Prediction of Efficiencies and Mass Transfer on a Stage with Multicomponent Systems

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In this paper methods are developed for predicting total transfer rates and efficiencies when systems of more than two components are contacted in equilibrium stage devices. The method is based on the linearized theory of multicomponent mass transfer which gives the point rates of mass transfer in a multicomponent system in terms of binary mass transfer coefficients and the physical properties of the multicomponent system when concentration differences are small enough so that all concentration dependent properties may be treated as constant (*5, 6*). The results of the theory follow. (The results are stated in terms of vapor-liquid systems. With minor modifications they also apply to liquid-liquid systems.)

The rate of transfer across the interface from the vapor to the liquid at any point in an $n + 1$ component system in terms of the overall driving force based on the vapor phase is in vector-matrix notation (*6*)

$$(N) = [K_y]\{(\bar{y}) - (y^*)\} \tag{1}$$

where

$$(N) = \begin{pmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ N_n \end{pmatrix} \tag{2}$$

$$(\bar{y}) = \begin{pmatrix} \bar{y}_1 \\ y_2 \\ \cdot \\ \cdot \\ \bar{y}_n \end{pmatrix} \tag{3}$$

$$(y^*) = [M]\,(\bar{x}) \tag{4}$$

$$(\bar{x}) = \begin{pmatrix} \bar{x}_1 \\ \bar{x}_2 \\ \cdot \\ \cdot \\ \bar{x}_n \end{pmatrix} \tag{5}$$

and $[M]$ is the equilibrium constant matrix.

The overall mass transfer coefficient matrix $[K_y]$ is related to the individual vapor and liquid side mass transfer coefficient matrices by the equation

$$[K_y]^{-1} = [k_y]^{-1} + [M]\,[k_x]^{-1} \tag{6}$$

and $[k_y]$ and $[k_x]$ are obtained as follows. For constant physical properties and fixed geometry and hydrodynamics the binary mass transfer coefficients are given by

$$k_y = k_y(D_y) \tag{7}$$

$$k_x = k_x(D_x) \tag{8}$$

that is the binary mass transfer coefficient of a phase is a given function of the binary diffusion coefficient of that phase D_y or D_x. If the transfer at the interface is equimolal countercurrent, k_y and k_x may be taken as independent of the magnitude of the fluxes.

Now it has been shown (*5, 6*) that with the following assumptions (the concentration differences are small enough so that all physical properties, including the elements of the diffusion coefficient matrix, may be taken as constant within each phase; the individual mass transfer coefficient matrices obtained with constant interfacial concentrations are the same as those obtained under actual conditions; the individual mass transfer coefficient matrices do not depend upon the magnitude of the fluxes) the mass transfer coefficient matrices in the multicomponent system with the same hydrodynamics and geometry as in the above binary system are given by

$$[k_y] = k_y([D_y]) \tag{9}$$

$$[k_x] = k_x([D_x]) \tag{10}$$

where the matrix functions are given by Sylvester's theorem (*1, 6*), and $[D_y]$ and $[D_x]$ are the multicomponent diffusion coefficient matrices of the vapor and liquid respectively. The matrix $[D_y]$ is defined by the basic flux equation (*6*)

$$(\underline{j}) = -[D_y]\,(\nabla C) \tag{11}$$

where for the present work the reference velocity is taken to be the molar average. $[D_y]$ is a property of the gas mixture which may be obtained for mixtures of any number of ideal gases from the Maxwell-Stefan equations. The components of $[D_y]$, $D_{y\,ij}$ vary with composition, and by the first assumption these elements are taken as constant at some average composition. The errors introduced by this assumption do not appear to be serious (*5*).

$[D_x]$ may be defined by an equation similar to (12)[*] and is a property of the liquid mixture. There is no reliable method of predicting $[D_x]$ in general. So far only a few measurements exist (*5*) and these only for ternary liquids. A zero-order approximation is to take

$$[D_x] = D_{xm}I \tag{12}$$

where D_{xm} is a weighted average of the diffusion coefficients of the binary pairs. A first-order approximation for ternary mixtures is to use the empirical equation of Shuck and Toor developed for relatively ideal mixtures (*3*), but the only reliable method at present is direct measurement.

The second assumption above is implied by the binary Equations (7) and (8) which state that the mass transfer coefficient of each phase does not depend upon the diffusional behavior of the other phase. This assumption, which is generally made in binary work and is contained in essentially all mass transfer models, is not expected to cause serious errors.

The third assumption should be valid when the transfer is close to equimolal countercurrent (low total flux) and concentration differences are small. If the transfer cannot be treated as equimolal countercurrent, k_y and k_x depend upon the total flux at the interface and so do $[k_y]$

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[*] Strictly speaking D_x and $[D_x]$ are measured in a volume average reference frame, and they should be converted to the present molar average reference frame [and the correlation in Equation (8) adjusted accordingly]. This would only be worth doing if $[D_x]$ were known accurately.

and $[k_x]$. When the former relationships are known, the latter can be predicted (*5, 6*), but this added complexity is hardly justified at present.

It was pointed out earlier that the matrix functions in Equations (9) and (10) are defined by Sylvester's theorem. Hence $[k_y]$ in explicit form is (*1, 6*)

$$[k_y] = k_y([D_y]) = \sum_{l=1}^{n} k_y(D_{yl})\ [Z_o(D_{yl})] \tag{13}$$

where

$$[Z_o(D_{yl})] = \frac{\underset{j\neq l}{\pi}\ (D_{yj}I - [D_y])}{\underset{j\neq l}{\pi}\ (D_{yj} - D_{yl})} \tag{13a}$$

and the D_{yl}, $l = 1, 2. . , n$, are the characteristic roots of the matrix $[D_y]$. If any roots are repeated, the confluent form of Sylvester's theorem (*1, 6*) is used in place of Equation (13). The equation for $[k_x]$ is obtained by replacing y by x in the above equations.

It is to be noted that the $k_y\ (D_{yl})$ which appear in Equation (13) are the binary mass transfer coefficients which would be obtained for a binary diffusion coefficient of D_{yl}. Hence $[k_y]$ and $[k_x]$ are expanded in terms of the diffusion coefficient matrix and the n characteristic binary mass transfer coefficients (which have been called *combine* mass transfer coefficients) (*5, 6*). If for example Equation (7) has the form $k_y = bD_y^p$, where b and p are constants, then $k_y\ (D_{yl})$ in Equation (13) is $b\ D_{yl}^p$.

It is to be further noted that Equation (1) may now be written symbolically as

$$(N) = K_y([D_y], [D_x], [M])\ \{(\bar{y}) - (y^*)\} \tag{14}$$

and that it is a formal matrix generalization of the standard binary expression (*2*)

$$N_i = K_y\ (D_y, D_x, m_i)\ \{\bar{y}_i - y_i^*\} \tag{15}$$

This formal generalization is ubiquitous, as will be seen.

The above scheme then gives the rates of transfer across the interface in a multicomponent system in terms of the compositions, equilibrium constants, mass transfer coefficients, and physical properties of the two phases.

POINT EFFICIENCIES

One now wishes to integrate Equation (1) over the system. Consider first the transfer at a vertical plane on say a distillation tray. The liquid is assumed to be well mixed vertically.

Since G is constant, a material balance on each component gives

$$G\,d(\bar{y}) = -\ (N)a\,dh \tag{16}$$

and combination with Equation (1) gives

$$\frac{d(\bar{y})}{dh} = \frac{d(\bar{y} - y^*)}{dh} = -\ [K_y]\frac{a}{G}\ (\bar{y} - y^*) \tag{17}$$

If the entering bulk gas compositions are given by $\bar{y}_i(o)$ and the exit by $\bar{y}_i(e)$, and if $[K_y]a$ is taken as constant (small concentration changes), then the solution to Equation (17) is

$$(\bar{y}(e) - y^*) = \exp\{-[\mathcal{N}]\}\ (\bar{y}(o) - y^*) \tag{18}$$

where $[\mathcal{N}]$ the overall transfer unit matrix based on the vapor side is defined by

$$[\mathcal{N}] = [K_y]\frac{ah}{G} \tag{19}$$

and h is now the total height of liquid.

Equations (18) and (19) are straightforward generalizations of their binary counterparts (*2*). (The subscripts *oy* would have to be used on $\mathcal{N}$ if one wanted to be consistent with usual binary notation.) To continue the analogy with binaries define individual vapor and liquid side transfer units as

$$[\mathcal{N}_y] = [k_y]\frac{ah}{G} \tag{20}$$

$$[\mathcal{N}_x] = [k_x]\frac{ah}{G} \tag{21}$$

Then from Equations (19) through (21) and (6) obtain

$$[\mathcal{N}]^{1-} = [\mathcal{N}_y]^{-1} + [M]\frac{G}{L}[\mathcal{N}_x]^{-1} \tag{22}$$

and from Equations (20) and (13)

$$[\mathcal{N}_y] = \mathcal{N}_y([D_y]) = \sum_{l=1}^{n} \mathcal{N}_y(D_{yl})\ [Z_o(D_{yl})] \tag{23}$$

and similarly for the liquid phase.

Thus the exit compositions at a point are given in terms of $[\mathcal{N}]$ which is related to $[\mathcal{N}_y]$ and $[\mathcal{N}_x]$ which in turn are given in terms of the binary transfer units and the multicomponent diffusion coefficients by Equation (23) and its liquid counterpart. Note that in general there are n binary transfer units for the vapor $\mathcal{N}_y(D_{y1})$, $\mathcal{N}_y(D_{y2})$, . ., $\mathcal{N}_y(D_{yn})$ and n for the liquid, that $\mathcal{N}_y(D_{yl})$ is the number of vapor side transfer units which would be obtained in a binary system with a diffusion coefficient of D_{yl}, while $\mathcal{N}_x(D_{xl})$ is the number of liquid side transfer units in a binary system which has the diffusion coefficient D_{xl}.

Once $[\mathcal{N}]$ is obtained, the exponential in Equation (18) may be expanded in terms of the characteristic roots of $[\mathcal{N}]$ by Sylvester's theorem

$$\exp\{-[\mathcal{N}]\} = \sum_{l=1}^{n} \exp\{-\mathcal{N}_l\}\ [Z_o(\mathcal{N}_l)] \tag{24}$$

If the vapor side controls [see Equation (22)]

$$[\mathcal{N}] \rightarrow [\mathcal{N}_y] = \mathcal{N}_y([D_y])$$

and the expansion can then be carried out simply in terms of the characteristic roots of $[D_y]$. If liquid side controls, the behavior is analogous to the above.

The above results show that Equation (18) may be written as

$$(\bar{y}(e) - y^*) = \exp\{-\mathcal{N}([D_y],[D_x],[M])\}\ (\bar{y}(o) - y^*) \tag{18a}$$

which is the formal generalization of the analogous binary equation (*2*).

If the liquid and vapor composition and temperature are uniform across the tray, Equation (18) may be used directly for design. Otherwise further integration is needed. Before giving an example of the integration the point efficiency may be calculated.

In either case it is convenient to define an overall point vapor efficiency matrix by the equation

$$[\bar{y}(e) - \bar{y}(o)] = [E]\ [y^* - \bar{y}(o)] \tag{25}$$

By comparison with Equation (18)

$$[E] = I - \exp\{-[\mathcal{N}]\} \tag{26}$$

or in expanded form from Equation (24)

$$[E] = \sum_{l=1}^{n} \{1 - \exp\{-\mathcal{N}_l\}\}\ [Z_o(\mathcal{N}_l)] \tag{27a}$$

$$= \sum_{l=1}^{n} E(\mathcal{N}_l)\ [Z_o(\mathcal{N}_l)] \tag{27b}$$

with $[Z_o(\mathcal{N}_l)]$ given by Equation (13*a*) with D replaced by $\mathcal{N}$. Notice that the $E(\mathcal{N}_l)$ are the binary efficiencies which correspond to the roots $\mathcal{N}_l$.

Now define point multicomponent vapor efficiencies in the usual manner (*2*)

$$E^{(i)} = \frac{\overline{y_i}(e) - \overline{y_i}(o)}{y_i^* - \overline{y_i}(o)} \tag{28}$$

or

$$(\overline{y}(e) - \overline{y}(o)) = \begin{bmatrix} E^{(1)} & & & \\ & E^{(2)} & & \\ & & \cdot & \\ & & & \cdot \; E^{(n)} \end{bmatrix} (y^* - \overline{y}(o)) \tag{29}$$

and compare with Equation (25)

$$E^{(i)} = \sum_{j=1}^{n} E_{ij} \frac{y_j^* - \overline{y_j}(o)}{y_i^* - \overline{y_i}(o)} \tag{30}$$

The E_{ij} are the elements of $[E]$ which are obtained from Equation (27).

Equation (30) shows that the multicomponent efficiencies depend upon concentration differences as well as upon $[\mathcal{N}]$. Whenever there is coupling, that is if any of the cross diffusion $D_{y,\,ij}$, $D_{x,\,ij}$ or M_{ij} $(i \neq j)$ are not zero, E_{ij} $(i \neq j)$ will not be zero, and the efficiencies $E^{(i)}$ may differ markedly from the binary efficiencies.

In general the $E^{(i)}$ can be negative or greater than 100%, and the calculations given earlier (*4*), although less general than the present method, demonstrate the effects to be expected.

All the above results of course can be obtained in terms of the liquid side instead of the vapor side.

STAGE EFFICIENCIES

Overall tray efficiencies are obtained by integrating Equation (18) across the tray. Based on the results obtained so far one might expect that if property changes are small across the tray the result for any particular type of flow is just the vector-matrix generalization of the binary result for that flow. Thus if the gas enters the tray with a uniform composition, if the liquid flow across the tray is uniform vertically, if there is no diffusion or mixing in the flow direction, and if $[M]$ is constant, the direct generalization of the Lewis equation (Equation 239, reference *2*) is

$$(\overline{y}(e) - \overline{y}(o)) = \frac{L}{G}[M]^{-1}\left\{ e^{[M]\frac{G}{L}[E]} - I \right\} (y^*(e) - \overline{y}(o)) \tag{31}$$

Writing the material balances and integrating Equation (18) across the tray confirms this result. One expects other cases to come out the same way. In any case for any particular situation the integration is easily carried out, leading to the conclusion that the linearized multicomponent problem is solved once the binary problem is solved.

As before Equation (31) (or similar forms obtained for other types of flow) is best used directly for design calculations. If the Murphree vapor efficiency (*2*) of each component

$$\hat{E}^{(i)} = \frac{\overline{y_i}(e) - \overline{y_i}(o)}{y_i^*(e) - \overline{y_i}(o)} \tag{32}$$

is desired, then define a vapor stage efficiency matrix by writing Equation (31) as

$$(\overline{y}(e) - \overline{y}(o)) = [\hat{E}]\,(y^*(e) - \overline{y}(o)) \tag{33}$$

so

$$[\hat{E}] = \frac{L}{G}[M]^{-1}\left\{ e^{[M]\frac{G}{L}[E]} - I \right\} \tag{34}$$

and from Equations (32) and (33)

$$\hat{E}^{(i)} = \sum_{j=1}^{n} E_{ij} \frac{y_j^*(e) - y_j(o)}{y_i^*(e) - y_i(o)} \tag{35}$$

The conclusions concerning the behavior of these overall tray efficiencies are similar to those reached earlier concerning the point efficiencies.

Results analogous to those obtained in this study also apply to packed columns and other contacting devices. These will be considered later.

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NOTATION

a = interfacial area per unit volume, (ft.)$^{-1}$
b = constant
(C) = column vector whose elements are the concentration in the vapor phase
D_y = binary diffusion coefficient in vapor phase, sq.ft./hr.
D_x = binary diffusion coefficient in liquid phase, sq.ft./hr.
$[D_y]$ = diffusion coefficient matrix in vapor phase
$[D_x]$ = diffusion coefficient matrix in liquid phase
D_{yl} = characteristic roots of $[D_y]$, sq.ft./hr.
D_{xl} = characteristic roots of $[D_x]$, sq.ft./hr.
E = point vapor efficiency
$E^{(i)}$ = point vapor efficiency of species i
$[E]$ = point vapor efficiency matrix
E_{ij} = elements of $[E]$
$\hat{E}^{(i)}$ = Murphree vapor stage efficiency of species i
$[\hat{E}]$ = vapor stage efficiency matrix
$\hat{E}_{ij}$ = elements of $[\hat{E}]$
G = superficial molar mass velocity of vapor, lb. moles/hr.sq.ft.
h = height of liquid, ft.
I = identity matrix
$(\underline{j})$ = column vector whose elements are fluxes with respect to molar average velocity
k_x = mass transfer coefficient of liquid phase, lb. moles/hr.sq.ft.
k_y = mass transfer coefficient of vapor phase, lb. moles/hr.sq.ft.
$[k_x]$ = multicomponent mass transfer coefficient matrix of liquid phase
$[k_y]$ = multicomponent mass transfer coefficient matrix of vapor phase
K_y = overall mass transfer coefficient based on vapor phase, lb. moles/hr.sq.ft.
$[K_y]$ = overall multicomponent mass transfer coefficient matrix based on vapor phase
L = superficial molar mass velocity of liquid, lb. moles/hr.sq.ft.
m_i = binary vapor-liquid equilibrium constant of species i
M_{ij} = elements of $[M]$
$[M]$ = multicomponent equilibrium constant matrix
n = number of components minus 1
N_i = flux of species i at the interface with respect to a fixed coordinate, lb. moles/hr.sq.ft.
(N) = column vector with elements N_i

$\mathcal{N}_x$ = number of liquid phase transfer units
$\mathcal{N}_y$ = number of vapor phase transfer units
$[\mathcal{N}_x]$ = liquid phase transfer unit matrix
$[\mathcal{N}_y]$ = vapor phase transfer unit matrix
$\mathcal{N}$ = number of overall vapor transfer units
$[\mathcal{N}]$ = overall vapor transfer unit matrix
$\mathcal{N}_i$ = characteristic roots of $[\mathcal{N}]$
p = constant
x_i = mole fraction of species i in liquid
(x) = column vector whose elements are x_i
y_i = mole fraction of species i in vapor
(y) = column vector whose elements are y_i
$(y(o))$ = column vector whose elements are the mole fractions in the vapor entering the stage
$(y(e))$ = column vector whose elements are the mole fractions in the vapor leaving the stage
y_i^* = mole fraction in equilibrium with $\bar{x}_i$
(y^*) = column vector whose elements are y_i^*
$(y^*(e))$ = column vector whose elements are the mole fractions in vapor in equilibrium with liquid leaving the stage
$[Z_o]$ = matrix defined by Equation (13*a*)
( ) = column vector of order n
[ ] = square matrix of order n

Superscripts

$-$ = bulk average value

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Application of Benedict-Webb-Rubin Equation of State to Hydrogen Sulfide-Hydrocarbon Mixtures

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The BWR equation of state relates pressure, volume, temperature, and composition of gaseous systems. Used in conjunction with a computer the equation is an important tool for making engineering calculations. The equation is intended for use in a region up to twice the critical density. As an example for a typical natural gas twice the critical density corresponds to about 6,000 lb./sq. in. abs. at 200°F.

The simplest form of the BWR equation is

$$P = RTd + \left(B_oRT - A_o - \frac{C_o}{T^2} \right) d^2 + (bRT - a)d^3 + a\,\alpha\, d^6 + \frac{cd^3}{T^2}(1 + \gamma d^2) \exp(-\gamma d^2) \tag{1}$$

Equation (1) can be used for pure compounds when the constants are known. In order to apply the equation to mixtures it is necessary to calculate the constants for the mixtures from the constants for the pure compounds contained in the mixtures. The rules for combining constants can be found in the literature (*4*). The Lorentz form of the combination rule for B_o was used in this work.

The constants for light hydrocarbons, nitrogen, carbon dioxide, and miscellaneous other compounds have been developed previously (*1, 2, 3, 4, 8*).* However a satisfactory set of constants for hydrogen sulfide in hydrogen sulfide-hydrocarbon systems has not been published. Because of the need to predict performance of sour gas reservoirs and to calculate the behavior of sour gases in absorption plants, pipe lines, compressors, etc., the authors have developed a set of hydrogen sulfide constants. These constants were developed by a mathematical analysis of experimental data and the results are presented in the following sections.

PROCEDURE

The procedure which was used to develop the BWR constants for hydrogen sulfide consisted of three principal steps:

1. Select experimental data from hydrogen sulfide-methane system.
2. Calculate the constants to fit these data.
3. Evaluate the constants for use in multicomponent systems.

1. The hydrogen sulfide-methane system was chosen as the basis for the constants because studies by the authors showed that the available experimental data for this system (*5*) were more accurate than the data available for other binary or multicomponent systems. Also the use of the constants for engineering calculations will generally be for gases with a high concentration of methane.

The data were chosen to cover the range of pressures from 600 to 5,000 lb./sq.in.abs. and temperatures from 160° to 280°F. Two different hydrogen sulfide-methane compositions were used with seven different pressures and three different temperatures to give a combination of forty-two data points.

2. By using the hydrogen sulfide-methane data described above with the BWR constants for methane (*2*) and the mixture rules the authors calculated a set of hydrogen sulfide constants which gave the best results. By best results is meant a minimum value of the sum of the squares of the difference between observed and computed pressures divided by the observed pressures. This function will be referred to as the *object function* and can be written as

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* Incorrect values of A_o for n-hexane and isopentane have been published. The correct values are n-hexane: A_o = 54,443.4, isopentane: A_o = 48,253.6