Real-World
Modeling of Distillation

Previously, simulations based on nonequilibrium, or rate-based, models were considered impractical due to their complexity. However, with ever-increasing computing power, these simulations are not only feasible, but in some circumstances they should be regarded as mandatory.

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C HEMICAL ENGINEERS HAVE BEEN solving their distillation problems using the equilibrium stage model since Sorel first used the model for the distillation of alcohol over 100 years ago. Seader *(1)* has provided an elegant history of the first century of equilibrium stage modeling. Real distillation and absorption processes, however, normally do not operate at equilibrium.

In recent years, it has become more common to simulate distillation and absorption as a mass-transfer-rate-based operation, using what have become known as nonequilibrium, or rate-based, models. This article presents a brief outline of nonequilibrium modeling and provides pointers to the growing literature in this field.

Modeling the old-fashioned way

To model a plant like the one shown in Figure 1, we decompose the entire plant into smaller units. In this case, the plant contains a distillation column that is shown enlarged in the center panel of the figure. There are many ways to model

an entire column, but the most common approach is to divide the column into a number of discrete "stages," as depicted in the third panel. Thus, the question to be addressed first is: *How do we model these stages*?

The equations that model equilibrium stages are known as the MESH equations. MESH is an acronym referring to the different types of equation that are used in the model:
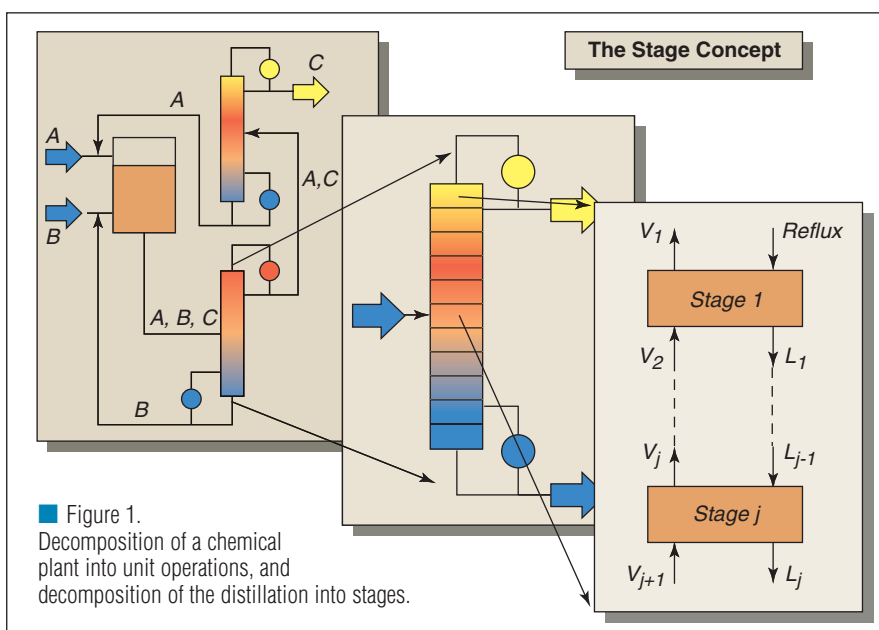
■ Figure 1.
Decomposition of a chemical plant into unit operations, and decomposition of the distillation into stages.

The Stage Concept

V_1 Reflux

Stage 1

V_2 L_1

V_j L_{j-1}

Stage j

V_{j+1} L_j

• M stands for material balances
• E stands for equilibrium relationships (to express the assumption that the streams leaving the stage are in equilibrium with each other)
• S stands for summation equations (mole fractions are perverse quantities and won't sum to unity unless you force them to)
• H stands for heat or enthalpy balances (processes conserve energy, as well as mass).

There are few mathematical models in any branch of engineering that are as well-suited to computer solutions and that have prompted the development of as many different algorithms as have the MESH equations. It would not be too far from the truth to claim that it is equilibrium stage calculations that brought computing into chemical engineering — and chemical engineers to computers *(1)*.

The equilibrium stage model is so simple in concept, so elegant from the mathematical viewpoint, the basis for so many commercial column simulation programs, and been used to simulate and design so many real columns, that it seems almost heretical to mention that the model is fundamentally flawed. However, chemical engineers have long been aware of the fact that the streams leaving a real tray or section of a packed column are not in equilibrium with each other. In fact, the separation actually achieved depends on the rates of mass transfer from the vapor to the liquid phases, and these rates depend on the extent to which the vapor and liquid streams are *not* in equilibrium with each other. The next question is: *What have we done about this fundamental weakness*?

The conventional way around this shortcoming

of what is referred to frequently as the rigorous model (with some disregard for semantic accuracy), is to employ efficiencies. Several kinds of efficiency have been used in distillation column modeling and design, including the overall, Murphree, Hausen and vaporization efficiencies. The Murphree efficiency *(2)* is arguably the most widely employed by distillation engineers and is defined by:

$$E_{i,MV} = \frac{\bar{y}_{iL} - \bar{y}_{iE}}{y_{iL}^* - \bar{y}_{iE}} \tag{1}$$

where the overbars indicate the average mole fraction in the entering (*E*) and leaving (*L*) streams, as depicted in Figure 2.
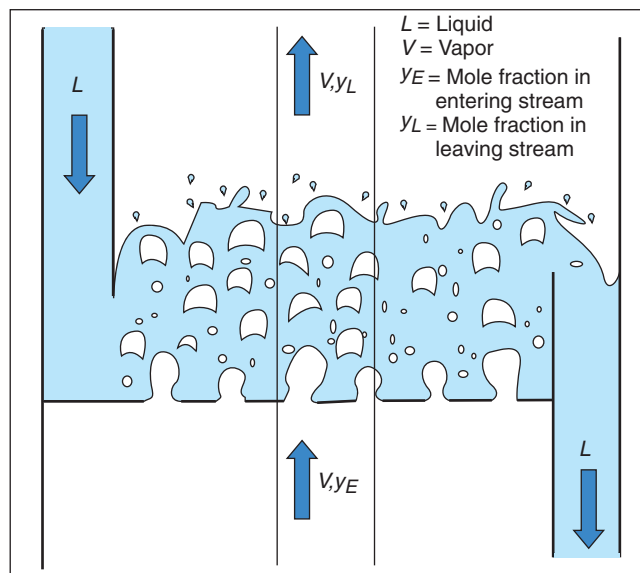
For packed columns, we use something analogous to the

Figure 2. Idealized flow patterns on a distillation column tray.

stage efficiency called the HETP (Height Equivalent to a Theoretical Plate). In practice, efficiencies and HETPs often are estimated simply from past experience with similar processes. However, for new processes, this approach is of no use whatsoever (and often fails even for old ones). Chemical engineers have, therefore, devoted a great deal of effort to devising methods for estimating efficiencies and HETPs *(3, 4)*.

These different kinds of efficiencies all attempt to represent the extent to which the real trays in a tray column (or the entire column itself) depart from equilibrium. The HETP is a number that is easy to use in column design. However, there are several drawbacks to employing efficiencies and HETPs in a computer simulation based on the equilibrium stage model:

• There is no consensus on which definition of efficiency is best (although many distillation experts will admit to a preference for Murphree-type efficiencies).
• The Murphree vapor-phase efficiency is not the same

Nomenclature

c	= number of components, dimensionless
c_t	= total concentration, mol/m^3
d	= driving force for mass transfer, m^{-1}
$D_{i,k}$	= Maxwell-Stefan diffusivity, m^2/s
$E_{i,MV}$	= Murphree tray efficiency, dimensionless
f	= proportionality coefficient
k	= mass transfer coefficient, m/s
K	= vapor-liquid equilibrium constant,
N_i	= molar flux of species i, mol/m^2-s
P	= pressure, Pa
p	= partial pressure, Pa
R	= gas constant, J/mol-K
t	= time, s
T	= temperature, K
u	= average velocity
x	= mole fraction, dimensionless
y	= mole fraction, dimensionless

Greek letters

κ	= mass transfer coefficient of binary pair in multicomponent mixture, m/s
μ	= Chemical potential, J/mol
η	= distance along diffusion path, dimensionless

Subscripts

i	= component index
I	= referring to interface
j	= stage index
k	= alternative component index
m	= reaction index
t	= total

Superscripts

F	= referring to feed stream
I	= referring to interface
L	= referring to liquid phase
V	= referring to vapor phase

as the liquid-phase efficiency on the same tray (the Hausen efficiency does not share this property).

- The generalized Hausen efficiencies (sometimes known as Standart efficiencies *(5)*) are the most fundamentally sound, but are impractically complicated to calculate and are never used in practice.
- Vaporization efficiencies, favored by some in the past because they are easy to include in computer programs, are not often used today.
- Efficiencies vary from component to component, and from tray to tray, in a multicomponent mixture. Very rarely is this fact taken into account in a simulation model that uses efficiencies.
- Efficiencies vary from stage to stage in a tray column. HETPs are a function of height in a packed column. These behaviors of efficiencies and HETPs are often not accounted for in conventional column simulation software.

These weaknesses of the standard model have been known for a long time *(6)*. Thus, our third question is: *How should we deal with the shortcomings of the standard model?*

Modeling in the real world

In recent years, a new approach to the modeling of distillation and absorption processes has become available — the so-called nonequilibrium, or rate-based, models. These models treat these classical separation processes as the mass-transfer-rate-governed processes that they really are.

The building blocks of the nonequilibrium model shown in Figure 3 are sometimes referred to as the MERSHQ equations, where:

- M represents material balances
- E represents energy balances
- R represents mass- and heat-transfer rate equations
- S represents summation equations
- H represents hydraulic equations for pressure drop
- Q represents equilibrium equations.

Some of these equations are also used in building equilibrium stage models; however, there are crucial differences in the way in which the conservation and equilibrium equations are used in the two types of model. In a nonequilibrium model, separate balance equations are written for each distinct phase. Figure 3 shows that the material balance for each phase includes terms to represent the mass transferred from one phase to the other. For the equation used in the equilibrium stage model, the sum of the phase balances yields the material balance for the stage as a whole. The energy balance is treated in a similar way — it is split into two parts, one for each phase, each part containing a term for the rate of energy transfer across the phase interface.

Modeling distillation and related operations as the rate-based processes that they really are requires us to face up to the challenge of modeling interfacial mass and energy transfer in tray and packed columns. This is something that we do not do in the conventional equilibrium stage model (although we face essentially the same problem if efficiencies

are to be estimated from a mathematical model *(3, 4)*). The molar fluxes at a vapor liquid interface may be expressed as:
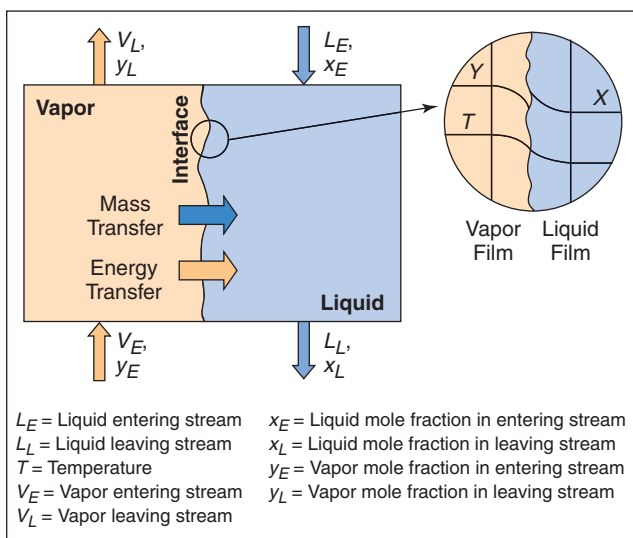
$$N_i^V = c_i^V k_i^V (y_i^V - y_i^I) \tag{2}$$

$$N_i^L = c_i^L k_i^L (x_i^I - x_i^L) \tag{3}$$

where c_i^V and c_i^L are the molar densities of the superscripted phases, y_i^V is the mole fraction in the bulk vapor phase, x_i^L is the mole fraction in the bulk liquid phase, and x_i^I and y_i^I are the mole fractions of species i at the phase interface. k_i^V and k_i^L are the mass-transfer coefficients for the vapor and liquid phases.
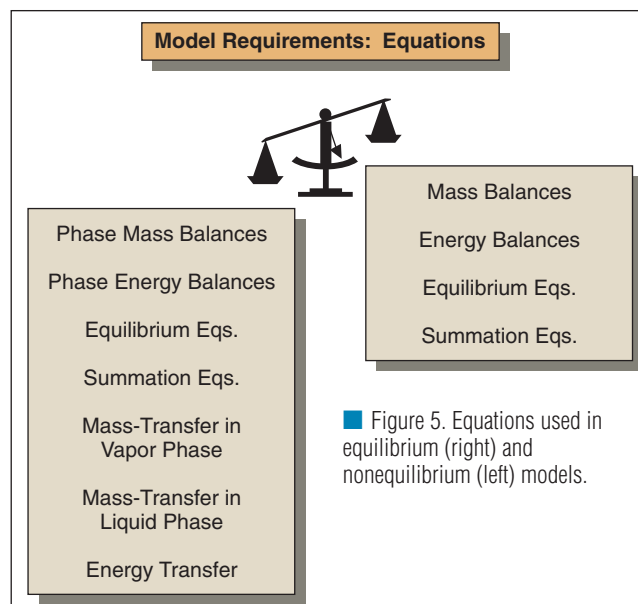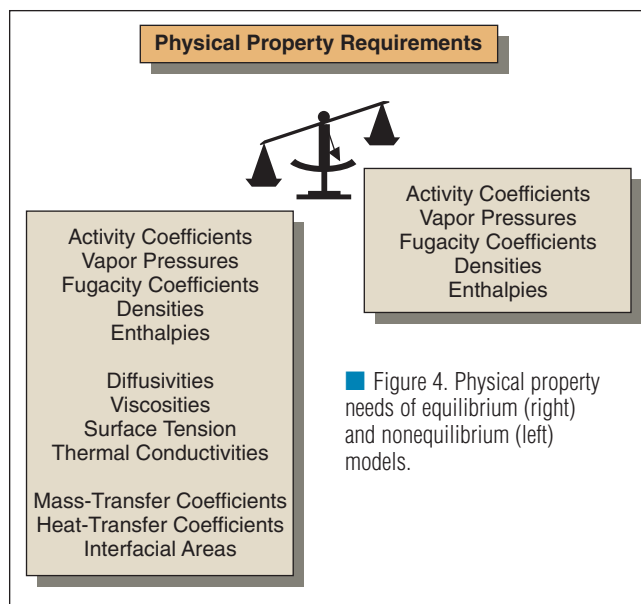
The inclusion in the model of the mass transport equations introduces the mole fractions at the interface, something we have not had to deal with so far, at least not explicitly. It is common to assume that the mole fractions at the interface are in equilibrium with each other. We may, therefore, use the very familiar equations from phase equilibrium thermodynamics to relate the interface mole fractions:

$$y_i^I = K_i x_i^I \tag{4}$$

where the superscript I denotes the interface compositions and K_i is the vapor-liquid equilibrium ratio for component i. These K-values are evaluated at the interface compositions and temperature using the same thermodynamic models used in conventional equilibrium stage simulations. The interface composition and temperature must, therefore, be computed during a nonequilibrium column simulation. In equilibrium stage calculations, the equilibrium equations are used to relate the composition of the streams leaving the stage and the K-values are evaluated at the composition of the two exiting streams and the stage temperature (usually assumed to be the same for both phases).

L_E = Liquid entering stream
L_L = Liquid leaving stream
T = Temperature
V_E = Vapor entering stream
V_L = Vapor leaving stream

x_E = Liquid mole fraction in entering stream
x_L = Liquid mole fraction in leaving stream
y_E = Vapor mole fraction in entering stream
y_L = Vapor mole fraction in leaving stream

■ Figure 3. Schematic diagram of a nonequilibrium stage.

■ Figure 4. Physical property needs of equilibrium (right) and nonequilibrium (left) models.

■ Figure 5. Equations used in equilibrium (right) and nonequilibrium (left) models.

Physical properties

Figure 4 identifies the major physical property requirements. It is obvious that nonequilibrium models are more demanding of physical property data than are equilibrium stage models (except when tray-efficiency or HETP and equipment-design calculations are carried out, but those are done after a simulation and are not needed to carry out the column simulation). The only physical properties required for an equilibrium stage simulation are those needed to calculate the K-values and enthalpies. Those same properties are needed for nonequilibrium models as well.

Mass-transfer coefficients and interfacial areas must be computed from empirical correlations or theoretical models. There are many correlations for mass-transfer coefficients in the literature (3, 4). These coefficients depend on the column design, as well as its method of operation.
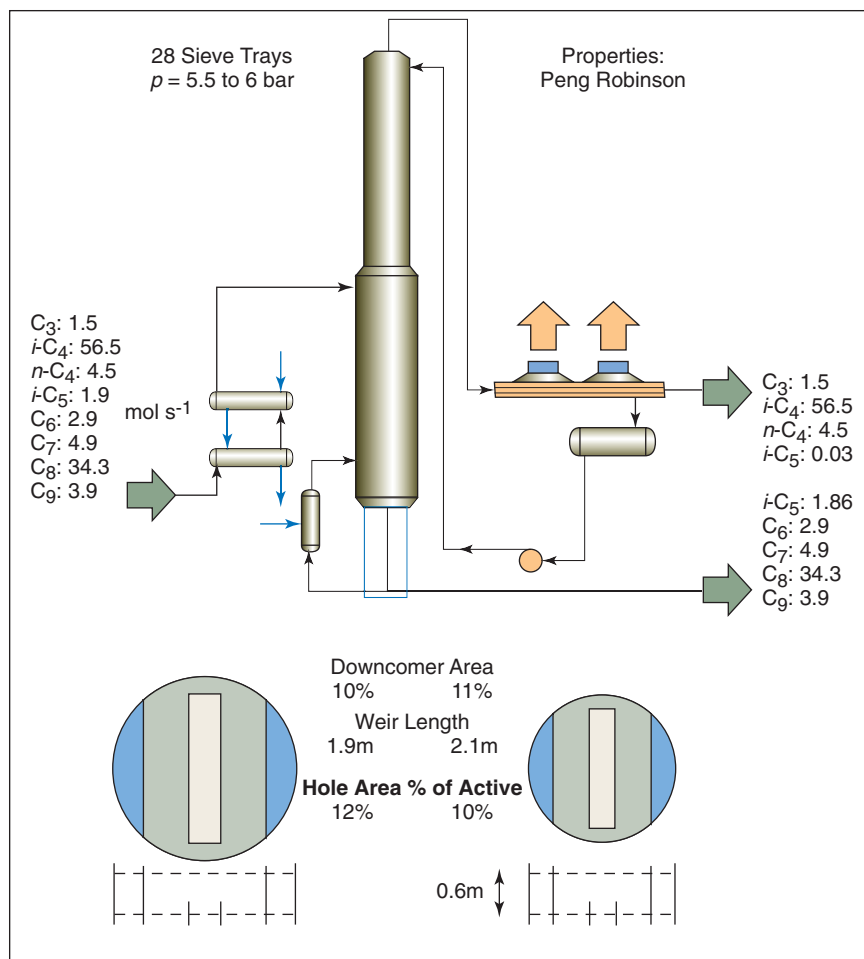
We do not believe that the need for additional physical properties should be a reason not to use a nonequilibrium stage model. Estimation methods are available for these properties, although they are typically much less accurate than methods for evaluating thermodynamic properties (7). However, these properties are needed only in so far as they are required to estimate mass-transfer coefficients. In fact, the sensitivity of these coefficients to any of these properties is not that large, and the fact that we do not always have accurate estimation methods should not act as a deterrent to their use. Rather, it should serve as a spur to more research and to the development of better methods for transport property prediction and estimation in much the same way as the need for reliable phase equilibrium models has served as motivation for the development of methods to predict thermodynamic properties.

Equipment design

The estimation of mass-transfer coefficients and interfacial areas from empirical correlations nearly always requires us to know something about the column design. At the very least, we need to know the diameter and type of internal (although usually we need to know more than that, since most empirical correlations for mass-transfer coefficients have some dependency on equipment design parameters, such as the weir height of trays). This need for complete equipment design details suggests that nonequilibrium models cannot be used in preliminary process design (before any actual equipment design has been carried out). However, this is not true. Column design methods are available in the literature, as well as in most process simulation programs. It is straightforward to simultaneously solve equipment sizing calculations and stage-equilibrium calculations (8). This does not add significantly to the difficulty of the calculations, and it allows nonequilibrium models to be used at all stages of process simulation, including preliminary design, detailed plant design and simulation, troubleshooting and retrofitting. In fact, nonequilibrium models can be particularly valuable in troubleshooting and retrofitting, even to the point of helping identify what particular equipment design detail might be responsible for a column failing to do what it was designed to do.

Solving the model equations

There has been so much work done on developing computational methods for solving the equilibrium stage model equations that we may essentially use the same approaches to solve the nonequilibrium model equations (8). The equations required by the two kinds of model are summarized in Figure 5. The fact that the nonequilibrium model in-

28 Sieve Trays
p = 5.5 to 6 bar

Properties:
Peng Robinson

C_3: 1.5
i-C_4: 56.5
n-C_4: 4.5
i-C_5: 1.9
C_6: 2.9
C_7: 4.9
C_8: 34.3
C_9: 3.9

mol s^{-1}

C_3: 1.5
i-C_4: 56.5
n-C_4: 4.5
i-C_5: 0.03

i-C_5: 1.86
C_6: 2.9
C_7: 4.9
C_8: 34.3
C_9: 3.9

Downcomer Area
10%   11%

Weir Length
1.9m   2.1m

Hole Area % of Active
12%   10%

0.6m

■ Figure 6. Debutanizer adapted from Example 9.1 in Ref. 9.
The simulation program created the tray design.

nonequilibrium model, it must be remembered, does not use efficiencies. McCabe-Thiele diagrams *(9)* can be constructed from the results of a nonequilibrium simulation (Figure 8), and are just as useful for understanding column behavior as they are for binary distillation. Note how the triangles do not touch the equilibrium line.

Example 2: A not-so-simple absorber. Consider the simple packed column depicted in Figure 9. The rich ammonia and air mixture enters at the bottom where the ammonia is absorbed. The enthalpy of absorption is released, causing the temperature of the liquid to rise. As a result, water evaporates. The mass transfer process in the gas therefore involves three species — ammonia, water and (essentially stagnant) air. Toward the top of the column, the gas encounters cold entering water. Therefore, water vapor condenses near the top of the column, and we now have co-diffusion of ammonia and water through air. We should not ignore water vaporization at the bottom and condensation at the top in the analysis. The resulting tempera-

■ Figure 7. Murphree efficiency profiles (predict-
ed) for the debutanizer shown in Figure 6.

volves more equations is not a concern. In our experience, the equations of both models are about equally simple (or difficult) to solve.
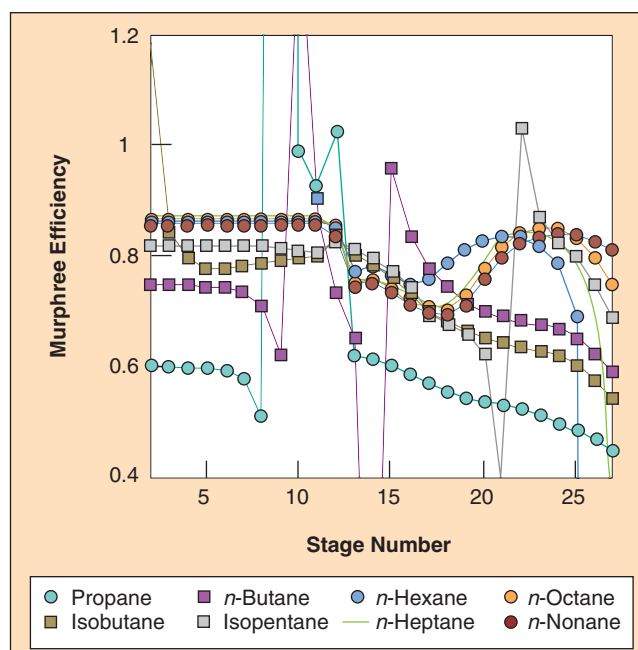
Numerical solution of the nonequilibrium model equations provides the chemical engineer with all of the quantities normally associated with the conventional equilibrium stage model — temperatures, flowrates, mole fractions, etc. Nonequilibrium-model calculations also provide a great deal of additional information, such as physical and transport property profiles, and equipment design and operating data.
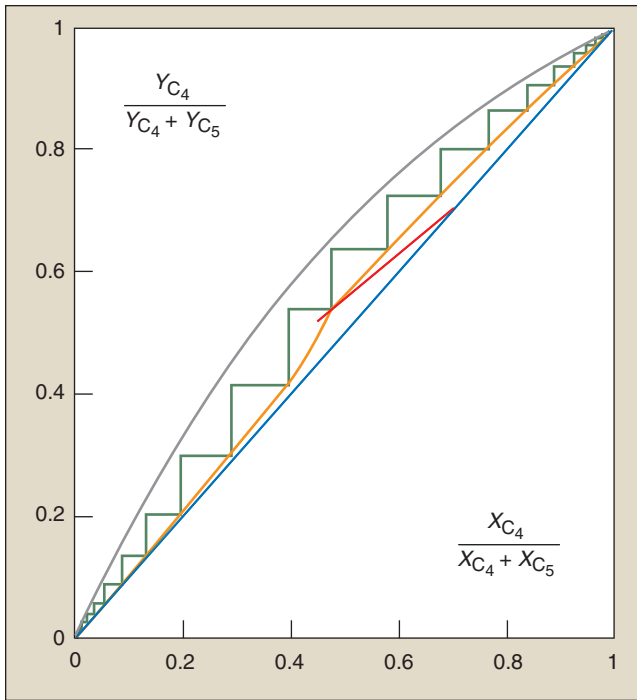
Example 1: A simple debutanizer. Consider the simple debutanizer shown in Figure 6. The flowrate and composition profiles do not differ to any significant extent from the results that you would obtain with a conventional equilibrium stage model (although the number of stages and feed stage location would be different). However, a nonequilibrium model can also provide considerable additional information, such as mass-transfer rates and predicted efficiency profiles (Figure 7). The

Legend:
○ Propane   ■ *n*-Butane   ○ *n*-Hexane   ○ *n*-Octane
■ Isobutane   ■ Isopentane   — *n*-Heptane   ● *n*-Nonane

■ Figure 8. McCabe-Thiele diagram for the debutanizer shown in Figure 6.

ture profiles along the column show a pronounced bulge near the bottom (Figure 9).

The Maxwell-Stefan approach

Equations 2 and 3 are included in all basic mass transfer texts and chemical engineering handbooks, and are taught to all chemical engineers in undergraduate chemical engineering degree programs. Strictly speaking, these equations are valid only for binary systems and under conditions where the rates of mass transfer are low. Most industrial distillation and absorption processes, however, involve more than two different chemical species.

The most fundamentally sound way to model mass transfer in multicomponent systems is to use the Maxwell-Stefan (MS) theory *(11–13)*. In our opinion, the MS approach to mass transfer should be what is taught to students, but rarely is that done, even at the graduate level; most texts give little or no serious attention to the matter of mass transfer in systems with more than two components (exceptions include the texts by Seader and Henley *(9)* and Benitez *(14)*).

The MS equation for diffusion in a binary ideal gas mixture is:

$$d_1 = f_{12} x_1 x_2 (u_1 - u_2) \qquad (5)$$

where d_1 is the driving force for diffusion and u_i is the average velocity of species i.

This expression may be derived using nothing more complicated than Newton's second law — the sum of the forces acting on the molecules of a particular species is directly proportional to the rate of change of momentum (Ref. 11 provides a more complete derivation). The rate of change of momentum between different species is proportional to the concentrations (mole fractions) of the different species and to their relative velocity. In Eq. 5, f_{12} is the coefficient of proportionality and is related to a friction factor. Eq. 5 is more often written in the form:

$$d_1 = \frac{x_1 x_2 (u_1 - u_2)}{D_{12}} \qquad (6)$$

where D_{12} is the MS diffusion coefficient.

The MS equations are readily extended to multicomponent systems simply by adding similar terms on the right-hand side to account for momentum exchanged between each pair of differing types of molecules. For a ternary mixture, for example, we would have two terms on the right, one of momentum exchange between molecules of types 1 and 2, and a second term for momentum transfer between molecules of types 1 and 3:

$$d_1 = \frac{x_1 x_2 (u_1 - u_2)}{D_{12}} - \frac{x_1 x_3 (u_1 - u_3)}{D_{13}} \qquad (7)$$

with the equations for species 2 and 3 obtained by rotating the subscripts.
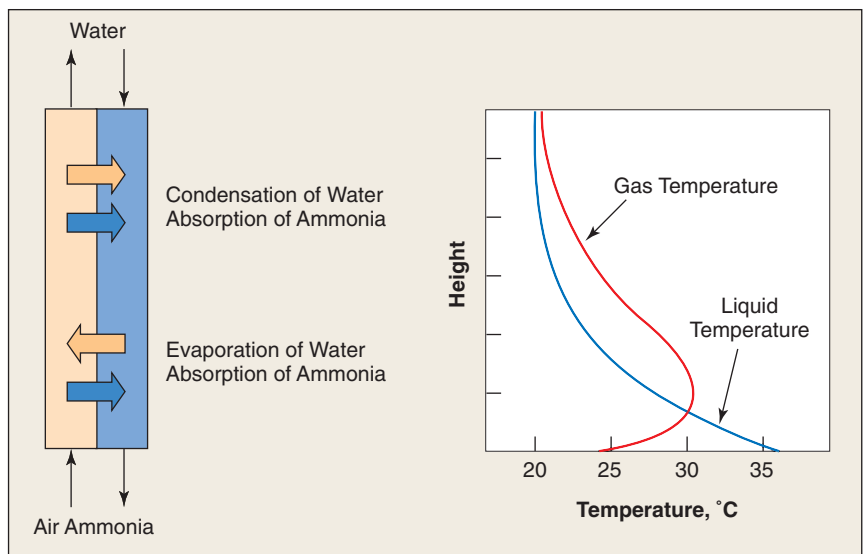
■ Figure 9. Ammonia absorber adapted from Example 8.8 in (10).

The generalization of this expression to mixtures with any number of different species is:

$$d_1 = -\sum_{k=1}^{c} \frac{x_i x_k (u_i - u_k)}{D_{ik}} \tag{8}$$

which is more familiar to us in the form:

$$d_1 = -\sum_{k=1}^{c} \frac{x_i N_k - x_k N_i}{c_t D_{ik}} \tag{9}$$

where we have replaced the velocities with the molar fluxes $N_i = c_i u_i$.

For an ideal gas mixture, the driving force is the partial pressure gradient:

$$d_1 = \frac{1}{P}\frac{dp_i}{dz} = \frac{dx_i}{dz} \tag{10}$$

Solving the MS equations might involve the computation of various matrices and functions thereof *(11)*. In practice, we most often employ a simple film model for mass transfer with a simple difference approximation to the MS equations:

$$\Delta x_i = -\sum_{k=1}^{c} \frac{\bar{x}_i N_k - \bar{x}_k N_i}{c_t \kappa_{ik}} \tag{11}$$

where $\bar{x}_i$ is the average mole fraction over the film. The MS mass-transfer coefficients κ_{ij} can be estimated from existing correlations. For a nonideal fluid, the driving force is related to the chemical potential gradient:

$$d_i = \frac{x_i}{RT}\frac{d\mu_i}{dz} \tag{12}$$

The difference approximation of this expression is somewhat more involved, since we have to include the derivative of the activity (or fugacity) coefficient *(13)*.

Example 3: The need for rigorous Maxwell-Stefan-based nonequilibrium models. The differences in column composition profiles predicted by a rigorous nonequilibrium model that incorporates the MS equations may differ significantly from those predicted by an equilibrium stage model. Consider the experimental work of Springer *et al. (15)* on the distillation of water (1), ethanol (2) and acetone (3) carried out in a 10-tray column operated at total reflux. The residue curve map for this system is shown in Figure 10a. This system shows a binary minimum boiling azeotrope between water and ethanol; an almost-straight distillation boundary connects the azeotrope with pure acetone.

A measured composition profile, carried out in the region to the left of the distillation boundary, is shown in Figure 10b. Simulations of the column, starting with the vapor composition at the column top, are also shown. It is evident that the nonequilibrium model is able to follow the experimentally observed column trajectories much better than the equilibrium model. The differences in the column composition trajectories are due to differences in the component Murphree efficiencies (Figure 10c).

Differences in component efficiencies could have a significant impact on a column design that aims for a specific purity at either ends of the column. For example, for the water (1), ethanol (2) and acetone (3) system operat-
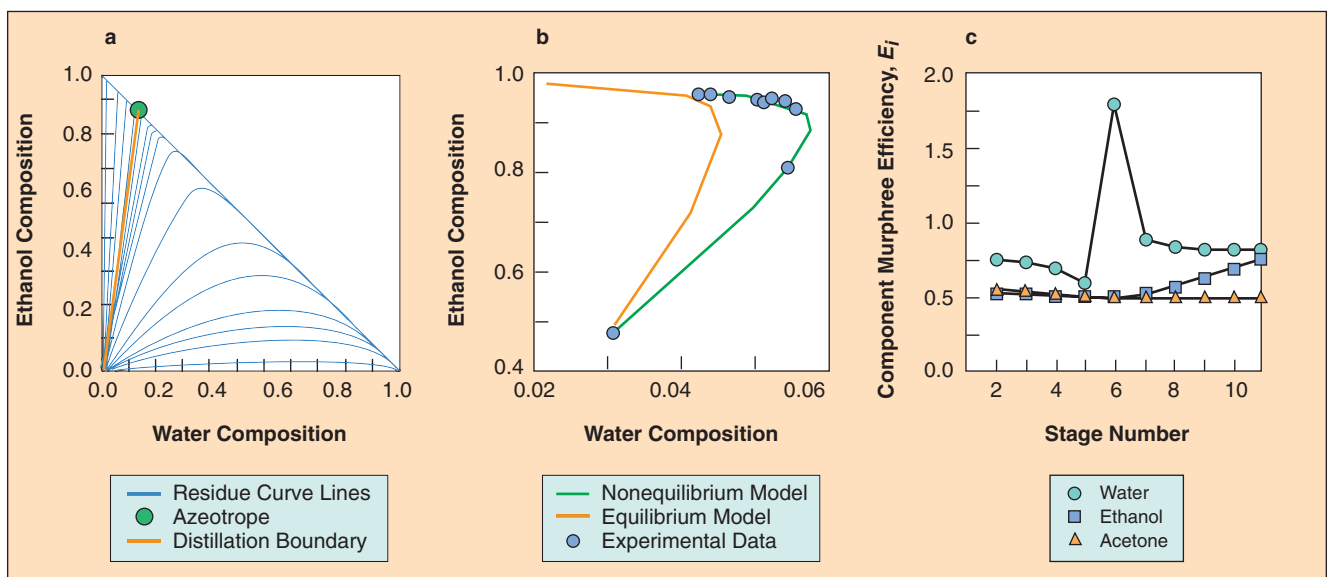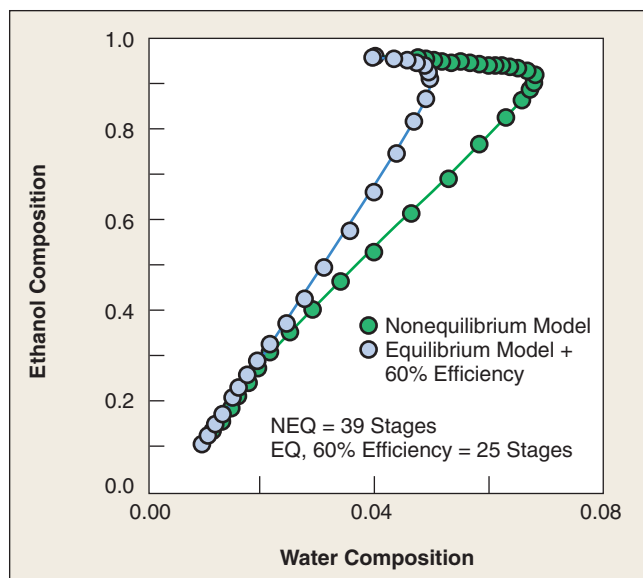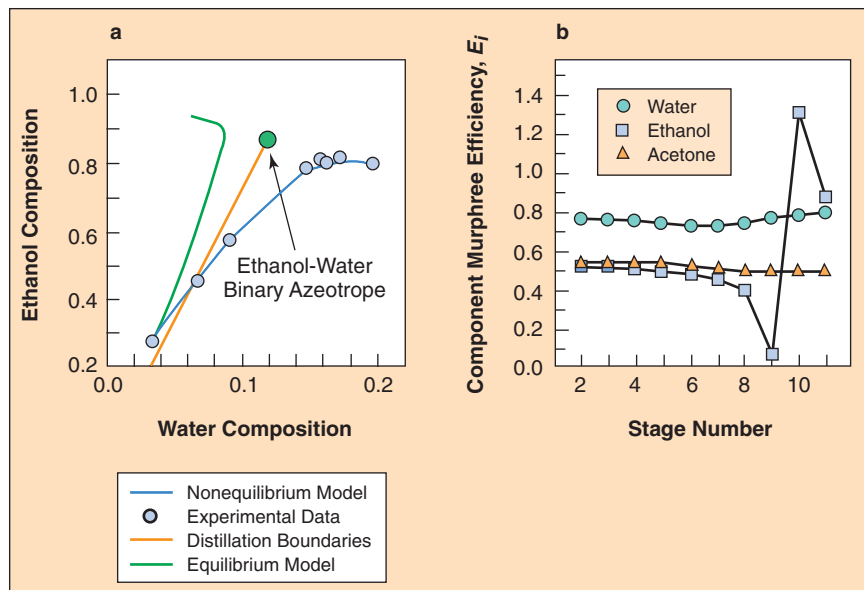

■ Figure 10. Distillation of water (1), ethanol (2) and acetone (3) in a bubble cap tray column: (a) residue curve map; (b) experimental composition trajectory for Run 6, compared with the nonequilibrium and equilibrium simulations; and (c) component Murphree efficiencies for Run 6 (15).

■ Figure 11. Comparison of nonequilibrium and equilibrium models for distillation of water (1), ethanol (2) and acetone (3) in a bubble cap tray column with the objective of reaching 96% ethanol purity at the top.

■ Figure 12. Distillation of water (1), ethanol (2) and acetone (3) in a bubble cap tray column: (a) experimental composition trajectory for Run 26, compared with the nonequilibrium and equilibrium simulations; and (b) Component Murphree efficiencies for Run 26 (15).

ing in the region to the left of the distillation boundary, let us demand a purity of 96% ethanol at the top of the column. For a specified feed composition and reflux ratio, the column composition trajectories for the nonequilibrium model and the equilibrium model (assuming 60% efficiencies for all components) are presented in Figure 11. The nonequilibrium model suggests that 39

stages are needed to reach the specified 96% ethanol purity at the top, whereas the equilibrium model indicates that only 25 stages are needed. In this case, the nonequilibrium model takes "the scenic route" to reach the desired top purity. Ignoring the differences in component efficiencies may lead to severe underdesign.
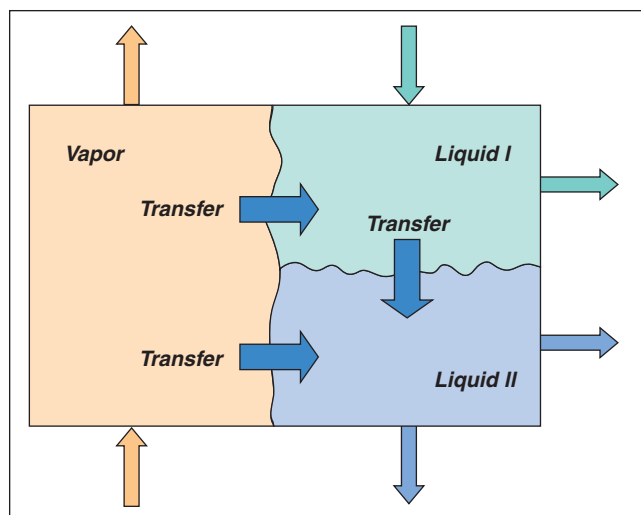
Columns operating close to the distillation boundary may experience much more exotic differences in the column composition trajectories predicted by the nonequilibrium and equilibrium models. For operation with the same water, ethanol and acetone system, Figure 12a shows that the experiments cross the straight-line distillation boundary (15), something that is forbidden by the equilibrium model (16). The nonequilibrium model is able to retrace this boundary-crossing trajectory, whereas the equilibrium model remains on one side of the distillation boundary. The nonequilibrium model predicts that the column gets progressively richer in water as we proceed down the column to the reboiler, whereas the equilibrium model anticipates that the column gets enriched in ethanol as the reboiler is approached. The root cause of this behavior lies with the differences in the efficiencies of the individual species (Figure 12b); the component efficiency of ethanol varies significantly from tray to tray. Comparing the component efficiency values in Figures 10c and 12b reveals that even though the mass transfer parameters used in the nonequilibrium model are identical for these two runs, the calculated component efficiency values bear no resemblance to one another. This underlines the difficulty of trying to emulate the performance of the nonequilibrium model by fudging component efficiency values. There is no way that this can be achieved.

Other applications

The principles outlined above are applicable to a wide range of related processes. Below, we very briefly consider some of these applications.

Three-phase distillation. Three-phase distillation remains relatively poorly understood compared to conventional distillation operations involving just a single liquid phase. Simulation methods currently in use for three-phase systems employ the equilibrium stage model (16). It is important to be able to correctly predict the location of the stages where a second liquid phase can form (to determine the appropriate location for a sidestream decanter, for example). The limited experimental data available suggest that efficiencies can be low and highly variable. Clearly, a model based on the assumption of equilibrium on every

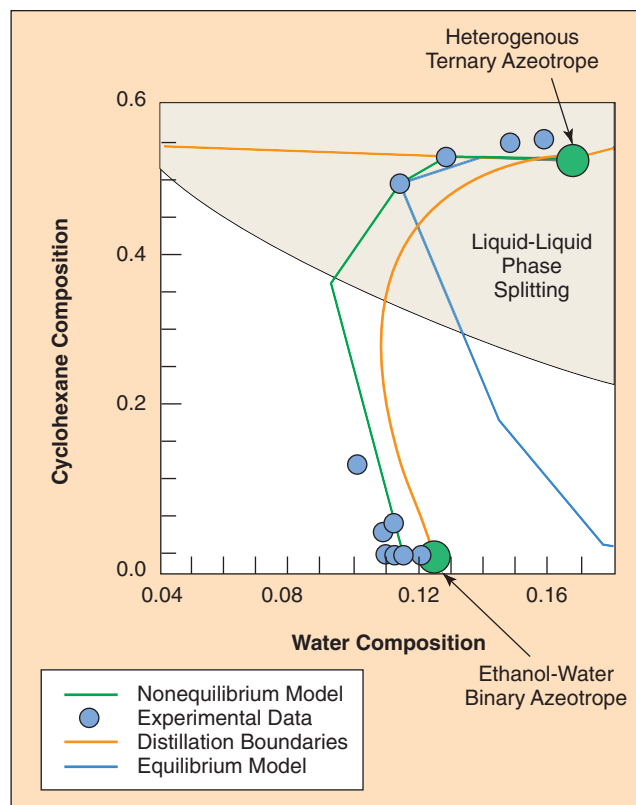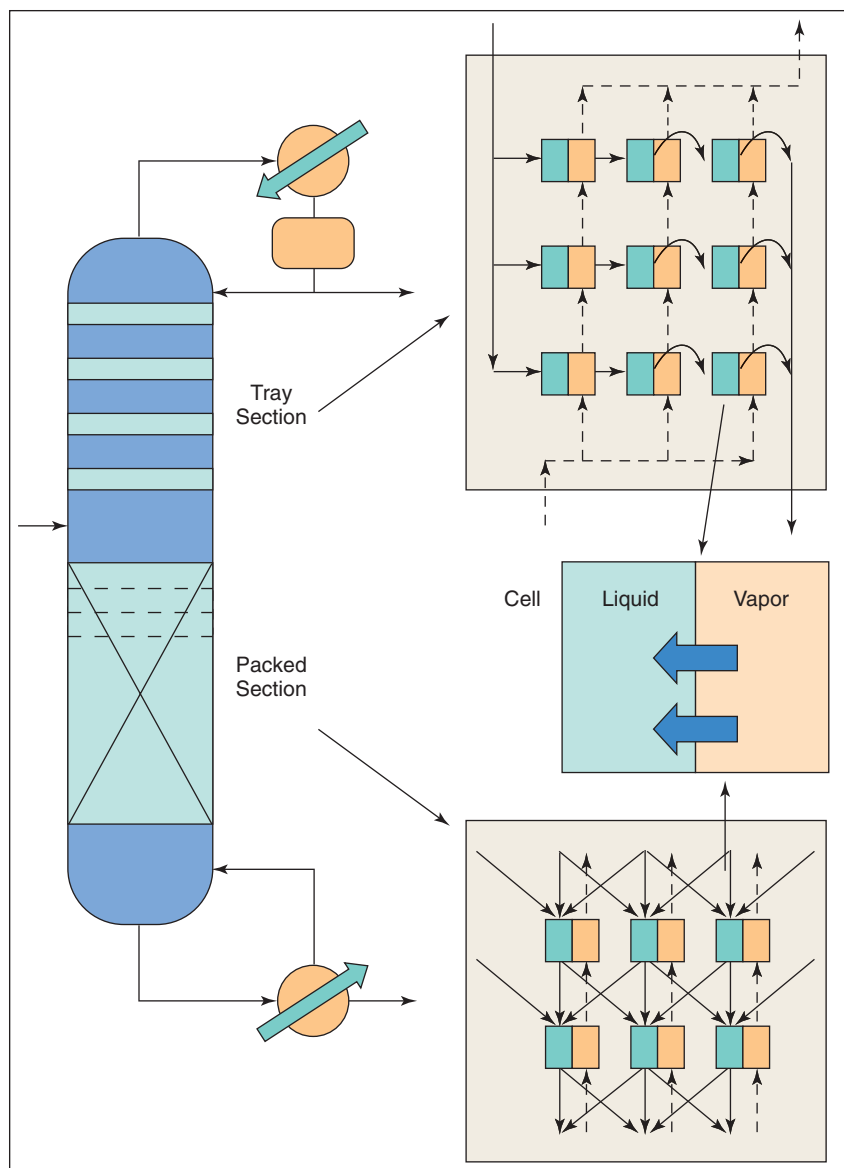■ Figure 13. Schematic representation of a three-phase nonequilibrium stage.

■ Figure 14. Distillation of water (1), cyclohexane (2), ethanol (3) and acetone (3) in a bubble cap tray column: experimental composition trajectory, compared with the nonequilibrium and equilibrium simulations (17).

stage cannot predict column performance. Springer and others *(17)* stress the limitations of simulation models assuming equal Murphree efficiencies for all components in the mixture.

It is straightforward in principle to extend the ideas that underlie nonequilibrium models to systems with more than two phases, as first shown by Lao and Taylor *(18)*. A complete nonequilibrium model for the system depicted in Figure 13 contains three phase balances, each of which contains terms for mass transfer to or from both of the other two phases. In addition, the model contains up to six sets of the MS equations, two for each phase boundary (vapor–liquid I, vapor–liquid II, and liquid I–liquid II). Three sets of equilibrium equations, one for each possible interface, complete the model. In practice, it is quite likely that the vapor phase and a dispersed liquid phase see only a continuous liquid phase, thereby considerably simplifying the model *(17)*.

Example 4. Heterogeneous azeotropic system. Sometimes the curvature of the distillation boundary is such that its crossing by the equilibrium stage model is allowable *(16)*. This is illustrated in Figure 14 for the water (1), cyclohexane (2) and ethanol (3) system. For a column operating at total reflux with the top composition corresponding to the heterogenous ternary azeotrope, the equilibrium model has no difficulty crossing the curved distillation boundary from the convex side, moving in the direction of high water compositions and proceeding down the column. However, the experimental data of Springer *et al. (17)* show that the boundary is not crossed in practice and the column composition trajectories are anticipated very well by a nonequilibrium model.

Reactive distillation. The design and operation issues for reactive distillation processes are considerably more complex than those of either conventional reactors or conventional distillation columns. The introduction of an *in situ* separation function within the reaction zone leads to complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalyzed processes) and chemical kinetics. For such systems, the chemical reaction influences the efficiencies to such an extent that the concept loses its meaning *(19)*.

Building a nonequilibrium model of a reactive separation process is not as straightforward as building an equilibrium stage model, in which we simply add a term to account for reaction to the liquid-phase material balances. It must be recognized that no single nonequilibrium model can deal with all possible situations. Separate models are needed depending on whether the reaction takes place within only the liquid phase or if a solid phase is present to catalyze the reaction. Refer to Refs. 16, 19 and 20 for further discussion.

Gas absorption. Efficiencies in gas absorption tend to be much lower than in distillation, sometimes as low as 5%. In addition, many important gas absorption processes involve chemical reactions. It does not seem to

■ Figure 15. The nonequilibrium cell model.

in the liquid phase). Models of this sort have been used with some success in the modeling of amine-based gas treating processes *(22)*.

Distillation column dynamics. One of the key points of this article is that nonequilibrium models should be used when efficiencies are unknown, cannot be reliably predicted, and are low and/or highly variable. Efficiencies in any process depend strongly on the properties of the mixture, whether or not chemical reactions are involved, and (last, but by no means least in importance) the type of column employed and the way in which it is operated. If a column is not at steady state, then efficiencies vary with time as a result of changes to flowrates and composition. Thus, equilibrium stage models with efficiencies should not be used to model the dynamic behavior of distillation and absorption columns. Nonequilibrium models for column dynamics are described in Refs. 23–25.

Nonequilibrium cell model. An issue that is not adequately addressed by most models is that of vapor and liquid flow patterns on distillation trays or maldistribution in packed columns. Since reaction rates and chemical equilibrium constants depend on the local concentrations and temperature, they may vary along the flow path of liquid on a tray, or from side to side in a packed column. For such systems, the residence time distribution could be very important.

To deal with this shortcoming of earlier models, nonequilibrium cell models have been developed *(26–28)*. The distinguishing feature of this model is that the stages are divided into a number of contacting cells (Figure 15). These cells describe just a small section of the tray or packing, and by choosing an appropriate set of cell connections, one can very easily study the influence of flow patterns on the distillation process.

Flow patterns on distillation trays are modeled by choosing an appropriate number of cells in each flow direction. A column of cells can model plug flow in the vapor phase, and multiple columns of cells can model plug flow in the liquid phase as depicted in Figure 15. Backmixing may also be taken into account by using an appropriate number of cells. Flow patterns in packed columns are evaluated by means of a cell flow model *(27)*.

make a great deal of sense to employ an equilibrium stage model for systems so far removed from equilibrium. In fact, although equilibrium stage models for such systems are used, it has long been more common to use mass-transfer-rate-based models to design gas absorption processes *(21)*. Nonequilibrium models apply more or less unchanged in principle to gas absorption (with or without reaction). The only differences between the models are the inclusion of different sub-models for the reaction kinetics and thermodynamic properties. Many absorption processes involve dilute mixtures, and the rate relationships in Eqs. 2 and 3 suffice (the latter modified by the inclusion of an enhancement factor to account for any chemical reaction

Available software

AspenTech developed RateFrac, in collaboration with Koch Engineering, Inc. This implementation is based largely on the nonequilibrium model described in the original papers by Krishnamurthy and Taylor *(29, 30)*, with the important additional capability of being able to handle systems with chemical reactions. The influence of reaction on mass transfer is modeled by means of enhancement factors. RateFrac has one mass-transfer coefficient model for each type of column internal, but it has the facilities to add user models for the calculation of transfer coefficients, pressure drop and interfacial area. RateFrac can use any of the thermodynamic packages that exist within AspenPlus, and can model columns with sidestreams, interstage heaters/coolers and pumparounds. Complex specifications can designated for product purity or internal streams. RateFrac is especially useful for modeling columns with chemical reactions that influence the separation. Illustrations of the use of RateFrac are described in Seader and Henley *(9)*. For more information, visit www.aspentech.com/includes/product.cfm?IndustryID=0&ProductID=110

CHEMCAD from Chemstations, Inc. (www.chemsta-

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Further Reading

For further reading, visit www.chemsep.org/publications

tions.net) contains a nonequilibrium model for both steady-state and dynamic simulation.

ChemSep *(31)* incorporates some of the most recent developments in nonequilibrium modeling. Many correlations for the mass-transfer coefficients, interfacial area and flow models are built into ChemSep. It also contains a variety of thermodynamic and physical property models. ChemSep can also provide a detailed design of the equipment selected for the simulation. This allows the program to simulate columns for preliminary design purposes. It has a limited component library but allows the user to add components with a databank manager. ChemSep is available through CACHE (www.cache.org) for educational use only. Applications of ChemSep are discussed in Refs. 9, 14, 31. For more information, visit www.chemsep.org.

Many other models have been implemented primarily for research purposes and are not available to others.

Conclusion

Within the last two decades, a new way of simulating multicomponent distillation operations has come of age. These nonequilibrium, or rate-based, models abandon the idea that the vapor and liquid streams in a distillation column ever are in equilibrium with each other. The idea of modeling distillation as a mass-transfer-rate-based operation is hardly new. Equations 2 and 3 (albeit in different units) actually appear in the classic paper by E.V. Murphree *(2)* that introduced us to efficiencies. Murphree went so far as to say: "the use of the general [mass-transfer] equation in rectifying column problems would cause the calculations to become very much involved, and it is therefore not considered feasible for practical purposes." Nowadays, such calculations not only are feasible, there are circumstances where they should be regarded as mandatory.

Of course, models based on equilibrium stage concepts will not be abandoned, nor is there any need for us to do so. For design of new columns in which the column configuration is not fixed, it is best to start with the equilibrium model to determine the configuration, optimum reflux ,etc. *(16)*. The final design should be checked against the nonequilibrium model because, as we have seen, it is possible for the predictions of the nonequilibrium model to differ considerably from those of the equilibrium model.

Nonequilibrium models are of great value in simulating existing columns. No longer is it necessary to guess the number of equilibrium stages, the location of the feed and any intermediate product streams, and the individual component efficiencies in order to try and model a column that no longer is performing as intended.

Reactive distillation is an emerging application that has introduced additional complications. Here it is not uncommon to assume equilibrium with regard to mass transfer, but allow for finite reaction rates. This is fine for conceptual design. But for equipment sizing, the problem of determining column heights remains. For reactive distillation,

HETPs and efficiencies have no physical meaning, as these are also influenced by reaction.

Rigorous nonequilibrium models require the use of the MS equations to properly describe mass transfer in multicomponent systems. These equations have, in fact, been with us for much longer than has the equilibrium stage model (see Ref. 11 for original citations). The application of the MS equations to modeling mass transfer in distillation is also not all that recent. Lewis and Chang *(32)*, in a remarkably prescient paper that appears to have been largely ignored, used the MS equations to investigate the mechanism of rectification. They wrote: "engineers generally are unfamiliar with them" — a situation that has persisted until relatively recent times. Not only do the MS equations allow us to model mass transfer in conventional operations like distillation, absorption and extraction, they also describe transport in many less common separation processes, such as membrane processes. Indeed, the MS formulation of mass transfer provides a rational basis for unifying the treatment of separation processes *(33)*.   **CEP**

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