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Preface

The Maxwell–Stefan approach to mass transfer

Mass transfer is the basis of separations. Fick's law of diffusion still underpins our mass transfer design equations. The limitations of Fick's law to describe molecular diffusion are well documented and it is now generally accepted that the most convenient and general approach to interphase mass transfer is the Maxwell–Stefan approach; this approach has been available for use by chemical engineers for more than a century. This approach has its roots in the theory of irreversible thermodynamics and allows for the influence of driving forces other than the chemical potential gradient, such as the electrostatic and gravitational potentials. The theory is further capable of dealing with mixtures with any number of components. The papers in this special issue of *The Chemical Engineering Journal* highlight the need to adopt the Maxwell–Stefan approach in a wide variety of applications in chemical engineering. They were presented at a two-day international symposium *Maxwell–Stefan Approach to Mass Transfer*, held in Amsterdam on 18 and 19 November 1994 and sponsored by the Dutch National Graduate School in Chemical Engineering (*Onderzoekschool Procestechnologie*).

Transport in ionic systems

Wesselingh et al., explore the Maxwell–Stefan description of ion exchange and suggest estimation procedures for the ionic diffusion coefficients. Curiously, the plus-plus ionic diffusivities can be negative!

Kraaijeveld et al., develop the Maxwell–Stefan approach to the description of mass transfer across electrodialysis membranes.

Diffusion in membranes and porous media

The Maxwell–Stefan approach can be extended to the description of diffusion in porous media and adsorbents by considering the medium as a pseudo-species in the mixtures. This approach is equivalent to the dusty gas model, which is well established in chemical engineering practice. ***Arnost and Schneider*** show that the dusty gas model is capable of accurately modelling dynamic transport of ternary mixtures of non-adsorbable gases through porous solids.

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 by considering the vacant sites as pseudo-species. The Maxwell–Stefan theory for micropore diffusion requires the use of the surface chemical potential gradients as proper driving forces. The Maxwell–Stefan theory brings out clearly the interplay between micropore mobility and adsorption strength. There are exciting separation possibilities offered by microporous carbon or zeolite membranes for separating hydrocarbons from a gaseous mixture containing hydrogen. The hydrocarbons are much more strongly adsorbed than hydrogen and are preferentially transported across the membrane. ***Kapteijn et al.*** have shown that for modelling of the steady-state transport of binary mixtures of light hydrocarbons across a zeolite membrane, the use of the Maxwell–Stefan equations is necessary. The more strongly adsorbed species has the higher flux through the membrane. ***Krishna and van den Broeke*** have modelled the transient diffusion process across zeolite membranes and have demonstrated the power of the Maxwell–Stefan formulation to predict the observed, curious, maximum in the transient flux of the component with the lower adsorption strength.

Srinivasan et al. have provided experimental confirmation of the need for the use of the chemical potential gradient driving forces for diffusion-selective separation of oxygen–nitrogen using carbon molecular sieves.

Diffusion with chemical reaction

Reactions involving a change in the number of molecules will generate pressure gradients when they are carried out in porous catalysts. When there is an increase in the number of molecules in the reaction, the pressure within the pellet is expected to be higher than at the surface, while the reverse is true when there is a decrease in number of molecules. *Nan et al.* have considered the influence of both (i) reaction stoichiometry and (ii) imposed pressure drop on the effectiveness factor inside catalyst pellets.

Veldsink et al. have demonstrated the need for using the Maxwell–Stefan formulation for describing mass transport across a catalytic membrane; their simulations show that the Fick formulation can, in some cases, lead to serious errors.

Kuijlaars et al. have considered two typical processes for the deposition of thin films on silicon wafers in microelectronics manufacturing: the deposition of tungsten from WF_6 and the deposition of polycrystalline silicon from SiH_4. The two-dimensional axisymmetric equations for the hydrodynamics and the concentration distributions in a multiple wafer low pressure chemical vapour deposition reactor were solved numerically using three different models to describe gaseous phase diffusion: (i) Fick's law, (ii) Wilke's effective diffusivity approach, and (iii) the Maxwell–Stefan equations. They show that the use of Fick's law or Wilke's approach can lead to inconsistent results when the reactants and products are present is relatively high concentrations.

The non-equilibrium stage model for column design

The equilibrium stage approach is firmly embedded into our design philosophy for distillation columns. After calculating the number of equilibrium stages, we arrive at the number of actual stages by introducing the efficiency concept. But component efficiencies are all different and component efficiencies can even be negative. 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 stage approach must incorporate the proper Maxwell–Stefan description of interphase mass transfer. Also, simultaneous heat transfer effects need to be included into the model formulation. 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; 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 the non-equilibrium stage approach is the lack of generally applicable mass transfer correlations for trays and packings.

The incorporation of the proper mixing model for either phase in a tray or packed column is an essential factor to be considered. ***Kooijman and Taylor*** develop appropriate computational procedures for handling a variety of "mixedness" situations.

Rao et al. have extended the available models for mass transfer in tray columns to include the influence of entrainment on tray efficiencies.

Zimmermann et al. have extended the non-equilibrium stage model for extraction columns to take account of drop size distributions. They combine the Maxwell–Stefan approach to interphase mass transfer with population balances and, additionally, take proper account of phase hydrodynamics. They report good agreement between model predictions and experiment.

Integrated separations within reactors

Separation processes usually follow the reaction step and there is a need to adopt an integral approach to reaction and separation. There is increasing attention 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. A dramatic example of the benefits of in situ separation within the reactor is afforded by the Eastman Chemicals process for methyl acetate where the conventionally used reactor followed by several distillation columns was replaced by one integral reactive distillation column with considerable economic advantages. The design of the reactive distillation column, however, requires proper attention to modelling and the rate based approach is indispensable.

Combination of reaction and distillation can lead to new effects such as multiple steady states and hysteresis. ***Sundmacher and Hoffmann*** report experienced oscillations in their experiments with catalytic distillation for MTBE synthesis. A rigorous dynamic model, including Maxwell–Stefan mass transfer equations, thermodynamic non-idealities, and thermal effects, needs to be developed for handling reactive distillation systems; this remains a challenge for the future.

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