

SEPARATION TECHNOLOGY: THE NEXT TEN YEARS

Edited by John Garside

INSTITUTION OF CHEMICAL ENGINEERS

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The Editor



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Garside was appointed professor at UMIST in 1982. He is the 1994/5 President of the Institution of Chemical Engineers.

PREFACE

Separations are at the heart of chemical and process engineering. Many of the separation processes that are now most widely employed have been known for very many years, indeed three of those considered in this book — drying, crystallization and distillation — have probably been used for thousands of years. In the 1860s crystallization, or more accurately precipitation, was central to one of the earliest inorganic chemical processes, the production of sodium bicarbonate by the Solvay process. The more recent development of diffusional gas/liquid separations had its origins in the growth of the oil industry; such developments are closely linked to the evolution of the unit operations concept and the establishment of chemical engineering as one of the primary engineering disciplines.

Major well-documented changes are now under way in the chemical and process industries, particularly in Western Europe, North America and increasingly in Asia. There are enormous pressures to reduce costs, especially in the manufacture of commodity products, together with a growing emphasis on the quality and diversity of speciality products. One obvious result of these trends is the need to reduce the cost and improve the efficiency of the more traditional separations while also accelerating the development and commercialization of new separation technologies. These newer separation processes increasingly depend on distinguishing between subtle differences in the molecular structure of components to be separated — between isomers or between chiral molecules, for example. This emphasizes the need to understand the basis of such separations at the molecular level. It contrasts with the traditional, phenomenological viewpoint which focuses on the larger size scales that have been central to the well-established separations. Consequently it will become more and more necessary to integrate the molecular, the micro and the macro scales — to link the nanometer to the meter length scale — much more effectively than is managed at present. Indeed, this need to understand better the underlying fundamentals of all separations is a theme that runs through all the contributions to this book. It leads to the recognition of the need to combine the science and understanding of the underlying phenomena with the engineering

and technology, with the equipment design techniques and with the development of specific applications.

This book presents a survey of a number of separation processes. It starts with a broad overview of separations which highlights some of the most exciting current ideas and challenges. A number of specific separation processes are then considered. Some are traditional — distillation, crystallization and drying — and here the authors emphasize new approaches and applications in fundamental understanding and equipment design. Others — adsorption and the spectrum of bioseparations — are newer and changing very rapidly. Here the authors concentrate on the most recent developments and achievements and look forward to the opportunities that exist for new applications. The final chapter highlights the importance of integrating separations into the overall process at an early stage and the advantages of so doing.

The chapters in this book are based on contributions to a conference organized by the North Western Branch of the Institution of Chemical Engineers and held at UMIST, Manchester on 18 May 1994. It is a pleasure to acknowledge the help of the other members of the organizing committee — Mike Adams, Stuart Gardiner, Malcolm Preston, Robin Smith and Tony Thompson — in initiating and developing the programme for that meeting. They join me in thanking the authors for their enthusiastic efforts in producing their contributions that will, I am sure, form a valuable and lasting contribution to the field.

John Garside

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1. IMPROVE SEPARATIONS!

Rajamani Krishna and Johannes Wesselingh

In order to achieve world class performance from separation processes, more attention must be paid to several areas of separation. Five areas are summarized on this page; the chapter is structured under headings corresponding to these five areas.

(1) Improved modelling of interphase mass transfer processes. Fick's law of diffusion is inadequate to handle the problems of today and tomorrow. The Maxwell-Stefan approach to diffusion is recommended for use in place of Fick's law. This approach takes proper account of thermodynamic non-idealities and the influence of external force fields. Furthermore, the Maxwell-Stefan approach can be extended to handle intra-particle diffusion in macro- and microporous adsorbents and membranes. The Maxwell-Stefan theory provides some insights into the development of innovative separation processes.

(2) Hydrodynamics of two phase flow on distillation, absorption and extraction plate and packed columns needs to be better understood. A unified approach to G-L and L-L hydrodynamics will provide improved design procedures and help reduce scale-up costs.

(3) Improvement of design procedures. Traditionally distillation, absorption and extraction columns have been designed using the equilibrium stage approach. There are persuasive reasons for adopting the non-equilibrium or rate-based approaches as a routine design tool.

(4) Separation equipment is far too big and intensification is required.

(5) Separation technologists must invade the territory of the reactor engineer and devise innovative methods for *in situ* product removal. This will improve selectivity and overall process economics.

PREAMBLE

In separation equipment many different processes occur on different scales. The largest scale is that of a complete plant, with units such as distillation columns or membrane systems. These might have dimensions of hundreds or tens of metres. There can be many such units, coupled in complicated ways, with any number of recycles and energy recovery loops. Equipment consists of smaller parts such as trays with their plates and downcomers and membrane modules with flow distributors. The dimensions of such parts are of the order of metres. The flow on trays or in modules shows smaller patterns again, which might be described as mixing or maldistribution. Near solid surfaces or other phase boundaries, turbulence dies out and transport is governed by diffusion. These phenomena are on a scale of micrometres. Diffusion scales in membranes or sorbents can be smaller again. Diffusivities and equilibria at phase interfaces are governed by phenomena that occur on an even smaller scale, that of molecules, with dimensions of about one nanometer.

In order to achieve world class performance from separation processes there is a need to improve understanding of, and aim for improvements in, the various phenomena at each scale of observation and occurrence. Starting at the smallest scale, there have been developments in the understanding of molecular diffusion.

**ADOPT A MORE FUNDAMENTAL AND GENERAL APPROACH
TO MASS TRANSFER!**

Mass transfer is the basis of separations. Fick's law of diffusion still underpins mass transfer design equations (for example, King, 1980). The limitations of Fick's law to describe molecular diffusion is well documented and it has been convincingly argued that the most convenient and general approach to inter-phase mass transfer is the Maxwell-Stefan approach (Wesselingh and Krishna, 1990; Taylor and Krishna, 1993; Krishna, 1993a; Krishna, 1993b). This approach is simple to comprehend and even teach at the first level separations course. The basis of the Maxwell-Stefan theory can be explained as follows. To achieve separation there needs to be relative motion between the molecular species. This relative motion is achieved by exerting a force on the species to be moved. From the theory of irreversible thermodynamics it can be derived that the force per mole of species is the chemical potential gradient (see Figure 1.1 on page 11). In the Maxwell-Stefan formulation of diffusion a linear relation is

postulated between the chemical potential gradient and the relative velocity between the diffusing species (see Figure 1.2 on page 12). The constant of proportionality can be interpreted as a kind of drag coefficient and the Maxwell-Stefan diffusivity can be simply interpreted as an inverse drag coefficient. For a two-component mixture, the Fick diffusivity equals the Maxwell-Stefan diffusivity times a thermodynamic non-ideality factor (Figure 1.2). The Fick diffusion coefficient lumps together two different concepts: (a) the drag between diffusing species and (b) thermodynamic non-idealities in the mixture; consequently its behaviour can be complex. This is why the Fick diffusivity performs ‘strangely’ in the vicinity of the phase transition points. At phase transition points the thermodynamic correction factor defined in Figure 1.2 tends to vanish and, consequently, the Fick diffusivity approaches vanishingly small values. Figure 1.3 on page 12 shows that for methanol-*n*-hexane the Fick diffusivity reduces by a factor 20 as the critical point is approached. This dramatic behaviour can be attributed to the behaviour of the thermodynamic factor. The Maxwell-Stefan diffusivity is practically constant over the whole composition range (see Figure 1.3). Several separation processes operate close to phase transition points, crystallization being the prime example. Figure 1.4 on page 13 shows the sharp reduction in the Fick diffusivity of glycine in water as the degree of supersaturation is increased. The Maxwell-Stefan diffusivity, on the other hand, is well behaved and its value remains practically constant (Clark and Rowley, 1986).

Mixtures encountered in practice are almost always multicomponent — that is, they contain three or more species. Though Fick’s law can be generalized to multicomponent mixtures by defining a matrix of Fick diffusivities, the elements of this matrix lose their simple meaning; the non-diagonal elements can assume negative values. The extension of the Maxwell-Stefan equations to multicomponent mixtures is straightforward. The force exerted on molecular species 1 is balanced by friction experienced by species 1 with species 2, 3 (Figure 1.5 on page 13). Since molecular species differ in size, shape, polarity and so on, differences in the 1–2, 1–3, 1–4 Maxwell-Stefan pair diffusivities can be expected even for ideal gases. Such differences in diffusivities can cause uphill transport of a particular species. Figure 1.6 on page 14 shows transient diffusion experiments for the system methane-argon-hydrogen in a Loschmidt apparatus. For argon the composition-time profiles are not monotonous and exhibit a maximum and a minimum in the bottom and top compartments respectively (Figure 1.6). These extremes signify the fact that for

a certain time period argon must be diffusing against its own driving force. Uphill diffusion of any species is not a violation of the second law of thermodynamics; this species is being 'pumped' uphill by the other transferring species which produce the extra entropy to compensate for entropy consumption by the species which transfers against its own gradient. Neglect of such interaction effects causes prediction of condensation instead of evaporation of acetone during vapour-liquid mass transfer in the system acetone-benzene-helium (see Figure 1.7 on page 14). This example shows that the predictions of the conventional approaches and the Maxwell-Stefan approach can be qualitative in nature.

Another important consequence of multicomponent interactions in practice is that component Murphree point efficiencies in multicomponent distillation can assume negative values. Figure 1.8 on page 15 shows the experimental results obtained by Vogelpohl for the system acetone-methanol-water in a sieve tray column. The component Murphree efficiency of water on tray 10 is -150 %. Negative component Murphree efficiency values are 'curious' only if it is assumed that the flux of any component is engendered by its own composition gradient. A fundamental Maxwell-Stefan approach, which has its roots in irreversible thermodynamics, shows that the flux of any component is inextricably linked to the driving forces of all the species in the mixture (see Figure 1.5 on page 13). Multicomponent 'interaction' effects can be used to devise new separation techniques. Condensation of an azeotropic mixture of 2-propanol and water in the presence of air will lead to a condensate composition which is richer in the faster diffusing species water vapour; see Figure 1.9 on page 15. There is a possibility of 'breaking' azeotropes by making the azeotrope condense in the presence of an inert gas. This concept has been verified experimentally (Fullarton and Schlunder, 1986). Conceptually speaking, the function of the inert gas in this separation is akin to that of an 'inert' membrane. Indeed, the most convenient way of modelling membrane transport is to view the membrane as a pseudo-species (see later).

Chemical potential gradients are not the only forces causing separations; electrostatic potential gradients, gravity and centrifugal force fields can also be used to cause relative motion of species (see Figure 1.10 on page 16). The total force expressed in Figure 1.10 is balanced by friction caused by relative motion of the species, as discussed earlier (Figure 1.5). Some separations involve ionic species — for example, ion exchange and electrodialysis. The driving forces for motion of the positive and negative ions are shown at the top of Figure 1.11 (see page 16). The electrostatic force is multiplied by the

charge of the species and so it is clear that forces are 'directional', the transport rates being direction dependent. Figure 1.11 illustrates this dramatic effect for ion exchange (Kraaijeveld and Wesselingh, 1993). Deliberate use of electric fields can enhance mass transfer rates across liquid-liquid interfaces (Stichlmair *et al.*, 1992); see Figure 1.12 on page 17.

Membrane separations are currently gaining in importance (Wankat, 1990; Wesselingh and Krishna, 1990). The membrane phase can be modelled as a homogeneous or heterogeneous phase — that is, one containing pores or channels (see Figure 1.13 on page 17). The mass transfer relations for membrane transport can be set up as for 'bulk' fluid mixtures (Figure 1.5 and Figure 1.10) by considering the membrane phase as a pseudo-species in the mixture (Figure 1.13); this approach is essentially analogous to the dusty gas model for intraparticle diffusion (Jackson, 1977; Mason and Malinauskas, 1983). The design of membrane and adsorption separations requires proper modelling of the diffusion processes in bulk fluids, solids and in macro- and micropores (see Figure 1.14 on page 18). The Maxwell-Stefan (= dusty gas model) formulation is essential to the design of pressure swing adsorption processes where adsorption and desorption take place in different transport regimes, bulk or Knudsen (Farooq and Ruthven, 1991).

Separations based on microporous adsorbents such as zeolites, microporous carbons and carbon molecular sieves will gain increasing attention and application in the future. The mechanism of transport of molecules inside micropores is by activated movement of adsorbed species along the sorption sites, and the motion of sorbed species can be modelled using the Maxwell-Stefan formulation (Figure 1.15 on page 18) by considering the vacant sites as pseudo-species. The Maxwell-Stefan diffusivity can be related simply to the jump frequency of sorbed species and to the average jump distance (Krishna, 1993a; Krishna, 1993b). The experimental results of Kapteijn *et al.* (1994) for the Maxwell-Stefan diffusivity of *n*-butane in silicalite shows an Arrhenius temperature dependence, typical of activated processes (see Figure 1.16 on page 19). The Maxwell-Stefan micropore diffusion model further shows that the Fick diffusivity increases strongly with increasing surface coverage (see Figure 1.17 on page 19). The consequences of this result is that the transfer rates increase with increasing surface coverage: a self-acceleration effect. On the other hand, desorption should be a self-decelerating effect (Figure 1.17). Experimental results for adsorption and desorption of methane in a packed bed of carbon molecular sieves confirms that adsorption proceeds much faster than desorption

(see Figure 1.18 on page 20). Desorption of a component is the rate-determining step and counter-sorption of mixtures can be expected to be asymmetric; this is confirmed for counter-sorption of methane-nitrogen in microporous carbons. Replacing strongly adsorbed methane by nitrogen proceeds much more slowly than replacement of weakly adsorbed nitrogen by methane (see Figure 1.19 on page 20). The self-accelerating transport of adsorbed species as predicted by the Maxwell-Stefan theory (Figure 1.17) provides us with exciting new separation possibilities. Sircar (1992) has shown those offered by microporous carbon membranes for separating hydrocarbons from a gaseous mixture containing hydrogen (see Figure 1.20 on page 21). The hydrocarbons are much more strongly adsorbed than hydrogen and are preferentially transported across the membrane.

MODEL MULTIPHASE FLOW HYDRODYNAMICS IN TRAY AND PACKED COLUMNS PROPERLY AND GENERALLY!

Figure 1.21 on page 21 pictures tray hydrodynamics in G-L and L-L tray columns. It is a sad commentary on chemical engineering academics that the hydrodynamics can still not be described well enough to be able to predict mass transfer rates to a sufficient degree of accuracy. There is a wealth of empirical data held by the company Fractionation Research Incorporated (FRI) but this is not available to the academic community and the net result is that teachers end up having to describe the AIChE tray efficiency procedure of 1958 to students; witness the treatment in the standard text of King (1980). The AIChE method does not take cognizance of flow regimes and flow regime transitions on trays and cannot be generally valid. For description of the froth regime a realization of the analogies with gas-solid fluidized beds will be beneficial. The fluid bed 'two-phase' model has been used with some degree of success for tray efficiency prediction (Taylor and Krishna, 1993). More time must be spent in quantifying multiphase tray hydrodynamics — for example, measure bubble sizes, rise velocities, jet penetration distances. The influence of system pressure on gas-solid fluid bed hydrodynamics is known to be extremely significant and will affect regime transitions. The influence of pressure on regime transitions on tray columns has not been studied enough, despite the fact that there are several applications in which the distillation tray column operates under high pressures (ethane-ethene, propane-propene separations). Increased system pressure will reduce the density differences between vapour and liquid phases

in distillation columns and the hydrodynamics will approach that of liquid-liquid systems. Prediction methods for sieve tray liquid-liquid extraction efficiencies are, perhaps, even more uncertain than for sieve tray distillation columns. This situation needs to be corrected. Ideally fluid-fluid hydrodynamics in trays and packed columns should be treated in a consistent and general way. A unified approach to fluid-fluid hydrodynamics allows rational treatment of supercritical extraction as has been shown by De Haan (1991).

IMPROVE COLUMN DESIGN PROCEDURES!

The equilibrium stage approach is firmly embedded into the design philosophy for distillation columns. After calculating the number of equilibrium stages, the number of actual stages emerges by introducing the efficiency concept. But component efficiencies are all different and can even be negative (see Figure 1.8 on page 15). The definition of the efficiency itself is fraught with uncertainty and inconsistencies. The correct and general approach to distillation column design is not to use the equilibrium stage approach but to attack, head-on, the complete non-equilibrium problem by taking account of the heat and mass transfer processes on trays (see Figure 1.22 on page 22). The non-equilibrium stage approach must incorporate the proper Maxwell-Stefan description of interphase mass transfer. Also simultaneous heat transfer effects need to be incorporated into the model formulation. The non-equilibrium stage design procedure can be developed logically in a manner which can be taught to students (Taylor and Krishna, 1993). The incentive to adopt the non-equilibrium stage model approach is that column profile predictions using this approach and the traditional approaches can be markedly different (see Figure 1.23 on page 22); such differences could have a significant effect on column design. With increasing computational power one of the major objections to the use of the non-equilibrium stage approach will vanish. The major bottleneck in the use of this approach is the lack of generally applicable mass transfer correlations for trays and packings, as noted earlier.

INTENSIFY SEPARATIONS!

Manufacturers of distillation structured packings and vendors of dryers usually boast about the fact that these can be supplied on massive scales (see Figures 1.24 and 1.25 on page 23). But this 'BIG IS BEAUTIFUL' slogan is not very

impressive. The aim should be to make distillation columns smaller by intensifying operations. The Hige centrifugal distillation column exemplifies a welcome trend. Would it be possible to replace the truly gigantic spray drying equipment found in FCC catalyst manufacturing facilities (Figure 1.25) by high efficiency and compact microwave-assisted short contact equipment?

INTEGRATE SEPARATIONS WITHIN REACTORS!

Separation processes usually follow the reaction steps and there is a need to adopt an integral approach to reaction and separation (see Figure 1.26 on page 24). Increasing attention is being paid to *in situ* product removal within the reactor; this will be beneficial for equilibrium-limited reactions and for reactions in which the desired product can undergo undesirable side reactions. The most dramatic example of the benefits of *in situ* separation within the reactor is afforded by the Eastman Kodak process for methyl acetate where the reactor, which is conventionally followed by several distillation columns, was replaced — with considerable economic advantages — by one integral reactive distillation column. The design of the reactive distillation column requires proper attention to modelling, however, and the rate based approach (as explained earlier) is indispensable. Combination of reaction and distillation can lead to new effects such as multiple steady states and hysteresis (see Figure 1.27 on page 24) and special attention must be paid to column dynamics and control even in the design stage (Doherty and Buzad, 1992).

Some other examples where *in situ* product separation can be beneficial to the process are discussed below. *In situ* extraction of product can be beneficial for preventing undesirable side reactions (see Figure 1.28 on page 25). *In situ* supercritical extraction increases the selectivity of biocatalysed reactions (see Figure 1.29 on page 25). *In situ* product removal through permselective membrane walls of a catalytic reactor offers many possibilities of improving overall performance and selectivities (see Figures 1.30 and 1.31 on page 26). Selective hydrogen removal in dehydrogenation reactors enhances conversions considerably (see Figure 1.32 on page 27). Separation technologists must increasingly invade the territory of the reactor engineer in order to arrive at optimum process solutions. Selectivity advantages in reactors will pay in the long run; this is the WRAP (Waste Reduction Always Pays) principle.

CONCLUSIONS

In order to prepare chemical engineers for the challenging separation tasks of the future, students must learn a more general interphase mass transfer theory using the Maxwell-Stefan approach. Multiphase hydrodynamics in trays and packed columns is insufficiently understood and there is a need for a concerted effort to develop a common, unified approach. Design procedures must routinely integrate interphase mass transfer, heat transfer, phase equilibria and hydrodynamics. Separation equipment is often too huge and this is one reason why the image of the chemical industry is not very high in the public eye. Separation intensification will go a long way towards achieving public acceptance. The classic thinking of reaction-followed-by-separation must give way to an integral (reaction + separation) approach.

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