MATHEMATICAL MODELING OF DISTILLATION OPERATION

FROM NON-EQUILIBRIUM APPROACH

BY

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FROM NON-EQUILIBRIUM APPROACH

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ABSTRACT


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Dissertation directed by:

Dr. Ching-Rong Huang
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A new method for mathematical modeling of a distillation
operation from non-equilibrium approach has been studied.
The primary purpose of the study was to develop a model to
simulate the mechanism of mass transfer between a continuous
phase and the bubbles of a dispersed phase in a distillation
column.  The second major purpose of this work was to utilize
and test the model of estimating the tray efficiency.

Distillation was considered to be purely a mass trans-
fer process, where the less volatile component is transferred
from vapor to liquid phase, and the more volatile component

from liquid to vapor phase. The theoretical analysis of mass transfer consisted of (1) convective mass transfer during bubble formation and (2) unsteady-state molecular diffusion of bubbles to the continuous phase. In a plate column, plug flow was assumed as the liquid flow pattern across the plate, from the submerged inlet weir to the overflow outlet weir. The material and energy balances were modeled to a section perpendicular to the direction of liquid flow on the plate.

The model was used in studying the following: (1) a binary separation using a one-stage column having a single-bubble cap; (2) a binary separation in a multi-stage column with a single-bubble cap; (3) a binary separation in a multi-stage column with a given multi-cap arrangement; and (4) a ternary separation in a multi-stage column with two-bubble caps. The comparisons of the model predictions, with the data obtained from published literature, showed that the model can successfully simulate distillation operations.

# ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

The use of distillation as a separation and purifica-
tion process is very common in the petroleum and chemical
industries.  Distillation is an operation which separates
the components of a mixture based on the differences in
their vapor pressures and volatilities.  It is a typical
mass transfer process which consists of certain design of
trays or packings that bring the gas into intimate contact
with the liquid.  Separation can be obtained by repeating the
vaporization and condensation steps.  The ultimate application
of distillation is for the purpose of separating binary or
multi- components in a mixture to produce products which meet
certain specifications.

The energy and mass-transfer processes in an actual
distillation column are very complex.  The difficulty of
the process is avoided by creating a hypothetical column
whose contact stages are ideal equilibrium stages as shown
in Figure 1.  By deffinition, the vapor and liquid phases,
leaving an equilibrium stage, are in complete equilibrium
with each other from a thermodynamic point of view.  Thermo-

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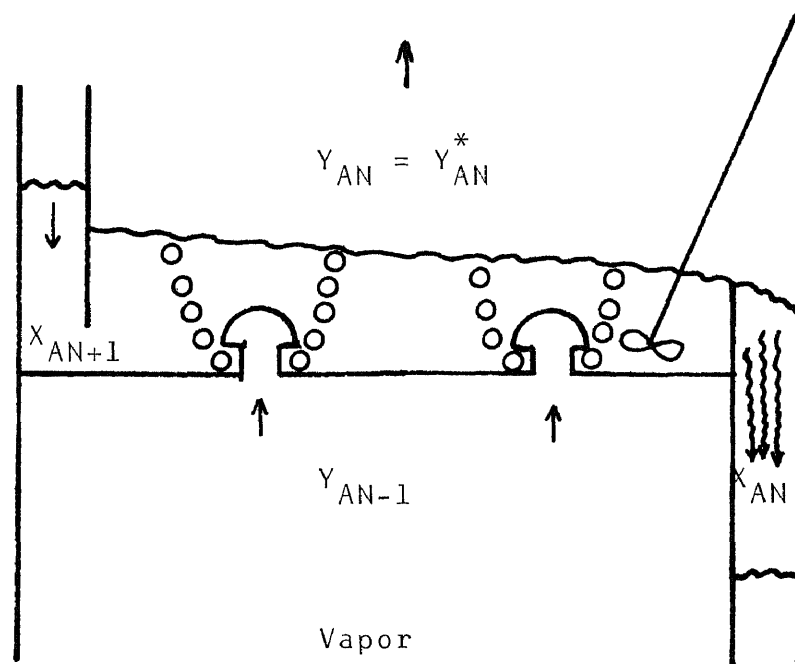
Fig.1    Sketch of a hypothetical ideal bubble-cap tray.

ic relationships can be used to relate the concentrations

ese two equilibrium phases.  These concentrations of

s, leaving a hypothetical equilibrium stage, must be

cted by introducing the tray efficiency.  The Murphree

iency is defined as:

$$E_G = \frac{Y_{N-1} - Y_N}{Y_{N-1} - Y_N^*}$$
(1-1)

$Y_{N-1}$ : vapor concentration to tray

$Y_N$   : vapor concentration from tray

$Y_N^*$  : vapor concentration in equilibrium with liquid.

efficiency compares the separation actually reached in

. stage to the separation that can possibly be reached

ideal equilibrium stage.


'igure 2 illustrates the location of a pseudo-equilib-

urve.  This curve is used in place of the true equilib-

elationship by means of Murphree efficiency to deter-

he compositions of phases leaving a real stage.  There-

it is important, that this mass transfer operation must

en into account in predicting stage efficiencies.

investigators focused on the effects of physical pro-

s and vapor-liquid equilibria on tray efficiencies.

st known correlations were proposed by Drickamer and

rd (10), where tray efficiency was related to average

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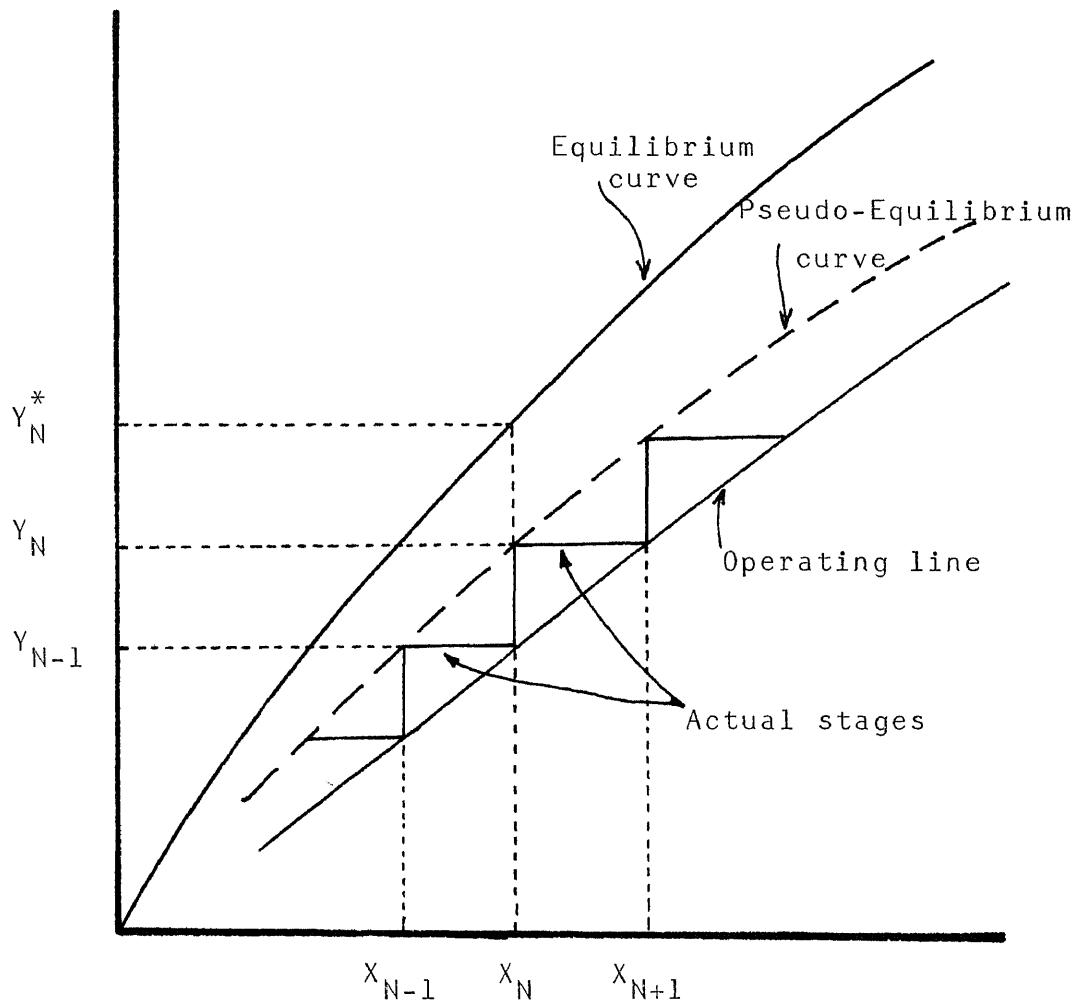
Fig. 2    Location of the pseudo-equilibrium curve showing
          the Murphree plate efficiency and determination
          of actual stages.

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liquid viscosity; and O'Connell(26), who examined the effects of relative volatility on tray efficiency.

This study considers the distillation operation which involves mass transfer between a continuous phase and a dispersed pahse. These two phases are intimately mixed, which can be achieved by using a bubble cap tray, a sieve tray, or a perforated tray. The work combines the effects of physical properties, vapor-liquid equilibria, and tray hydraulics in a mass transfer model. The theoretical analysis of this model consists of mass transfer by (1) convective mass transfer during bubble formation, and (2) unsteady-state molecular diffusion of bubbles to the liquid phase. In a tray column, plug flow is assumed as the liquid flow pattern across the plate, from the submerged inlet weir to the overflow outlet weir. The material and energy balances are modeled to a section perpendicular to the direction of liquid flow on the plate. The vapor-liquid equilibrium relationship assumes that the vapor phase is ideal (Dalton's and Raoult's laws are applicable) and that the liquid phase can be theoretically represented by the UNIFAC (11) method. As for necessary physical properties, empirical correlations are used in estimating diffusivity, density, viscosity, enthalpy, etc.

Chapter Two deals with the mathematical analysis in the separation of binary and multicomponent mixtures. The method in predicting the stage efficiency is also discussed. Chapter Three presents the results and conclusions of the study that the model is applied in the following operations: (1) a binary separation using a one-stage column having a single-bubble cap; (2) a binary separation in a multi-stage column with a single-bubble cap; (3) a binary separation in a multi-stage column with a given multi-cap arrangement; and (4) a ternary separation in a multi-stage column with two-bubble caps. Some recommendations are made in Chapter Four. The objective of this thesis is to develop a model that represents the distillation operation, and ultimately using this model to predict the stage efficiency.

CHAPTER II


THEORY


A large portion of chemical engineering design is con-

cerned with separation operations.  Many of these are diffu-

sional operations of the phase-contacting type such as dis-

tillation, absorption and extraction.  In distillation, the

less volatile component is transferred from the vapor to the

liquid phase.  These two phases are intimately mixed and then

separated and led independently to the adjacent stages.  The

intimate contact between phases can be achieved by using a

bubble-cap tray, a sieve tray, or a variable orifice tray.

Figure 3 schematically illustrates the vapor is issued from

the slots in a bubble-cap.  The mass-transfer mechanism con-

sists of two parts: (1) mass-transfer during bubble formation,

and (2) mass-transfer during bubble rising.  It is generally

assumed that the mass exchange rate during bubble formation

is significant.  Therefore, it is most important to take

this into account.  However, this transfer mechanism is very

complex, it is far beyond the knowledge to obtain an analy-

tical solution to represent this phenomenon.  An empirical

correlation developed by Skelland (36) is used to calculate

the mass exchange rate during bubble formation which will be
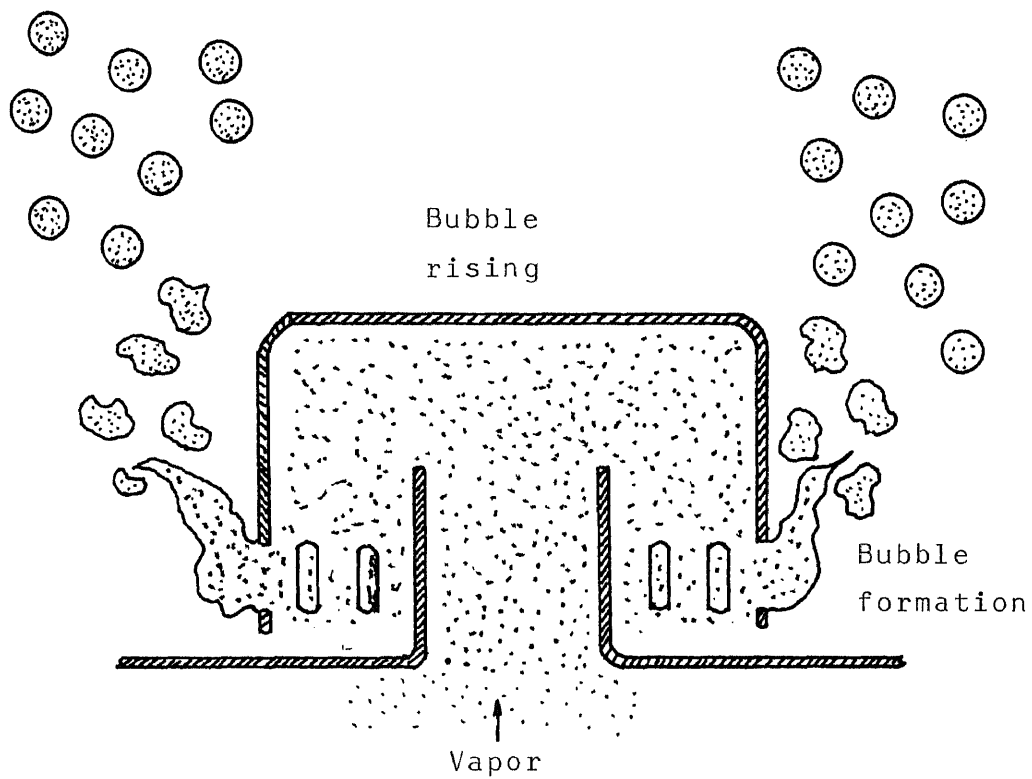
Fig. 3 Schematic illustration of gas issuing from
a slot in a bubble-cap.

discussed in Section C.  The mass-transfer during bubble rising
can be split into two parts, the transfer of a binary system
and the transfer of a multicomponent mixture.  The subjects
are discussed in Section A and Section B respectively.


A.  Mathematical Modeling Of Unsteady-State Mass-Transfer
    From A Spherical Gas Bubble To Liquid Media Of A Binary
    System


During bubble rising, a less volatile component transfers
from liquid to vapor phase, and a more volatile component simul-
taneous transfers back into the vapor phase.  The discontinuous
phase may be regarded as the spherical bubbles, in which mass-
transfer occurs by unsteady-state molecular diffusion as shown
in Figure 4.  The following assumptions are made:

1.  The concentration of solute (component A, which is
    a heavier component or a less volatile component) is
    uniform at $C_{AO}$ throughout the sphere at the start of
    diffusion (t = 0).

2.  Diffusion is radial, there is no variation in con-
    centration with angular position, and physical pro-
    perties are constant.

3.  The resistance to transfer in the media surrounding
    the sphere is considered, so that at the surface of
    the sphere, there is a gas film resistance.

4.  At the vapor-liquid interface, gas phase concentration
    is in equilibrium with the concentration of bulk
    liquid phase.

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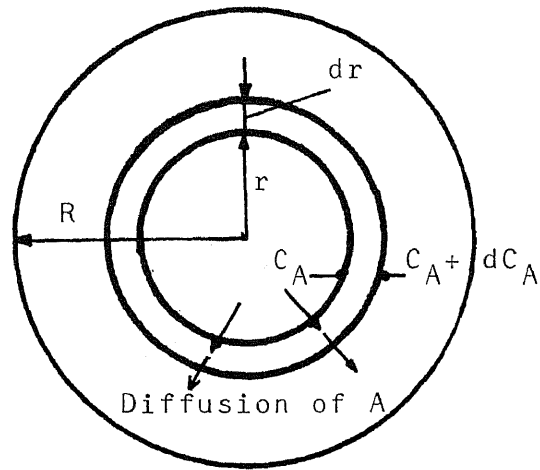
(a)
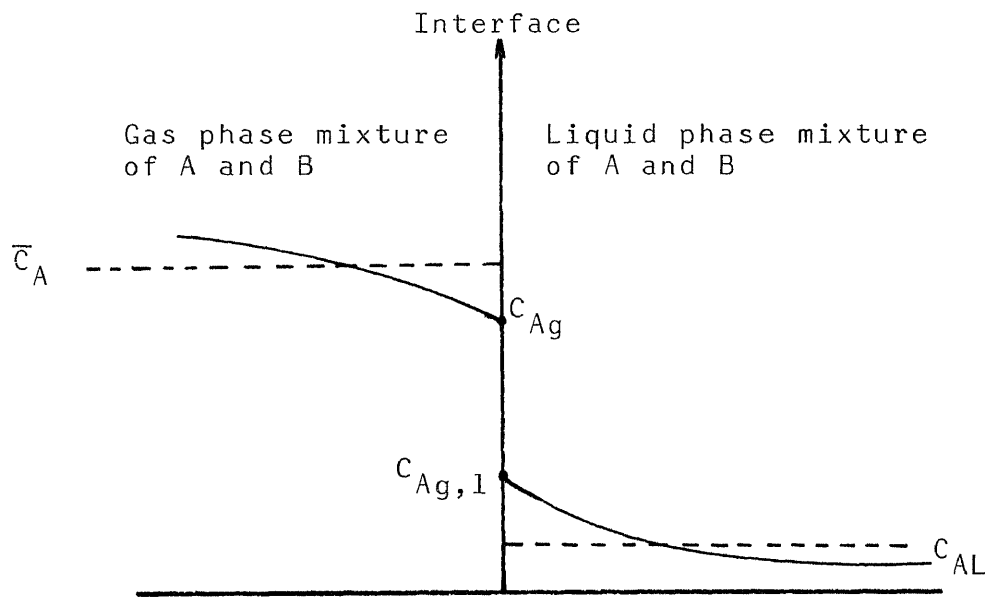


(b)

Fig. 4    (a) Section of a sphere in which mass transfer is
          occuring by unsteady-state molecular diffusion;
          (b) concentration profile of A (heavier component)
          in the neighborhood of a gas-liquid interface.

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By referring to Figure 4, the center of the sphere is the origin of coordinates; the concentration at the surface of radius r is $C_A$, and at the surface r+dr is $C_A + dC_A$. A control volume is defined as a region between these two surfaces at r and r+dr. The rate of solute A flows into the control volume is

$$-D(4\pi r^2)\frac{\partial C_A}{\partial r} \qquad (2-1)$$

where D is the diffusivity coefficient. The rate of solute A flows out the control volume is

$$-D(4\pi(r+dr)^2)\left(\frac{\partial C_A}{\partial r} + \frac{\partial}{\partial r}\left(\frac{\partial C_A}{\partial r}\right)dr\right) \qquad (2-2)$$

The net flow rate of solute A into the control volume is obtained by subtracting equation (2-2) from equation (2-1), the result is

$$4\pi D\left(r^2\frac{\partial^2 C_A}{\partial r^2}dr + 2r\frac{\partial C_A}{\partial r}dr\right) \qquad (2-3)$$

The rate of accumulation of solute A in the control volume is

$$(4\pi r^2 dr)\frac{\partial C_A}{\partial t} \qquad (2-4)$$

Combine equation (2-3) with equation (2-4) yields

$$\frac{\partial C_A}{\partial t} = D\left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r}\right) \qquad (2-5)$$

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The initial condition and boundary conditions follow from the assumptions above are:

I.C.     at $t = 0$, $C_A = C_{A0}$

B.C.(1)  at $r = 0$, $C_A$ = finite

B.C.(2)  at $r = R$, $-D\dfrac{\partial C_A}{\partial r}\Big|_{r=R} = K_G(\overline{C}_A - C_{Agl})$

The B.C.(2) can be rewritten as

$$\text{at } r = R, \quad -D\frac{\partial C_A}{\partial r}\Big|_{r=R} = K_G\left(\frac{\int_o^R C_A 4\pi r^2 dr}{(4/3)\pi R^3} - C_{Agl}\right)$$

where  $R$      = the radius of the sphere

$\overline{C}_A$      = average concentration of A inside the sphere

$C_{Agl}$    = the gas phase concentration which is in equilibrium with the existing liquid phase concentration

$K_G$      = overall gas phase mass transfer coefficient.

Introducing the dimensionless variables,

$$\Theta = \frac{C_{A0} - C_A}{C_{A0} - C_{Agl}} \ , \quad \eta = \frac{r}{R}, \text{ and } \tau = \frac{Dt}{R^2}$$

equation (2-5) becomes

$$\frac{\partial \Theta}{\partial \tau} = \frac{\partial^2 \Theta}{\partial \eta^2} + \frac{2}{\eta} \frac{\partial \Theta}{\partial \eta} \qquad (2\text{-}6)$$

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with the initial condition and boundary conditions:

I.C.      at $\tau = 0$, $\Theta = 0$

B.C.(1)   at $\eta = 0$, $\Theta =$ finite

B.C.(2)   at $\eta = 1$, $\left.\dfrac{\partial \Theta}{\partial \eta}\right|_{\eta=1} = N_{sh}\left[1 - 3\displaystyle\int_{0}^{1} \Theta\, \eta^2\, d\eta\right]$

where $N_{sh}$ is the Sherwood number defined by:

$$N_{sh} = \frac{K_G\, R}{D}$$

Equation (2-6) can be solved by taking Laplace Transformation with respect to $\tau$, then

$$S\overline{\Theta} - \overline{\Theta}(0,\eta) = \frac{\partial^2 \overline{\Theta}}{\partial \eta^2} + \frac{2}{\eta}\frac{\partial \overline{\Theta}}{\partial \eta} \qquad (2\text{-}7)$$

and the boundary conditions become

B.C.(1)   at $\eta = 0$, $\overline{\Theta} =$ finite

B.C.(2)   at $\eta = 1$, $\left.\dfrac{\partial \overline{\Theta}}{\partial \eta}\right|_{\eta=1} = N_{sh}\left[\dfrac{1}{s} - 3\displaystyle\int_{0}^{1} \overline{\Theta}\, \eta^2\, d\eta\right]$

The second term on the left hand side of equation (2-7) is zero as the initial condition stated.

Define a new variable, let

$$f = \eta\overline{\theta} \tag{2-8}$$

Inserting equation (2-8) into equation (2-7), equation (2-7) can be simplified as

$$\frac{d^2 f}{d\eta^2} - sf = 0 \tag{2-9}$$

There is a general solution for equation (2-9), which is

$$\overline{\theta} = \frac{C_1}{\eta} \text{Sinh}(\sqrt{s}\ \eta) + \frac{C_2}{\eta} \text{Cosh}(\sqrt{s}\ \eta) \tag{2-10}$$

where $C_1$ and $C_2$ are arbitrary constants. With boundary condition (1), $C_2$ has to be equal to zero; otherwise, $\overline{\theta}$ will be undefined at $\eta = 0$. Equation (2-10) then becomes

$$\overline{\theta} = \frac{C_1}{\eta} \text{Sinh}(\sqrt{s}\ \eta) \tag{2-11}$$

Constant $C_1$ can be determined by applying boundary condition (2). Inserting equation (2-11) into boundary condition (2), the left hand side can be rewritten as

$$\frac{\partial \overline{\theta}}{\partial \eta}\bigg|_{\eta=1} = -C_1 \text{Sinh}\sqrt{s} + C_1 \sqrt{s}\ \text{Cosh}\sqrt{s} \tag{2-12}$$

and the right hand side of boundary condition (2) becomes

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$$N_{sh}\left(\frac{1}{s} - 3\int_0^1 \bar{\Theta}\, \eta^2\, d\eta\right) = \frac{N_{sh}}{s} - \frac{3C_1 N_{sh}}{s}\left(\sqrt{s}\, \mathrm{Cosh}\sqrt{s} - \mathrm{Sinh}\sqrt{s}\right) \qquad (2\text{-}13)$$

By combining L.H.S. with R.H.S., $C_1$ can be obtained.  The result is

$$C_1 = \frac{N_{sh}}{(s + 3\, N_{sh})\left(\sqrt{s}\, \mathrm{Cosh}\sqrt{s} - \mathrm{Sinh}\sqrt{s}\right)} \qquad (2\text{-}14)$$

Therefore, the solution for $\bar{\Theta}$ is

$$\bar{\Theta} = \frac{N_{sh}\, \mathrm{Sinh}(\sqrt{s}\, \eta)}{(s + 3\, N_{sh})\left(\sqrt{s}\, \mathrm{Cosh}\sqrt{s} - \mathrm{Sinh}\sqrt{s}\right)\eta} \qquad (2\text{-}15)$$

Equation (2-15) needs to employ the technique of inverse Laplace Transformation to obtain a final solution for $\Theta$.  In order to find all the residues, equation (2-15) can be re-written as a polynomial expression by introducing the definitions of the hyperbolic sine and hyperbolic cosine,

$$\bar{\Theta} = \frac{N_{sh}}{(s + 3\, N_{sh})}\ *$$

$$\frac{\left(\sqrt{s}\,\eta + \frac{(\sqrt{s}\eta)^3}{3!} + \frac{(\sqrt{s}\eta)^5}{5!} + \frac{(\sqrt{s}\eta)^7}{7!} + \ldots\right)}{\left[\sqrt{s}\left(1 + \frac{(\sqrt{s})^2}{2!} + \frac{(\sqrt{s})^4}{4!} + \frac{(\sqrt{s})^6}{6!} + \ldots\right) - \left(\sqrt{s} + \frac{(\sqrt{s})^3}{3!} + \frac{(\sqrt{s})^5}{5!} + \ldots\right)\right]\eta} \qquad (2\text{-}16)$$

with further simplifications, equation (2-16) becomes

$$\overline{\theta} = \frac{N_{sh}}{(s + 3\,N_{sh})} \frac{1}{s} \frac{(1 + \frac{\eta^2}{3!}\,s + \frac{\eta^4}{5!}\,s^2 + \frac{\eta^6}{7!}\,s^3 + \ldots)}{(\frac{1}{3} + \frac{1}{30}\,s + \frac{1}{840}\,s^2 + \ldots)} \qquad (2\text{-}17)$$

It is obvious that there is a simple pole at s = 0, a simple pole at s + 3 $N_{sh}$ = 0, and a simple pole at $\sqrt{s}$ Cosh$\sqrt{s}$ = Sinh$\sqrt{s}$. The residue at pole s = 0 can be obtained by taking the limit on equation (2-17) as s approachs zero,

$$\lim_{s \to 0} s \; \frac{N_{sh}}{(s + 3\,N_{sh})} \frac{1}{s} \frac{(1 + \frac{\eta^2}{3!}\,s + \frac{\eta^4}{5!}\,s^2 + \frac{\eta^6}{7!}\,s^3 + \ldots)}{(\frac{1}{3} + \frac{1}{30}\,s + \frac{1}{840}\,s^2 + \ldots)} \; e^{s\tau} \qquad (2\text{-}18)$$

and the result is equal to 1. The residue at pole s + 3 $N_{sh}$ = 0 can be derived as following:

$$\lim_{s \to -3N_{sh}} (s + 3N_{sh}) \frac{N_{sh}}{(s + 3N_{sh})} \frac{(1 + \frac{\eta^2}{3!}\,s + \frac{\eta^4}{5!}\,s^2 + \frac{\eta^6}{7!}\,s^3 + \ldots)}{s(\frac{1}{3} + \frac{1}{30}\,s + \frac{1}{840}\,s^2 + \ldots)} \; e^{s\tau}$$

$$= N_{sh} \; e^{-3N_{sh}\tau} \; \frac{Sin(\sqrt{3N_{sh}}\;\eta)}{(\sqrt{3N_{sh}}\;Cos\sqrt{3N_{sh}} - Sin\sqrt{3N_{sh}})\;\eta} \qquad (2\text{-}19)$$

The simple pole at $\sqrt{s}$ Cosh$\sqrt{s}$ - Sinh$\sqrt{s}$ = 0 is an eigenfunction. By introducing a new variable $\alpha_n$, and letting s = $-\alpha_n^2$, this function can be rewritten as

$$\alpha_n = Tan\,(\alpha_n) \qquad (2\text{-}20)$$

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Many eigenvalues are satisfied with this eigenfunction as
illustrated in Figure 5. A computer program in search of
these eigenvalues is given in Appendix A, and the first
fifteen eigenvalues are listed in Table I. The residue of
equation (2-15) and its equivalent (2-17) at $s = -\alpha_n^2$ can then
be obtained as

$$\lim_{s \to -\alpha_n^2} (s + \alpha_n^2) \frac{N_{sh} \, Sinh(\sqrt{s} \, \eta)}{(s + 3N_{sh})(\sqrt{s} \, Cosh\sqrt{s} - Sinh\sqrt{s}) \, \eta} \, e^{s\tau}$$

$$= \frac{2 \, N_{sh} \, Sin(\alpha_n \eta)}{(3N_{sh} - \alpha_n^2) \, (Sin \, \alpha_n) \, \eta} \, e^{-\alpha_n^2 \tau} \qquad (2\text{-}21)$$

Once, all the residues are found, the final solution can be
written as

$$\Theta = 1 + \frac{N_{sh} \, Sin(\sqrt{3N_{sh}} \, \eta)}{(\sqrt{3N_{sh}} \, Cos\sqrt{3N_{sh}} - Sin\sqrt{3N_{sh}}) \, \eta} \, e^{-3N_{sh}\tau}$$

$$+ \sum_{n=1}^{\infty} \frac{2 \, N_{sh} \, Sin(\alpha_n \, \eta)}{(3N_{sh} - \alpha_n^2)(Sin \, \alpha_n)\eta} \, e^{-\alpha_n^2 \tau} \qquad (2\text{-}22)$$

By the definition of dimensionless variable $\Theta$, equation
(2-22) becomes

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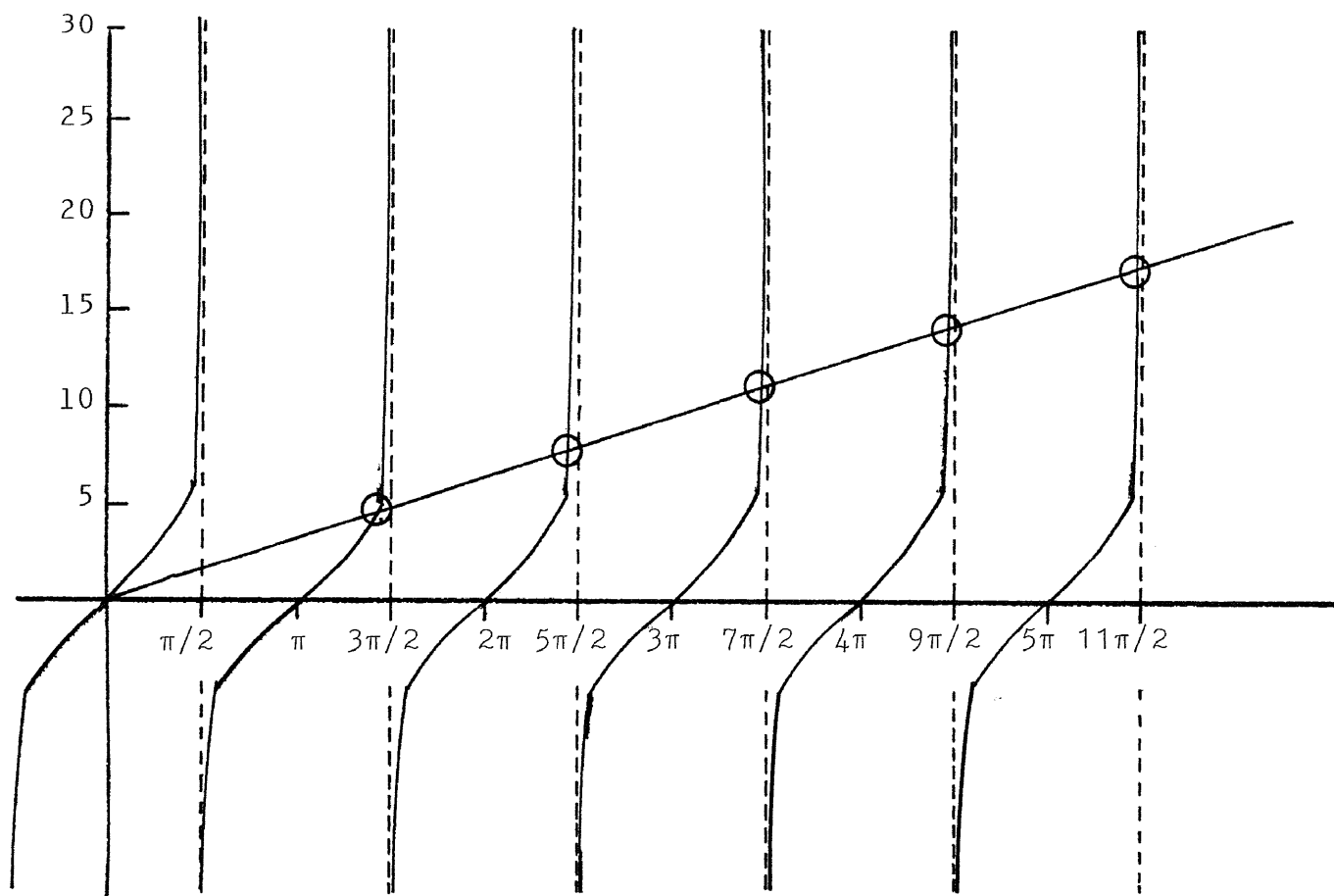
Fig. 5  Sketch of an eigenfunction ( X = TAN X ) and its eigenvalues.

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Table I

Eigenvalues of $\alpha_n = TAN\ \alpha_n$

$\alpha_1$ = 4.4934095

$\alpha_2$ = 7.7252518

$\alpha_3$ = 10.9041217

$\alpha_4$ = 14.0661939

$\alpha_5$ = 17.2207553

$\alpha_6$ = 20.3713030

$\alpha_7$ = 23.5194525

$\alpha_8$ = 26.6660542

$\alpha_9$ = 29.8115988

$\alpha_{10}$ = 32.9563890

$\alpha_{11}$ = 36.1006222

$\alpha_{12}$ = 39.2444323

$\alpha_{13}$ = 42.3879136

$\alpha_{14}$ = 45.5311340

$\alpha_{15}$ = 48.6741442

$$C_A = C_{AO} - (C_{AO} - C_{Agl}) \left[ 1 + \frac{N_{sh} \, Sin(\sqrt{3N_{sh}} \, \eta)}{(\sqrt{3N_{sh}} \, Cos\sqrt{3N_{sh}} - Sin\sqrt{3N_{sh}}) \, \eta} \, e^{-3N_{sh}\tau} \right.$$

$$\left. + \sum_{n=1}^{\infty} \frac{2 \, N_{sh} \, Sin(\alpha_n \eta)}{(3N_{sh} - \alpha_n^2)(Sin \, \alpha_n) \, \eta} \, e^{-\alpha_n^2 \tau} \right] \qquad (2\text{-}23)$$

The rate of transfer at time t across the surface of the sphere is

$$4\pi R^2 N_{Ar}(t) = -4\pi R^2 D \left( \frac{\partial C_A}{\partial r} \right) \Big|_{r=R} \qquad (2\text{-}24)$$

$\frac{\partial C_A}{\partial r}$ can be evaluated at r = R from equation (2-23), then

$$N_{Ar}(t) = -(C_{AO} - C_{Agl}) \left[ \frac{N_{sh} \, e^{-3N_{sh}\tau}}{R} \right.$$

$$\left. + \sum_{n=1}^{\infty} \frac{2 \, N_{sh} \, (\alpha_n \, Cos\alpha_n - Sin \, \alpha_n)}{(3N_{sh} - \alpha_n^2)(Sin \, \alpha_n) \, R} \, e^{-\alpha_n^2 \tau} \right] \qquad (2\text{-}25)$$

The total mass-transfer up to time t is $N_A^{\prime}$, where

$$N_A^{\prime} = 4\pi R^2 \int_o^t N_{Ar}(t) \, dt$$

$$= 4\pi R^2 (C_{AO} - C_{Agl}) \left[ \frac{R}{3} (1 - e^{-3N_{sh}\tau}) \right.$$

$$\left. + \sum_{n=1}^{\infty} \frac{2N_{sh}(\alpha_n \, Cos \, \alpha_n - Sin \, \alpha_n) \, R}{(3N_{sh} - \alpha_n^2)(Sin \, \alpha_n) \, \alpha_n^2} (1 - e^{-\alpha_n^2 \tau}) \right] \qquad (2\text{-}26)$$

The total transfer per unit surface up to time t is

$$\frac{N_A'}{4\pi R^2} = (C_{A0} - C_{Agl})\left[\frac{R}{3}(1 - e^{-3N_{sh}\tau})\right.$$

$$\left. + \sum_{n=1}^{\infty} \frac{2 N_{sh}(\alpha_n \cos \alpha_n - \sin \alpha_n) R}{(3 N_{sh} - \alpha_n^2)(\sin \alpha_n)\alpha_n^2}(1 - e^{-\alpha_n^2\tau})\right] \qquad (2\text{-}27)$$

A material balance on the transfer up to time t is

$$(C_{A0} - \overline{C}_A)\frac{4}{3}\pi R^3 = N_A' \qquad (2\text{-}28)$$

in which $\overline{C}_A$ is the average concentration throughout the
sphere at t.  The dimensionless average concentration $\Theta'$ is
defined as

$$\Theta' = \frac{C_{A0} - \overline{C}_A}{C_{A0} - C_{Agl}}$$

$$= (1 - e^{-3N_{sh}\tau}) + \sum_{n=1}^{\infty} \frac{6N_{sh}(\alpha_n \cos \alpha_n - \sin \alpha_n)}{(3N_{sh} - \alpha_n^2)(\sin \alpha_n)\alpha_n^2}(1 - e^{-\alpha_n^2\tau}) \quad (2\text{-}29)$$

A computer program for calculation $1-\Theta'$ with various $\tau$ and
Sherwood number is given in Appendix B.  The result is presented
in Figure 6.  It is important to note that as time increases,
the $1-\Theta'$ curve is levelled off, which indicates after a certain
amount of time, the mass-transfer rate reaches a limiting
value.
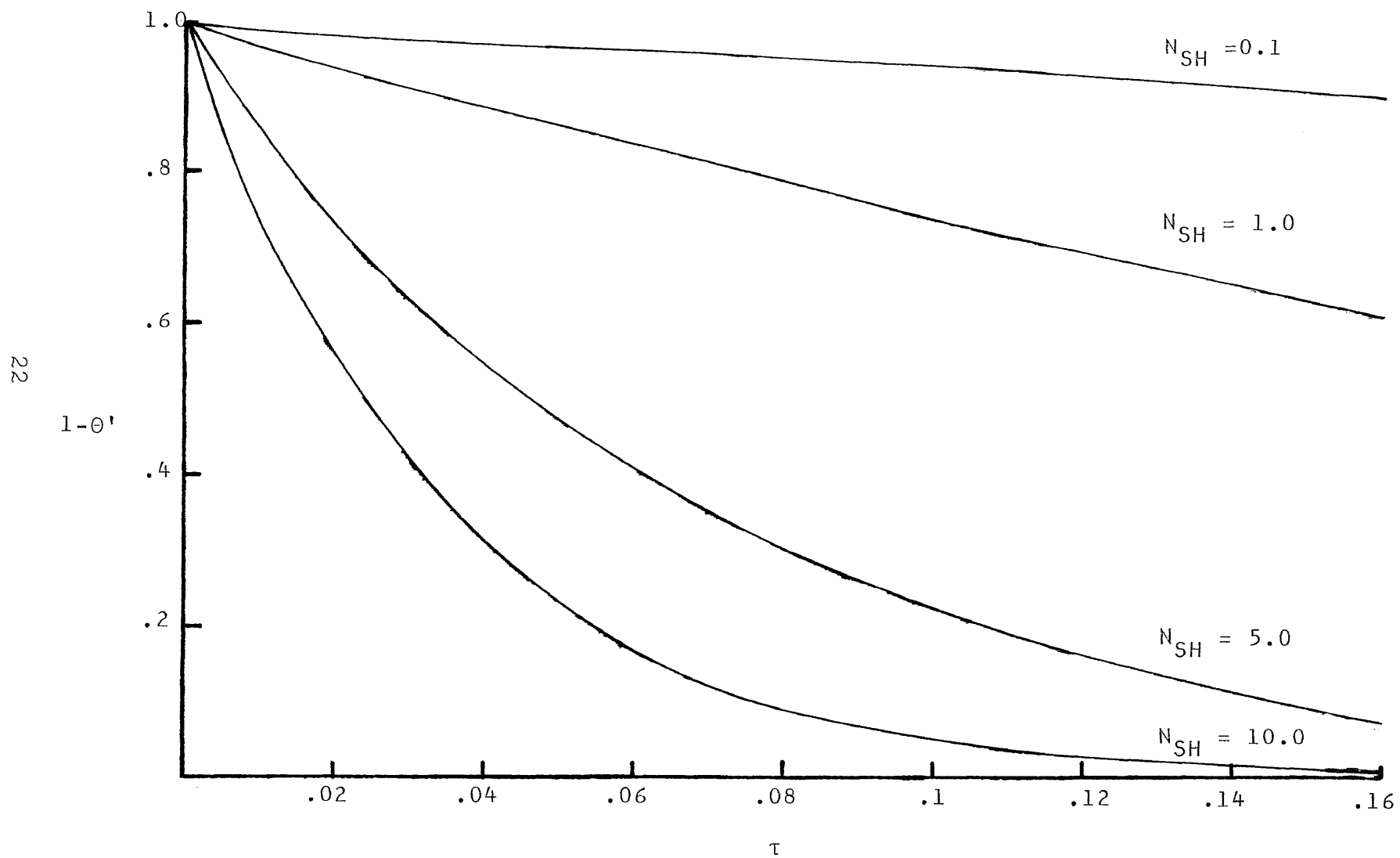
Fig. 6   Sketch of dimensionless average concentration
Vs. dimensionless time and Sherwood number.

Equation (2-27) can also be written in the form of mole fraction of A, that is

$$\frac{N_A'}{4\pi R^2} = C\,(Y_{A0} - Y_{Agl})\left[\frac{R}{3}\,(1 - e^{-3N_{sh}\tau})\right.$$

$$\left.+ \sum_{n=1}^{\infty} \frac{2\,N_{sh}\,R(\alpha_n\,\text{Cos}\,\alpha_n - \text{Sin}\,\alpha_n)}{(3N_{sh} - \alpha_n^2)(\text{Sin}\,\alpha_n)\,\alpha_n^2}\,(1 - e^{-\alpha_n^2\tau})\right] \qquad (2\text{-}30)$$

where  $C = C_A + C_B$ = molar density of gas mixture

$C_A$ = molar concentration of A

$Y_A = C_A/C$ = mole fraction of A

A new variable, $Q_r$, defined as overall mass-transfer up to time t during bubble rising can be expressed as

$$Q_r = \left(\frac{N_A'}{4\pi R^2}\right) A_{eff} \qquad (2\text{-}31)$$

where $A_{eff}$ is the effective contact area of all the bubbles issued from the slots in a bubble-cap.  For convenience, equation (2-31) can be rewritten as

$$Q_r = (Y_{A0} - Y_{Agl})\,F(N_{sh}, \tau, \alpha_n, A_{eff}) \qquad (2\text{-}32)$$

where

$$F(N_{sh}, \tau, \alpha_n, A_{eff}) = \left[\frac{R}{3}\,(1 - e^{-3N_{sh}\tau})\right.$$

$$\left.+ \sum_{n=1}^{\infty} \frac{2\,N_{sh}\,R\,(\alpha_n\,\text{Cos}\,\alpha_n - \text{Sin}\,\alpha_n)}{(3N_{sh} - \alpha_n^2)(\text{Sin}\,\alpha_n)\,\alpha_n^2}\,(1 - e^{-\alpha_n^2\tau})\right]\,C\,A_{eff} \qquad (2\text{-}33)$$

## B. Mathematical Analysis Of Mass-Transfer During Bubble Rising Of A Multicomponent System

Multicomponent diffusion is the transport process in which the concentration gradient of one component affects the flux of a second component. The study on the effects of multicomponent diffusion are split into parallel efforts of theoreticians and of ecperimentalists. The theoreticians initiated their studies with the Maxwell equation(23),

$$\nabla X_i = \sum_{j=1}^{n} \frac{X_i \, X_j}{d_{ij}} (V_j - V_i) \qquad (2\text{-}34)$$

where $d_{ij}$ in gases is a binary diffusion coefficient, and the $V_i$'s are component velocities. This equation suggested, on the basis of kinetic theory, that multicomponent diffusion in dilute gases can be described by a summation of binary-like diffusion terms. At the same time, Onsager(27) proposed an equation which is favored by experimentalists,

$$- j_i = \sum_{j=1}^{n-1} D_{ij} \, \nabla C_j \qquad (2\text{-}35)$$

where $j_i$ is the flux relative to the volume-average velocity. This form of the equation was preferred by experimentalists because the $D_{ij}$ are easier to measure experimentally. The scientific development of multicomponent diffusion becomes faster after Onsager and Maxwell's initial efforts to establish

the experimental nature and mathematical analysis of determining the diffusion coefficient. After many research projects have been accomplished, it resulted to the following conclusions as stated by Cussler(8): (1) it is generally believed that the multicomponent diffusion is often a small effect. (2) All flux equations proposed by different investigators are equivalent with each other. (Although, in some cases, the form of equation is more complex than the others.) (3) A binary solution to a mass-transfer problem without chemical reaction is sufficient to allow the multicomponent solution to be written down in an equivalent form.

This section presents the basic mathematical analysis necessary for describing the phenomenon of mass-transfer during bubble rising of a multicomponent system. A linearization method proposed by Toor(42) is introduced in order to reduce the equations of diffusion in a multicomponent system to a set of equivalent binary diffusion equations. Then, solutions to the equations of multicomponent mass-transfer may be written as matrix mass-transfer equations. The chief mathematical results are that multicomponent diffusion coefficients can be predicted from binary diffusion coefficients, and solutions to the multicomponent mass-transfer problems may be obtained in terms of solutions to equivalent binary problems.

As explained in Section A, equation (2-5) can be written for a binary system. The governing equation for each of the N-1 independent components in a N component mixture can also be written in an equivalent form as

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{N-1} D_{ij} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r}\right) \quad i = 1, \ldots, N-1 \qquad (2\text{-}36)$$

with initial condition and boundary conditions:

I.C.     at $t = 0$, $C_i = C_{i0}$     $i = 1, \ldots, N-1$

B.C.(1)  at $r = 0$, $C_i = $ finite   $i = 1, \ldots, N-1$

B.C.(2)  at $r = R$, $\displaystyle - \sum_{j=1}^{N-1} D_{ij} \frac{\partial C_i}{\partial r}\bigg|_{r=R}$

$$= \sum_{j=1}^{N-1} K_G' (\overline{C}_i - C_{igl}) \quad i = 1, \ldots, N-1$$

where $K_G'$ is the overall gas-phase mass-transfer coefficient which is a function of $D_{ij}$.

If the $C_i$ are written as the elements of a column vector (C), the concentration vector; and the $D_{ij}$ as the elements of a matrix (D), the diffusion coefficient matrix; then in matrix notation, equation (2-36) and initial, boundary conditions become

$$\frac{\partial(C)}{\partial t} = (D) \left( \frac{\partial^2(C)}{\partial r^2} + \frac{2}{r} \frac{\partial(C)}{\partial r} \right) \qquad (2-37)$$

I.C.     at $t = 0$, $(C) = (C_0)$

B.C.(1)  at $r = 0$, $(C)$ = finite

B.C.(2)  at $r = R$, $-(D) \frac{\partial(C)}{\partial r}\big|_{r=R} = (K_G') \left[ (\overline{C}) - (C_{gl}) \right]$

where $(K_G')$ is an overall mass-transfer coefficient matrix since it is a function of $(D)$.

Equation (2-37) and boundary condition (2) are now partially linearized by assuming that the matrix $(D)$ may be treated as concentration independent. Toor(42) indicated that the errors caused by this assumption are not seriuos even for the moderate concentration changes.

The determination of concentration profiles has been developed through the efforts of Toor(42). It begins with continuity and flux equations for multicomponent mass-transfer problems. Toor assumed that there exists a non-singular matrix $(t)$ which can diagonalize matrix $(D)$:

$$(t)^{-1} (D) (t) = (\sigma) = \begin{pmatrix} \sigma_1 & & \\ & \sigma_2 & \\ & & \sigma_3 \end{pmatrix} \qquad (2-38)$$

where $(t)^{-1}$ is the inverse of $(t)$, and $(\sigma)$ is the diagonal matrix of the eigenvalues of the diffusion coefficient matrix $(D)$. Defining a new combined concentration $(\psi)$ as:

$$(C) = (t) \, (\psi) \tag{2-39}$$

Equation (2-37) then becomes

$$(t) \, \frac{\partial(\psi)}{\partial t} = (D) \, (t) \left[ \frac{\partial^2(\psi)}{\partial r^2} + \frac{2}{r} \frac{\partial(\psi)}{\partial r} \right] \tag{2-40}$$

with initial condition and boundary conditions:

I.C.     at $t = 0$, $(t) \, (\psi) = (t) \, (\psi_o)$

B.C.(1)  at $r = 0$, $(t) \, (\psi) = $ finite

B.C.(2)  at $r = R$, $- (D) \, (t) \, \frac{\partial(\psi)}{\partial r} \Big|_{r=R}$

$$= (K'_G) \, (t) \left[ (\overline{\psi}) - (\psi_{gl}) \right]$$

Now, multiply both sides of equation (2-40) and its initial condition and boundary conditions by $(t)^{-1}$. A new set of equations can be obtained.

$$\frac{\partial(\psi)}{\partial t} = (\sigma) \, \left( \frac{\partial^2(\psi)}{\partial r^2} + \frac{2}{r} \frac{\partial(\psi)}{\partial r} \right) \tag{2-41}$$

I.C.     at $t = 0$, $(\psi) = (\psi_o)$

B.C.(1)  at $r = 0$, $(\psi) = $ finite

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B.C.(2)  at $r = R$, $- (\sigma) \left.\dfrac{\partial(\psi)}{\partial r}\right|_{r=R} = (K_G'') \left[ (\overline{\psi}) - (\psi_{g1}) \right]$

where $(K_G'')$ is a function of $(\sigma)$.

Introducing the dimensionless variables,

$$\Theta_1 = \frac{(\psi_0) - (\psi)}{(\psi_0) - (\psi_{g1})} \text{ , and } \tau_1 = \frac{(\sigma)\,t}{R^2}$$

equation (2-41) then becomes

$$\frac{\partial \Theta_1}{\partial \tau_1} = \frac{\partial^2 \Theta_1}{\partial \eta^2} + \frac{2}{\eta}\,\frac{\partial \Theta_1}{\partial \eta} \qquad\qquad (2\text{-}42)$$

with initial condition and boundary conditions:

I.C.    at $\tau_1 = 0$, $\Theta_1 = 0$

B.C.(1)  at $\eta = 0$, $\Theta_1 = $ finite

B.C.(2)  at $\eta = 1$, $\dfrac{\partial \Theta_1}{\partial \eta} = N_{sh1} \left( 1 - 3\displaystyle\int_0^1 \Theta_1\,\eta^2\,d\eta \right)$

where $N_{sh1}$ is the Sherwood number, and a function of $(\sigma)$.

Equation (2-42) and its initial, boundary conditions have exactly the same mathematical form as equation (2-6) for a binary system.  As a result, the exact same solution structure for a binary system can be expected for the multi-component system:

$$\Theta_1 = 1 + \frac{N_{sh1} \, Sin(\sqrt{3N_{sh1}} \, \eta)}{(\sqrt{3N_{sh1}} \, Cos \, \sqrt{3N_{sh1}} - Sin \, \sqrt{3N_{sh1}}) \, \eta} \, e^{-3N_{sh1}\tau_1}$$

$$+ \sum_{n=1}^{\infty} \frac{2 \, N_{sh1} \, Sin(\alpha_n \, \eta)}{(3N_{sh1} - \alpha_n^2)(Sin \, \alpha_n) \, \eta} \, e^{-\alpha_n^2 \, \tau_1} \tag{2-43}$$

It is convenient to define a new function, $F_1(\sigma_i, \, \eta, \, \tau_i)$, to represent the right hand side of equation (2-43). Equation (2-43) becomes

$$\frac{(\psi_0) - (\psi)}{(\psi_0) - (\psi_{gl})} = F_1(\sigma_i, \, \eta, \, \tau_i) \tag{2-44}$$

Then, the final solution for $(\psi)$ can be written as

$$(\psi) = (\psi_0) - F_1(\sigma_i, \, \eta, \, \tau_i) \left[ (\psi_0) - (\psi_{gl}) \right] \tag{2-45}$$

This result is completely analogous to the binary result of equation (2-23). There are only two real differences. First, instead of the actual concentration $C_i$, we now have a new combined concentration, $\psi_i$. Second, instead of the binary diffusion coefficient D, we now have the eigenvalues $\sigma_i$. However, the concentrations in equation (2-45) are not those actually measured. To convert equation (2-45) back into the actual observed concentration, first rewrite equation (2-39) as

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$$(\psi) = (t)^{-1} (C) \qquad\qquad (2\text{-}46)$$

by multiply both sides by $(t)^{-1}$. Insert equation (2-46)
into equation (2-45), and multiply both sides by $(t)$ to
obtain a final solution as below

$$(C) = (C_0) - (t) \, F_1(\sigma_i, \, \eta, \, \tau_i) \, (t)^{-1} \left[ (C_0) - (C_{gl}) \right] \qquad (2\text{-}47)$$

Thus, equation (2-47) is the concentration profiles in a
multicomponent system in terms of the binary solution to the
problem, where the binary diffusion coefficient is replaced
by each eigenvalue of the diffusion coefficient matrix.

Following the same derivation procedure as in Section A
for a binary system, the overall mass-transfer up to time t
in terms of mole fraction of component i during bubble rising
can be obtained as

$$(Q_r) = (t) \, F_2(\sigma_i, \, \eta, \, \tau_i, \, A_{eff}) \, (t)^{-1} \left[ (Y_0) - (Y_{gl}) \right] \qquad (2\text{-}48)$$

where

$$F_2(\sigma_i, \, \eta, \, \tau_i, \, A_{eff}) = \left[ \frac{R}{3} (1 - e^{-3N_{shi}\tau_i}) \right.$$

$$+ \sum_{n=1}^{\infty} \frac{2 \, N_{shi} \, (\alpha_n \, \text{Cos} \, \alpha_n - \text{Sin} \, \alpha_n) \, R}{(3 \, N_{shi} - \alpha_n^2)(\text{Sin} \, \alpha_n) \, \alpha_n^2} (1 - e^{-\alpha_n^2 \tau_i}) \Big] C \, A_{eff} \quad (2\text{-}49)$$

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$$C \quad = \sum_{i}^{N} C_i = \text{molar density of gas mixture}$$

$$C_i \quad = \text{molar concentration of component i}$$

$$Y_i \quad = C_i/C = \text{mole fraction of component i}$$

$$N_{shi} \quad = \frac{K(\sigma_i) \ R}{\sigma_i} = \text{Sherwood number}$$

$$\tau_i \quad = \frac{\sigma_i \ t}{R} = \text{dimensionless time}$$

$$K(\sigma_i) = \text{overall mass-transfer coefficients}$$

$$A_{eff} \quad = \text{effective contact area of all bubbles}$$

It is possible to obtain analytical solutions for concentration profiles in a ternary system. To illustrate how this is done, one starts with the estimation of the multicomponent diffusion coefficients. For dilute gases, the ternary diffusion coefficients for the generalized Fick's law diffusion coefficients can be written down in terms of the generalized Stefan-Maxwell(23) diffusion coefficients as

$$D_{11} = \frac{d_{13} \left[ d_{12} \ (Y_2 + Y_3) + d_{23} \ Y_1 \right]}{S} \qquad (2\text{-}50)$$

$$D_{12} = \frac{Y_1 \ d_{13} \ (d_{23} - d_{12})}{S} \qquad (2\text{-}51)$$

$$D_{21} = \frac{Y_2 \ d_{13} \ (d_{23} - d_{12})}{S} \qquad (2\text{-}52)$$

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$$D_{22} = \frac{d_{23}\left[d_{13}(Y_1 + Y_3) + d_{13}\,Y_2\right]}{S} \qquad (2\text{-}53)$$

$$S = Y_1\,d_{23} + Y_2\,d_{13} + Y_3\,d_{12} \qquad (2\text{-}54)$$

where $d_{13}$, $d_{23}$, $d_{12}$ are binary diffusion coefficients, and $Y_1$, $Y_2$, $Y_3$ are the mole fractions of each component. The various binary diffusion coefficients can be predicted from the kinetic theory. Therefore, the multicomponent diffusion coefficients, $D_{ij}$ (i=j), "main diffusion coefficients"; and $D_{ij}$ (i≠j), "cross diffusion coefficients"; can be obtained from these binary diffusion coefficients.

For a ternary system, equation (2-39) can be rewritten as

$$C_i = \sum_{k=1}^{2} t_{ik}\,\psi_k \qquad i = 1,\ 2 \qquad (2\text{-}55)$$

where

$$\begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix} = \begin{pmatrix} 1 & \dfrac{D_{12}}{D_{22} - \sigma_1} \\ \dfrac{D_{22} - \sigma_2}{D_{12}} & 1 \end{pmatrix} = \begin{pmatrix} 1 & \dfrac{D_{11} - \sigma_1}{D_{21}} \\ \dfrac{D_{21}}{D_{11} - \sigma_2} & 1 \end{pmatrix} \qquad (2\text{-}56)$$

and equation (2-38) becomes

$$\begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix}^{-1} \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix} = \begin{pmatrix} \sigma_1 & \\ & \sigma_2 \end{pmatrix} \qquad (2\text{-}57)$$

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where

$$\sigma_1 = \tfrac{1}{2}\left(D_{11} + D_{22} + \sqrt{(D_{11} - D_{22})^2 + 4\,D_{12}\,D_{21}}\right) \qquad (2\text{-}58)$$

$$\sigma_2 = \tfrac{1}{2}\left(D_{11} + D_{22} - \sqrt{(D_{11} - D_{22})^2 + 4\,D_{12}\,D_{21}}\right) \qquad (2\text{-}59)$$

$$\begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix}^{-1} = \begin{pmatrix} 1 & \dfrac{D_{12}}{\sigma_1 - D_{22}} \\ \dfrac{\sigma_2 - D_{22}}{D_{12}} & 1 \end{pmatrix} = \begin{pmatrix} 1 & \dfrac{\sigma_1 - D_{11}}{D_{21}} \\ \dfrac{D_{21}}{\sigma_2 - D_{11}} & 1 \end{pmatrix} \qquad (2\text{-}60)$$

Equation (2-47), the concentration profile, can be re-written for a ternary system as

$$C_i = C_{i0} - \sum_{j=1}^{2}\sum_{k=1}^{2} t_{ij}\, F_1(\sigma_j,\, \eta,\, \tau_j)\, t_{jk}^{-1}\,(C_{i0} - C_{igl}) \qquad (2\text{-}61)$$

which in terms of component A and B can be rearranged to give

$$C_A = C_{A0} - \left[\frac{(D_{11} - \sigma_2)\,(C_{A0} - C_{Agl}) + D_{12}\,(C_{B0} - C_{Bgl})}{\sigma_1 - \sigma_2}\right] F_1(\sigma_1, \eta, \tau_1)$$

$$- \left[\frac{(D_{11} - \sigma_1)\,(C_{A0} - C_{Agl}) + D_{12}\,(C_{B0} - C_{Bgl})}{\sigma_2 - \sigma_1}\right] F_1(\sigma_2, \eta, \tau_2) \qquad (2\text{-}62)$$

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and

$$C_B = C_{B0} - \left[ \frac{D_{21} (C_{A0} - C_{Agl}) + (D_{22} - \sigma_2) (C_{B0} - C_{Bgl})}{\sigma_1 - \sigma_2} \right] F_1(\sigma_1, \eta, \tau_1)$$

$$- \left[ \frac{D_{21} (C_{A0} - C_{Agl}) + (D_{22} - \sigma_1) (C_{B0} - C_{Bgl})}{\sigma_2 - \sigma_1} \right] F_1(\sigma_2, \eta, \tau_2) \quad (2\text{-}63)$$

where $F_1(\sigma_i, \eta, \tau_i)$ is expressed as in equation (2-44).

The overall mass-transfer up to time t during a bubble rising in terms of mole fraction of component A and B for a ternary system can be expressed as following:

$$Q_{r,A} = \left[ \frac{(D_{11} - \sigma_2)(Y_{A0} - Y_{Agl}) + D_{12}(Y_{B0} - Y_{Bgl})}{\sigma_1 - \sigma_2} \right] F_2(\sigma_1, \eta, \tau_1, A_{eff})$$

$$+ \left[ \frac{(D_{11} - \sigma_1)(Y_{A0} - Y_{Agl}) + D_{12}(Y_{B0} - Y_{Bgl})}{\sigma_2 - \sigma_1} \right] F_2(\sigma_2, \eta, \tau_2, A_{eff}) \quad (2\text{-}64)$$

$$Q_{r,B} = \left[ \frac{D_{21}(Y_{A0} - Y_{Agl}) + (D_{22} - \sigma_2)(Y_{B0} - Y_{Bgl})}{\sigma_1 - \sigma_2} \right] F_2(\sigma_1, \eta, \tau_1, A_{eff})$$

$$+ \left[ \frac{D_{21}(Y_{A0} - Y_{Agl}) + (D_{22} - \sigma_1)(Y_{B0} - Y_{Bgl})}{\sigma_2 - \sigma_1} \right] F_2(\sigma_2, \eta, \tau_2, A_{eff}) \quad (2\text{-}65)$$

where $F_2(\sigma_i, \eta, \tau_i, A_{eff})$ is expressed as in equation (2-49).

## C. Empirical Correlation Of Mass-Transfer During Bubble Formation

The mechanism of mass-transfer of the distillation operation in a stage consists of two parts. They are (1) the mass-transfer during bubble formation, and (2) the mass transfer during bubble rising. Sections A and B have presented the analytical solutions of mass exchange rate for a binary and a ternary system during bubble rising. However, due to the complex phenomenon of the mass-transfer during bubble formation, it is difficult to obtain an analytical solution to represent this transport process. This section presents an empirical correlation proposed by Skelland(36) to simulate the rate of mass transfer during bubble formation.

The rate of mass transfer during bubble formation in a plate can be written as

$$Q_f = K_{df} \, A_f \, (Y_{AI} - Y_{Agl}) \qquad\qquad (2\text{-}66)$$

where  $Q_f$ = the rate of mass-transfer during bubble formation

$K_{df}$ = overall coefficients of mass transfer during bubble formation

$A_f$ = total interfacial area during bubble formation

$Y_{AI}$ = mole fraction of component A in disperse-phase enter to stage

$Y_{Agl}$ = disperse-phase mole fraction of A that in equilibrium with existing continuous-phase mole fraction in stage

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If the bubble is assumed to grow as a sphere, Skelland[36]
suggested that the interfacial area, $A_f$, can be related to
the bubble diameter and the number of perforations per plate.
In the equation

$$A_f = \frac{3}{5} N_o \pi d_p^2 \qquad (2\text{-}67)$$

$d_p$ is the bubble diameter and $N_o$ is the number of perforations
per plate.


The overall coefficient of mass-transfer during bubble
formation can be represented as

$$K_{df} = \frac{(k_{cf}^* \; k_{df}^*)}{k_{cf}^* + k_{df}^* \; \alpha} \qquad (2\text{-}68)$$

where $k_{df}^*$ = individual disperse-phase coefficient of mass
transfer during bubble formation

$k_{cf}^*$ = individual continuous-phase coefficient of mass
transfer during bubble formation

$\alpha$ = slope of the equilibrium curve

Skelland and Hemler[37] used least-squares statistical tech-
niques to correlate 23 experimental measurements to obtain
an empirical correlation for $k_{df}^*$. This equation,

$$k_{df}^* = 0.0432 \; \frac{d_p}{t_f}\left(\frac{\rho}{M}\right)_{Av} \left(\frac{u_o^2}{d_p g}\right)^{0.089} \left(\frac{d_p^2}{t_f D_d}\right)^{-0.334} \left(\frac{\mu_d}{\sqrt{\rho_d d_p \sigma g_c}}\right)^{-0.601} \qquad (2\text{-}69)$$

has an average absolute deviation of about 26 percent.

A similar study was performed by Skelland and Minhas$^{(38)}$. They proposed an equation to estimate $k_{cf}^*$ as

$$K_{cf}^* = 0.386 \left(\frac{d_p}{t_f}\right)\left(\frac{\rho}{M}\right)_{Av}\left(\frac{D_c}{t_f}\right)^{0.5}\left(\frac{\rho_c \sigma g_c}{\Delta\rho g t_f \mu_c}\right)^{0.407}\left(\frac{g\, t_f^2}{d_p}\right)^{0.148} \qquad (2\text{-}70)$$

This equation correlated 20 data points with an average absolute deviation of 11 percent.

In equation (2-69) and equation (2-70), $t_f$ is the time of formation of a single bubble, it can be expressed as

$$t_f = \frac{2}{3}\frac{d_p^3}{d_o^2 u_o} \qquad (2\text{-}71)$$

and $d_o$ = orifice or perforation diameter

$u_o$ = velocity of disperse-phase through orifice

$g$ = acceleration due to gravity

$g_c$ = conversion factor

$M$ = mean molecular weight of phases under consideration

$\rho$ = mean densities of phases under consideration

$\sigma$ = surface tension

$\mu_c$, $\mu_d$ = viscosities of continuous and disperse phases

$D_c$, $D_d$ = diffusivity coefficients of solute in continuous and disperse phases

$\rho_c$, $\rho_d$, $\Delta\rho$ = densities of continuous and disperse phases; absolute values of $\rho_c - \rho_d$.

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## D.  Mathematical Simulation Of The Distillation Operation In A Stagewise Column

Stagewise columns are widely used in gas-liquid contacting operations such as distillation, gas absorption, and stripping.  These types of operation achieve intimate contact between the vapor phase and liquid phase in a discontinuous manner.  The stage may take the form of bubble-cap plate, sieve plate, or a variable orifice plate.  The plate contact device is designed to contact the vapor and liquid in such a manner that area and time of contact are maximized so as to approach the equilibrium stage.  This section presents a method that uses plate-to-plate calculations involving material and enthalpy balances, vapor-liquid equilibrium relationship, physical properties, tray hydraulics, and rate of mass-transfer to determine the quantities of liquid and vapor, the temperature of each plate, and the composition of each stream from each plate.

## D.1  Binary Separation

A schematic representation of a plate is shown in Figure 7.  The vapor $V_{n-1}$ rising to the plate n from plate n-1 and the liquid $L_{n+1}$ falling from plate n+1 to plate n,
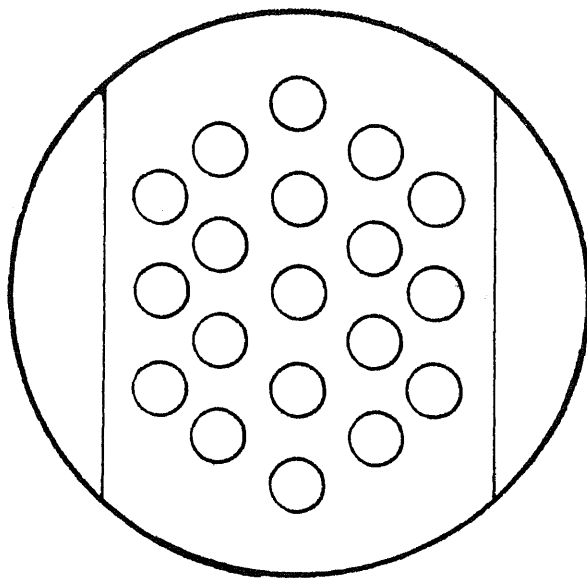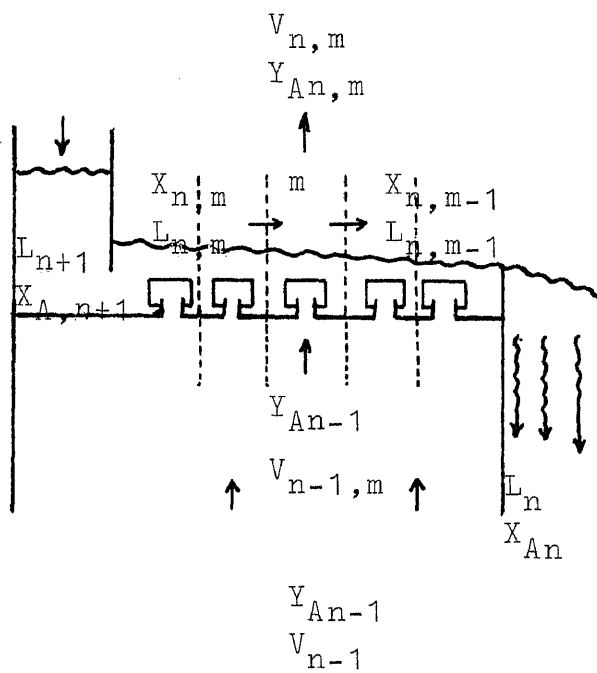
Fig. 7 (a) Top view of the layout of a bubble-cap tray;
(b) Side view of a bubble-cap tray as separated
into several regions. Material and energy balances
can be made on each region.

the vapor and liquid phases are intimately contacted by
bubble-caps. In the plate, plug flow is assumed as the liquid
flow pattern across from the submerged inlet weir to the over-
flow outlet weir. The material and energy balances combined
with the rate of mass-transfer equations are modeled to a
section perpendicular to the direction of liquid flow on the
plate. The vapor-liquid equilibrium relationship assumed
that the vapor phase is ideal and that the liquid phase can
be represented by the UNIFAC equation(11).

As illustrated in Figure 7, the plate can be separated
into several regions that perpendicular to the direction of
liquid flow. If there are N bubble-caps on the plate, the
flow rate of vapor passes through each bubble-cap is $V_{n-1}/N$.
Now, assume that the mth region on the plate has $N_m$ bubble-
caps, then the flow rate of vapor enters the mth region,
$V_{n-1,m}$, is $N_m V_{n-1}/N$. Take the mth region in consideration,
the overall material balances around the mth region can be
written as

$$V_{n-1,m} + L_{n,m} = V_{n,m} + L_{n,m-1} \qquad (2-72)$$

The component material balance is

$$V_{n-1,m} Y_{A,n-1} + L_{n,m} X_{A,n,m} = V_{n,m} Y_{A,n,m} + L_{n,m-1} X_{A,n,m-1}$$

$$(2-73)$$

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The energy balance is

$$V_{n-1,m} H_v(Y_{A,n-1}, T_{n-1}) + L_{n,m} h_l(X_{A,n,m}, T_n)$$

$$= V_{n,m} H_V(Y_{A,n,m}, T_n) + L_{n,m-1} h_l(X_{A,n,m-1}, T_n) \qquad (2-74)$$

The rate of mass-transfer during bubble formation is

$$Q_f = K_{df,n,m} A_{f,n,m} (Y_{A,n-1} - Y_{Agl,n,m}) \qquad (2-75)$$

which can also be written as

$$Q_f = V_{n-1,m} (Y_{A,n-1} - Y_{A0,n,m}) \qquad (2-76)$$

The rate of mass-transfer during bubble rising is

$$Q_r = (Y_{A0,n,m} - Y_{Agl,n,m}) F(N_{sh}, \tau, \alpha_n, A_{eff}) \qquad (2-77)$$

The overall rate of mass-transfer including bubble rising
and formation is

$$Q_f + Q_r = V_{n-1,m} Y_{A,n-1} - V_{n,m} Y_{A,n,m} \qquad (2-78)$$

The overall material balance around the plate n is

$$V_{n-1} + L_{n+1} = V_n + L_n \qquad (2-79)$$

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The component material balance around the plate n is

$$V_{n-1} \, Y_{A,n-1} + L_{n+1} \, X_{A,n+1} = V_n \, Y_{A,n} + L_n \, X_{A,n} \qquad (2\text{-}80)$$

The energy balance around the plate n is

$$V_{n-1} \sum_{i=1}^{2} H_V(Y_{i,n-1}, \, T_{n-1}) + L_{n+1} \sum_{i=1}^{2} h_l(X_{i,n+1}, \, T_{n+1})$$

$$= V_n \sum_{i=1}^{2} H_V(Y_{i,n}, \, T_n) + L_n \sum_{i=1}^{2} h_l(X_{i,n}, \, T_n) \qquad (2\text{-}81)$$

The restriction on fractional concentrations are

$$X_{A,n} + X_{B,n} = 1 \qquad \text{and} \qquad Y_{A,n} + Y_{B,n} = 1 \qquad (2\text{-}82)$$

where the variables used in equation (2-72) to equation (2-82) are

$V_{n-1}$ = the flow rate of vapor entering the plate n

$V_n$ = the flow rate of vapor leaving the plate n

$L_{n+1}$ = the flow rate of liquid entering the plate n

$L_n$ = the flow rate of liquid leaving the plate n

$Y_{A,n-1}$ = the mole fraction of A in vapor phase entering the plate n

$Y_{A,n}$ = the mole fraction of A in vapor phase leaving the plate n

$X_{A,n+1}$ = the mole fraction of A in liquid phase entering the plate n

$X_{A,n}$ = the mole fraction of A in liquid phase leaving the plate n

$Y_{Agl,n,m}$ = the mole fraction of A in vapor phase which is in equilibrium with the existing liquid in nth plate mth region

$Y_{AO,n,m}$ = the initial mole fraction of A in vapor phase after bubble formed in nth plate mth region

$H_v$ = enthalpy of vapor

$h_l$ = enthalpy of liquid

$F(N_{sh}, \tau, \alpha_n, A_{eff})$ = as defined in equation (2-33)

The procedure to achieve these plate-to-plate calculations is as following:

1. $Y_{Agl,n,m}$ is in equilibrium with $X_{A,n,m-1}$ can be calculated by using the UNIFAC method.

2. $Y_{AO,n,m}$ can be solved by combining equation (2-75) with equation (2-76), the result is

$$Y_{AO,n,m} = Y_{A,n-1} - \frac{K_{df,n,m} \, A_{f,n,m}}{V_{n-1,m}} (Y_{A,n-1} - Y_{Agl,n,m}) \quad (2\text{-}83)$$

3. There are insufficient equations to evaluate the composition and the quantity of $V_{n,m}$. However, one can initially assume that $V_{n,m} = V_{n-1,m}$ (constant molar overflow is assumed) to proceed the calculations.

4. $Y_{A,n,m}$ can be obtained by combining equations (2-76), (2-77), and (2-78) as

$$Y_{A,n,m} = Y_{AO,n,m} \frac{V_{n-1,m}}{V_{n,m}} - (Y_{AO,n,m} - Y_{Agl,n,m}) \frac{F(N_{sh},\tau,\alpha_n,A_{eff}}{V_{n,m}}$$

$$(2\text{-}84)$$

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5. $L_{n,m}$ can be solved by using equation (2-72).

6. The mole fraction of A of liquid entering the mth region can then be calculated by using the equation below

$$X_{A,n,m} = \frac{V_{n,m}\,Y_{A,n,m} + L_{n,m-1}\,X_{A,n,m-1} - V_{n-1,m}\,Y_{A,n-1}}{L_{n,m}} \quad (2-85)$$

7. A new quantity of $V_{n,m}$ can be evaluated by using equation (2-74), and a new composition $Y_{A,n,m}$ can be obtained by inserting the new value of $V_{n,m}$ into equation (2-84). Convergence is checked by $|Y_{A,n,m,new} - Y_{A,n,m,old}| <$ specified error. The speed of convergence depends on how strong the molal latent heat varies with the temperature and composition, and that the molal heat capacities varies with temperature. Repeat step 4 to step 7 if necessary, and as soon as the absolute error falls below the specified maximum error, the calculation is stoped and proceed to next region.

8. The local efficiency can be defined as

$$E_{local,m} = \frac{Y_{A,n,m} - Y_{A,n-1}}{Y_{Agl,n,m} - Y_{A,n-1}} \quad (2-86)$$

9. The average composition of vapor leaving the plate n can be obtained by

$$Y_{A,n,avg} = \frac{\sum_{m=1}^{m} Y_{A,n,m}}{m} \quad (2-87)$$

and the average plate efficiency can be defined as

$$E_{Avg} = \frac{\sum_{m=1}^{m} E_{local,m}}{m} \quad (2-88)$$

10. The quantity of vapor leaving the plate n is

$$V_n = \sum_{m=1}^{m} V_{n,m} \qquad (2\text{-}89)$$

and the quantity of liquid entering the plate n can be solved by using equation (2-79).

11. The next plate temperature, $T_{n+1}$, can be estimated by using equation (2-81), the result is

$$\sum_{i=1}^{2} h_l(X_{i,n+1}, T_{n+1}) = \left( V_n \sum_{i=1}^{2} H_v(Y_{i,n}, T_n) + L_n \right.$$

$$\left. \sum_{i=1}^{2} h_l(X_{i,n}, T_n) - V_{n-1} \sum_{i=1}^{2} H_v(Y_{i,n-1}, T_{n-1}) \right] / L_{n+1} \qquad (2\text{-}90)$$

The procedure mentioned above when combined with the specified operating conditions of a distillation column can solve the binary separation by repeating the plate-to-plate calculations from the bottom to the top of the column.

## D.2  Multicomponent Separation

The term multicomponent system can be used to describe
all systems containing more than two components.  For a sys-
tem having N components to form the mixture, there are N-1
independent equations that can be written for the component
material and energy balances.  The overall material balances,
component material balances, energy balances, and the rate
of mass-transfer equations apply to the multicomponent dis-
tillation operation are as following:  By referring to
Figure 7, the overall material balances around the mth
region can be written as

$$V_{n-1,m} + L_{n,m} = V_{n,m} + L_{n,m-1} \qquad (2\text{-}91)$$

The component material balances are

$$V_{n-1,m}\, Y_{i,n-1} + L_{n,m}\, X_{i,n,m}$$

$$= V_{n,m}\, Y_{i,n,m} + L_{n,m-1}\, X_{i,n,m-1} \qquad i = 1,\ \ldots,\ N\text{-}1 \qquad (2\text{-}92)$$

The energy balances around the mth region is

$$V_{n-1,m} \sum_{i=1}^{N} H_v(Y_{i,n-1},\ T_{n-1}) + L_{n,m} \sum_{i=1}^{N} h_l(X_{i,n,m},\ T_n)$$

$$= V_{n,m} \sum_{i=1}^{N} H_v(Y_{i,n,m},\ T_n) + L_{n,m-1} \sum_{i=1}^{N} h_l(X_{i,n,m-1},\ T_n) \qquad (2\text{-}93)$$

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The rate of mass-transfer during bubble formation for each component is

$$Q_{f,i} = K_{df,i,n,m} \, A_{f,n,m} \, (Y_{i,n-1} - Y_{igl,n,m}) \quad i = 1, \ldots, N-1$$

$$(2-94)$$

which can also be written as

$$Q_{f,i} = V_{n-1,m} \, (Y_{i,n-1} - Y_{i0,n,m}) \quad i = 1, \ldots, N-1 \quad (2-95)$$

The rate of mass-transfer during bubble rising for each component is

$$(Q_r)_{n,m} = (t)_{n,m} \, F_2(\sigma_i, \eta, \tau_i, A_{eff})_{n,m} \, (t)^{-1}_{n,m} \left[ (Y_0) - (Y_{gl}) \right]_{n,m}$$

$$(2-96)$$

The overall rate of mass-transfer including bubble rising and formation is

$$Q_{f,i} + Q_{r,i} = V_{n-1,m} \, Y_{i,n-1} - V_{n,m} \, Y_{i,n,m} \quad i = 1, \ldots, N-1$$

$$(2-97)$$

The overall material balance around the plate n is

$$V_{n-1} + L_{n+1} = V_n + L_n \qquad (2-98)$$

The component material balance around the plate n for each component is

$$V_{n-1} \, Y_{i,n-1} + L_{n+1} \, X_{i,n+1} = V_n \, Y_{i,n} + L_n \, X_{i,n} \qquad (2\text{-}99)$$

The energy balance around the plate n is

$$V_{n-1} \sum_{i=1}^{N} H_v(Y_{i,n-1}, \, T_{n-1}) + L_{n+1} \sum_{i=1}^{N} h_l(X_{i,n+1}, \, T_{n+1})$$

$$= V_n \sum_{i=1}^{N} H_v(Y_{i,n}, \, T_n) + L_n \sum_{i=1}^{N} h_l(X_{i,n}, \, T_n) \qquad (2\text{-}100)$$

The restriction of fractional concentrations is

$$\sum_{i=1}^{N} X_{i,n} = 1 \qquad \text{and} \qquad \sum_{i=1}^{N} Y_{i,n} = 1 \qquad (2\text{-}101)$$

where

$(Q_r)$ = the column vector of the rate of mass-transfer during bubble rising

$(Y_0)$ = the column vector of the initial mole fraction after bubble formed

$(Y_{gl})$ = the column vector of the mole fraction that in equilibrium with the existing liquid

The plate-to-plate calculation can be achieved by using numerical methods for a multicomponent separation. However, it is possible to obtain analytical plate-to-plate calculation for a ternary system. This will be further discussed below.

For a ternary system, equation (2-64) and equation (2-65) are used to substitute equation (2-96). The following procedure is used to solve s ternary separation.

1. $Y_{Agl,n,m}$ and $Y_{Bgl,n,m}$ can be evaluated from the UNIFAC method.

2. $Y_{A0,n,m}$ and $Y_{B0,n,m}$ can be obtained by the following equations respectively.

$$Y_{A0,n,m} = Y_{A,n-1} - \frac{K_{df,A,n,m} \, A_{f,n,m}}{V_{n-1,m}} \left( Y_{A,n-1} - Y_{Agl,n,m} \right)$$

$$(2\text{-}102)$$

$$Y_{B0,n,m} = Y_{B,n-1} - \frac{K_{df,B,n,m} \, A_{f,n,m}}{V_{n-1,m}} \left( Y_{B,n-1} - Y_{Bgl,n,m} \right)$$

$$(2\text{-}103)$$

3. There are insufficient equations to evaluate the compositions and the quantity of $V_{n,m}$. One can initially assume $V_{n,m} = V_{n-1,m}$ to proceed the calculations.

4. The exit concentrations of component A and B can be solved by combining equations (2-95), (2-97), (2-64), and (2-65). The results are

$$Y_{A,n,m} = Y_{A0,n,m} \frac{V_{n-1,m}}{V_{n,m}} - \left[ \frac{(D_{11}-\sigma_2)(Y_{A0}-Y_{Agl})+D_{12}(Y_{B0}-Y_{Bgl})}{\sigma_1 - \sigma_2} \right]_{n,m}$$

$$\frac{F_2(\sigma_1,n,\tau_1,A_{eff})_{n,m}}{V_{n,m}} - \left[ \frac{(D_{11}-\sigma_1)(Y_{A0}-Y_{Agl})+D_{12}(Y_{B0}-Y_{Bgl})}{\sigma_2 - \sigma_1} \right]_{n,m}$$

$$\frac{F_2(\sigma_2,n,\tau_2,A_{eff})_{n,m}}{V_{n,m}}$$

$$(2\text{-}104)$$

$$Y_{B,n,m} = Y_{B0,n,m} \frac{V_{n-1,m}}{V_{n,m}} - \left\{ \frac{D_{21}(Y_{A0}-Y_{Agl})+(D_{22}-\sigma_2)(Y_{B0}-Y_{Bgl})}{\sigma_1 - \sigma_2} \right\}_{n,m}$$

$$\frac{F_2(\sigma_1,\eta,\tau_1,A_{eff})_{n,m}}{V_{n,m}} - \left\{ \frac{D_{21}(Y_{A0}-Y_{Agl})+(D_{22}-\sigma_1)(Y_{B0}-Y_{Bgl})}{\sigma_2 - \sigma_1} \right\}_{n,m}$$

$$\frac{F_2(\sigma_2,\eta,\tau_2,A_{eff})_{n,m}}{V_{n,m}} \qquad\qquad (2\text{-}105)$$

5. $L_{n,m}$ can be solved by using equation (2-91).

6. The mole fractions of liquid entering the mth region for component A and B can be calculated by using equation (2-92).

7. The new quantity of $V_{n,m}$ can be evaluated by using equation (2-93). Convergence is checked by $|V_{n,m,new} - V_{n,m,old}|/V_{n,m,old} <$ specified error. Repeat step 4 to step 7 if necessary.

8. The local efficiency of component A and B are

$$E_{A,local,m} = \frac{Y_{A,n,m} - Y_{A,n-1}}{Y_{Agl,n,m} - Y_{A,n-1}} \qquad\qquad (2\text{-}106)$$

$$E_{B,local,m} = \frac{Y_{B,n,m} - Y_{B,n-1}}{Y_{Bgl,n,m} - Y_{B,n-1}} \qquad\qquad (2\text{-}107)$$

9. The average compositions of component A and B leaving the plate n are

$$Y_{A,n,avg} = \frac{\sum_{m=1}^{m} Y_{A,n,m}}{m} \qquad\qquad (2\text{-}108)$$

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$$Y_{B,n,avg} = \frac{\sum\limits_{m=1}^{m} Y_{B,n,m}}{m} \qquad (2\text{-}109)$$

and the average plate efficiencies of component A and B are

$$E_{A,avg} = \frac{\sum\limits_{m=1}^{m} E_{A,local,m}}{m} \qquad (2\text{-}110)$$

$$E_{B,avg} = \frac{\sum\limits_{m=1}^{m} E_{B,local,m}}{m} \qquad (2\text{-}111)$$

10. The quantity of vapor leaving the plate n is

$$V_n = \sum\limits_{m=1}^{m} V_{n,m} \qquad (2\text{-}112)$$

and the quantity of liquid entering the plate n can can be solved by using the equation (2-98).

11. The next plate temperature, $T_{n+1}$, can be estimated by using the equation (2-100), the result is

$$\sum\limits_{i=1}^{3} h_l(X_{i,n+1}, T_{n+1}) = \left[ V_n \sum\limits_{i=1}^{3} H_v(Y_{i,n}, T_n) + L_n \right.$$

$$\left. \sum\limits_{i=1}^{3} h_l(X_{i,n}, T_n) - V_{n-1} \sum\limits_{i=1}^{3} H_v(Y_{i,n-1}, T_{n-1}) \right]/L_{n+1} \qquad (2\text{-}113)$$

The procedure described above can be combined with the specific operating conditions of a ternary distillation separation to accomplish the plate-to-plate calculations from the bottom to the top of the column.

CHAPTER III


RESULTS AND CONCLUSIONS


In conjunction with this study on the mathematical
modeling of the distillation operation from non-equilibrium
approach, the following distillation operations were used to
verify the method proposed by the author: (1) a binary separa-
tion using a one-stage column having a single-bubble cap;
(2) a binary separation in a multi-stage column with a single-
bubble cap; (3) a binary separation in a multi-stage column
with a given multi-cap arrangement; and (4) a ternary separa-
tion in a multi-stage column with two-bubble caps.  The
results of the comparisons between the theoretical predictions
and the experimental data are presented in the catagories of
binary separation and ternary separation as following:


A.  Binary Separation

    A.1  Single-Stage, Single-Bubble Cap Column

         The effect of liquid composition on plate

    efficiency is studied.  Equipment consists of a

    one-stage column, 6-inch in diameter with one bubble

    cap on the plate.  There are 8 slots per cap, the

width of each slot in the bubble cap is 0.25-inch
and the liquid level on the plate is 13/16-inch
high.  Complete details of the equipment are given
by Carey(5).  Experimental work and theoretical
simulation are made by feeding various liquid compo-
sitions of benzene-toluene mixture in a single-plate
column which operates at total reflux condition.
The results show a slight effect of liquid composi-
tion on plate efficiency as illustrated in Figure 8.
A very good agreement can be observed when the theo-
retical predictions are compared with the experimental
data obtained by Carey(5).

A.2  Multi-Stage Column With Single-Bubble Cap On Each
     Plate

     The plate-to-plate analysis of the liquid are
performed in various types of experimental equip-
ment from a ten-plate column to a seven-plate column.
Both of the ten-plate and seven-plate columns have
single-bubble cap on each plate.  In a ten-plate
column, each bubble cap has 48 slots, with 3/16-
inch width of each slot and the liquid seal has 1.5-
inch high on the plate.  In a seven plate column,
there are 36 slots per cap, with 1-inch high of
liquid level on the plate and each slot has 1/8-
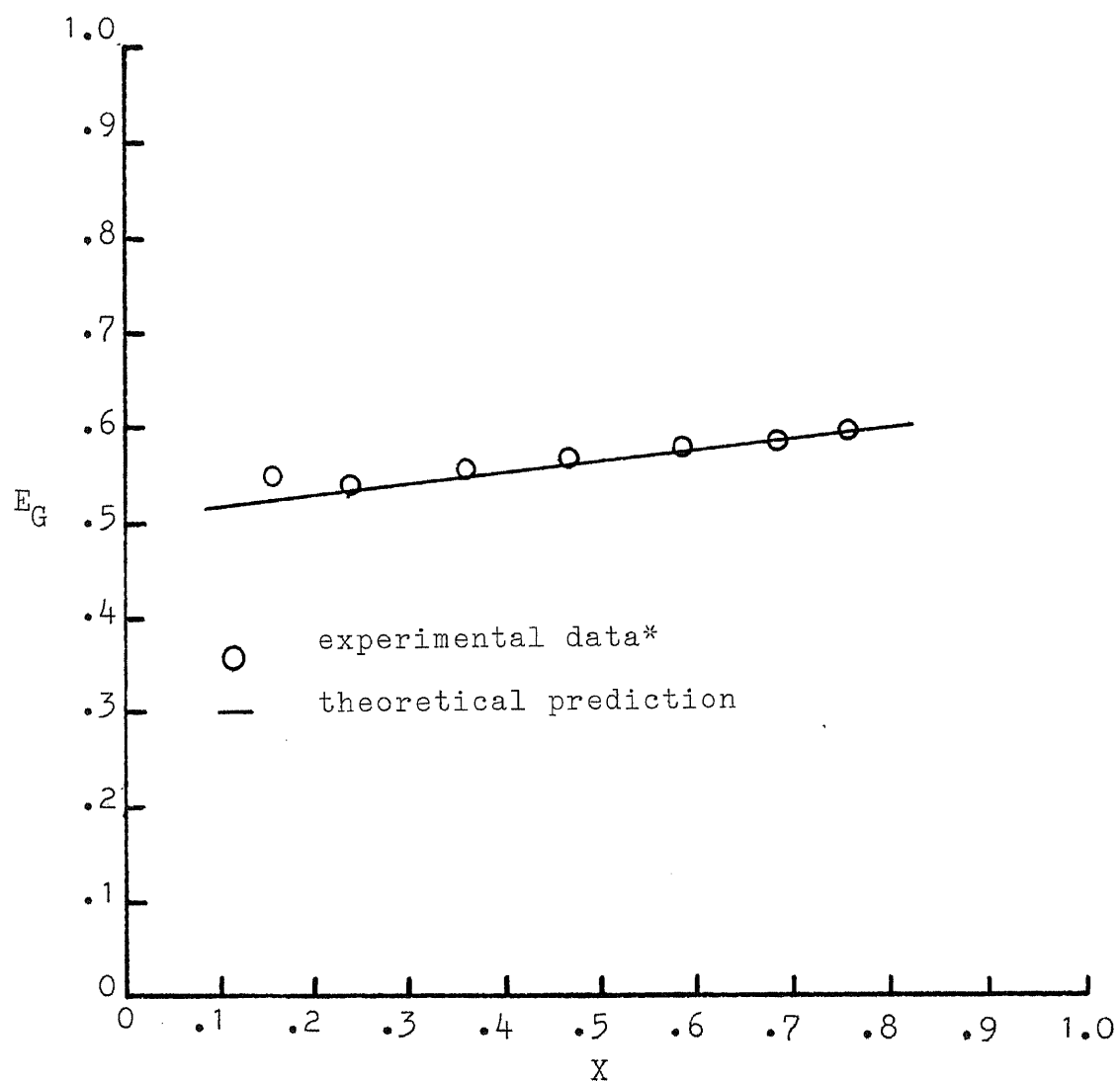
Fig. 8   Effect of composition on plate efficiency,
single plate column (Benzene-Toluene runs).

* Data from Carey(5).

inch of width. The experimental runs are conducted
with total reflux, the complete details for each run
are given by Carey(5).

The mathematical model proposed in this work is
used to simulate the operations with various operating
conditions. The plate-to-plate calculations are performed
to estimate the compositions of entering liquid phase and
exiting gas phase on each plate. A pseudo-equilibrium
curve can be located on the McCabe-Thiele diagram as
shown in Figure 9 and Figure 10, for the typical runs
in a seven-plate column and a ten-plate column respectively.
This pseudo-equilibrium curve represents the real compo-
sitions of liquid and gad phases on the actual stages.

The theoretical predictions listed in Table II are
the mathematical simulation results of five experimental
runs in a seven-plate column. A maximum error of 12.5
percent can be observed when the experimental data are
compared with these theoretical predictions in a seven-
plate column. Four sets of experimental runs are studied
in a ten-plate column. The results are tabulated in Table
III, a 19.1 percent of maximum error is found when the
comparisons are made between the theoretical predictions
and the experimental data.
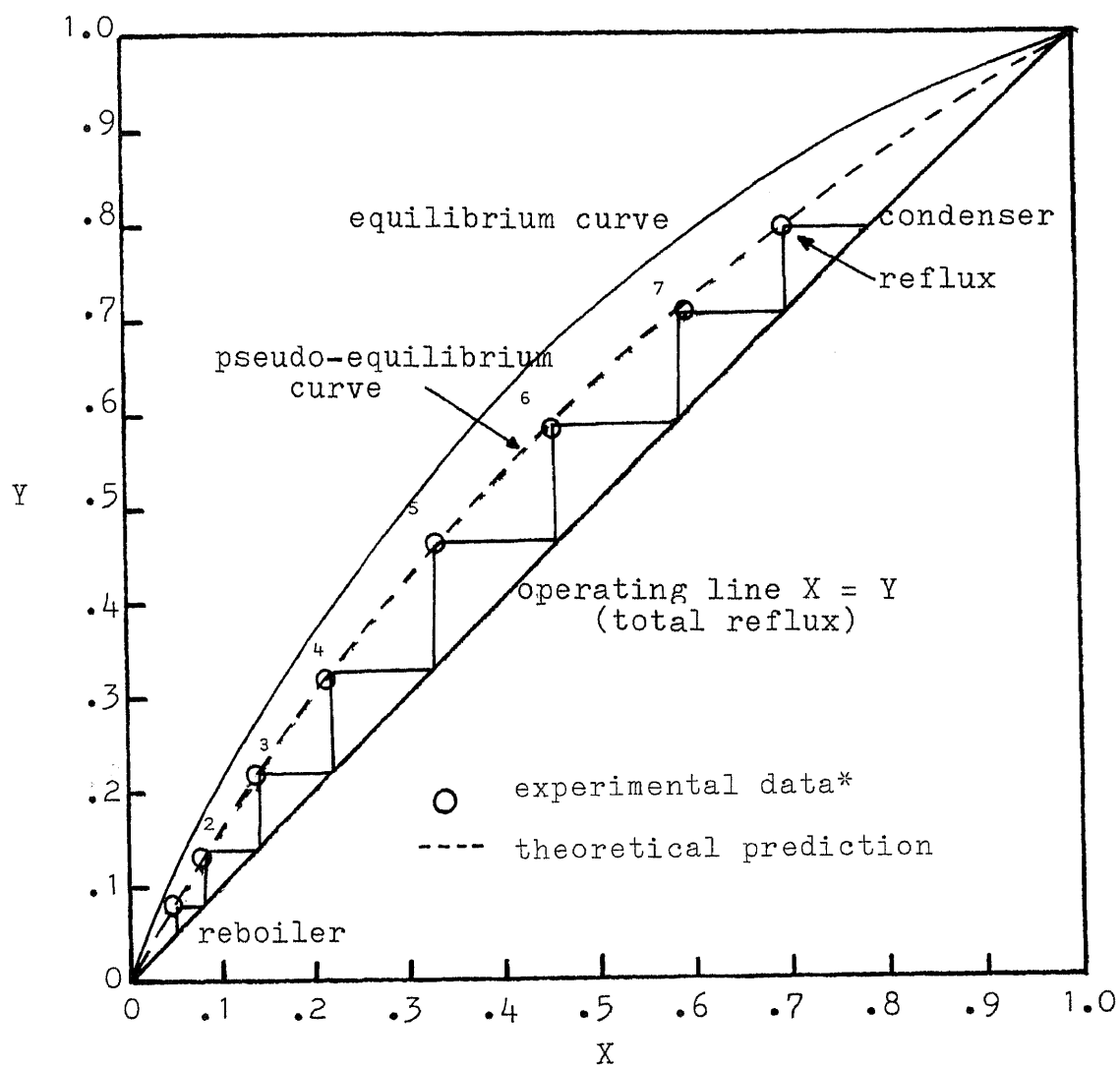
Fig. 9  McCabe and Thiele diagram for a 7-plate column,
showing pseudo-equilibrium curve and actual stages.

* Data from Carey(5).

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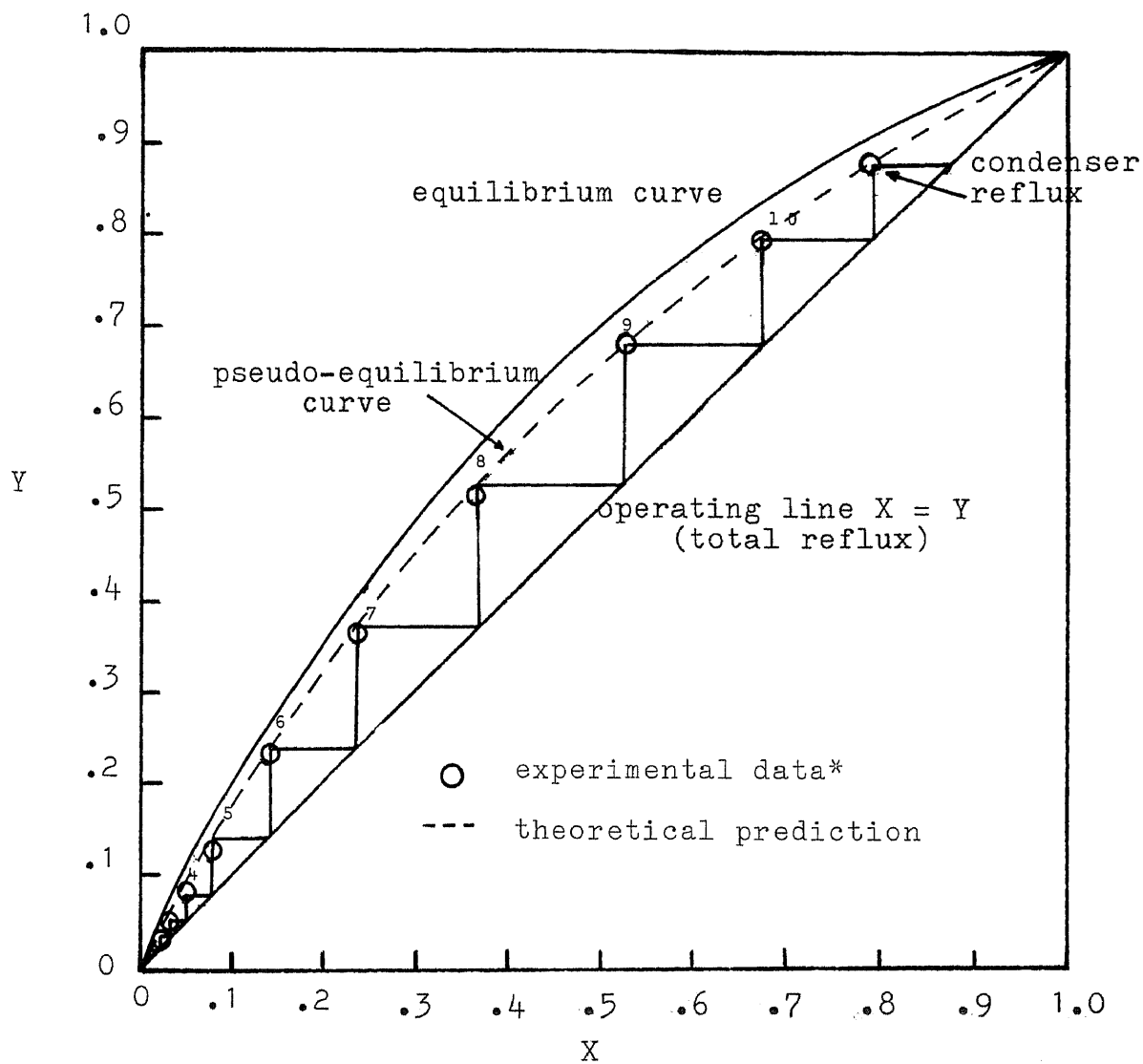
Fig. 10  McCabe and Thiele diagram for a 10-plate
        column, showing theoretical predicted
        pseudo-equilibrium curve and actual stages.

* Data from Carey(5).

Table II

Rectification of Benzene-Toluene Mixtures
With Total Reflux, In Seven-Plate Column

| Run | PW-1 | | | PW-2 | | | PW-3 | | | PW-4 | | | PW-7 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Expt. | *Calc. | % | Expt. | *Calc. | % | Expt. | *Calc. | % | Expt. | *Calc. | % | Expt. | *Calc. | |
| Still | .891 | | | .954 | | | .927 | | | .722 | | | .911 | | |
| Plate 1 | .859 | .828 | -3.6 | .905 | .926 | 1.6 | .861 | .872 | 1.3 | .64 | .603 | - 5.7 | - | .850 | - |
| 2 | .737 | .740 | .4 | .857 | .866 | 1.1 | .795 | .788 | - .9 | .462 | .474 | 2.6 | .75 | .76 | 1.3 |
| 3 | .624 | .731 | 1.1 | .775 | .784 | 1.1 | .678 | .671 | -1.0 | .385 | .353 | - 8.3 | .637 | .641 | .6 |
| 4 | .524 | .510 | -2.6 | .686 | .673 | -1.9 | .514 | .529 | 2.9 | .269 | .251 | - 6.6 | .5 | .505 | 1.0 |
| 5 | .4 | .391 | -2.2 | .541 | .542 | .2 | .383 | .386 | .8 | .187 | .173 | - 7.5 | .386 | .372 | -3.6 |
| 6 | .302 | .287 | -4.9 | .436 | .408 | -6.4 | .263 | .264 | .4 | .134 | .116 | -13.4 | .254 | .258 | 1.5 |
| 7 | .216 | .205 | -5.0 | .305 | .290 | -4.9 | .147 | .152 | 3.4 | .088 | .077 | -12.5 | .149 | .163 | 9.4 |

% = Percentage Error = $\dfrac{\text{Calculated} - \text{Experiment}}{\text{Experiment}}$ x 100%

* Data from Carey(5).

Table III

Rectification of Benzene-Toluene Mixtures
With Total Reflux, In Ten-Plate Column

| Run | G-8 | | | G-9 | | | G-10 | | | G-11 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Expt.* | Calc. | % | Expt.* | Calc. | % | Expt.* | Calc. | % | Expt.* | Calc. | % |
| Still | .988 | | | .925 | | | .969 | | | .97 | | |
| Plate 1 | .978 | .977 | - .1 | .867 | .868 | - .1 | .946 | .943 | - .3 | .942 | .935 | .3 |
| 2 | .964 | .958 | - .6 | .784 | .780 | - .5 | .898 | .899 | .1 | .907 | .902 | - .5 |
| 3 | .924 | .922 | - .2 | .663 | .656 | -1.1 | .826 | .825 | - .1 | .842 | .839 | -1.4 |
| 4 | .871 | .862 | -1.0 | .513 | .506 | -1.3 | .728 | .716 | -1.6 | .731 | .723 | -1.1 |
| 5 | .786 | .765 | -2.6 | .357 | .356 | - .3 | .58 | .572 | -1.3 | .595 | .581 | -2.3 |
| 6 | .646 | .631 | -2.3 | .228 | .230 | .8 | .420 | .416 | - .9 | .429 | .424 | -1.2 |
| 7 | .488 | .473 | -3.1 | .140 | .141 | .7 | .279 | .276 | -1.1 | .284 | .282 | - .7 |
| 8 | .341 | .322 | -5.5 | .080 | .083 | 3.7 | .177 | .171 | -3.4 | .179 | .176 | -1.6 |
| 9 | .214 | .202 | -5.6 | .041 | .048 | 14.5 | .108 | .101 | -6.5 | .11 | .104 | -5.4 |
| 10 | .127 | .120 | -5.5 | .021 | .025 | 19.1 | .054 | .058 | 7.4 | .065 | .060 | -7.7 |

$$\% = \text{Percentage Error} = \frac{\text{Calculated} - \text{Experiment}}{\text{Experiment}} \times 100\%$$

* Data from Carey(5).

A.3  Multi-Stage Column With A Given Multi-Cap Arrange-
      ment On The Stage

   A.3-1  Ten-Plate Column With Two Bubble Caps On
          Each Plate


        The separation of carbon tetrachloride-toluene

   mixture is studied in a ten-plate column.  The

   column is 6-inch in diameter with two bubble caps

   on each plate.  The slots, twelve to a cap, are   .

   0.5-inch high and 0.25-inch wide.  The details of

   the column design are given by Huffman(19).  A

   typical run at total reflux and one atmosphere

   total pressure was conducted in this ten-plate

   column by Huffman(19).  The mathematical simula-

   tion of this operation is done by a sample computer

   program listed in Appendix E.  The result is illus-

   trated in Figure 11 as the concentration and temper-

   ature profiles are plotted vs. plate number.  Differ-

   ences can be found in between the theoretical pre-

   dictions and the experimental data on top four

   plates.  It is assumed that the differences are

   due to a particularly high efficiency (161%) of the

   top plate that was found in the experimental run

   and the inherited errors of the plate-to-plate

   calculations.
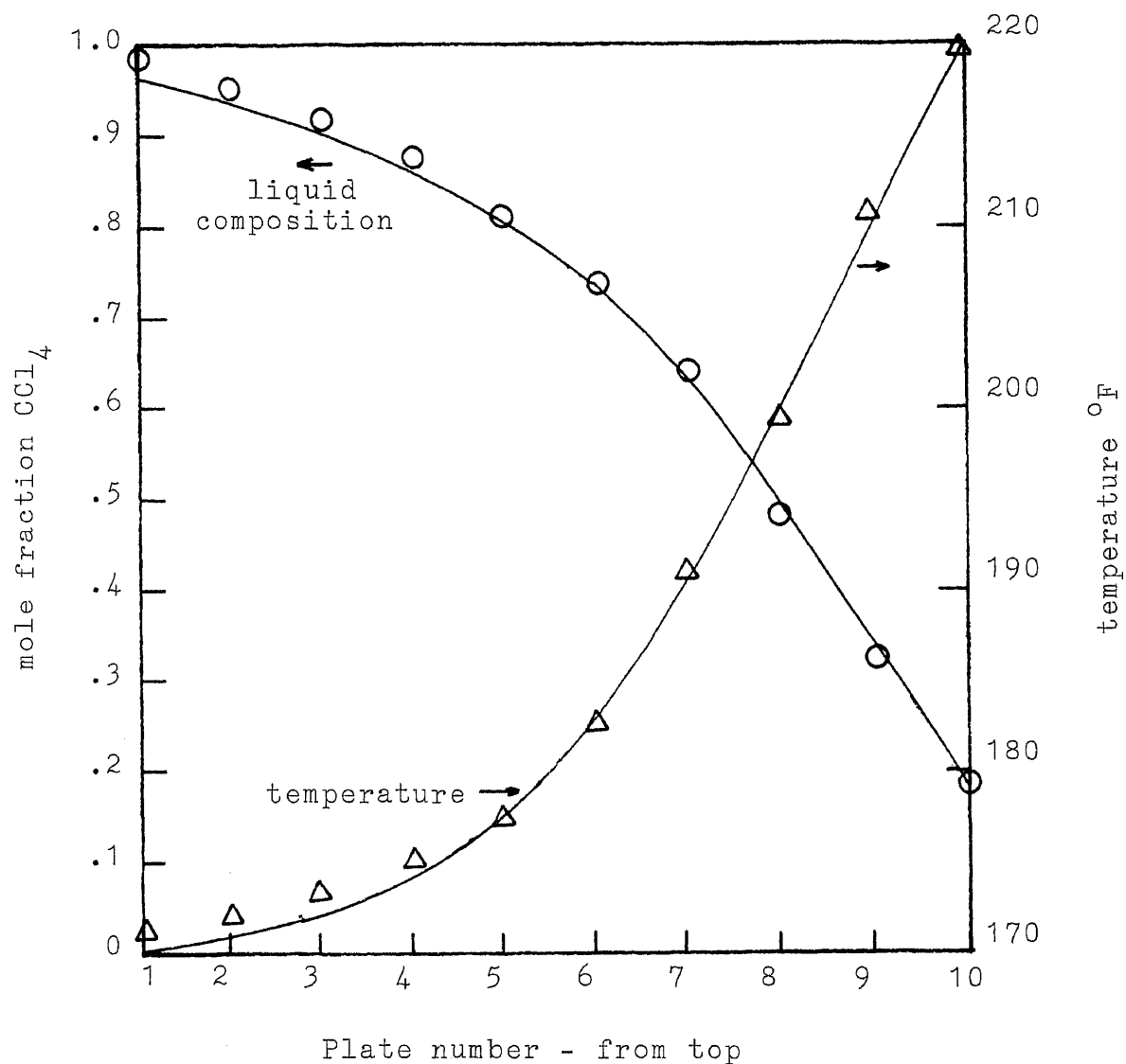
Fig. 11 Temperature and liquid composition on plates at total reflux for $CCl_4$-toluene separation.

O △ experimental data from Huffman(21)

—— theoretical prediction

A.3-2   Three-Plate Column With Ten Bubble Caps On
        Each Plate

Ethanol-water fractionation is used to study the
variation with liquid composition of local efficiency
at the center of a plate.  The equipment contains
three plates, each plate carries ten 3-inch bubble
caps with a 3-4-3 arrangement.  Each cap has 38 slots
with 1/8-inch of width.  The liquid level on the
plate is $1\frac{1}{4}$-inch.  The details of the column design
are given by Shilling(35).  Experimental runs were
made by Shilling at total reflux and 740 mmHg of total
pressure.  The mathematical simulation on this study
shows the liquid composition has little effect on the
local efficiency.  The result is shown in Figure 12.
It also shows that the theoretical predictions of
the local efficiencies are in good aggrement with
the experimental data.


B.   Ternary Separation


The separation of benzene-toluene-m-xylene mixture
is studied.  The reason to study the ternary separation
is because analytical plate-to-plate calculations can be
employed.  Two sets of experimental runs are used to
compare with the theoretical predictions.  The experi-
mental data are taken from the work done by Nord(25).
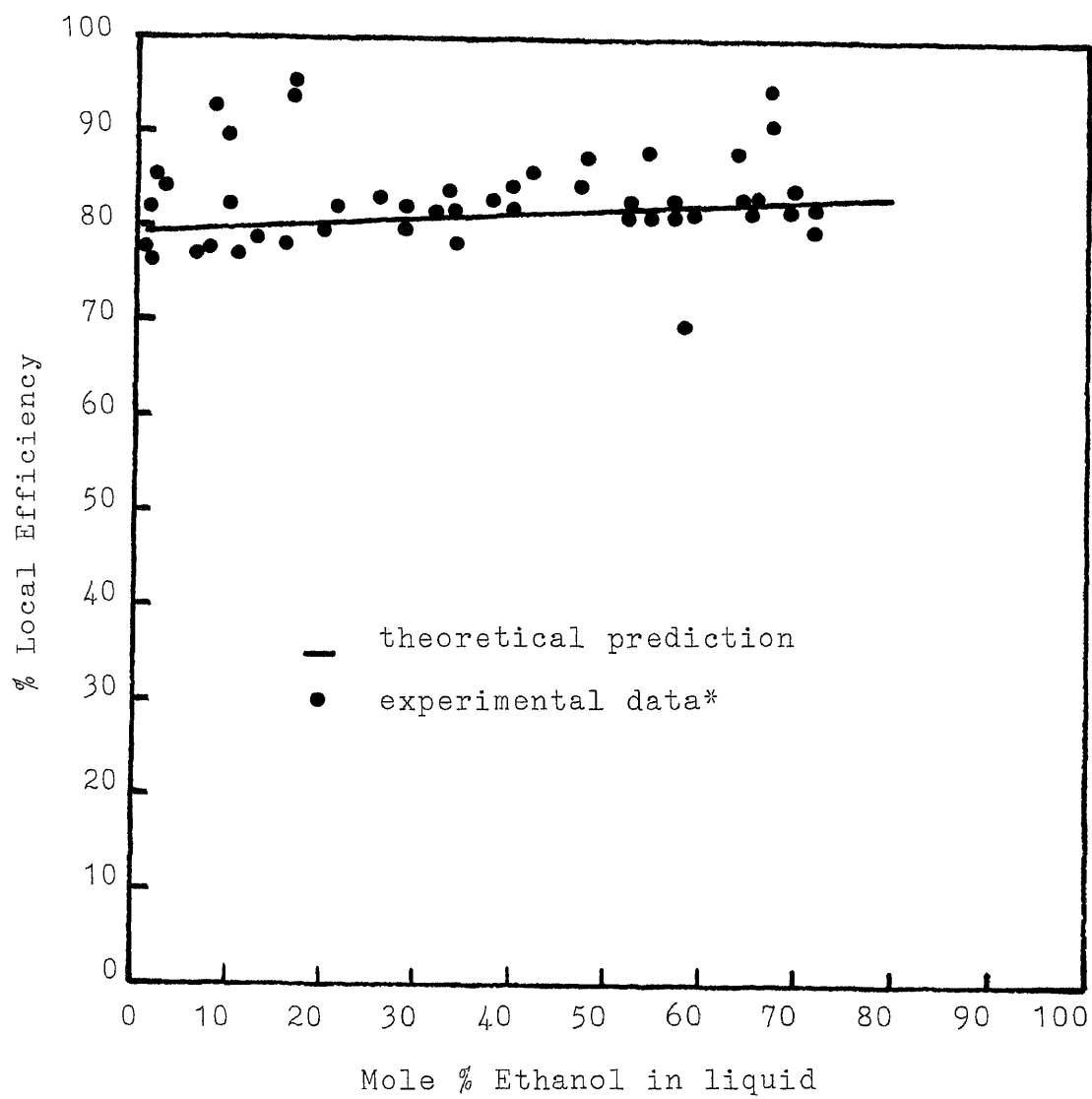
Fig. 12   Local efficiency vs. liquid composition at
          center of plate for ethanol-water separation


* Data from Shilling(35).

The experimental equipment that used by Nord consists
of a ten-plate column, 6-inch in diameter with two bubble
caps per plate.  The slots in the bubble caps are 0.5-
inch high and 0.25-inch wide and the liquid level on the
plate is about 0.5-inch above the center of the slots.
Complete details of the column design are given by
Huffman[19].  Experimental runs were made at total re-
flux.  Thus, by material balance it is evident that the
composition of the liquid leaving the plate is the same
as the average-vapor composition entering the plate.  The
mathematical simulation results are plotted as the liquid
composition vs. plate number as shown in Figure 13 and
Figure 14.  Good aggreement can be observed when the
results are compared with the experimental data (run-11
and run-12 in Nord's work).  A computer simulation pro-
gram for a ternary separation is attached in Appendix F.


C.  Conclusions


    The objectives of this work are (1) to develop a
mathematical model to simulate the mechanism of mass-
transfer in a distillation column, and (2) to develop a
method to achieve the plate-to-plate calculations to
quantitatively determine the compositions of phases and
the plate efficiencies.  The theoretical simulation was
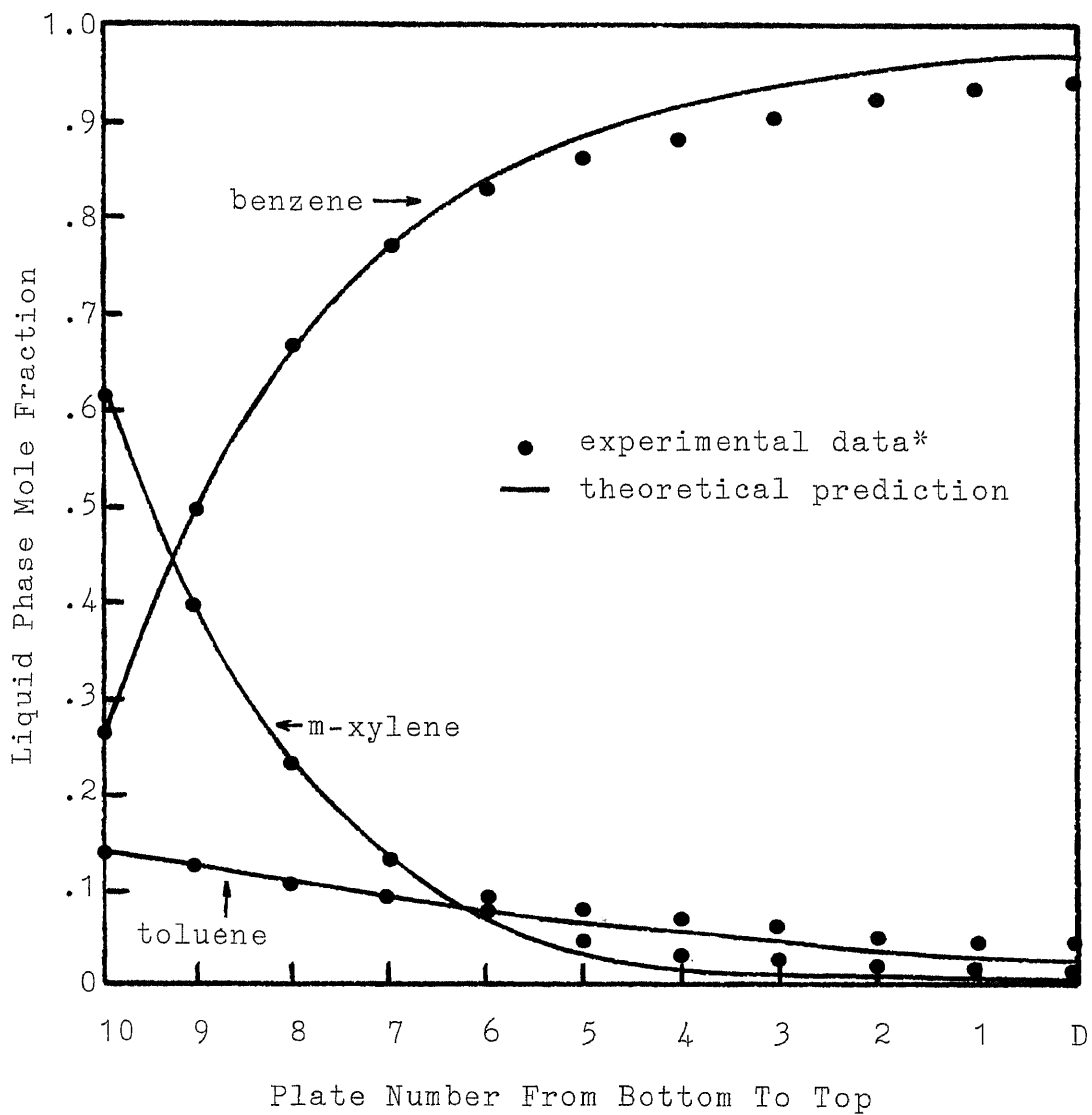
Fig. 13  Concentration profile plotted as liquid compo-
sition vs. plate number (benzene-toluene-m-
xylene separation, run - 11).

* Data from Nord(25).

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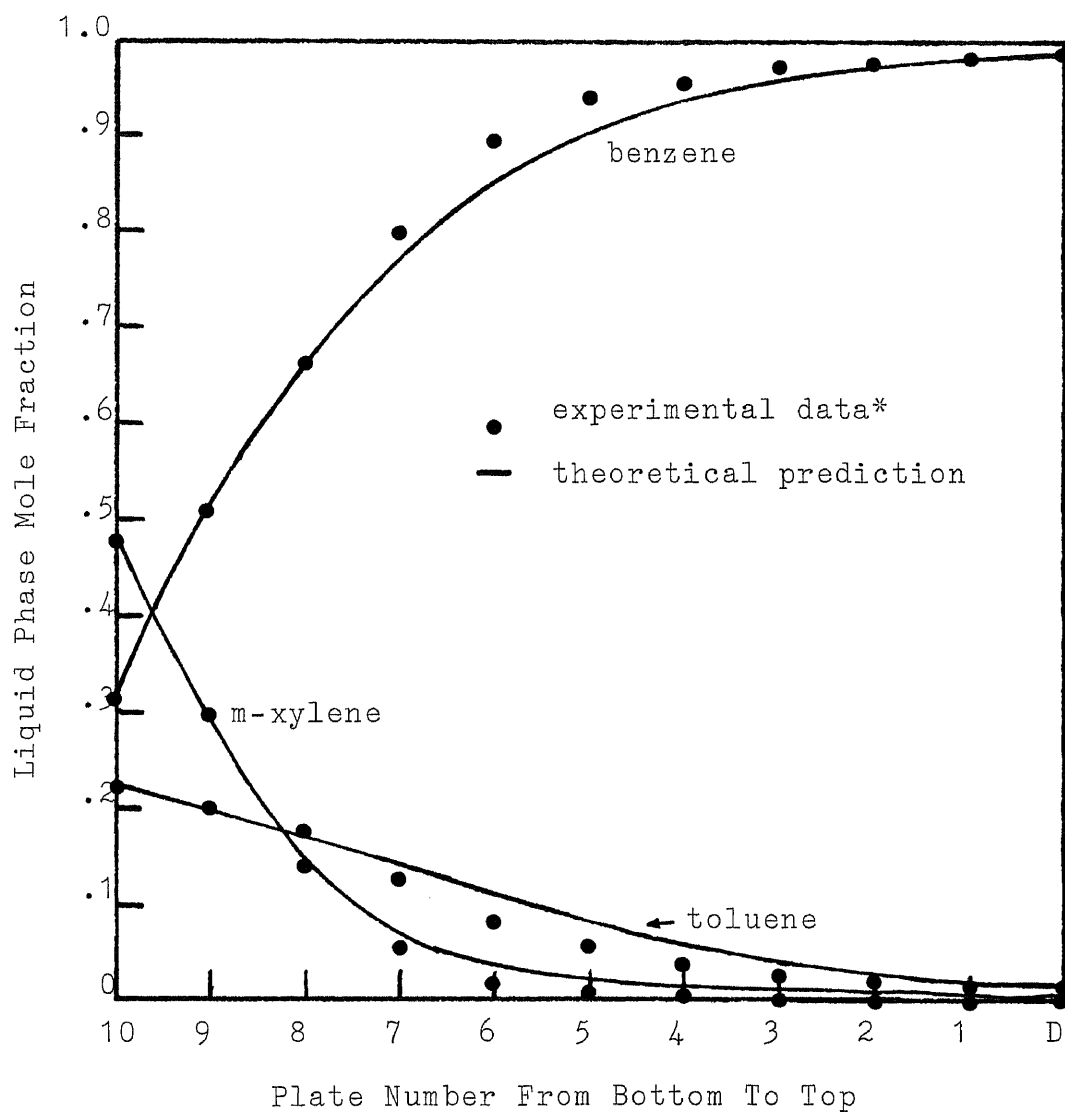
Fig. 14  Concentration profile plotted as liquid compo-
sition vs. plate number (benzene-toluene-m-
xylene separation, run - 12).

* Data from Nord(25).

tested with various distillation operations.  The results
show good agreement with the experimental data that was
obtained from the published literature.

This investigation is intended to eliminate the need for
experimental determination of stage efficiencies, since the
experimental work is usually require substantial cost in time,
money, and effort.  Furthermore, the applicability of such
experimental data measured on small-pilot-plant to large-
scale equipment is always an uncertain matter.  This work
consists of using the rate equation of mass-transfer during
the bubble formation and rising on each plate, and to define
the pseudo-equilibrium curve.  This curve is used in place of
the true equilibrium relationship to determine real composi-
tions of phases leaving a plate.  It is believed that the
method presented here provides a way to approach a successful
design of a distillation column.

Although, this work is successfully developed and it is
able to achieve the objectives that were set at the begining
of this project, it must not be thought that the design pro-
cedures outlined in this study for the stagewise column is
the final form of treatment.  This study is considered to
be an initial effort.

# CHAPTER IV

## RECOMMENDATIONS

1. In this work, the discussion of plate-to-plate calculations assumed that the pressure throughout the column is essentially constant. Actually, the pressure is not constant, or there would be no vapor flow from the bottom to the top of the column. Thus, the pressure does change from plate to plate. This pressure drop affects the vapor-liquid equilibrium relationship, and the vapor phase physical properties. Therefore, further study is suggested with regard to the effect of changing pressure.

2. The liquid flow pattern on the plate is assumed as plug flow in the present work. The liquid flow pattern is designed to give the best contact with the vapor, and requires the minimum hydraulic gradient or buildup of liquid across the plate. Various flow patterns such as backmixing, reverse, and double-cross, etc. do exist. In the future, the rate of mass-transfer equation combined with various flow patterns should be investigated.

APPENDIX A

COMPUTER PROGRAM IN SEARCH OF

EIGENVALUES OF FUNCTION X = TAN(X)

```
C       ********************************
C
C       MASS TRANSFER FROM A SINGLE BUBBLE
C       CONSIDER BOTH LIQUID AND GAS FILM RESISTANCE
C
C       THIS PROGRAM IS FOR FINDING EIGENVALUES OF
C       THE FUNCTION X-TAN(X)=0
C
C       ********************************
C
        COMMON/AREA1/BETA(500)
        DATA N/30/
        DO 1000 I=1,N
        CALL BTAFN(I)
 1000   CONTINUE
        CALL OUTPUT(N)
        STOP
        END




        FUNCTION TEST(X)
        IMPLICIT REAL*8(A-H,O-Z)
        TEST=DTAN(X)-X
        RETURN
        END
```

```
      SUBROUTINE BTAFN(I)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/AREA1/BETA(500)
      DATA TOL2,START,STEP /1.D-7,1.0D0,0.01D0/
      X0=START
      K=I-1
      IF(I.NE.1) X0=BETA(K)+STEP
  500 IF((TEST(X0)/TEST(X0+STEP)).LT.0.D0) GO TO 1000
      X0=X0+STEP
      GO TO 500
 1000 CONTINUE
      CALL RTFND(ROOT,X0,TOL2,STEP)
      BETA(I)=ROOT
      RETURN
      END




      SUBROUTINE RTFND(ROOT,X0,TOL,STEP)
      IMPLICIT REAL*8(A-H,O-Z)
      LOGICAL FSTTIM
      FSTTIM=.TRUE.
      X1=X0+STEP
      DO 1000 I=1,100
      X2=(X0*TEST(X1)-X1*TEST(X0))/(TEST(X1)-TEST(X0))
      IF(FSTTIM) GO TO 900
      IF(DABS(X2-X2STOR).LE.TOL) GO TO 1500
  900 IF((TEST(X2)/TEST(X0)).GT.0.D0) X0=X2
      IF((TEST(X2)/TEST(X1)).GT.0.D0) X1=X2
      FSTTIM=.FALSE.
      X2STOR=X2
 1000 CONTINUE
      WRITE(6,6833)
 6833 FORMAT(/40X,'DEFAULT ON ROOT')
 1500 ROOT=X2
      RETURN
      END




      SUBROUTINE OUTPUT(N)
      IMPLICIT REAL*8(A-H,O-Z)
      COMMON/AREA1/BETA(500)
      DO 5000 I=1,N
      WRITE(6,2000) I,BETA(I)
 2000 FORMAT(////,10X,'BETA (',I2,') = ',F12.7)
 5000 CONTINUE
      RETURN
      END
```

APPENDIX B


COMPUTER PROGRAM IN CALCULATING

DIMENSIONLESS AVERAGE CONCENTRATION

WITH VARIOUS DIMENSIONLESS TIME AND SHERWOOD NUMBER

```fortran
C     ******************************************************
C
C        MASS TRANSFER FROM A SINGLE BUBBLE
C        CONSIDER BOTH LIQUID AND GAS FILM RESISTANCE
C
C        CALCULATE DIMENSIONLESS CONCENTRATION WITH VARIOUS
C        DIMENSIONLESS LENGTH,TIME, AND SHERWOOD NUMBER
C
C     ******************************************************
C
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION BETA(100)
      DIMENSION TAU(9),ZI(14)
      DATA (TAU(I),I=1,9)/0.01D0,0.02D0,0.04D0,0.06D0,
     10.08D0,0.1D0,0.12D0,0.14D0,0.16D0/
      DATA (ZI(I),I=1,14)/0.02D0,0.04D0,0.06D0,0.08D0,
     10.1D0,0.2D0,0.3D0,0.4D0,0.5D0,0.6D0,0.7D0,0.8D0,
     10.9D0,1.0D0/
      DATA (BETA(I),I=1,10)/4.4934094D0,7.7252517D0,
     110.9041216D0,14.0661938D0,17.2207549D0,20.371303D0,
     123.5194525D0,26.6660542D0,29.8115988D0,32.956389D0/
      DATA EPS/1.D-14/
      DATA SH/7.D0/
      WRITE (6,103) SH
103   FORMAT(/,5X,'SHERWOOD NUMBER = ',F6.2)
      DO 50 J=1,9
      TIME=TAU(J)
      DO 60 K=1,14
      DLENTH=ZI(K)
      SUM=0.D0
      DO 1000 I=1,10
      ZZ=-(BETA(I)**2)
      Z=ZZ*TIME
      ZZ1=DEXP(Z)
      YY1=DSIN(BETA(I)*DLENTH)/DLENTH
      Y1=DSIN(BETA(I))
      Y2=(3.D0*SH)-(BETA(I)**2)
      YY2=(2.D0*SH)
      SU=YY2*ZZ1*YY1/(Y2*Y1)
      SSUM=SUM+SU
      TT=SSUM-SUM
      T=DABS(TT)
      IF (T-EPS) 3,3,5
5     SUM=SSUM
1000  CONTINUE
      TSUM=SUM
      GO TO 6
3     TSUM=SSUM
```

```
6        TY1=(3.DO*SH)**0.5
         TY11=3.DO*SH*TIME
         TY2=DEXP(-TY11)
         TY3=DSIN(TY1*DLENTH)
         TY4=DSIN(TY1)
         TY5=DCOS(TY1)
         TY6=TY1*TY5-TY4
         TY7=SH*TY2*TY3/TY6
         TY8=TY7/DLENTH
         TTUM=1.DO+TY8+TSUM
         WRITE (6,100) I,TIME,DLENTH,TTUM
100      FORMAT(/,5X,'ANSWER  WITH  SUMMATION TERMS =',
        *I3,/,5X,'DIMENSIONLESS TIME = ',F7.3,/,5X,
        *'DIMENSIONLESS LENGTH = ',F7.3,/,5X,
        *'DIMENSIONLESS CONCENTRATION IN CAO-CAG FORM = ',F14.7)
         TTTTM=1.DO-TTUM
         WRITE (6,102) TTTTM
102      FORMAT(/,10X,'DIMENSIONLESS CONCENTRATION IN
        1CAG-CAGL FORM = ',F16.7)
60       CONTINUE
50       CONTINUE
         STOP
         END
```

APPENDIX C


PREDICTION OF VAPOR-LIQUID EQUILIBRIUM RELATIONSHIP


Effective design of a complex distillation operation requires quantitative informations on phase equilibria in binary and multicomponent mixtures.  Experimental vapor-liquid equilibria data are often available for binary mixtures.  However, it is rather difficult to obtain the vapor-liquid equilibrium relationships experimentally for multicomponent systems.  Therefore, it is highly desirable to predict the vapor-liquid equilibrium relationships for multicomponent systems from the available experimental data.


A very useful correlation, UNIFAC, was proposed to predict the liquid phase activity coefficient using molecular structure.  UNIFAC is an abbreviation for universal quasi-chemical functional group activity coefficients.  It is based on the quasichemical theory of liquid solutions which was proposed by Guggenheim(17), generalized by Abrams and Prausnitz(1), applied to the functional groups within the molecules (rather than the molecules themselves) by Fredenslund(11), and later revised by Fredenslund(12) and Skjold-Jorgensen(39) to extend its range of applicability. This group contribution method assumes that the physical

properties of the fluid can be calculated from the sum of
contributions made by various functional groups (e.g., $-CH_3$;
$-OH$; $-CH_2$; $-CO$; etc.) that form the molecules in the fluid.

The activity coefficients are calculated from two terms
as in equation (C-1), a combinatorial part, essentially due
to differences in size and shape of the molecules; and a
residual part, due to energetic interactions between the
groups.

$$\ln \gamma_i = \quad \ln \gamma_i^c \quad + \quad \ln \gamma_i^R \qquad \text{(C-1)}$$
$$\text{combinatorial} \quad \text{residual}$$

combinatorial part:

$$\ln \gamma_i^c = \ln \frac{\Phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\Theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{X_i} \sum_j X_j l_j \qquad \text{(C-2)}$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \qquad \text{(C-3)}$$

$$\Theta_i = \frac{q_i X_i}{\sum_j q_j X_j} \qquad \text{(C-4)}$$

$$\Phi_i = \frac{r_i X_i}{\sum_j r_j X_j} \qquad \text{(C-5)}$$

$$r_i = \sum_k \nu_k^{(i)} R_k \qquad \text{(C-6)}$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \qquad \text{(C-7)}$$

$$Z = 10 \qquad \text{(C-8)}$$

residual part:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad \text{(C-9)}$$

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \Theta_m \Psi_{mk} \right) - \sum_m \left( \Theta_m \Psi_{km} / \sum_n \Theta_n \Psi_{nm} \right) \right] \qquad \text{(C-10)}$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad \text{(C-11)}$$

$$X_m = \frac{\sum_i \nu_i^{(i)} X_i}{\sum_i \sum_k \nu_k^{(i)} X_i} \qquad \text{(C-12)}$$

$$\Psi_{nm} = \exp \left[ -(a_{nm}/T) \right] \qquad \text{(C-13)}$$

where  $r_i$   = molecular van der Waals volume

$q_i$   = molecular surface areas

$\nu_k^{(i)}$ = always an integer, number of groups of type k in molecule i

$\Gamma_k$   = group residual activity coefficient

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing only molecules of type i

$X_m$   = fraction of group m in the mixture.

The three types of group parameters needed are listed in
Table IV and Table V: group volume parameters $(R_k)$, group
surface area parameters $(Q_k)$, and group interaction parameters
$(a_{mn}$ and $a_{nm})$. The indicies k, m, and n represent different
groups.

Figure 15 to Figure 22, and Table VI and Table VII show
the comparisons made between experimental data and the pre-
dictions by UNIFAC method of various systems at different
temperatures. The results indicate that the UNIFAC method
can be used to predict activity coefficients in the absence
of experimental data.

Table IV


UNIFAC Group Volume and Surface-Area Parameters*

| main group | sub group | no. | $R_k$ | $Q_k$ | sample group assignment | |
|---|---|---|---|---|---|---|
| 1 "$CH_2$" | $CH_3$ | 1 | 0.9011 | 0.848 | hexane: | 2 $CH_3$, 4 $CH_2$ |
| | $CH_2$ | 2 | 0.6744 | 0.540 | 2-methylpropane: | 3 $CH_3$, 1 CH |
| | CH | 3 | 0.4469 | 0.228 | 2,2-dimethylpropane: | 4 $CH_3$, 1 C |
| | C | 4 | 0.2195 | 0.000 | | |
| 2 "C=C" | $CH_2$=CH | 5 | 1.3454 | 1.176 | 1-hexene: | 1 $CH_3$, 3 $CH_2$, 1 $CH_2$=CH |
| | CH=CH | 6 | 1.1167 | 0.867 | 2-hexene: | 2 $CH_3$, 2 $CH_2$, 1 CH=CH |
| | $CH_2$=C | 7 | 1.1173 | 0.988 | 2-methyl-1-butene: | 2 $CH_3$, 1 $CH_2$, 1 $CH_2$=C |
| | CH=C | 8 | 0.8886 | 0.676 | 2-methyl-2-butene: | 3 $CH_3$, 1 CH=C |
| | C=C | 9 | 0.6605 | 0.485 | 2,3-dimethylbutene-2: | 4 $CH_3$, 1 C=C |
| 3 "ACH" | ACH | 10 | 0.5313 | 0.400 | benzene: | 6 ACH |
| | AC | 11 | 0.3652 | 0.120 | styrene: | 1 $CH_2$=CH, 5 ACH, 1 AC |
| 4 "$ACCH_2$" | $ACCH_3$ | 12 | 1.2663 | 0.968 | toluene: | 5 ACH, 1 $ACCH_3$ |
| | $ACCH_2$ | 13 | 1.0396 | 0.660 | ethylbenzene: | 1 $CH_3$, 5 ACH, 1 $ACCH_2$ |
| | ACCH | 14 | 0.8121 | 0.348 | cumene: | 2 $CH_3$, 5 ACH, 1 ACCH |
| 5 "OH" | OH | 15 | 1.000 | 1.200 | 2-propanol: | 2 $CH_3$, 1 CH, 1 OH |
| 6 "$CH_3OH$" | $CH_3OH$ | 16 | 1.4311 | 1.432 | methanol: | 1 $CH_3OH$ |
| 7 "$H_2O$" | $H_2O$ | 17 | 0.92 | 1.40 | water: | 1 $H_2O$ |
| 8 "ACOH" | ACOH | 18 | 0.8952 | 0.680 | phenol: | 5 ACH, 1 ACOH |
| 9 "$CH_2CO$" | $CH_3CO$ | 19 | 1.6724 | 1.488 | ketone group is 2nd carbon; 2-butanone: | 1 $CH_3$, 1 $CH_2$, 1 $CH_3CO$ |
| | $CH_2CO$ | 20 | 1.4457 | 1.180 | ketone group is any other carbon; 3-pentanone: | 2 $CH_3$, 1 $CH_2$, 1 $CH_2CO$ |
| 10 "CHO" | CHO | 21 | 0.9980 | 0.948 | acetaldehyde: | 1 $CH_3$, 1 CHO |
| 11 "CCOO" | $CH_3COO$ | 22 | 1.9031 | 1.728 | butyl acetate: | 1 $CH_3$, 3 $CH_2$, 1 $CH_3COO$ |
| | $CH_2COO$ | 23 | 1.6764 | 1.420 | butyl propanoate: | 2 $CH_3$, 3 $CH_2$, 1 $CH_2COO$ |
| 12 "HCOO" | HCOO | 24 | 1.2420 | 1.188 | ethyl formate: | 1 $CH_3$, 1 $CH_2$, 1 HCOO |
| 13 "$CH_2O$" | $CH_3O$ | 25 | 1.1450 | 1.088 | dimethyl ether: | 1 $CH_3$, 1 $CH_3O$ |
| | $CH_2O$ | 26 | 0.9183 | 0.780 | diethyl ether: | 2 $CH_3$, 1 $CH_2$, 1 $CH_2O$ |
| | CH-O | 27 | 0.6908 | 0.468 | diisopropyl ether: | 4 $CH_3$, 1 CH, 1 CH-O |
| | $FCH_2O$ | 28 | 0.9183 | 1.1 | tetrahydrofuran: | 3 $CH_2$, 1 $FCH_2O$ |
| 14 "$CNH_2$" | $CH_3NH_2$ | 29 | 1.5959 | 1.544 | methylamine: | 1 $CH_3NH_2$ |
| | $CH_2NH_2$ | 30 | 1.3692 | 1.236 | propylamine: | 1 $CH_3$, 1 $CH_2$, 1 $CH_2NH_2$ |
| | $CHNH_2$ | 31 | 1.1417 | 0.924 | isopropylamine: | 2 $CH_3$, 1 $CHNH_2$ |
| 15 "CNH" | $CH_3NH$ | 32 | 1.4337 | 1.244 | dimethylamine: | 1 $CH_3$, 1 $CH_3NH$ |
| | $CH_2NH$ | 33 | 1.2070 | 0.936 | diethylamine: | 2 $CH_3$, 1 $CH_2$, 1 $CH_2NH$ |
| | CHNH | 34 | 0.9795 | 0.624 | diisopropylamine: | 4 $CH_3$, 1 CH, 1 CHNH |
| 16 "$(C)_3N$" | $CH_3N$ | 35 | 1.1865 | 0.940 | trimethylamine: | 2 $CH_3$, 1 $CH_3N$ |
| | $CH_2N$ | 36 | 0.9597 | 0.632 | triethylamine: | 3 $CH_3$, 2 $CH_2$, 1 $CH_2N$ |
| 17 "$ACNH_2$" | $ACNH_2$ | 37 | 1.0600 | 0.816 | aniline: | 5 ACH, 1 $ACNH_2$ |
| 18 "pyridine" | $C_5H_5N$ | 38 | 2.9993 | 2.113 | pyridine: | 1 $C_5H_5N$ |
| | $C_5H_4N$ | 39 | 2.8332 | 1.833 | 3-methylpyridine: | 1 $CH_3$, 1 $C_5H_4N$ |
| | $C_5H_3N$ | 40 | 2.667 | 1.553 | 2,3-dimethylpyridine: | 2 $CH_3$, 1 $C_5H_3N$ |
| 19 "CCN" | $CH_3CN$ | 41 | 1.8701 | 1.724 | acetonitrile: | 1 $CH_3CN$ |
| | $CH_2CN$ | 42 | 1.6434 | 1.416 | propionitrile: | 1 $CH_3$, 1 $CH_2CN$ |
| 20 "COOH" | COOH | 43 | 1.3013 | 1.224 | acetic acid: | 1 $CH_3$, 1 COOH |
| | HCOOH | 44 | 1.5280 | 1.532 | formic acid: | 1 HCOOH |

* Taken from Gmehling(14).

Table IV (continued)

| main group | sub group | no. | $R_k$ | $Q_k$ | sample group assignment | |
|---|---|---|---|---|---|---|
| 21 "CCl" | CH₂Cl | 45 | 1.4654 | 1.264 | 1-chlorobutane: | 1 CH₃, 2 CH₂, 1 CH₂Cl |
| | CHCl | 46 | 1.2380 | 0.952 | 2-chloropropane: | 2 CH₃, 1 CHCl |
| | CCl | 47 | 1.0060 | 0.724 | 2-chloro-2-methylpropane: | 3 CH₃, 1 CCl |
| 22 "CCl₂" | CH₂Cl₂ | 48 | 2.2564 | 1.988 | dichloromethane: | 1 CH₂Cl₂ |
| | CHCl₂ | 49 | 2.0606 | 1.684 | 1,1-dichloroethane: | 1 CH₃, 1 CHCl₂ |
| | CCl₂ | 50 | 1.8016 | 1.448 | 2,2-dichloropropane: | 2 CH₃, 1 CCl₂ |
| 23 "CCl₃" | CHCl₃ | 51 | 2.8700 | 2.410 | chloroform: | 1 CHCl₃ |
| | CCl₃ | 52 | 2.6401 | 2.184 | 1,1,1-trichloroethane: | 1 CH₃, 1 CCl₃ |
| 24 "CCl₄" | CCl₄ | 53 | 3.3900 | 2.910 | tetrachloromethane: | 1 CCl₄ |
| 25 "ACCl" | ACCl | 54 | 1.1562 | 0.844 | chlorobenzene: | 5 ACH, 1 ACCl |
| 26 "CNO₂" | CH₃NO₂ | 55 | 2.0086 | 1.868 | nitromethane: | 1 CH₃NO₂ |
| | CH₂NO₂ | 56 | 1.7818 | 1.560 | 1-nitropropane: | 1 CH₃, 1 CH₂, 1 CH₂NO₂ |
| | CHNO₂ | 57 | 1.5544 | 1.248 | 2-nitropropane: | 2 CH₃, 1 CHNO₂ |
| 27 "ACNO₂" | ACNO₂ | 58 | 1.4199 | 1.104 | nitrobenzene: | 5 ACH, 1 ACNO₂ |
| 28 "CS₂" | CS₂ | 59 | 2.057 | 1.65 | carbon disulfide: | 1 CS₂ |
| 29 "CH₃SH" | CH₃SH | 60 | 1.8770 | 1.676 | methanethiol: | 1 CH₃SH |
| | CH₂SH | 61 | 1.6510 | 1.368 | ethanethiol: | 1 CH₃, 1 CH₂SH |
| 30 "furfural" | furfural | 62 | 3.1680 | 2.481 | furfural: | 1 furfural |
| 31 "DOH" | (CH₂OH)₂ | 63 | 2.4088 | 2.248 | 1,2-ethanediol: | 1 (CH₂OH)₂ |
| 32 "I" | I | 64 | 1.2640 | 0.992 | 1-iodoethane: | 1 CH₃, 1 CH₂, 1 I |
| 33 "Br" | Br | 65 | 0.9492 | 0.832 | 1-bromoethane: | 1 CH₃, 1 CH₂, 1 Br |
| 34 "C≡C" | CH≡C | 66 | 1.2920 | 1.088 | 1-hexyne: | 1 CH₃, 3 CH₂, 1 CH≡C |
| | C≡C | 67 | 1.0613 | 0.784 | 2-hexyne: | 2 CH₃, 2 CH₂, 1 C≡C |
| 35 "Me₂SO" | Me₂SO | 68 | 2.8266 | 2.472 | dimethyl sulfoxide: | 1 Me₂SO |
| 36 "ACRY" | ACRY | 69 | 2.3144 | 2.052 | acrylonitrile: | 1 ACRY |
| 37 "ClCC" | Cl(C=C) | 70 | 0.7910 | 0.724 | trichloroethylene: | 1 CH=C, 3 Cl(C=C) |
| 38 "ACF" | ACF | 71 | 0.6948 | 0.524 | hexafluorobenzene: | 6 ACF |
| 39 "DMF" | DMF-1 | 72 | 3.0856 | 2.736 | dimethylformamide: | 1 DMF-1 |
| | DMF-2 | 73 | 2.6322 | 2.120 | diethylformamide: | 2 CH₃, 1 DMF-2 |
| 40 "CF₂" | CF₃ | 74 | 1.4060 | 1.380 | perfluorohexane: | 2 CF₃, 4 CF₂ |
| | CF₂ | 75 | 1.0105 | 0.920 | | |
| | CF | 76 | 0.6150 | 0.460 | perfluoromethylcyclohexane: | 1 CH₃, 5 CH₂, 1 CF |

Table V


UNIFAC Interaction Parameters*


|  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| 1 CH₂ | 0.0 | −200.0 | 61.13 | 76.50 | 986.5 | 697.2 | 1318.0 | 1333.0 |
| 2 C=C | 2520.0 | 0.0 | 340.7 | 4102.0 | 693.9 | 1509.0 | 634.2 | 547.4 |
| 3 ACH | −11.12 * | −94.78 | 0.0 | 167.0 | 636.1 | 637.3 | 903.8 | 1329.0 |
| 4 ACCH₂ | −69.70 | −269.7 | −146.8 | 0.0 | 803.2 | 603.2 | 5695.0 | 884.9 |
| 5 OH | 156.4 | 8694.0 | 89.60 | 25.82 | 0.0 | −137.1 | 353.5 | −259.7 |
| 6 CH₃OH | 16.51 | −52.39 | −50.00 | −44.50 | 249.1 | 0.0 | −181.0 | −101.7 |
| 7 H₂O | 300.0 | 692.7 | 362.3 | 377.6 | −229.1 | 289.6 | 0.0 | 324.5 |
| 8 ACOH | 275.8 | 1665.0 | 25.34 | 244.2 | −451.6 | −265.2 | −601.8 | 0.0 |
| 9 CH₂CO | 26.76 | −82.92 | 140.1 | 365.8 | 164.5 | 108.7 | 472.5 | −133.1 |
| 10 CHO | 505.7 | n.a. | n.a. | n.a. | −404.8 | −340.2 | 232.7 | n.a. |
| 11 CCOO | 114.8 | 269.3 | 85.84 | −170.0 | 245.4 | 249.6 | 10000.0 | −36.72 |
| 12 HCOO | 90.49 | 91.65 | n.a. | n.a. | 191.2 | 155.7 | n.a. | n.a. |
| 13 CH₂O | 83.36 | 76.44 | 52.13 | 65.69 | 237.7 | 339.7 | −314.7 | n.a. |
| 14 CNH₂ | −30.48 | 79.40 | −44.85 | n.a. | −164.0 | −481.7 | −330.4 | n.a. |
| 15 CNH | 65.33 | −41.32 | −22.31 | 223.0 | −150.0 | −500.4 | −448.2 | n.a. |
| 16 (C)₃N | −83.98 | −188.0 | −223.9 | 109.9 | 28.60 | −406.8 | −598.8 | n.a. |
| 17 ACNH₂ | 5339.0 | n.a. | 650.4 | 979.8 | 529.0 | 5.182 | −339.5 | n.a. |
| 18 pyridine | −101.6 | n.a. | 31.87 | 49.80 | −132.3 | −378.2 | −332.9 | −341.6 |
| 19 CCN | 24.82 | 34.78 | −22.97 | −138.4 | 185.4 | 157.8 | 242.8 | n.a. |
| 20 COOH | 315.3 | 349.2 | 62.32 | 268.2 | −151.0 | 1020.0 | −66.17 | n.a. |
| 21 CCl | 91.46 | −24.36 | 4.680 | 122.9 | 562.2 | 529.0 | 698.2 | n.a. |
| 22 CCl₂ | 34.01 | −52.71 | 121.3 | n.a. | 747.7 | 669.9 | 708.7 | n.a. |
| 23 CCl₃ | 36.70 | −185.1 | 288.5 | 33.61 | 742.1 | 649.1 | 826.7 | n.a. |
| 24 CCl₄ | −78.45 | −293.7 | −4.700 | 134.7 | 856.3 | 860.1 | 1201.0 | 10000. |
| 25 ACCl | −141.3 | −203.2 | −237.7 | 375.5 | 246.9 | 661.6 | 920.4 | n.a. |
| 26 CNO₂ | −32.69 | −49.92 | 10.38 | −97.05 | 341.7 | 252.6 | 417.9 | n.a. |
| 27 ACNO₂ | 5541.0 | n.a. | 1824.0 | −127.8 | 561.6 | n.a. | 360.7 | n.a. |
| 28 CS₂ | −52.65 | 16.62 | 21.50 | 40.68 | 823.5 | 914.2 | 1081.0 | n.a. |
| 29 CH₃SH | −7.481 | n.a. | 28.41 | n.a. | 461.6 | 382.8 | n.a. | n.a. |
| 30 furfural | −25.31 | n.a. | 157.3 | 404.3 | 521.6 | n.a. | 23.48 | n.a. |
| 31 DOH | 140.0 | n.a. | 221.4 | 150.6 | 267.6 | n.a. | 0.0 | 838.4 |
| 32 I | 128.0 | n.a. | 58.68 | n.a. | 501.3 | n.a. | n.a. | n.a. |
| 33 Br | −31.52 | n.a. | 155.6 | 291.1 | 721.9 | n.a. | n.a. | n.a. |
| 34 C≡C | −72.88 | −184.4 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 35 Me₂SO | 50.49 | n.a. | −2.504 | −143.2 | −25.87 | 695.0 | −240.0 | n.a. |
| 36 ACRY | −165.9 | n.a. | n.a. | n.a. | n.a. | n.a. | 386.6 | n.a. |
| 37 ClCC | 41.90 | −3.167 | −75.67 | n.a. | 640.9 | 726.7 | n.a. | n.a. |
| 38 ACF | −5.132 | n.a. | −237.2 | −157.3 | 649.7 | 645.9 | n.a. | n.a. |
| 39 DMF | −31.95 | 37.70 | −133.9 | −240.2 | 64.16 | 172.2 | −287.1 | n.a. |
| 40 CF₂ | 147.3 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

Table V (continued)

|  | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|
| 1 $CH_2$ | 476.4 | 677.0 | 232.1 | 741.4 | 251.5 | 391.5 | 255.7 | 206.6 |
| 2 C=C | 524.5 | n.a. | 71.23 | 468.7 | 289.3 | 396.0 | 273.6 | 658.8 |
| 3 ACH | 25.77 | n.a. | 5.994 | n.a. | 32.14 | 161.7 | 122.8 | 90.49 |
| 4 $ACCH_2$ | −52.10 | n.a. | 5688.0 | n.a. | 213.1 | n.a. | −49.29 | 23.50 |
| 5 OH | 84.00 | 441.8 | 101.1 | 193.1 | 28.06 | 83.02 | 42.70 | −323.0 |
| 6 $CH_3OH$ | 23.39 | 306.4 | −10.72 | 193.4 | −180.6 | 359.3 | 266.0 | 53.90 |
| 7 $H_2O$ | −195.4 | −257.3 | 14.42 | n.a. | 540.5 | 48.89 | 168.0 | 304.0 |
| 8 ACOH | −356.1 | n.a. | −449.4 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 9 $CH_2CO$ | 0.0 | −37.36 | −213.7 | n.a. | 5.202 | n.a. | n.a. | n.a. |
| 10 CHO | 128.0 | 0.0 | n.a. | n.a. | 304.1 | n.a. | n.a. | n.a. |
| 11 CCOO | 372.2 | n.a. | 0.0 | 372.9 | −235.7 | n.a. | −73.50 | n.a. |
| 12 HCOO | n.a. | n.a. | −261.1 | 0.0 | n.a. | n.a. | n.a. | n.a. |
| 13 $CH_2O$ | 52.38 | −7.838 | 461.3 | n.a. | 0.0 | n.a. | 141.7 | n.a. |
| 14 $CNH_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | 0.0 | 63.72 | −41.11 |
| 15 CNH | n.a. | n.a. | 136.0 | n.a. | −49.30 | 108.8 | 0.0 | −189.2 |
| 16 $(C)_3N$ | n.a. | n.a. | n.a. | n.a. | n.a. | 38.89 | 865.9 | 0.0 |
| 17 $ACNH_2$ | −399.1 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 18 pyridine | −51.54 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 19 CCN | −287.5 | n.a. | −266.6 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 20 COOH | −297.8 | n.a. | −256.3 | 312.5 | −338.5 | n.a. | n.a. | n.a. |
| 21 CCl | 286.3 | −47.51 | n.a. | n.a. | 225.4 | n.a. | n.a. | n.a. |
| 22 $CCl_2$ | 423.2 | n.a. | −132.9 | n.a. | −197.7 | n.a. | n.a. | −141.4 |
| 23 $CCl_3$ | 552.1 | n.a. | 176.5 | 488.9 | −20.93 | n.a. | n.a. | −293.7 |
| 24 $CCl_4$ | 372.0 | n.a. | 129.5 | n.a. | 113.9 | 261.1 | 91.13 | −126.0 |
| 25 ACCl | 128.1 | n.a. | −246.3 | n.a. | n.a. | 203.5 | −108.4 | 1088.0 |
| 26 $CNO_2$ | −142.6 | n.a. | n.a. | n.a. | −94.49 | n.a. | n.a. | n.a. |
| 27 $ACNO_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 28 $CS_2$ | 303.7 | n.a. | 243.8 | n.a. | 112.4 | n.a. | n.a. | n.a. |
| 29 $CH_3SH$ | 160.6 | n.a. | n.a. | 239.8 | 63.71 | 106.7 | n.a. | n.a. |
| 30 furfural | 317.5 | n.a. | −146.3 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 31 DOH | n.a. | n.a. | 152.0 | n.a. | 9.207 | n.a. | n.a. | n.a. |
| 32 I | 138.0 | n.a. | 21.92 | n.a. | 476.6 | n.a. | n.a. | n.a. |
| 33 Br | −142.6 | n.a. | n.a. | n.a. | 736.4 | n.a. | n.a. | n.a. |
| 34 C≡C | 443.6 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 35 $Me_2SO$ | 110.4 | n.a. | 41.57 | n.a. | −122.1 | n.a. | n.a. | n.a. |
| 36 ACRY | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 37 ClCC | −8.671 | n.a. | −18.87 | n.a. | −209.3 | n.a. | n.a. | n.a. |
| 38 ACF | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 39 DMF | 97.04 | n.a. | n.a. | n.a. | −158.2 | n.a. | n.a. | n.a. |
| 40 $CF_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

|  | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|---|---|---|
| 1 $CH_2$ | 1245.0 | 287.7 | 597.0 | 663.5 | 35.93 | 53.76 | 24.90 | 104.3 |
| 2 C=C | n.a. | n.a. | 405.9 | 730.4 | 99.61 | 337.1 | 4584.0 | 5831.0 |
| 3 ACH | 668.2 | −4.449 | 212.5 | 537.4 | −18.81 | −144.4 | −231.9 | 3.000 |
| 4 $ACCH_2$ | 764.7 | 52.80 | 6096.0 | 603.8 | −114.1 | n.a. | −12.14 | −141.3 |
| 5 OH | −348.2 | 170.0 | 6.712 | 199.0 | 75.62 | −112.1 | −98.12 | 143.1 |
| 6 $CH_3OH$ | 335.5 | 580.5 | 36.23 | −289.5 | −38.32 | −102.5 | −139.4 | −67.80 |
| 7 $H_2O$ | 213.0 | 459.0 | 112.6 | −14.09 | 325.4 | 370.4 | 353.7 | 497.5 |
| 8 ACOH | n.a. | −305.5 | n.a. | n.a. | n.a. | n.a. | n.a. | 1827.0 |
| 9 $CH_2CO$ | 937.9 | 165.1 | 481.7 | 669.4 | −191.7 | −284.0 | −354.6 | −39.20 |
| 10 CHO | n.a. | n.a. | n.a. | n.a. | 751.9 | n.a. | n.a. | n.a. |
| 11 CCOO | n.a. | n.a. | 494.6 | 660.2 | n.a. | 108.9 | −209.7 | 54.47 |
| 12 HCOO | n.a. | n.a. | n.a. | −356.3 | n.a. | n.a. | −287.2 | n.a. |
| 13 $CH_2O$ | n.a. | n.a. | n.a. | 664.6 | 301.1 | 137.8 | −154.3 | 47.67 |
| 14 $CNH_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | −99.81 |
| 15 CNH | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 71.23 |
| 16 $(C)_3N$ | n.a. | n.a. | n.a. | n.a. | n.a. | −73.85 | −352.9 | −8.283 |
| 17 $ACNH_2$ | 0.0 | n.a. | −216.8 | n.a. | n.a. | n.a. | n.a. | 8455.0 |
| 18 pyridine | n.a. | 0.0 | −169.7 | −153.7 | n.a. | −351.6 | −114.7 | −165.1 |
| 19 CCN | 617.1 | 134.3 | 0.0 | n.a. | n.a. | n.a. | −15.62 | −54.86 |
| 20 COOH | n.a. | −313.5 | n.a. | 0.0 | 44.42 | −183.4 | 76.75 | 212.7 |
| 21 CCl | n.a. | n.a. | n.a. | 326.4 | 0.0 | 108.3 | 249.2 | 62.42 |
| 22 $CCl_2$ | n.a. | 587.3 | n.a. | 1821.0 | −84.53 | 0.0 | 0.0 | 56.33 |
| 23 $CCl_3$ | n.a. | 18.98 | 74.04 | 1346.0 | −157.1 | 0.0 | 0.0 | −30.10 |
| 24 $CCl_4$ | 1301.0 | 309.2 | 492.0 | 689.0 | 11.80 | 17.97 | 51.90 | 0.0 |
| 25 ACCl | 323.3 | n.a. | 356.9 | n.a. | −314.9 | n.a. | n.a. | −255.4 |
| 26 $CNO_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | −34.68 |
| 27 $ACNO_2$ | 5250.0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 514.6 |
| 28 $CS_2$ | n.a. | n.a. | 335.7 | n.a. | −73.09 | n.a. | −26.06 | −60.71 |
| 29 $CH_3SH$ | n.a. | n.a. | 125.7 | n.a. | −27.94 | n.a. | n.a. | n.a. |
| 30 furfural | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 48.48 | −133.1 |
| 31 DOH | 164.4 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 32 I | n.a. | n.a. | n.a. | n.a. | n.a. | −40.82 | 21.76 | 48.49 |
| 33 Br | n.a. | n.a. | n.a. | n.a. | 1169.0 | n.a. | n.a. | 225.8 |
| 34 C≡C | n.a. | n.a. | 329.1 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 35 $Me_2SO$ | n.a. | n.a. | n.a. | n.a. | n.a. | −215.0 | −343.6 | −58.43 |
| 36 ACRY | n.a. | n.a. | −42.31 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 37 ClCC | n.a. | n.a. | 298.4 | 2344.0 | 201.7 | n.a. | 85.32 | 143.2 |
| 38 ACF | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | −124.6 |
| 39 DMF | 335.6 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | −186.7 |
| 40 $CF_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

Table V (continued)

|  | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
|---|---|---|---|---|---|---|---|---|
| 1 $CH_2$ | 321.5 | 661.5 | 543.0 | 153.6 | 184.4 | 354.5 | 3025.0 | 335.8 |
| 2 C=C | 959.7 | 542.1 | n.a. | 76.30 | n.a. | n.a. | n.a. | n.a. |
| 3 ACH | 538.2 | 168.0 | 194.9 | 52.07 | -10.43 | -64.69 | 210.4 | 113.3 |
| 4 $ACCH_2$ | -126.9 | 3629.0 | 4448.0 | -9.451 | n.a. | -20.36 | 4975.0 | n.a. |
| 5 OH | 287.8 | 61.11 | 157.1 | 477.0 | 147.5 | -120.5 | -318.9 | 313.5 |
| 6 $CH_3OH$ | 17.12 | 75.14 | n.a. | -31.09 | 37.84 | n.a. | n.a. | n.a. |
| 7 $H_2O$ | 678.2 | 220.6 | 399.5 | 887.1 | n.a. | 188.0 | 0.0 | n.a. |
| 8 ACOH | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | -687.1 | n.a. |
| 9 $CH_2CO$ | 174.5 | 137.5 | n.a. | 216.1 | -46.28 | -163.7 | n.a. | 53.59 |
| 10 CHO | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 11 CCOO | 629.0 | n.a. | n.a. | 183.0 | n.a. | 202.3 | -101.7 | 148.3 |
| 12 HCOO | n.a. | n.a. | n.a. | n.a. | 4.339 | n.a. | n.a. | n.a. |
| 13 $CH_2O$ | n.a. | 95.18 | n.a. | 140.9 | -8.538 | n.a. | -20.11 | -149.5 |
| 14 $CNH_2$ | 68.81 | n.a. | n.a. | n.a. | -70.14 | n.a. | n.a. | n.a. |
| 15 CNH | 4350.0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 16 $(C)_3N$ | -86.36 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 17 $ACNH_2$ | 699.1 | n.a. | -62.73 | n.a. | n.a. | n.a. | 125.3 | n.a. |
| 18 pyridine | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 19 CCN | 52.31 | n.a. | n.a. | 230.9 | 21.37 | n.a. | n.a. | n.a. |
| 20 COOH | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 21 CCl | 464.4 | n.a. | n.a. | 450.1 | 59.02 | n.a. | n.a. | n.a. |
| 22 $CCl_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 177.6 |
| 23 $CCl_3$ | n.a. | n.a. | n.a. | 116.6 | n.a. | -64.38 | n.a. | 86.40 |
| 24 $CCl_4$ | 475.8 | 490.9 | 534.7 | 132.2 | n.a. | 546.7 | n.a. | 247.8 |
| 25 ACCl | 0.0 | -154.5 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 26 $CNO_2$ | 794.4 | 0.0 | 533.2 | n.a. | n.a. | n.a. | 139.8 | 304.3 |
| 27 $ACNO_2$ | n.a. | -85.12 | 0.0 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 28 $CS_2$ | n.a. | n.a. | n.a. | 0.0 | n.a. | n.a. | n.a. | n.a. |
| 29 $CH_3SH$ | n.a. | n.a. | n.a. | n.a. | 0.0 | n.a. | n.a. | n.a. |
| 30 furfural | n.a. | n.a. | n.a. | n.a. | n.a. | 0.0 | n.a. | n.a. |
| 31 DOH | n.a. | 481.3 | n.a. | n.a. | n.a. | n.a. | 0.0 | n.a. |
| 32 I | n.a. | 64.28 | n.a. | n.a. | n.a. | n.a. | n.a. | 0.0 |
| 33 Br | 224.0 | 125.3 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 34 C≡C | n.a. | 174.4 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 35 $Me_2SO$ | n.a. | n.a. | n.a. | n.a. | 85.70 | n.a. | 535.8 | n.a. |
| 36 ACRY | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 37 ClCC | n.a. | 313.8 | n.a. | 167.9 | n.a. | n.a. | n.a. | n.a. |
| 38 ACF | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 39 DMF | n.a. | n.a. | n.a. | n.a. | -71.00 | n.a. | -191.7 | n.a. |
| 40 $CF_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

|  | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
|---|---|---|---|---|---|---|---|---|
| 1 $CH_2$ | 479.5 | 298.9 | 526.5 | 689.0 | -0.505 | 125.8 | 485.3 | -2.859 |
| 2 C=C | n.a. | 523.6 | n.a. | n.a. | 237.3 | 320.4 | 320.4 | n.a. |
| 3 ACH | -13.59 | n.a. | 169.9 | n.a. | 69.11 | 389.3 | 245.6 | n.a. |
| 4 $ACCH_2$ | -171.3 | n.a. | 4284.0 | n.a. | n.a. | 101.4 | 5629.0 | n.a. |
| 5 OH | 133.4 | n.a. | -202.1 | n.a. | 253.9 | 44.78 | -143.9 | n.a. |
| 6 $CH_3OH$ | n.a. | n.a. | -399.3 | n.a. | -21.22 | -48.25 | -172.4 | n.a. |
| 7 $H_2O$ | n.a. | n.a. | -139.0 | 160.8 | n.a. | n.a. | 319.0 | n.a. |
| 8 ACOH | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 9 $CH_2CO$ | 245.2 | -246.6 | -44.58 | n.a. | -44.42 | n.a. | -61.70 | n.a. |
| 10 CHO | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 11 CCOO | n.a. | n.a. | 52.08 | n.a. | -23.30 | n.a. | n.a. | n.a. |
| 12 HCOO | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 13 $CH_2O$ | -202.3 | n.a. | 172.1 | n.a. | 145.6 | n.a. | 254.8 | n.a. |
| 14 $CNH_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 15 CNH | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 16 $(C)_3N$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 17 $ACNH_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | -293.1 | n.a. |
| 18 pyridine | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 19 CCN | n.a. | -203.0 | n.a. | 81.57 | -19.14 | n.a. | n.a. | n.a. |
| 20 COOH | n.a. | n.a. | n.a. | n.a. | -90.87 | n.a. | n.a. | n.a. |
| 21 CCl | -125.9 | n.a. | n.a. | n.a. | -58.77 | n.a. | n.a. | n.a. |
| 22 $CCl_2$ | n.a. | n.a. | 215.0 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 23 $CCl_3$ | n.a. | n.a. | 363.7 | n.a. | -79.54 | n.a. | n.a. | n.a. |
| 24 $CCl_4$ | 41.94 | n.a. | 337.7 | n.a. | -86.85 | 215.2 | 498.6 | n.a. |
| 25 ACCl | -60.70 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 26 $CNO_2$ | 10.17 | -27.70 | n.a. | n.a. | 48.40 | n.a. | n.a. | n.a. |
| 27 $ACNO_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 28 $CS_2$ | n.a. | n.a. | n.a. | n.a. | -47.37 | n.a. | n.a. | n.a. |
| 29 $CH_3SH$ | n.a. | n.a. | 31.66 | n.a. | n.a. | n.a. | 78.92 | n.a. |
| 30 furfural | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 31 DOH | n.a. | n.a. | -417.2 | n.a. | n.a. | n.a. | 302.2 | n.a. |
| 32 I | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 33 Br | 0.0 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 34 C≡C | n.a. | 0.0 | n.a. | n.a. | n.a. | n.a. | -119.8 | n.a. |
| 35 $Me_2SO$ | n.a. | n.a. | 0.0 | n.a. | n.a. | n.a. | -97.71 | n.a. |
| 36 ACRY | n.a. | n.a. | n.a. | 0.0 | n.a. | n.a. | n.a. | n.a. |
| 37 ClCC | n.a. | n.a. | n.a. | n.a. | 0.0 | n.a. | n.a. | n.a. |
| 38 ACF | n.a. | n.a. | n.a. | n.a. | n.a. | 0.0 | n.a. | n.a. |
| 39 DMF | n.a. | 6.699 | 136.6 | n.a. | n.a. | n.a. | 0.0 | n.a. |
| 40 $CF_2$ | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 0.0 |
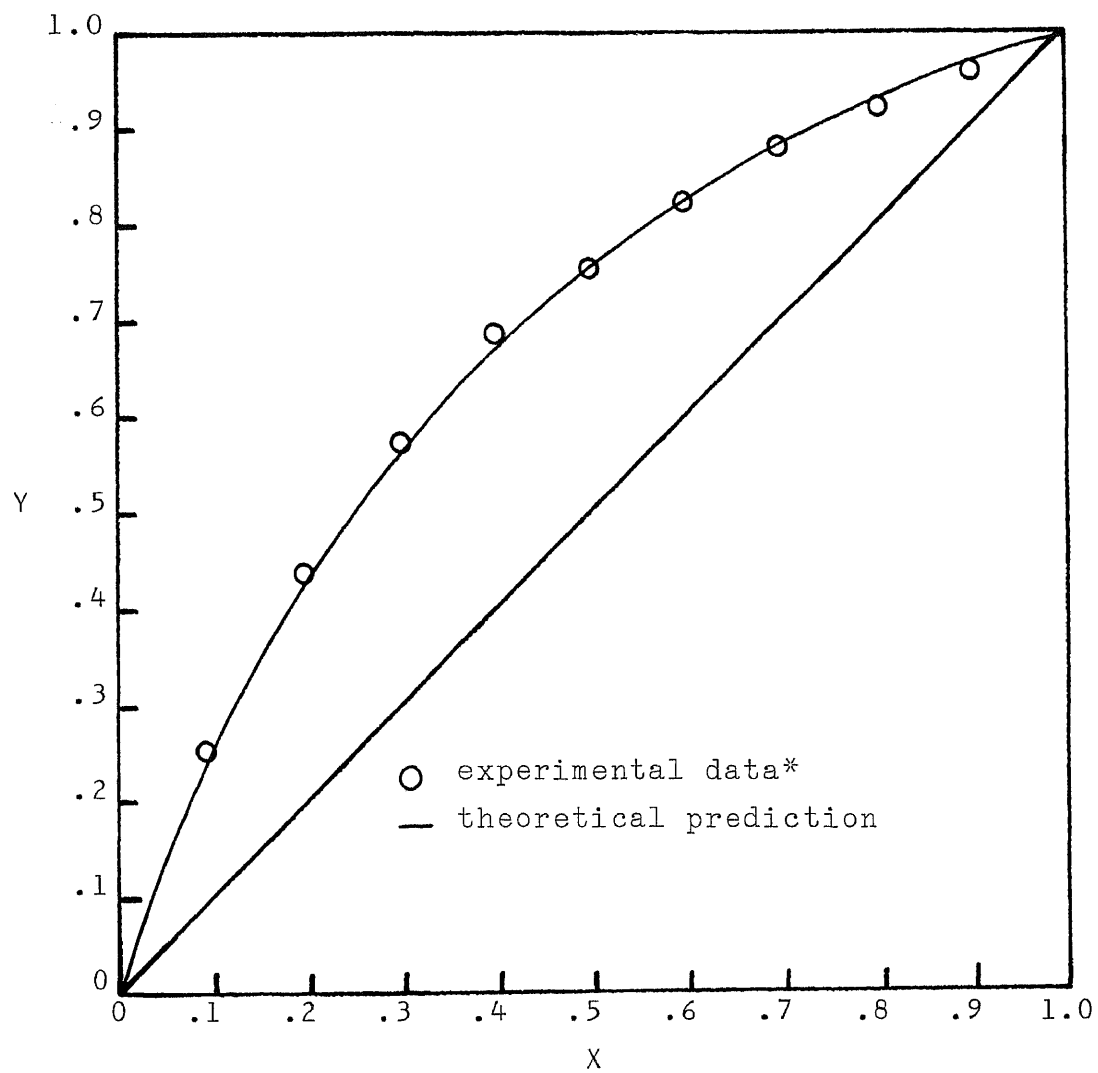
Fig. 15  X-Y diagram for Benzene-Toluene system at 20°C.

*  Data from Schmidt(34).
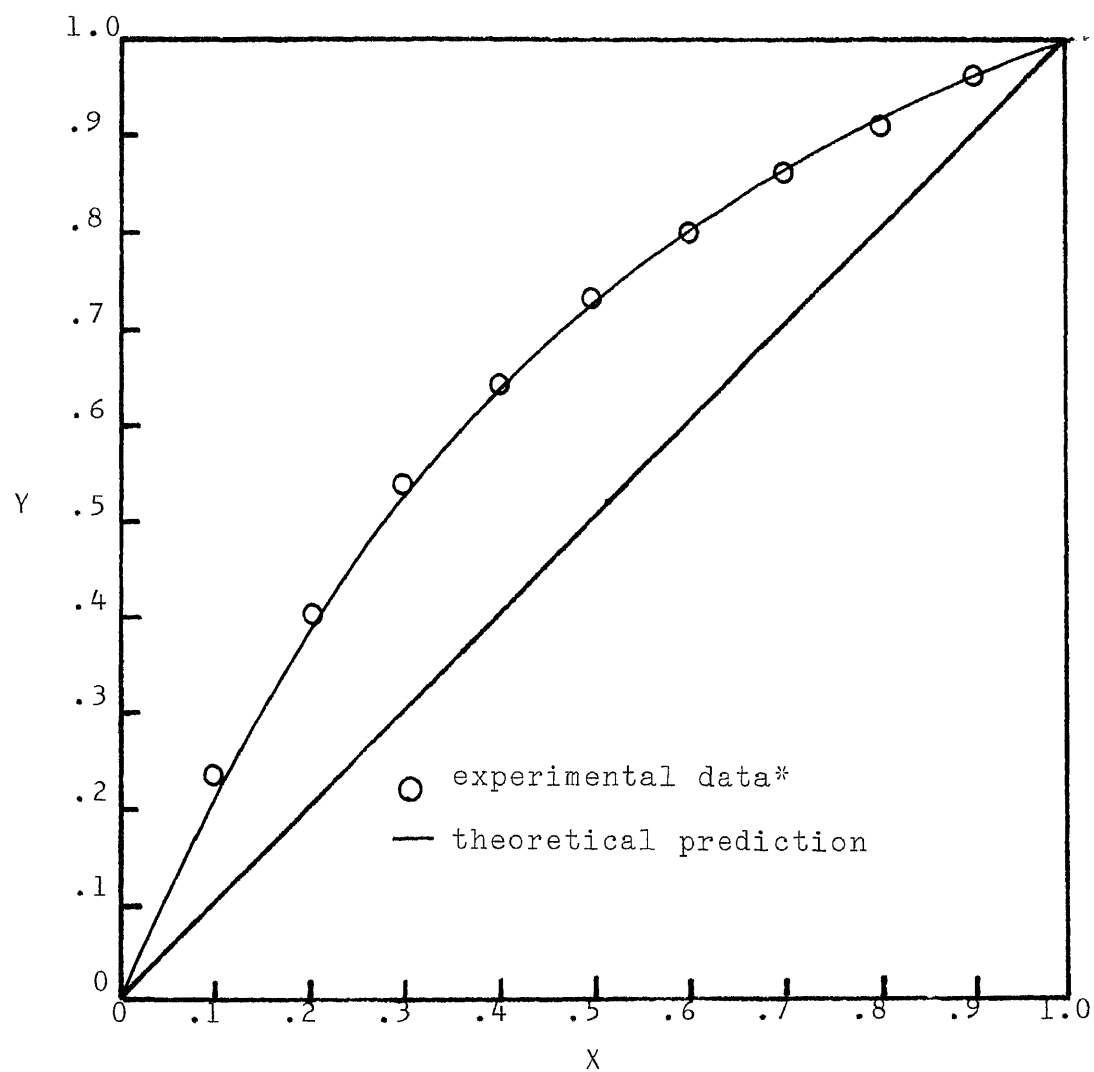
Fig. 16 X-Y diagram for Benzene-toluene system at 60 °C.


\* Data from Schmidt(34).

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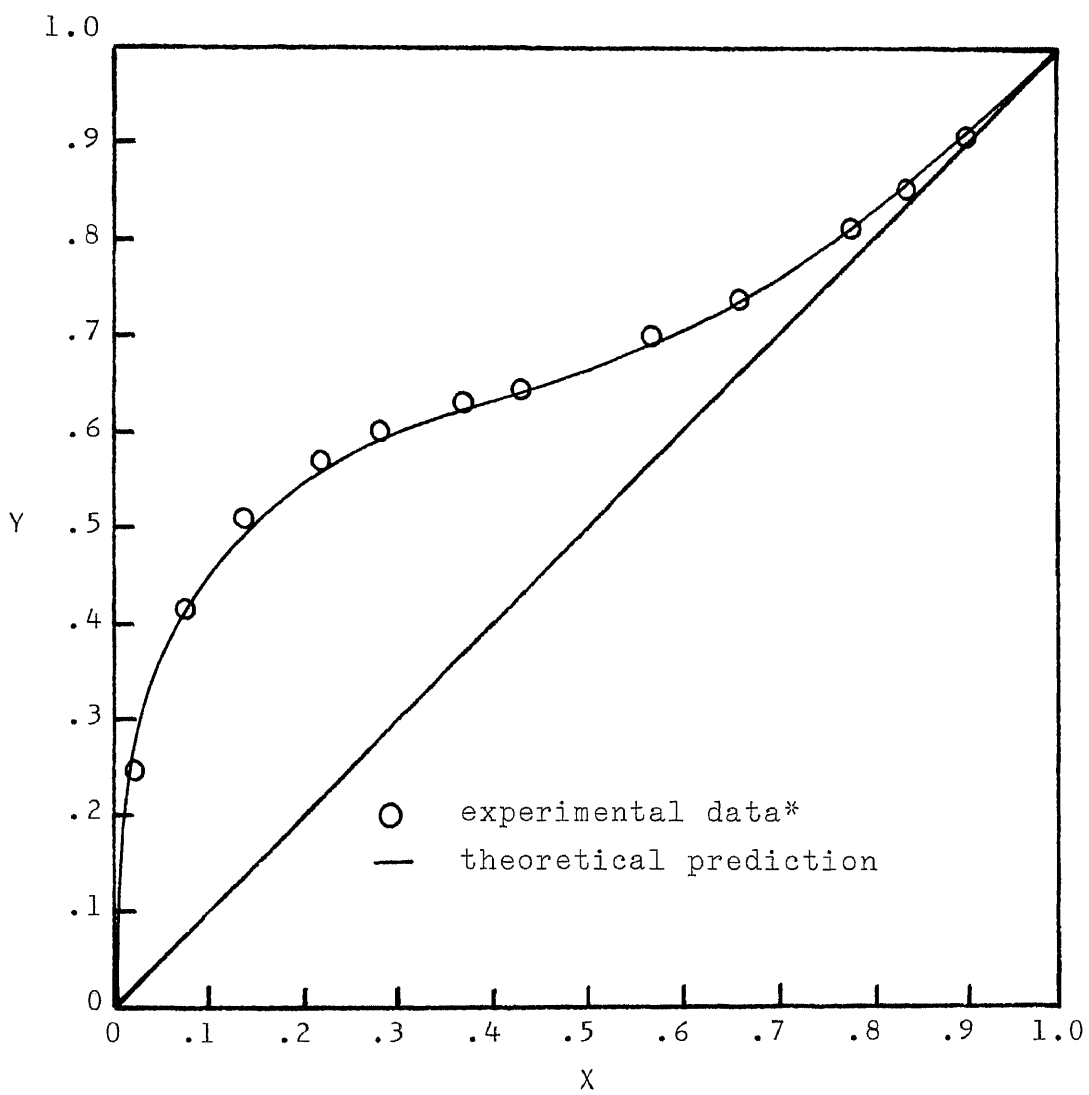
Fig. 17 X-Y diagram for Ethanol-Water system at 50°C.

* Data from Chaudhry(7).
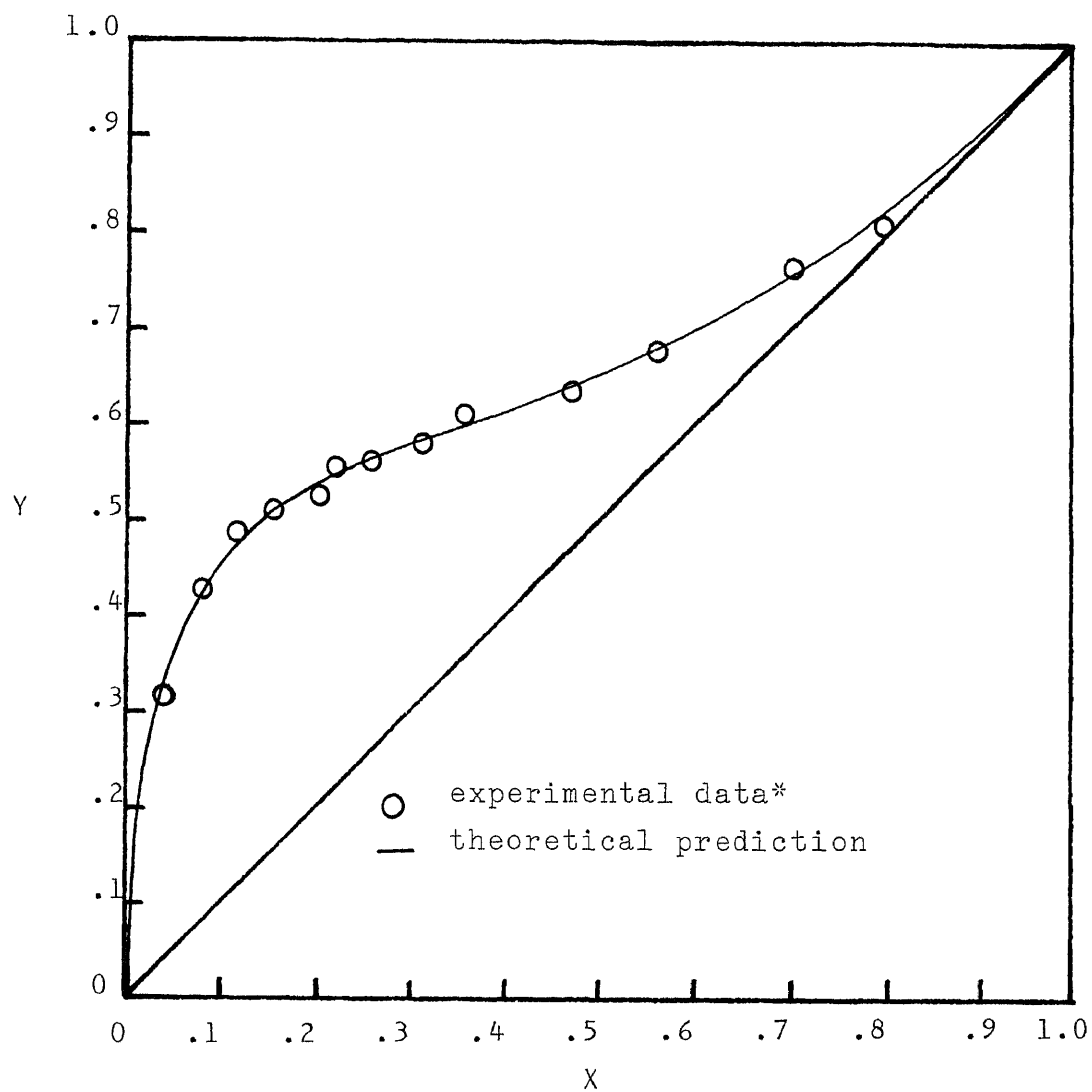
Fig. 18 X-Y diagram for Ethanol-Water system at 70°C.

* Data from Pemberton(28).
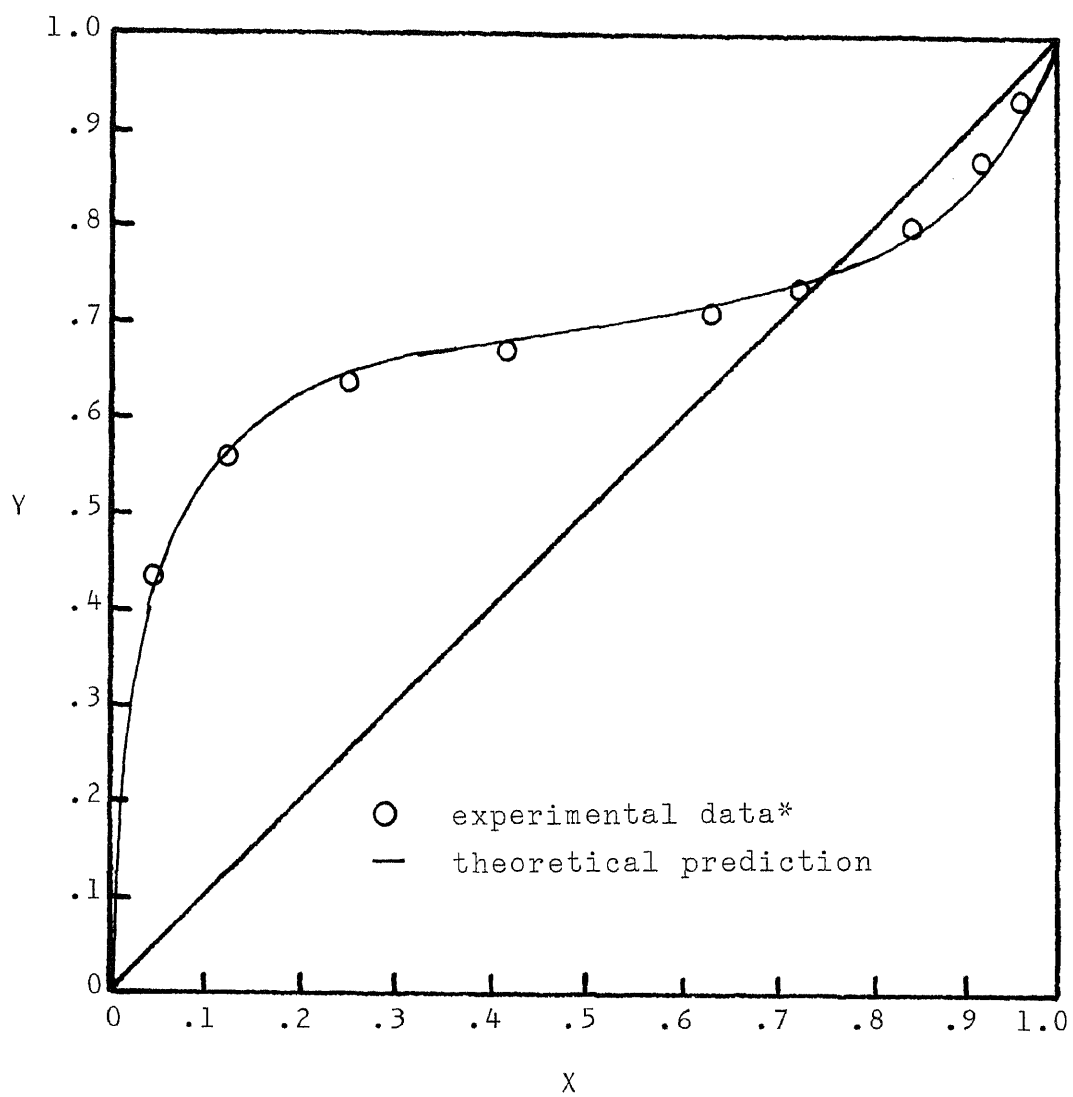
Fig.19   X-Y diagram for Ethanol-Toluene system at 55 °C.

*   Data from Kretschmer(22).

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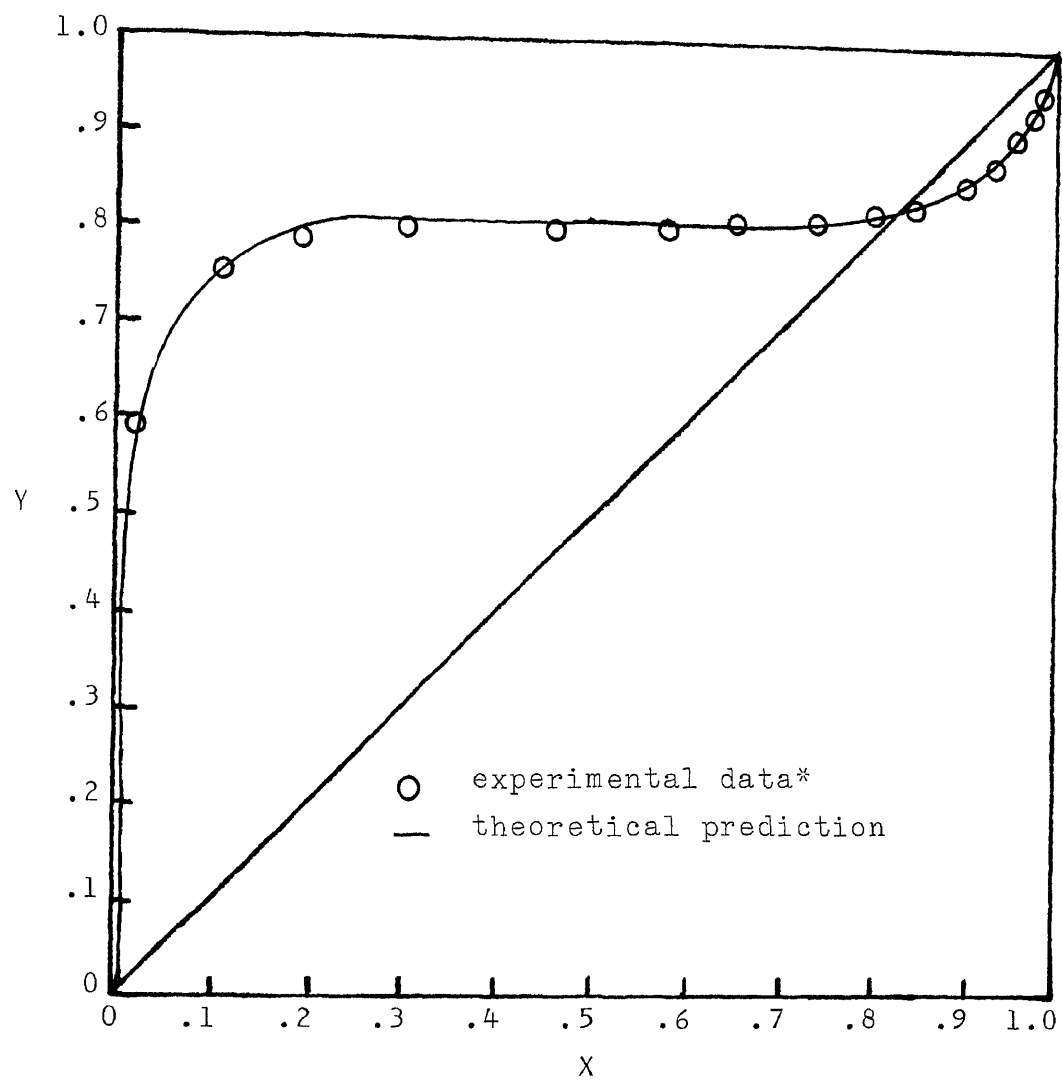
Fig. 20  X-Y diagram for Ethanol-N-Octane system at 45 °C.

* Data from Boublikova(3).
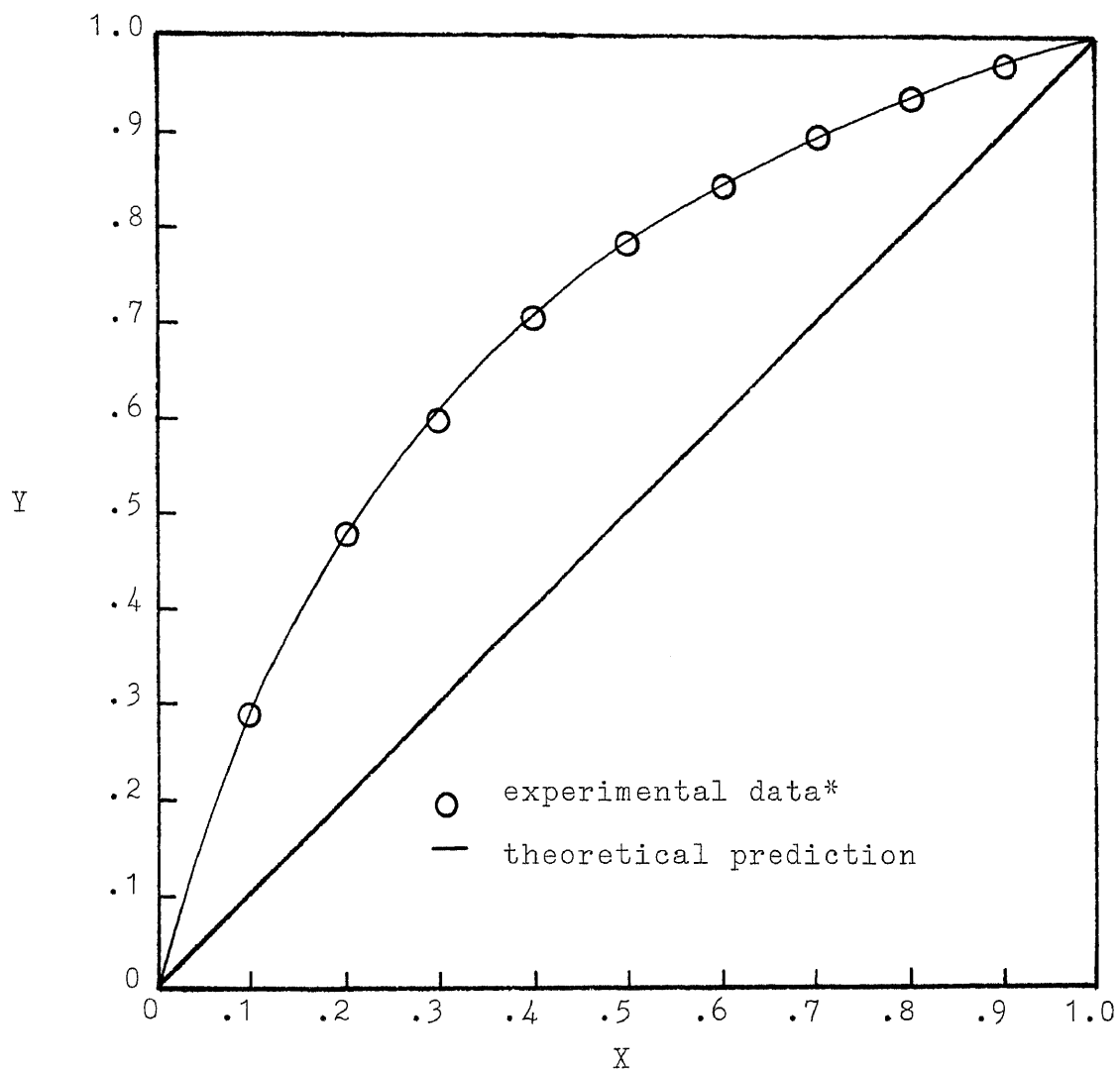
Fig. 21  X-Y diagram for tetrachloromethane-toluene
system at 40 C.

* Data from Kind(21).
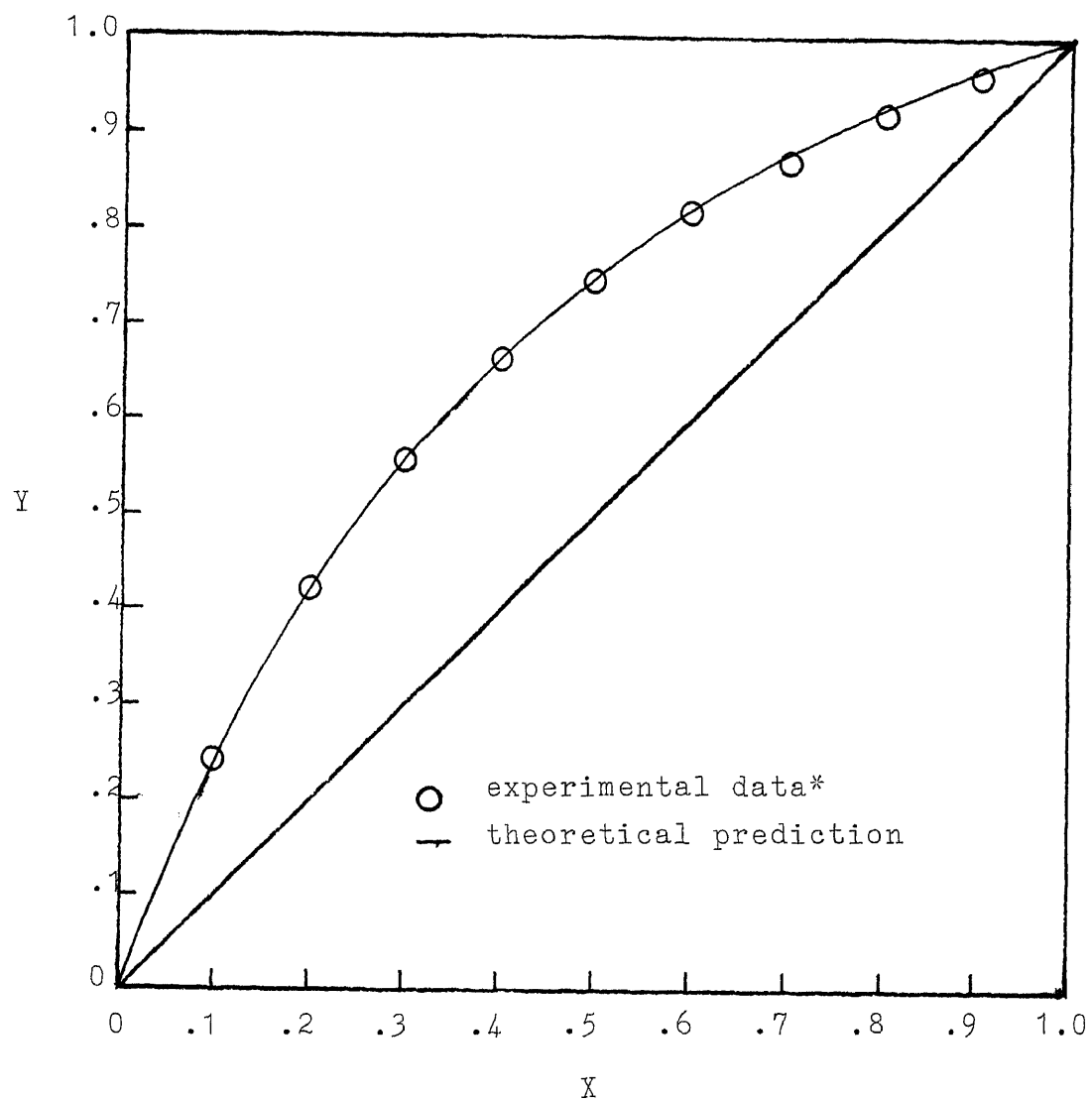
Fig. 22   X-Y diagram for tetrachloromethane-toluene
          system at 80 C.

\* Data from Kind(21).

Table VI


Comparisons Between Experimental Data And UNIFAC
Predicted Results For Acetone-Methanol-Water System

(1) Acetone     (2) Methanol     (3) Water

Temperature = 100 degree C


|  | Experimental Data* | | | | UNIFAC | |
| X1 | X2 | Y1 | Y2 | | Y1 | Y2 |
| --- | --- | --- | --- | --- | --- | --- |
| 0.270 | 0.670 | 0.323 | 0.648 | | 0.345 | 0.633 |
| 0.916 | 0.050 | 0.910 | 0.069 | | 0.895 | 0.066 |
| 0.607 | 0.330 | 0.621 | 0.339 | | 0.621 | 0.343 |
| 0.381 | 0.549 | 0.430 | 0.525 | | 0.444 | 0.524 |
| 0.257 | 0.640 | 0.324 | 0.621 | | 0.342 | 0.612 |
| 0.231 | 0.639 | 0.311 | 0.624 | | 0.322 | 0.620 |
| 0.177 | 0.654 | 0.259 | 0.657 | | 0.270 | 0.654 |
| 0.182 | 0.616 | 0.272 | 0.629 | | 0.283 | 0.626 |
| 0.494 | 0.294 | 0.593 | 0.295 | | 0.598 | 0.292 |
| 0.201 | 0.549 | 0.320 | 0.558 | | 0.319 | 0.569 |
| 0.220 | 0.478 | 0.368 | 0.489 | | 0.359 | 0.505 |
| 0.672 | 0.082 | 0.763 | 0.077 | | 0.769 | 0.073 |
| 0.379 | 0.299 | 0.541 | 0.296 | | 0.544 | 0.301 |
| 0.460 | 0.171 | 0.661 | 0.145 | | 0.653 | 0.161 |
| 0.144 | 0.440 | 0.308 | 0.495 | | 0.297 | 0.517 |
| 0.075 | 0.470 | 0.187 | 0.593 | | 0.186 | 0.608 |
| 0.091 | 0.269 | 0.275 | 0.442 | | 0.269 | 0.476 |
| 0.215 | 0.033 | 0.658 | 0.041 | | 0.678 | 0.039 |
| 0.119 | 0.119 | 0.503 | 0.156 | | 0.503 | 0.184 |
| 0.069 | 0.198 | 0.325 | 0.317 | | 0.325 | 0.349 |
| 0.033 | 0.204 | 0.208 | 0.411 | | 0.202 | 0.432 |
| 0.028 | 0.182 | 0.197 | 0.396 | | 0.196 | 0.416 |
| 0.024 | 0.107 | 0.248 | 0.271 | | 0.244 | 0.303 |
| 0.019 | 0.044 | 0.287 | 0.148 | | 0.295 | 0.162 |
| 0.015 | 0.034 | 0.256 | 0.126 | | 0.271 | 0.140 |


*Data from Griswold(16).


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Table VII


Comparisons Between Experimental Data And UNIFAC
Predicted Results For Acetone-Chloroform-Methanol System

(1) Acetone     (2) Chloroform     (3) Methanol
Temperature = 25 degree C

| Experimental Data* | | | | UNIFAC | |
| X1 | X2 | Y1 | Y2 | Y1 | Y2 |
| --- | --- | --- | --- | --- | --- |
| 0.404 | 0.521 | 0.384 | 0.549 | 0.375 | 0.481 |
| 0.200 | 0.099 | 0.348 | 0.146 | 0.318 | 0.148 |
| 0.531 | 0.390 | 0.591 | 0.323 | 0.559 | 0.308 |
| 0.264 | 0.098 | 0.419 | 0.121 | 0.390 | 0.124 |
| 0.441 | 0.436 | 0.446 | 0.395 | 0.426 | 0.379 |
| 0.412 | 0.446 | 0.370 | 0.380 | 0.385 | 0.398 |
| 0.402 | 0.197 | 0.396 | 0.400 | 0.379 | 0.361 |
| 0.354 | 0.466 | 0.455 | 0.194 | 0.424 | 0.182 |
| 0.660 | 0.309 | 0.710 | 0.210 | 0.741 | 0.207 |
| 0.300 | 0.507 | 0.239 | 0.484 | 0.236 | 0.498 |
| 0.302 | 0.297 | 0.320 | 0.361 | 0.308 | 0.317 |
| 0.487 | 0.237 | 0.526 | 0.186 | 0.524 | 0.188 |
| 0.196 | 0.725 | 0.104 | 0.742 | 0.113 | 0.720 |
| 0.191 | 0.593 | 0.105 | 0.667 | 0.113 | 0.611 |
| 0.615 | 0.184 | 0.649 | 0.121 | 0.664 | 0.119 |
| 0.487 | 0.095 | 0.583 | 0.091 | 0.586 | 0.074 |
| 0.723 | 0.204 | 0.778 | 0.123 | 0.786 | 0.118 |
| 0.586 | 0.089 | 0.675 | 0.074 | 0.663 | 0.058 |
| 0.713 | 0.104 | 0.804 | 0.086 | 0.762 | 0.057 |
| 0.093 | 0.853 | 0.041 | 0.849 | 0.040 | 0.821 |


* Data from Tamir (41 ).

APPENDIX D

ESTIMATIONS OF PHYSICAL PROPERTIES

1.  Surface Tension

The surface tension of pure liquid is calculated by
using the equations proposed by Miller(24):

$$\sigma = P_c^{\frac{2}{3}} \; T_c^{\frac{1}{3}} \; Q \; (1 - T_r)^{\frac{11}{9}} \qquad\qquad \text{(D-1)}$$

$$Q = 0.1207 \; (1 + \frac{T_{br} \; \ln P_c}{1 - T_{br}}) - 0.281 \qquad\qquad \text{(D-2)}$$

Equations (D-1) and (D-2) are basically for nonpolar
liquids, they are not applicable to compounds exhibiting
strong hydrogen bonding (alcohols, acids) and quantum
liquids ($H_2$, He, Ne).

Sprow-Prausnitz correlation(40) is used to calculate
the surface tension for mixtures.  For a binary system

$$\sigma_m = X_A \; \sigma_A + X_B \; \sigma_B - \frac{A}{2RT} \; (\sigma_A - \sigma_B)^2 \; X_A \; X_B \qquad \text{(D-3)}$$

and for a ternary system

$$\sigma_m = X_A \; \sigma_A + X_B \; \sigma_B + X_C \; \sigma_C - \frac{A}{3RT}(\sigma_A - \sigma_B)^2 \; X_A \; X_B$$

$$- \frac{A}{3RT} \; (\sigma_A - \sigma_C)^2 \; X_A \; X_C - \frac{A}{3RT} \; (\sigma_B - \sigma_C)^2 \; X_B \; X_C \quad \text{(D-4)}$$

where A is a partial molar surface area, which can be obtained by

$$A = \sum_{i=1}^{n} (V_i)^{\frac{2}{3}} (6.023 \times 10^{23})^{\frac{1}{3}} \qquad \text{(D-5)}$$

and $V_i$ is liquid molal volume, it can be related to critical volume as

$$V_i = 0.285 \; V_c^{1.048} \qquad \text{(D-6)}$$

The accuracy is normally within 5 percent range of using this method to estimate the surface tension.

2. Liquid Density

Goyal(15) proposed a correlation to estimate liquid density with the knowledge of critical properties, which is expressed as

$$\rho_1 = \frac{P_c \; M}{T_c} \left( \frac{0.0653}{Z_c^{0.773}} - 0.09 \; T_r \right) \qquad \text{(D-7)}$$

For mixtures of liquids, the mixing rule is applied, the density of liquid mixtures can be obtained by

$$\rho_m = \sum_i X_i \; \rho_{1i} \qquad \text{(D-8)}$$

This correlation for pure liquid density do not exceed 5 percent error.

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## 3. Gas Density

The average molecular weight of the gas is calculated from the compositions of the components existed in the mixture

$$M_{avg} = \sum_i Y_i M_i \qquad (D-9)$$

The average density of the gas can be calculated according to the Redlich-Kwong equation of state(30). As it is originally proposed,

$$P = \frac{RT}{V + b_m} - \frac{a_m}{T^{\frac{1}{2}} V (V + b_m)} \qquad (D-10)$$

The empirical mixing rules have found that

$$a_m = \sum_i \sum_j (Y_i Y_j a_{ij}) \qquad (D-11)$$

$$b_m = \sum_i Y_i b_i \qquad (D-12)$$

where

$$a_{ij} = \frac{0.4278 R^2 T_{cij}^{2.5}}{P_{cij}} \qquad (D-13)$$

$$b_{ij} = \frac{0.0867 R T_{ci}}{P_{ci}} \qquad (D-14)$$

The mixing rules for the calculation of $T_{cij}$ and $P_{cij}$ are:

$$T_{cij} = (T_{ci} T_{cj})^{\frac{1}{2}} \qquad (D-15)$$

and

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \qquad (D-16)$$

where

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \qquad (D-17)$$

$$V_{cij} = \left(\frac{V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}}}{2}\right)^3 \qquad (D-18)$$

For a binary system, $a_m$ in equation (D-11) can be expressed as

$$a_m = Y_1^2 a_{11} + 2 Y_1 Y_2 a_{12} + Y_2^2 a_{22} \qquad (D-19)$$

and for a ternary system, it can be expressed as

$$a_m = Y_1^2 a_{11} + Y_2^2 a_{22} + Y_3^2 a_{33} + 2 Y_1 Y_2 a_{12}$$

$$+ 2 Y_1 Y_3 a_{13} + 2 Y_2 Y_3 a_{23} \qquad (D-20)$$

Once $a_m$ and $b_m$ for the mixtures are determined, then the average volume can be calculated as

$$V_{avg} = \frac{ZRT}{P} \qquad (D-21)$$

where

$$Z = \frac{1}{1-h} - \frac{a_m}{b_m \, R \, T^{\frac{3}{2}}} \left( \frac{h}{1+h} \right) \qquad \text{(D-22)}$$

$$h = \frac{b_m}{ZRT} \qquad \text{(D-23)}$$

Combining equation (D-22) with equation (D-23), Z can be solved with iteration method. By inserting Z, system pressure, and temperature into equation (D-21), the average volume V can be obtained. Therefore, the average density of the gas mixture can be determined as

$$\rho = \frac{M_{avg}}{V_{avg}} \qquad \text{(D-24)}$$

4. Gas Viscosity

The gas viscosity is computed by Bromley and Wilke method(4). In the equation

$$\mu^0 = \frac{33.3 \, (M \, T_c)^{\frac{1}{2}}}{V_c^{\frac{2}{3}}} \left[ f(1.33 \, T_r) \right] \qquad \text{(D-25)}$$

$\mu^0$ is expressed in micropoise, $T_c$ in $^\circ K$, and $V_c$ in cc./gmole. The function $\left[ f(1.33 \, T_r) \right]$ is represented analytically by Scheibel(33) as shown in the equation (D-26)

$$f(1.33 \, T_r) = 1.058 \, T_r^{0.645} - \frac{0.261}{(1.9 \, T_r)^{0.9 \, \log(1.9 \, T_r)}} \qquad \text{(D-26)}$$

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The viscosities of gas mixtures can be obtained
with Herning's correlation(18)

$$\mu_m^0 = \frac{\sum Y_i \, \mu_i \, (M_i)^{\frac{1}{2}}}{\sum Y_i \, (M_i)^{\frac{1}{2}}} \qquad \text{(D-27)}$$

The method used for computing the viscosities of pure
gases give 3 and 13 percent average and maximum errors.
The correlation used to calculate the viscosities of
gas mixtures represents the data with the average and
maximum deviations of 1.5 and 5 percent.


5.  Liquid Viscosity

The liquid viscosity is calculated by van Velzen
equation(43)

$$\log \eta_1 = B \left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad \text{(D-28)}$$

where  $\eta_1$ = liquid viscosity, cp

  T  = temperature, $^\circ K$

and B and $T_o$ are related to structure.  The B and $T_o$
values for common compounds are tabulated in the data
bank of the book written by Reid(31).


For liquid mixtures, the Kendall-Monroe equation(20)
is used

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$$\mu_m^{\frac{1}{3}} = X_1 \, \mu_1^{\frac{1}{3}} + X_2 \, \mu_2^{\frac{1}{3}} \qquad\qquad (D\text{-}29)$$

This equation relates the viscosities of miscible liquid mixtures to the pure-component viscosities.

6. Gas-Phase Diffusivity

The empirical correlation suggested by Fuller(13) is used to calculate the gas-phase diffusivities. The equation is

$$D_{AB} = \frac{10^{-3} \, T^{1.75} \left[ (M_A + M_B)/M_A \, M_B \right]^{\frac{1}{2}}}{P \left[ (\Sigma V)_A^{\frac{1}{3}} + (\Sigma V)_B^{\frac{1}{3}} \right]^2} \qquad (D\text{-}30)$$

where T is in kelvin and P in atmospheres. The values of the atomic diffusion volumes, $\Sigma V$, were determined by a regression analysis of 340 experimental diffusion coefficient values of 153 binary systems. For simple, non-polar systems at moderate temperatures, this correlation gives less than 5 to 10 percent errors.

7. Liquid-Phase Diffusivity

Wilke-Chang technique(44) is a widely used correlation for liquid-phase diffusivity. It is shown in the following equation

$$D_{AB}^{L} = 7.4 \times 10^{-8} \frac{(\phi \, M_B)^{\frac{1}{2}}}{\eta_B \, V_A^{0.6}} \qquad (D\text{-}31)$$

where  $D_{AB}^{L}$  = mutual diffusion coefficient of solute A
in solvent B, $cm^2$/sec

$M_B$   = molecular weight of solvent B

$\eta_B$   = viscosity of solvent B, cp

$V_A$   = molal volume of solute A at its normal
boiling temperature, $cm^3$/g mole

$\phi$    = association factor of solvent B, dimensionless

The value of $V_A$ can be estimated by equation (D-6). Wilke
and Chang recommend that $\phi$ be chosen as 2.6 if the solvent
is water, 1.9 for methanol, 1.5 for ethanol, and 1.0 for
unassociated solvents. This correlation gives an average
error about 10 percent.

8. Vapor Pressure

Antoine's equation(2) is used to calculate the vapor
pressure. It is a widely used equation

$$\ln P = A - \frac{B}{T + C} \qquad (D\text{-}32)$$

The values A, B, and C are tabulated in the data bank
of the book written by Reid(31). The temperature used
in equation (D-32) is in kelvin and pressure is in
millimeters of mercury.

## 9. Enthalpy

The enthalpy depends strongly on temperature. It can be calculated by integrating heat capacity at constant pressure, $C_p$, from a reference temperature $(T_r)$ to the system temperature $(T_s)$. The liquid enthalpy can be expressed as

$$h_l = \int_{T_r}^{T_s} C_{pl}(T) \, dT \qquad (D-33)$$

where $C_{pl}(T)$ is in polynomial form as

$$C_{pl}(T) = A + BT + CT^2 + DT^3 \qquad (D-34)$$

The polynomial coefficients for heat capacity at constant pressure can be obtained from the data bank in the book written by Reid(31). For liquid mixture, the enthalpy $h_{lm}$ can be calculated in the form as shown below

$$h_{lm} = \sum_i X_i \, h_{li} \qquad (D-35)$$

The vapor mixture enthalpy may be estimated by

$$H_{vm} = \sum_i Y_i \, h_{li} + \sum_i Y_i \, \lambda_i \qquad (D-36)$$

where $\lambda_i$ is the heat of vaporization of individual component. The method of estimating the heat of vaporization is discussed in the following section.

## 10. Heat of Vaporization

The heat of vaporization is estimated by Carruth correlation(6)

$$\frac{\lambda}{RT_c} = 7.08 \, (1 - T_r)^{0.354} + 10.95 \, \omega \, (1 - T_r)^{0.456} \qquad (D-37)$$

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where $\omega$ is acentric factor, and $T_r$ is reduced temperature. This correlation is one of the most accurate and convenient methods to estimate the heat of vaporization.

11. Overall Gas-Phase Mass-Transfer Coefficient

The overall mass-transfer coefficient is calculated by using Rowe's correlation(32). Rowe and his coworkers suggested that the overall mass-transfer coefficient can be estimated via Sherwood number. The equation is

$$N_{sh} = 2.0 + 0.76 \ (Re)^{\frac{1}{2}} \ (Sc)^{\frac{1}{3}} \qquad (D-38)$$

where $N_{sh}$ = Sherwood number = $\dfrac{K_G \ R}{D}$

Re = Reynolds number = $\dfrac{d \ \rho \ v}{\mu}$

Sc = gas phase Schmidt number = $\dfrac{\mu}{D \ \rho}$

d  = diameter of bubbles

v  = velocity of bubbles

$\rho$  = gas phase density

$\mu$  = gas phase viscosity

D  = diffusivity coefficient

12. Bubble diameter, contact area and time

Many investigations have been done on bubbles

rising in the liquids.  Davidson and Amick(9) found a
relation between the bubble frequency and the orifice
diameter.  The relation is

$$N_m = 9.1 \ q^{0.13} \ r^{0.43} \qquad\qquad (D\text{-}39)$$

where  $N_m$ = frequency, bubbles per second

$q$ = gas flow rate, cc./sec

$r$ = orifice radius, cm

Quigley(29) and his coworkers suggested that the bubble
diameters were unaffected by the liquid seal and by the
density and surface tension of the liquid.  In the
equation

$$D_B = 0.222 \ D_o^{0.33} \ Q_G^{0.125} \ \mu^{0.02} + 3.02\text{x}10^{-4} \ Q_G^{1.09} \quad (D\text{-}40)$$

$D_B$ is the bubble diameter (diameter of a sphere of equal
volume), $Q_G$ is gas flow rate per orifice, $D_o$ is orifice
diameter, $\mu$ is liquid viscosity.  Quigley also presented
the following equations

$$V_R = 4.1\text{x}10^3 \ Q_G^{0.16} \qquad\qquad (D\text{-}41)$$

$$A = 1.46\text{x}10^{-3} \ Q_G^{0.84}/D_B \qquad\qquad (D\text{-}42)$$

$$t = Z/V_R \qquad\qquad (D\text{-}43)$$

where  $V_R$ = rising velocity

$A$ = area of bubbles (assumed spherical)

t  =  contact area

Z  =  liquid seal


    All the physical properties that were discussed in
this appendix are necessary to proceed the calculations
in this work.  Some of the calculated physical proper-
ties are listed in Table VIII, which are compared with
the available experimental data.  The result shows good
agreement with the data.

Table VIII

Comparisons of Calculated Physical
Properties With Experimental Data

Surface Tension (dyne/cm)

| | Temperature (°C) | Data[1] | Calculated |
|---|---|---|---|
| Benzene | 25 | 28.23 | 27.42 |
| Diethyl Ether | 25 | 16.47 | 16.42 |
| 42.3% Diethyl Ether & 57.7% Benzene | 25 | 21.81 | 21.68 |

Gas Viscosity (micropoise)

| | Temperature (°C) | Data[2] | Calculated |
|---|---|---|---|
| Nitrogen | 40 | 182 | 178.6 |
| | 60 | 190 | 186.57 |
| Water | 40 | 101 | 98.7 |
| | 60 | 111 | 105.34 |
| Ammonia | 40 | 105 | 103.3 |
| | 60 | 111 | 107.92 |

Liquid Viscosity (centipoise)

| | Temperature (°C) | Data[1] | Calculated |
|---|---|---|---|
| Water | 20 | 1.005 | 0.989 |
| | 40 | 0.656 | 0.638 |
| Isobutyl Alcohol | 20 | 3.98 | 4.009 |
| | 40 | 2.30 | 2.197 |

Liquid Density (g/cc)

| | Temperature (°C) | Data[1] | Calculated |
|---|---|---|---|
| Water | 30 | 0.995 | 0.981 |
| | 40 | 0.992 | 0.972 |
| Cyclohexanol | 30 | 0.949 | 0.908 |
| | 40 | 0.932 | 0.899 |

Gas Phase Diffusivity (ft$^2$/hr)

| | Temperature (°C) | Data[2] | Calculated |
|---|---|---|---|
| He - $H_2O$ | 25 | 3.52 | 3.25 |
| | 60 | 4.25 | 4.14 |
| Air - $H_2O$ | 25 | 1.01 | 0.97 |
| | 60 | 1.24 | 1.18 |
| Air - $NH_3$ | 25 | 0.98 | 0.94 |
| | 60 | 1.21 | 1.14 |
| He - Isobutyl Alcohol | 25 | 1.41 | 1.21 |
| | 60 | 1.71 | 1.47 |
| $N_2$ - Isobutyl Alcohol | 25 | 0.35 | 0.36 |
| | 60 | 0.43 | 0.44 |

Data[1] - Data from Reid(31).

Data[2] - Data from Williams(45).

APPENDIX E


COMPUTER PROGRAM FOR A BINARY

SEPARATION IN A DISTILLATION COLUMN

```
        IMPLICIT REAL*8(A-H,O-Z)
        REAL LRIN,LROUT
        DIMENSION HV(15),HL(15)
        DATA NTOL/10/
        DATA NREGIN/2/
        DATA NBUBLE/2/
        DATA PCLMN/760.DO/
        DATA QVAP/104.6DO/
C       QVAP = AIR FLOW RATE IN FT*FT*FT/HR
C              PER INCH WIDTH OF ORIFICE
C       NTOAL = TOTAL NUMBER OF TRAYS
C       NREGIN = THE REGION THAT CAN BE DIVIDED ON EACH TRAY
C       NBUBLE = NUMBER OF BUBBLE CAPS ON EACH TRAY
        QGIN=QVAP/NBUBLE
        DATA TPLATE,XAOUT,YAOUT/377.59DO,0.879DO,0.879DO/
        XAIN=XAOUT
        YAIN=YAOUT
        CALL UNIFAC(XAIN,TPLATE,YAEQ,VOLTY)
        YAGL=YAEQ
        RELATE=VOLTY
        CALL PROPER(XAIN,YAIN,TPLATE,RELATE,QGIN,HRIN,G,QMOLEV)
        FLOW=QMOLEV
        VRIN=FLOW
        XA=XAIN
        YA=YAIN
        CALL ENTHPY(TPLATE,XA,YA,ENTHVM,ENTHLM)
        HVINI=ENTHVM
        HLINI=ENTHLM
        DO 5500 NP=1,NTOL
        XAIN=XAOUT
        YAIN=YAOUT
        YASUMO=0.DO
        EFSUMO=0.DO
        DO 6700 NR=1,NREGIN
        CALL UNIFAC(XAIN,TPLATE,YAEQ,VOLTY)
        YAGL=YAEQ
        RELATE=VOLTY
        CALL PROPER(XAIN,YAIN,TPLATE,RELATE,QGIN,HRIN,G,QMOLEV)
        FORM=G
        RISN=HRIN*VRIN
        LRIN=VRIN*2.DO
        YAI=YAIN-FORM*(YAIN-YAGL)
        VROUT=VRIN
        YAOUT=(VRIN/VROUT)*YAI-(YAI-YAGL)*(RISN/VROUT)
        LROUT=LRIN-(VRIN-VROUT)
        XAOUT=(VROUT*YAOUT+LRIN*XAIN-VRIN*YAIN)/LROUT
        XA=XAOUT
        YA=YAOUT
        EFFICN=(YAOUT-YAIN)/(YAGL-YAIN)
        WRITE (6,8877) EFFICN
        YASUMO=YASUMO+YA
        EFSUMO=EFSUMO+EFFICN
        XAIN=XA
6700    CONTINUE
```

```
      YAOUT=YASUMO/NREGIN
      EFAVG=EFSUMO/NREGIN
      WRITE (6,9919)
9919  FORMAT(/,10X,50('$'))
      WRITE (6,9919)
      WRITE (6,9919)
      WRITE (6,6564) NP
6564  FORMAT(/,10X,'***** THE PLATE NUMBER = ',I3,2X,'*****')
      WRITE (6,7655) TPLATE,YAOUT,XAOUT,VROUT
      WRITE (6,8898) YAOUT,YAIN,YAGL
      WRITE (6,8897) EFAVG
8897  FORMAT(/,10X,' THE AVERAGE PLATE EFFICIENCY = ',F11.6)
      WRITE (6,9919)
      WRITE (6,9919)
      WRITE (6,9919)
C        THIS SECTION ESTIMATE NEXT PLATE TEMPERATURE
      XA=XAOUT
      YA=YAOUT
      CALL ENTHPY(TPLATE,XA,YA,ENTHVM,ENTHLM)
      HV(NP)=ENTHVM
      E=(VROUT*HV(NP)+LRIN*HLINI-VRIN*HVINI)/LROUT
      TNXT=TPLATE
      CALL TEMP(XA,E,TNXT)
      TPLATE=TNXT
      HVINI=HV(NP)
      CALL ENTHPY(TPLATE,XA,YA,ENTHVM,ENTHLM)
      HLINI=ENTHLM
5500  CONTINUE
7655  FORMAT(/,10X,'THE PLATE TEMPERATURE IS ',F16.6,/,10X
     1,'THE OUTLET GAS COMPOSITION AFTER ADJUST TEMPERATURE IS
     1 ',F11.6,/,10X,'THE INLET LIQUID COMPOSITION IS
     1 ',F11.6,/,10X,'THE OUTLET GAS FLOW RATE IN G MOLE/HR IS
     1 ',F16.6)
8898  FORMAT(/,10X,'YAOUT =',F11.6,' YAIN =',F11.6,' YAGL =',
     1F11.6)
8877  FORMAT(/,10X,'THE PLATE LOCAL EFFICIENCY IS ',F11.6)
      STOP
      END
```

```
      SUBROUTINE UNIFAC(XAIN,TPLATE,YAEQ,VOLTY)
        IMPLICIT REAL*8(A-H,O-Z)
C******************************************************************
C
C      THIS SECTION IS WRITTEN FOR PREDICTING
C     TOLUENE-CCL4 BINARY SYSTEM BY
C      USING UNIFAC METHOD
C
C******************************************************************
C
C       THE SYSTEM IS HEAVIER (1) = TOLUENE
C       THE SYSTEM IS LIGHTER (2) = CCL4
C
      DIMENSION R1(4),R2(4),Q1(4),Q2(4)
      DIMENSION NU1(4),NU2(4),AMN(8,8),PSI(8,8)
      DIMENSION E(8),THEMX(8),GROMX(8)
C
C******************************************************************
C
C      DATA FILE AS FOLLOWING FORM
C
C     COMPONENT        MAIN GROUPS     R      Q     NU
C     ------------------------------------------------------------
C         A                1          XX     YY     ZZ
C                          2          XX     YY     ZZ
C                          3          XX     YY     ZZ
C                          4  .       XX     YY     ZZ
C
C         . . . . . . . . . . . . . . . . . . . . . . . . . . . .
C         B                5          XX     YY     ZZ
C                          6          XX     YY     ZZ
C                 .        7          XX     YY     ZZ`
C                          8          XX     YY     ZZ
C     ------------------------------------------------------------
C
C     1-8 : TYPES OF FUNCTIONAL GROUP
C     R   : DATA FROM TABLE
C     Q   : DATA FROM TABLE
C     NU  : NUMBER OF FUNCTIONAL GROUPS IN COMPONENT
C
C      INTERACTION PARAMETERS AMN(I,J)
C
C          1        2        3        4        5        6        7        8
C     ------------------------------------------------------------------------
C  1 I A(1,1)  A(1,2)  A(1,3)  A(1,4)  A(1,5)  A(1,6)  A(1,7)  A(1,8)
C  2 I A(2,1)  . . . . . . . . . . . . . . . . . . . . .         A(2,8)
C  3 I A(3,1)  . . . . . . . . . . . . . . . . . . . .           A(3,8)
C  4 I         . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
C  5 I         . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
C  6 I
C  7 I
C  8 I A(8,1)  A(8,2)  A(8,3)  A(8,4)  A(8,5)  A(8,6)  A(8,7)  A(8,8)
C     ------------------------------------------------------------------------
C
C
C******************************************************************
```

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```
C
C       CHECK (1) TOLUENE, (2) CCL4
        DATA (R1(K),K=1,4)/1.2663D0,0.5313D0,0.D0,0.D0/
        DATA (R2(K),K=1,4)/3.39D0,0.0D0,0.D0,0.D0/
        DATA (Q1(K),K=1,4)/0.968D0,0.400D0,0.D0,0.D0/
        DATA (Q2(K),K=1,4)/2.91D0,0.0D0,0.D0,0.D0/
        DATA (NU1(K),K=1,4)/1,5,0,0/
        DATA (NU2(K),K=1,4)/1,0,0,0/
        DATA (AMN(1,J),J=1,8)/0.D0,-146.8D0,0.D0,0.D0,
       *-141.3D0,0.0D0,0.D0,0.D0/
        DATA (AMN(2,J),J=1,8)/167.0D0,0.D0,0.D0,0.D0,
       *3.0D0,0.0D0,0.D0,0.D0/
        DATA (AMN(3,J),J=1,8)/0.D0,0.D0,0.D0,0.D0,
       *0.D0,0.D0,0.D0,0.D0/
        DATA (AMN(4,J),J=1,8)/0.D0,0.D0,0.D0,0.D0,
       *0.D0,0.D0,0.D0,0.D0/
        DATA (AMN(5,J),J=1,8)/134.7D0,-4.7D0,0.D0,0.D0,
       *0.D0,0.0D0,0.D0,0.D0/
        DATA (AMN(6,J),J=1,8)/0.0D0,0.0D0,0.D0,0.D0,
       *0.0D0,0.D0,0.D0,0.D0/
        DATA (AMN(7,J),J=1,8)/0.D0,0.D0,0.D0,0.D0,
       *0.D0,0.D0,0.D0,0.D0/
        DATA (AMN(8,J),J=1,8)/0.D0,0.D0,0.D0,0.D0,
       *0.D0,0.D0,0.D0,0.D0/
C
C       ANTOINE CONSTANTS FOR VAPOR PRESSURE
C
        DATA ANTA1,ANTB1,ANTC1/16.0137D0,3096.52D0,-53.67D0/
        DATA ANTA2,ANTB2,ANTC2/15.8742D0,2808.19D0,-45.99D0/
        T=TPLATE
        P1S=DEXP(ANTA1-(ANTB1/(T+ANTC1)))
        P2S=DEXP(ANTA2-(ANTB2/(T+ANTC2)))
        WRITE (6,212) P1S,P2S
212     FORMAT(/,10X,'VAPOR PRESSURE FOR COMPONENT 1 IS ',F11.6,
       */,10X,'FOR COMPONENT 2 IS ',F11.6)
C
        DATA Z/10.D0/
        X1=XAIN
        X2=1.D0-X1
C
        PR1=NU1(1)*R1(1)+NU1(2)*R1(2)+NU1(3)*R1(3)+NU1(4)*R1(4)
        PR2=NU2(1)*R2(1)+NU2(2)*R2(2)+NU2(3)*R2(3)+NU2(4)*R2(4)
        QQ1=NU1(1)*Q1(1)+NU1(2)*Q1(2)+NU1(3)*Q1(3)+NU1(4)*Q1(4)
        QQ2=NU2(1)*Q2(1)+NU2(2)*Q2(2)+NU2(3)*Q2(3)+NU2(4)*Q2(4)
C
        T1=(PR1*X1)+(PR2*X2)
        PHI1=(PR1*X1)/T1
        PHI2=(PR2*X2)/T1
        T2=(QQ1*X1)+(QQ2*X2)
        THETA2=(QQ2*X2)/T2
        THETA1=(QQ1*X1)/T2
        TL1=(Z/2.D0)*(PR1-QQ1)-(PR1-1.0D0)
        TL2=(Z/2.D0)*(PR2-QQ2)-(PR2-1.0D0)
        C1=DLOG(PHI1/X1)
```

```
      C2=DLOG(THETA1/PHI1)
      C3=(X1*TL1)+(X2*TL2)
      C11=DLOG(PHI2/X2)
      C22=DLOG(THETA2/PHI2)
      COMBI1=C1+(Z/2.DO)*QQ1*C2+TL1-(PHI1/X1)*C3
      COMBI2=C11+(Z/2.DO)*QQ2*C22+TL2-(PHI2/X2)*C3
C
C

      DO 11 I=1,8
      DO 12 J=1,8
      PSI(I,J)=DEXP(-AMN(I,J)/T)
12    CONTINUE
11    CONTINUE
C
C
      FOR PURE TOLUENE A1=ACCH3=1,A2=ACH=5,A3=0,A4=0
C
      FG1=NU1(1)+NU1(2)+NU1(3)+NU1(4)
      FGX1=NU1(1)/FG1
      FGX2=NU1(2)/FG1
      FGX3=NU1(3)/FG1
      FGX4=NU1(4)/FG1
      F1=Q1(1)*FGX1+Q1(2)*FGX2+Q1(3)*FGX3+Q1(4)*FGX4
      THET11=Q1(1)*FGX1/F1
      THET12=Q1(2)*FGX2/F1
      THET13=Q1(3)*FGX3/F1
      THET14=Q1(1)*FGX4/F1
      B1=THET11*PSI(1,1)+THET12*PSI(2,1)+THET13*PSI(3,1)+
     *THET14*PSI(4,1)
      B2=THET11*PSI(1,2)+THET12*PSI(2,2)+THET13*PSI(3,2)+
     *THET14*PSI(4,2)
      B3=THET11*PSI(1,3)+THET12*PSI(2,3)+THET13*PSI(3,3)+
     *THET14*PSI(4,3)
      B4=THET11*PSI(1,4)+THET12*PSI(2,4)+THET13*PSI(3,4)+
     *THET14*PSI(4,4)
      D1=THET11*PSI(1,1)/B1+THET12*PSI(1,2)/B2+THET13*PSI(1,3)
     */B3+THET14*PSI(1,4)/B4
      D2=THET11*PSI(2,1)/B1+THET12*PSI(2,2)/B2+THET13*PSI(2,3)
     */B3+THET14*PSI(2,4)/B4
      D3=THET11*PSI(3,1)/B1+THET12*PSI(3,2)/B2+THET13*PSI(3,3)
     */B3+THET14*PSI(3,4)/B4
      D4=THET11*PSI(4,1)/B1+THET12*PSI(4,2)/B2+THET13*PSI(4,3)
     */B3+THET14*PSI(4,4)/B4
      PGRA1=Q1(1)*(1.DO-DLOG(B1)-D1)
      PGRA2=Q1(2)*(1.DO-DLOG(B2)-D2)
      PGRA3=Q1(3)*(1.DO-DLOG(B3)-D3)
      PGRA4=Q1(4)*(1.DO-DLOG(B4)-D4)
C
C
      FOR PURE CCL4 B5=CCL4=1,B6=0,B7=0,B8=0
C
      FG2=NU2(1)+NU2(2)+NU2(3)+NU2(4)
      FGX5=NU2(1)/FG2
      FGX6=NU2(2)/FG2
      FGX7=NU2(3)/FG2
      FGX8=NU2(4)/FG2
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      F2=Q2(1)*FGX5+Q2(2)*FGX6+Q2(3)*FGX7+Q2(4)*FGX8
      THET25=Q2(1)*FGX5/F2
      THET26=Q2(2)*FGX6/F2
      THET27=Q2(3)*FGX7/F2
      THET28=Q2(4)*FGX8/F2
      B5=THET25*PSI(5,5)+THET26*PSI(6,5)+THET27*PSI(7,5)+
     *THET28*PSI(8,5)
      B6=THET25*PSI(5,6)+THET26*PSI(6,6)+THET27*PSI(7,6)+
     *THET28*PSI(8,6)
      B7=THET25*PSI(5,7)+THET26*PSI(6,7)+THET27*PSI(7,7)+
     *THET28*PSI(8,7)
      B8=THET25*PSI(5,8)+THET26*PSI(6,8)+THET27*PSI(7,8)+
     *THET28*PSI(8,8)
      D5=THET25*PSI(5,5)/B5+THET26*PSI(5,6)/B6+THET27*PSI(5,7)
     */B7+THET28*PSI(5,8)/B8
      D6=THET25*PSI(6,5)/B5+THET26*PSI(6,6)/B6+THET27*PSI(6,7)
     */B7+THET28*PSI(6,8)/B8
      D7=THET25*PSI(7,5)/B5+THET26*PSI(7,6)/B6+THET27*PSI(7,7)
     */B7+THET28*PSI(7,8)/B8
      D8=THET25*PSI(8,5)/B5+THET26*PSI(8,6)/B6+THET27*PSI(8,7)
     */B7+THET28*PSI(8,8)/B8
      PGRB5=Q2(1)*(1.D0-DLOG(B5)-D5)
      PGRB6=Q2(2)*(1.D0-DLOG(B6)-D6)
      PGRB7=Q2(3)*(1.D0-DLOG(B7)-D7)
      PGRB8=Q2(4)*(1.D0-DLOG(B8)-D8)
C
C
C
C
C
C
C     FOR THE MIXTURE, X1 = HEAVIER
C
C     THERE ARE TWO CASES :
C     (1) WITHOUT ANY SAME FUNCTIONAL GROUPS IN THESE
C         TWO COMPOUNDS, THEN AMN(I,J) = SAME SIZE
C         XM = NUM(1)*X1/SUM(NUM1(K)*X1+NUM2(K)*X2)
C     (2) WITH SAME FUNCTIONAL GROUPS IN THESE TWO
C         COMPOUNDS, THEN RECALCULATE NUM(K)
C         ALSO AMN(I,J) WILL BE SMALLER SIZED
C         XM = NUM1(K)*X1+NUM(K)*X2/SUM(NUM1(K)*X1+NUM2(K)*X2
C
C     FOLLOWING FORMULAS ARE FOR THE CASE (1)
C
      F3=(X1*FG1)+(X2*FG2)
      XA1=(X1*NU1(1))/F3
      XA2=(X1*NU1(2))/F3
      XA3=(X1*NU1(3))/F3
      XA4=(X1*NU1(4))/F3
      XB5=(X2*NU2(1))/F3
      XB6=(X2*NU2(2))/F3
      XB7=(X2*NU2(3))/F3
      XB8=(X2*NU2(4))/F3
      F4=(Q1(1)*XA1)+(Q1(2)*XA2)+(Q1(3)*XA3)+(Q1(4)*XA4)
     *+(Q2(1)*XB5)+(Q2(2)*XB6)+(Q2(3)*XB7)+(Q2(4)*XB8)
      THEMX(1)=(Q1(1)*XA1)/F4
      THEMX(2)=(Q1(2)*XA2)/F4
```

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        THEMX(3)=(Q1(3)*XA3)/F4
        THEMX(4)=(Q1(4)*XA4)/F4
        THEMX(5)=(Q2(1)*XB5)/F4
        THEMX(6)=(Q2(2)*XB6)/F4
        THEMX(7)=(Q2(3)*XB7)/F4
        THEMX(8)=(Q2(4)*XB8)/F4
        DO 1100 M=1,8
        E(M)=THEMX(1)*PSI(1,M)+THEMX(2)*PSI(2,M)+
       *THEMX(3)*PSI(3,M)+THEMX(4)*PSI(4,M)+
       *THEMX(5)*PSI(5,M)+THEMX(6)*PSI(6,M)+
       *THEMX(7)*PSI(7,M)+THEMX(8)*PSI(8,M)
1100    CONTINUE
        DO 1200 N=1,8
        GROMX(N)=(1.DO-DLOG(E(N))-((THEMX(1)*PSI(N,1))/E(1)+
       *(THEMX(2)*PSI(N,2))/E(2)+(THEMX(3)*PSI(N,3))/E(3)+
       *(THEMX(4)*PSI(N,4))/E(4)+(THEMX(5)*PSI(N,5))/E(5)+
       *(THEMX(6)*PSI(N,6))/E(6)+(THEMX(7)*PSI(N,7))/E(7)+
       *(THEMX(8)*PSI(N,8))/E(8)))
1200    CONTINUE
        GR1A=Q1(1)*GROMX(1)
        GR2A=Q1(2)*GROMX(2)
        GR3A=Q1(3)*GROMX(3)
        GR4A=Q1(4)*GROMX(4)
        GR5B=Q2(1)*GROMX(5)
        GR6B=Q2(2)*GROMX(6)
        GR7B=Q2(3)*GROMX(7)
        GR8B=Q2(4)*GROMX(8)
        RESD1=NU1(1)*(GR1A-PGRA1)+NU1(2)*(GR2A-PGRA2)+NU1(3)*
       *(GR3A-PGRA3)+NU1(4)*(GR4A-PGRA4)
        RESD2=NU2(1)*(GR5B-PGRB5)+NU2(2)*(GR6B-PGRB6)+NU2(3)*
       *(GR7B-PGRB7)+NU2(4)*(GR8B-PGRB8)
C
C
C
        TOT1=RESD1+COMBI1
        TOT2=RESD2+COMBI2
        ACT1=DEXP(TOT1)
        ACT2=DEXP(TOT2)
        PT=(X1*ACT1*P1S)+(X2*ACT2*P2S)
        Y1=(X1*ACT1*P1S)/PT
        VOLTY=Y1/X1
        WRITE (6,4433) X1,Y1,ACT1
4433    FORMAT(//,5X,'X1 = ',F8.4,5X,'Y1 = ',F8.4,
       15X,'ACT1 = ',F8.4)
        WRITE (6,7766) PT
7766    FORMAT(/,10X,' CALCULATED P = ',F10.4)
        WRITE (6,3344) VOLTY
3344    FORMAT(/,10X,'EQUILIBRIUM CONSTANT IS ',F11.6)
        X2=1.DO-X1
        Y2=1.DO-Y1
        WRITE (6,3355) X2,Y2
3355    FORMAT(/,10X,'X2 = ',F8.4,10X,'Y2 = ',F8.4)
        YAEQ=Y1
        RETURN
        END
```

```
      SUBROUTINE PROPER(XAIN,YAIN,TPLATE,RELATE,QGIN,HRIN,G,
     1QMOLEV)
       IMPLICIT REAL*8(A-H,O-Z)
C*****************************************************************
C
C
C      THIS PROGRAM IS TO CALCULATE ALL THE PROPERTIES
C      NECESSARY TO PROCED THE CALCULATIONS FOR DISTILLATION
C
C
C*****************************************************************
C
C
C      THE PLATE TEMPERATURE,AND COMPOSITION HAVE TO BE
C      INTRODUCED INTO THIS PROGRAM
C        THE TEMPERATURE IN DEGREE K
      DIMENSION BETA(20)
      DIMENSION TC(3),WM(3),VC(3),TB(3),PC(3)
      DIMENSION ZC(3),V(3),ROHL(3),DA(3),DB(3)
      DIMENSION TBR(3),TR(3),Q(3),A(3),SIG(3)
      DIMENSION PR(3)
      DIMENSION ETAG(3),FETA(3),FEP(3),ETAPUR(3)
      DIMENSION VLA(3),ETAL(3),VISB(3),VISTO(3)
C
C      TC,PC,VC ARE THE CRITICAL PROPERTIES FOR TEM. PRESSURE,
C        AND VOLUME
C      WM IS MOLECULAR WEIGHT, TB IS BOILING POINT
C
      DATA TC(1),PC(1),VC(1)/591.7D0,40.6D0,316.D0/
      DATA TC(2),PC(2),VC(2)/556.4D0,45.0D0,276.D0/
      DATA TB(1),WM(1)/383.8D0,92.141D0/
      DATA TB(2),WM(2)/349.7D0,153.823D0/
      DATA ZC(1),ZC(2)/0.264D0,0.272D0/
      DATA VISB(1),VISTO(1)/467.33D0,255.24D0/
      DATA VISB(2),VISTO(2)/540.15D0,290.84D0/
      DATA SUMVA,SUMVB/111.14D0,94.5D0/
C      SUMVA,SUMVB ARE FOR GAS PHASE DAB, PAGE 554 IN REID
      WRITE (6,7755)
7755  FORMAT(///,10X,'### THIS SECTION REPORTS PROPERTIES ###')
C      COLUMN PRESSURE IS CONSTANT
      DATA PCLMN/760.D0/
      P=PCLMN/760.D0
      T=TPLATE
      XA=XAIN
      YA=YAIN
      Q1=QGIN
      YB=1.D0-YA
      XB=1.D0-XA
C
      DO 10 I=1,2
      TBR(I)=TB(I)/TC(I)
      TR(I)=T/TC(I)
       PR(I)=P/PC(I)
```

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```
C          THIS SECTION CALCULATE SURFACE TENSION
C        PAGE 604 IN REID
C
       Q(I)=0.1207D0*(1.D0+((TBR(I)*DLOG(PC(I)))/(1.D0-TBR(I))
      1))-0.281D0
       AA=2.D0/3.D0
       BB=1.D0/3.D0
       CC=11.D0/9.D0
C
       SIG(I)=(PC(I)**AA)*(TC(I)**BB)*Q(I)*((1.D0-TR(I))**CC)
      WRITE (6,22) I,SIG(I)
22     FORMAT(/,10X,'SURFACE TENSION FOR PURE COMPONENT (',
      *I2,' ) IS ',F11.6,' DYNE/CM')
C
C        THE ABOVE EQUATION FOR SIG IS FOR NON-HYDROGEN BONDED
C
       V(I)=0.285D0*(VC(I)**1.048D0)
C      V(I) PAGE 59 IN REID
       A(I)=(V(I)**AA)*((6.023D23)**BB)
C
C        THIS SECTION CALCULATE LIQUID DENSITY
C      PAGE 3-230 IN PERRY HANDBOOK
C
       ROHL(I)=(PC(I)*WM(I)/TC(I))*((0.0653D0/(ZC(I)**0.773))-
      *0.09D0*TR(I))
      WRITE (6,222) I,ROHL(I)
222    FORMAT(/,10X,'DENSITY OF PURE LIQUID ',I2,' IS ',F11.6)
C
C        THIS SECTION CALCULATE CONSTANTS FOR GAS DENSITY
C      PAGE 270-277 IN SMITH&VAN NESS
C      REDLICH-KWONG EQUATION OF STATE IS USED
C
       DB(I)=(0.0867D0*82.05D0*TC(I)/PC(I))
       DA(I)=(0.4278D0*82.05D0*(TC(I)**2.5))/PC(I)
C
C        THIS SECTION CALCULATES GAS PHASE VISCOSITY
C      PAGE 3-247 IN PERRY HANDBOOK
C
       ETAG(I)=(33.3D0*DSQRT(WM(I)*TC(I)))/(VC(I)**AA)
       FEP(I)=0.91D0*DLOG10(1.9D0*TR(I))
       FETA(I)=1.058D0*(TR(I)**0.645)-0.261D0/((1.9D0*TR(I))**
      1FEP(I))
       ETAPUR(I)=ETAG(I)*FETA(I)*1.D-4
      WRITE (6,330) I,ETAPUR(I)
330    FORMAT(/,10X,'VISCOSITY,PURE GAS  COMPONENT ',I2,' IS ',
      *F11.6,'  CENTIPOISE')
C
C        THIS SECTION CALCULATES LIQUID VISCOSITY
C      PAGE 629 IN REID
C
       VLA(I)=VISB(I)*((1.D0/T)-(1.D0/VISTO(I)))
       ETAL(I)=10.D0**(VLA(I))
      WRITE (6,335) I,ETAL(I)
335    FORMAT(/,10X,'VISCOSITY FOR PURE LIQUID COMPONENT',I2,
      *' IS ',F11.6,'  CENTIPOSE')
```

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```
10          CONTINUE
       AM=(A(1)+A(2))/2.DO
       BM=AM/(2.DO*8.314D7*T)
       SIGM=XA*SIG(1)+XB*SIG(2)-BM*((SIG(1)-SIG(2))**2)*XA*XB
      WRITE (6,110) SIGM
110     FORMAT(/,10X,'SURFACE TENSION FOR THE MIXTURE IS ',
     *F11.6,' DYNE/CM')
       DSIG=DABS(SIG(1)-SIG(2))
       WRITE (6,5088) DSIG
5088   FORMAT(/,10X,'THE INTERFACIAL TENSION IS ',F11.6)
C
C       THIS SECTION CALCULATE DENSITY FOR GAS MIXTURE
C       PAGE 270-277 IN SMITH&VAN NESS
C
       TC12=DSQRT(TC(1)*TC(2))
       VC12=((VC(1)**BB+VC(2)**BB)/2.DO)**3
       ZC12=(ZC(1)+ZC(2))/2.DO
       PC12=(ZC12*82.05DO*TC12)/VC12
       DA12=(0.4278DO*82.05DO*82.05DO*(TC12**2.5))/PC12
       DBM=YA*DB(1)+YB*DB(2)
       DAM=YA*YA*DA(1)+2.DO*YA*YB*DA12+YB*YB*DA(2)
C
       ZNEW=1.DO
       DO 100 J=1,100
       ZOLD=ZNEW
       H=(DBM*P)/(ZOLD*82.05DO*T)
       ZNEW=(1.DO/(1.DO-H))-(DAM/(DBM*82.05DO*(T**1.5)))*(H/(
     11.DO+H))
      WRITE (6,2222) J,ZNEW
2222    FORMAT(/,10X,'COMPRESBILITY FACTOR IS  ON TERMS ',I3,
     *' IS ',F11.7)
       IF (DABS((ZNEW-ZOLD)/ZOLD) .LT. 1.D-4) GO TO 101
100     CONTINUE
C
101     VGM=ZNEW*82.05DO*T/P
       WMAVG=(YA*WM(1)+YB*WM(2))
      WMAVL=(XA*WM(1)+XB*WM(2))
       ROHGM=WMAVG/VGM
       ROHLM=XA*ROHL(1)+XB*ROHL(2)
      WRITE (6,111) ROHGM,ROHLM
111     FORMAT(/,10X,'DENSITY OF MIXTURE FOR GAS IS ',F11.6,
     */,10X,'     FOR LIQUID IS ',F11.6,' G/ CM**3')
C
C       THIS SECTION CALCULATES VISCOSITY FOR GAS MIXTURE
C       PAGE 411 IN REID
C
       ETM1=YA*DSQRT(WM(1))
       ETM2=YB*DSQRT(WM(2))
       ETAM=(ETAPUR(1)*ETM1+ETAPUR(2)*ETM2)/(ETM1+ETM2)
      WRITE (6,331) ETAM
331     FORMAT(/,10X,' VISCOSITY FOR GAS MIXTURE IS ',F11.6,
     *' CENTIPOISE')
C       THIS SECTION CALCULATE VISCOSITY FOR LIQUID MIXTURE
C       PAGE 3-247 IN PERRY HANDBOOK
```

```
          VISCOL=(XA*(ETAL(1)**BB)+XB*(ETAL(2)**BB))**3
          WRITE (6,336) VISCOL
336       FORMAT(/,10X,'VISCOSITY FOR LIQUID MIXTURE IS',F11.6,
     *'   CENTIPOSE')
C
C         THIS SECTION CALCULATE DIFFUSIVITY COEFFICIENT
C         IN GAS PHASE
C       PAGE 554 IN REID
C
          DC1=DSQRT((WM(1)+WM(2))/(WM(1)*WM(2)))
          DC2=(1.D-3)*(T**1.75)*DC1
          DC3=P*((SUMVA**BB+SUMVB**BB)**2)
          DAB=DC2/DC3
         WRITE (6,338) DAB
338       FORMAT(/,10X,'DIFFUSIVITY COEFFICIENT IN GAS PHASE IS ',
     *F11.6,'CM*CM/SEC')
C
C         THIS SECTION CALCULATE LIQUID PHASE DIFFUSIVITY
C         COEFFICIENT
C         PAGE 557 IN REID
C
          DATA HIP/2.6D0/
C
C         HIP DEPENDS ON THE SYSTEM, PAGE 568 IN REID
C
          DABLO=(7.4D-8)*((DSQRT(HIP*WM(2))*T)/(ETAL(2)*(V(2)**
     *10.6)))
          DBALO=(7.4D-8)*((DSQRT(HIP*WM(1))*T)/(ETAL(1)*(V(1)**
     *10.6)))
          DLAB=(DABLO**XB)*(DBALO**XA)
          WRITE (6,348) DLAB
348       FORMAT(/,10X,'DIFFUSIVITY COEFFICIENT, LIQUID PHASE IS ',
     *F11.6,'CM*CM/SEC')
C
C         THIS SECTION CALCULATE THE BUBBLE DIAMETER, RISING
C         VELOCITY
C         AND THE CONTACT AREA, CONTACT TIME
C
C         Q1=GAS FLOW RATE IN FT**3/HR PER INCH WIDTH OF SLOT
C
C         WIDTH OF SLOT IS 1/4 , 12 SLOTS PER CAP, TOTAL 3 INCHES
C         INCHES
C         QFLOWG IS THE VOLUMETRIC FLOW RATE OF VAPOR FLOW
C
          DATA NSLOT/12/
          QGAS=Q1*4.D0/16.D0
          QFLOWG=Q1*3.0D0
C
C         ETAM = GAS MIXTURE VISCOSITY IN CENTIPOISE
C         UETAM = VISCOSITY IN LB/FT HR, 1 CP = 2.42 LB/FT HR
C
          UETAM=ETAM*2.42D0
C
C         DIAMETER OF SLOT IN FT = 1/4 INCHES
C         DEPTH OF LIQUID SEAL IS 1 INCHES, IN FT
```

```
C
      DSLOT=(4.DO/16.DO)*(1.DO/12.DO)
      HSEAL=(1.0DO)*(1.DO/12.DO)
      DBUBL=0.222DO*(DSLOT**0.33)*(QGAS**0.125)*(UETAM**0.02)+
     *(3.02D-4)*(QGAS**1.09)
C     DBUBL IN FT
      DCMBL=DBUBL*30.48DO
C     DCMBL IN CM
      WRITE (6,5010) DCMBL
5010  FORMAT(/,10X,'THE BUBBLE DIAMETER IS ',F11.6,
     *'   CM')
      VBUBL=(4.1D3)*(QGAS**0.16)
C     VBUBL IN FT/HR
      VCMBL=VBUBL*(30.48DO/3600.DO)
C     VCMBL IN CM/SEC
      WRITE (6,5011) VCMBL
5011  FORMAT(/,10X,'RISING VELOCITY  IS ',F11.6,'    CM/SEC')
      ACNTAT=(1.46D-3)*(QGAS**0.84)/DBUBL
C     ACNTAT IS CONTACT AREA OF BUBBLES IN FT*FT PER FT OF
C     LIQUID SEAL
      ATAT=ACNTAT*HSEAL*30.48DO*30.48DO
C     ATAT CONTACT AREA IN CM*CM
      WRITE (6,5012) ATAT
5012  FORMAT(/,10X,'CONTACT AREA IS ',F11.6,'    CM*CM')
      TCNTAT=HSEAL/VBUBL
C     TCNTAT CONTACT TIME THROUGH THE LIQUID SEAL IN HOUR
      TCAT=TCNTAT*3600.DO
C     TCAT CONTACT TIME IN SECOND
      WRITE (6,5013) TCAT
5013  FORMAT(/,10X,'THE CONTACT TIME IS ',F11.6,'   SECOND')
      RCMBL=DCMBL/2.DO
      DITCAT=TCAT*DAB/(RCMBL*RCMBL)
      WRITE (6,5025) DITCAT
5025  FORMAT(/,10X,'THE DIMENSIONLESS TIME = ',F11.6)
C
C        THIS SECTION CALCULATE SHERWOOD NUMBER
C
      DRE=(DCMBL*VCMBL*ROHGM)/ETAM
      DSC=(ETAM/(DAB*ROHGM))
      SHRWOD=2.DO+0.76DO*DSQRT(DRE)*(DSC**BB)
      WRITE (6,5035) SHRWOD
5035  FORMAT(/,10X,'THE SHERWOOD NUMBER IS ',F11.6)
C
C        THIS SECTION CALCULATE PART OF MASS TRANSFER DURING
C     BUBBLE RISING
C
C        MASS TRANSFER FROM A SINGLE BUBBLE
C        CONSIDER BOTH LIQUID AND GAS FILM RESISTANCE
C
      DATA (BETA(I),I=1,10)/4.4934094DO,7.7252517DO,
     110.9041216DO,14.0661938DO,17.2207549DO,20.371303DO,
     123.5194525DO,26.6660542DO,29.8115988DO,32.956389DO/
      DATA EPS/1.D-14/
      SH=SHRWOD
```

```
         TIME=DITCAT
         SUM=0.DO
         DO 1000 I=1,10
         ZZ=-(BETA(I)**2)
         Z=ZZ*TIME
         ZZ1=DEXP(Z)
         YY1=BETA(I)*DCOS(BETA(I))
         Y1=DSIN(BETA(I))
         Y2=(3.DO*SH)-(BETA(I)**2)
         YY2=(2.DO*SH*RCMBL)
         SU=(YY2*(YY1-Y1)*(1.DO-ZZ1))/(Y2*Y1*BETA(I)*BETA(I))
         SSUM=SUM+SU
         TT=SSUM-SUM
         TO1=DABS(TT)
         IF (TO1-EPS) 3,3,5
5        SUM=SSUM
1000     CONTINUE
         TSUM=SUM
         GO TO 6
3        TSUM=SSUM
6        TY4=RCMBL/3.DO
         TY11=3.DO*SH*TIME
         TY2=DEXP(-TY11)
         TY6=TY4*(1.DO-TY2)
         TTUM=TY6+TSUM
C
C
C        THIS SECTION CONVERT THE VOLUMETRIC FLOW RATE OF VAPOR
C        TO MOLAR FLOW RATE IN G MOLE / HR
C
         QMOLEG=QFLOWG*(30.48DO**3)
         QMOLEV=QMOLEG*ROHGM/WMAVG
         WRITE (6,5099) QMOLEV
5099     FORMAT(/,10X,'THE MOLAR FLOW RATE FOR GAS IS ',
        1F11.6,'  G MOLE/HR')
         HRIN=ATAT*TTUM
         WRITE (6,5075) HRIN
5075     FORMAT(/,10X,'THE H FUNCTION DURING BUBBLE RISING IS ',
        1F16.6,'  G MOLE / HR')
C
C        THIS SECTION CALCULATE THE PART OF MASS TRANSFER DURING
C        BUBBLE FORMATION
C
         TF=(2.DO/3.DO)*((DCMBL**3)/((DSLOT*30.48DO)**2)*VCMBL)
         AF=(3.DO/5.DO)*NSLOT*3.1415968DO*DCMBL*DCMBL
         CKF0=DCMBL/TF
         CKF1=((ROHGM+ROHLM)/2.DO)/WMAVG
         CKF2=(VCMBL*VCMBL)/(DCMBL*980.66DO)
         CKF3=DCMBL*DCMBL/(TF*DAB)
         CKF4=ETAM/DSQRT(ROHGM*DCMBL*SIGM)
         CKDF=0.0432DO*CKF0*CKF1*(CKF2**0.089)*(CKF3**(-0.334))*
        1(CKF4**(-0.601))
         CKF5=DLAB/TF
         CKF6=(ROHLM*SIGM)/((DABS(ROHGM-ROHLM))*980.66DO*TF*
        1VISCOL)
```

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```
      CKF7=980.6600*TF*TF/DCMBL
      CKF8=((ROHGM+ROHLM)/2.DO)/WMAVL
      CKCF=0.386DO*CKFO*CKF8*(CKF5**0.5)*(CKF6**0.407)*(CKF7**
     10.148)
      RRR11=RELATE
      CKKF=(CKCF*CKDF)/(CKCF+RRR11*CKDF)
      G=CKKF*AF*3600.DO
      WRITE (6,5095) G
5095  FORMAT(/,10X,' FUNCTION G DURING BUBBLE FORMATION IS ',
     1F11.6,'   G MOLE / HR')
      WRITE (6,646)
646   FORMAT(/,10X,'#### END OF PROPERTIES REPORTING ####')
      RETURN
      END
```

```fortran
      SUBROUTINE ENTHPY(TPLATE,XA,YA,ENTHVM,ENTHLM)
      IMPLICIT REAL*8(A-H,O-Z)
C
C     THIS SECTION CALCULATE THE ENTHALPIES FOR LIQUID PHASE
C     AND GAS PHASE, ALSO LATENT HEAT IS ESTIMATED
C     CP DATA FROM REID, PAGE 629
C     LATENT HEAT FROM PAGE 201 IN REID
C
      DIMENSION CPGA(3),CPGB(3),CPGC(3),CPGD(3)
      DIMENSION ENTHLV(3),ENTHLL(3)
      DIMENSION OMEGA(3)
      DIMENSION TC(3)
      DATA CPGA(1),CPGB(1),CPGC(1),CPGD(1)/-5.817D0,1.224D-1,
     1-6.605D-5,1.173D-8/
      DATA CPGA(2),CPGB(2),CPGC(2),CPGD(2)/9.725D0,4.893D-2,
     1-5.421D-5,2.112D-8/
      DATA OMEGA(1),OMEGA(2)/0.257D0,0.194D0/
      DATA TC(1),TC(2)/591.7D0,556.4D0/
      T=TPLATE
      XB=1.D0-XA
      YB=1.D0-YA
C
      DO 303 NL=1,2
      PP1=CPGA(NL)*(T-298.D0)
      PP2=(CPGB(NL)/2.D0)*((T**2)-(298.D0**2))
      PP3=(CPGC(NL)/3.D0)*((T**3)-(298.D0**3))
      PP4=(CPGD(NL)/4.D0)*((T**4)-(298.D0**4))
      ENTHLV(NL)=PP1+PP2+PP3+PP4
C     ENTHLV IS IN CALORIES/G MOLE
C
      TR=T/TC(NL)
      CH=7.08D0*((1.D0-TR)**0.354)
      CG=10.95D0*OMEGA(NL)*((1.D0-TR)**0.456)
      CLAMDA=1.987D0*TC(NL)*(CH+CG)
      ENTHLL(NL)=ENTHLV(NL)-CLAMDA
303   CONTINUE
      ENTHVM=YA*ENTHLV(1)+YB*ENTHLV(2)
      ENTHLM=XA*ENTHLL(1)+XB*ENTHLL(2)
      RETURN
      END
```

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```fortran
      SUBROUTINE TEMP(XA,E,TNXT)
      IMPLICIT REAL*8(A-H,O-Z)
C
C     THIS ROUTINE USE NEWTON-RAPHSON'S METHOD
C     TO ESTIMATE THE NEXT PLATE TEMPERATURE
C
      DIMENSION CPGA(3),CPGB(3),CPGC(3),CPGD(3)
      DIMENSION ENTHLL(3),ENTHLV(3),DENTHL(3)
      DIMENSION OMEGA(3)
      DIMENSION TC(3)
      DATA CPGA(1),CPGB(1),CPGC(1),CPGD(1)/-5.817D0,1.224D-1
     1-6.605D-5,1.173D-8/
      DATA CPGA(2),CPGB(2),CPGC(2),CPGD(2)/9.725D0,4.893D-2,
     1-5.421D-5,2.112D-8/
      DATA OMEGA(1),OMEGA(2)/0.257D0,0.194D0/
      DATA TC(1),TC(2)/591.7D0,556.4D0/
      T=TNXT
      XB=1.D0-XA
      DO 404 I=1,100
      DO 303 NL=1,2
      PP1=CPGA(NL)*(T-298.D0)
      PP2=(CPGB(NL)/2.D0)*((T**2)-(298.D0**2))
      PP3=(CPGC(NL)/3.D0)*((T**3)-(298.D0**3))
      PP4=(CPGD(NL)/4.D0)*((T**4)-(298.D0**4))
      ENTHLV(NL)=PP1+PP2+PP3+PP4
C     ENTHLV IS IN CALORIES/G MOLE
C
      TR=T/TC(NL)
      CH=7.08D0*((1.D0-TR)**0.354)
      CG=10.95D0*OMEGA(NL)*((1.D0-TR)**0.456)
      CLAMDA=1.987D0*TC(NL)*(CH+CG)
      ENTHLL(NL)=ENTHLV(NL)-CLAMDA
      DPP1=CPGA(NL)
      DPP2=CPGB(NL)*T
      DPP3=CPGC(NL)*(T**2)
      DPP4=CPGD(NL)*(T**3)
      DCH=-7.08D0*0.354D0*((1.D0-TR)**(-0.646))
      DCG=-10.95D0*OMEGA(NL)*0.456D0*((1.D0-TR)**(-0.544))
      DENTHL(NL)=DPP1+DPP2+DPP3+DPP4-1.987D0*(DCH+DCG)
303   CONTINUE
      F1=XA*ENTHLL(1)+XB*ENTHLL(2)-E
      DF1=XA*DENTHL(1)+XB*DENTHL(2)
      TNEW=T-(F1/DF1)
      IF((DABS(TNEW-T)/T) .LE. 1.D-5) GO TO 40
      T=TNEW
404   CONTINUE
      TNXT=T
      GO TO 50
40    TNXT=TNEW
50    WRITE (6,555) TNXT
555   FORMAT(/,10X,'THE NEXT PLATE TEMPERATURE = ',F11.5)
      RETURN
      END
```

APPENDIX F


COMPUTER PROGRAM FOR A TERNARY

SEPARATION IN A DISTILLATION COLUMN

```
      IMPLICIT REAL*8(A-H,O-Z)
      REAL LRIN,LROUT
      DIMENSION HV(15),HL(15)
      DATA NTOL/10/
      DATA NREGIN/2/
      DATA NBUBLE/2/
      DATA PCLMN/760.DO/
      DATA QVAP/141.6DO/
C     QVAP = AIR FLOW RATE IN FT*FT*FT/HR
C             PER INCH WIDTH OF ORIFICE
C     NTOAL = TOTAL NUMBER OF TRAYS
C     NREGIN = THE REGION THAT CAN BE DIVIDED ON EACH TRAY
C     NBUBLE = NUMBER OF BUBBLE CAPS ON EACH TRAY
      QGIN=QVAP/NBUBLE
      DATA TPLATE,XAOUT,YAOUT/377.59DO,0.616DO,0.616DO/
      DATA XBOUT,YBOUT/0.132DO,0.132DO/
      XAIN=XAOUT
      YAIN=YAOUT
      XBIN=XBOUT
      YBIN=YBOUT
      CALL UNIFAC(XAIN,XBIN,TPLATE,YAEQ,YBEQ,VOLTY1,
     1VOLTY2,VOLTY3)
      YAGL=YAEQ
      YBGL=YBEQ
      RELATA=VOLTY1
      RELATB=VOLTY2
      RELATC=VOLTY3
      CALL PROPER(XAIN,XBIN,YAIN,YBIN,TPLATE,RELATA,
     1RELATB,RELATC,QGIN,HRINA,HRINB,GA,GB,QMOLEV,
     1D11,D12,D22,D21,SG1,SG2)
      FLOW=QMOLEV
      VRIN=FLOW
      XA=XAIN
      YA=YAIN
      XB=XBIN
      YB=YBIN
      CALL ENTHPY(TPLATE,XA,XB,YA,YB,ENTHVM,ENTHLM)
      HVINI=ENTHVM
      HLINI=ENTHLM
      DO 5500 NP=1,NTOL
      XAIN=XAOUT
      YAIN=YAOUT
      XBIN=XBOUT
      YBIN=YBOUT
      YASUMO=0.DO
      YBSUMO=0.DO
      EFSUMO=0.DO
      EFBSUM=0.DO
      DO 6700 NR=1,NREGIN
      CALL UNIFAC(XAIN,XBIN,TPLATE,YAEQ,YBEQ,VOLTY1,
     1VOLTY2,VOLTY3)
      YAGL=YAEQ
      YBGL=YBEQ
      RELATA=VOLTY1
```

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```
      RELATB=VOLTY2
      RELATC=VOLTY3
      CALL PROPER(XAIN,XBIN,YAIN,YBIN,TPLATE,RELATA,
     1RELATB,RELATC,QGIN,HRINA,HRINB,GA,GB,QMOLEV,D11,
     1D12,D22,D21,SG1,SG2)
      FORMA=GA
      FORMB=GB
      RISNA=HRINA*VRIN
      RISNB=HRINB*VRIN
      LRIN=VRIN*2.D0
      YAI=YAIN-FORMA*(YAIN-YAGL)
      YBI=YBIN-FORMB*(YBIN-YBGL)
      VROUT=VRIN
      TRR1=(D11-SG2)*(YAI-YAGL)+D12*(YBI-YBGL)
      TOOR1=TRR1/(SG1-SG2)
      TRR11=(D11-SG1)*(YAI-YAGL)+D12*(YBI-YBGL)
      TOOR2=TRR11/(SG2-SG1)
      TRNEWA=TOOR1*RISNA+TOOR2*RISNB
      TRR2=D21*(YAI-YAGL)+(D22-SG1)*(YBI-YBGL)
      TOOR3=TRR2/(SG1-SG2)
      TRR22=D21*(YAI-YAGL)+(D22-SG1)*(YBI-YBGL)
      TOOR4=TRR22/(SG2-SG1)
      TRNEWB=TOOR3*RISNA+TOOR4*RISNB
      YAOUT=(VRIN/VROUT)*YAI-(TRNEWA/VROUT)
      YBOUT=(VRIN/VROUT)*YBI-(TRNEWB/VROUT)
      LROUT=LRIN-(VRIN-VROUT)
      XAOUT=(VROUT*YAOUT+LRIN*XAIN-VRIN*YAIN)/LROUT
      XBOUT=(VROUT*YBOUT+LRIN*XBIN-VRIN*YBIN)/LROUT
      XA=XAOUT
      YA=YAOUT
      XB=XBOUT
      YB=YBOUT
      EFFICN=(YAOUT-YAIN)/(YAGL-YAIN)
      EFFBCN=(YBOUT-YBIN)/(YBGL-YBIN)
      WRITE (6,8877) EFFICN
      YASUMO=YASUMO+YA
      YBSUMO=YBSUMO+YB
      EFBSUM=EFBSUM+EFFBCN
      EFSUMO=EFSUMO+EFFICN
      XAIN=XA
      XBIN=XB
6700  CONTINUE
      YAOUT=YASUMO/NREGIN
      YBOUT=YBSUMO/NREGIN
      EFAVG=EFSUMO/NREGIN
      EFBVG=EFBSUM/NREGIN
      WRITE (6,9919)
9919  FORMAT(/,10X,50('$'))
      WRITE (6,9919)
      WRITE (6,9919)
      WRITE (6,6564) NP
6564  FORMAT(/,10X,'***** THE PLATE NUMBER = ',I3,2X,'*****')
      WRITE (6,7655) TPLATE,YAOUT,XAOUT,VROUT
      WRITE (6,8898) YAOUT,YAIN,YAGL
```

```
      WRITE (6,9998) YBOUT,YBIN,YBGL,XBOUT
9998  FORMAT(/,10X,'OUTLET COMPOSITION FOR TOLUENE IS ',F11.6,
     1/,10X,'INLET COMPOSITION AND EQUILIBRIUM COMPOSITION ARE
     1',F11.6,5X,F11.6,/,10X,'INLET LIQUID COMPOSITION OF
     1TOLUENE IS ',F11.6)
      WRITE (6,8897) EFAVG
8897  FORMAT(/,10X,' THE AVERAGE PLATE EFFICIENCY = ',F11.6)
      XCOUT=1.DO-XAOUT-XBOUT
      YCOUT=1.DO-YAOUT-YBOUT
      WRITE (6,1171)
1171  FORMAT(/,10X,50('.'))
      WRITE (6,5551) XAOUT,YAOUT
5551  FORMAT(/,10X,'X-XYLENE  =',F11.6,8X,'Y-XYLENE  =',F11.6)
      WRITE (6,5552) XBOUT,YBOUT
5552  FORMAT(/,10X,'X-TOLUENE =',F11.6,8X,'Y-TOLUENE =',F11.6)
      WRITE (6,5553) XCOUT,YCOUT
5553  FORMAT(/,10X,'X-BENZENE =',F11.6,8X,'Y-BENZENE =',F11.6)
      WRITE (6,9919)
      WRITE (6,9919)
      WRITE (6,9919)
C        THIS SECTION ESTIMATE NEXT PLATE TEMPERATURE
      XA=XAOUT
      YA=YAOUT
      XB=XBOUT
      YB=YBOUT
      CALL ENTHPY(TPLATE,XA,XB,YA,YB,ENTHVM,ENTHLM)
      HV(NP)=ENTHVM
      E=(VROUT*HV(NP)+LRIN*HLINI-VRIN*HVINI)/LROUT
      TNXT=TPLATE
      CALL TEMP(XA,XB,E,TNXT)
      TPLATE=TNXT
      HVINI=HV(NP)
      CALL ENTHPY(TPLATE,XA,XB,YA,YB,ENTHVM,ENTHLM)
      HLINI=ENTHLM
5500  CONTINUE
7655  FORMAT(/,10X,'THE PLATE TEMPERATURE IS ',F16.6,/,10X
     1,'THE OUTLET GAS COMPOSITION AFTER ADJUST TEMPERATURE IS
     1 ',F11.6,/,10X,'THE INLET LIQUID COMPOSITION IS
     1 ',F11.6,/,10X,'THE OUTLET GAS FLOW RATE IN G MOLE/HR IS
     1  ',F16.6)
8898  FORMAT(/,10X,'YAOUT =',F11.6,' YAIN =',F11.6,' YAGL =',
     1F11.6)
8877  FORMAT(/,10X,'THE PLATE LOCAL EFFICIENCY IS ',F11.6)
      STOP
      END
```

```
      SUBROUTINE UNIFAC(XAIN,XBIN,TPLATE,YAEQ,YBEQ,VOLTY1,
     *VOLTY2,VOLTY3)
        IMPLICIT REAL*8(A-H,O-Z)
C*****************************************************************
C
C       THIS SECTION IS WRITTEN FOR PREDICTING
C       M-XYLENE - TOLUENE - BENZENE TERNARY SYSTEM
C       BY USING UNIFAC METHOD
C
C*****************************************************************
C
C          THE SYSTEM IS HEAVIEST (1) = M-XYLENE
C          THE SYSTEM IS HEAVIER (2) = TOLUENE
C          THE SYSTEM IS LIGHTEST (3) = BENZENE
C
      DIMENSION A(6,6),PSI(6,6)
      DIMENSION R1(2),R2(2),Q1(2),Q2(2),NU1(2),NU2(2)
      DIMENSION R3(2),Q3(2),NU3(2)
      DIMENSION THE1A(6)
      DIMENSION E(6),GRO1A(6)
C
C*****************************************************************
C
C          DATA FILE AS FOLLOWING FORM
C
C       COMPONENT        MAIN GROUPS        R        Q        NU
C       ----------------------------------------------------------
C           A                1             XX       YY       ZZ
C                            2             XX       YY       ZZ
C       ...............................................
C           B                3             XX       YY       ZZ
C                            4             XX       YY       ZZ
C       ...............................................
C           C                5             XX       YY       ZZ
C                            6             XX       YY       ZZ
C       ----------------------------------------------------------
C
C       1-6 : TYPES OF FUNCTIONAL GROUP
C       R   : DATA FROM TABLE
C       Q   : DATA FROM TABLE
C       NU  : NUMBER OF FUNCTIONAL GROUPS IN COMPONENT
C
C          INTERACTION PARAMETERS AMN(I,J)
C
C          1        2        3        4        5        6
C       ----------------------------------------------------------
C   1 I A(1,1) A(1,2) A(1,3) A(1,4) A(1,5) A(1,6)
C   2 I A(2,1) ........................
C   3 I A(3,1) ......................
C   4 I        ...................................
C   5 I        ...................................
C   6 I A(6,1) A(6,2) A(6,3) A(6,4) A(6,5) A(6,6)
C       ----------------------------------------------------------
C
C
```

```
C**********************************************************
C
C     CHECK (1) M-XYLENE, (2) TOLUENE, (3) BENZENE
C      M-XYLENE = 2 ACCH3, 4 ACH
C       TOLUENE = 1 ACCH3, 5 ACH
C       BENZENE = 6 ACH
C
      DATA (R1(K),K=1,2) /0.5313D0,1.2663D0/
      DATA (R2(K),K=1,2) /0.5313D0,1.2663D0/
      DATA (R3(K),K=1,2) /0.5313D0,0.0D0/
      DATA (Q1(K),K=1,2) /0.400D0,0.9681D0/
      DATA (Q2(K),K=1,2) /0.400D0,0.9681D0/
      DATA (Q3(K),K=1,2) /0.400D0,0.0D0/
      DATA (NU1(K),K=1,2) /4,2/
      DATA (NU2(K),K=1,2) /5,1/
      DATA (NU3(K),K=1,2) /6,0/
C
C     ANTOINE CONSTANTS FOR VAPOR PRESSURE
C
      DATA ANTA1,ANTB1,ANTC1/16.1390D0,3366.99D0,-58.04D0/
      DATA ANTA2,ANTB2,ANTC2/16.0137D0,3096.52D0,-53.67D0/
      DATA ANTA3,ANTB3,ANTC3/15.9008D0,2788.51D0,-52.36D0/
      DATA (A(1,J),J=1,6)/0.0D0,167.0D0,0.0D0,167.0D0,
     *0.0D0,0.0D0/
      DATA (A(2,J),J=1,6)/-146.8D0,0.0D0,-146.8D0,0.0D0,
     *-146.8D0,0.0D0/
      DATA (A(3,J),J=1,6) /0.0D0,167.0D0,0.0D0,167.0D0
     *,0.0D0,0.0D0/
      DATA (A(4,J),J=1,6) /-146.8D0,0.0D0,-146.8D0,0.0D0,
     *-146.8D0,0.0D0/
      DATA (A(5,J),J=1,6) /0.0D0,167.0D0,0.0D0,167.0D0 \
     *,0.0D0,0.0D0/
      DATA (A(6,J),J=1,6) /0.0D0,0.0D0,0.0D0,0.0D0,0.0D0,0.0D0/
      DATA Z/10.0D0/
      T=TPLATE
C
      P1S=DEXP(ANTA1-(ANTB1/(T+ANTC1)))
      P2S=DEXP(ANTA2-(ANTB2/(T+ANTC2)))
      P3S=DEXP(ANTA3-(ANTB3/(T+ANTC3)))
C
      PR1=NU1(1)*R1(1)+NU1(2)*R1(2)
      PR2=NU2(1)*R2(1)+NU2(2)*R2(2)
      PR3=NU3(1)*R3(1)+NU3(2)*R3(2)
      QQ1=NU1(1)*Q1(1)+NU1(2)*Q1(2)
      QQ2=NU2(1)*Q2(1)+NU2(2)*Q2(2)
      QQ3=NU3(1)*Q3(1)+NU3(2)*Q3(2)
      X1=XAIN
      X2=XBIN
      X3=1.D0-X1-X2
      F1=(PR1*X1)+(PR2*X2)+(PR3*X3)
      PHI1=(PR1*X1)/F1
      PHI2=(PR2*X2)/F1
      PHI3=(PR3*X3)/F1
      T1=(QQ1*X1)+(QQ2*X2)+(QQ3*X3)
```

```
       THETA1=(QQ1*X1)/T1
       THETA2=(QQ2*X2)/T1
       THETA3=(QQ3*X3)/T1
       TL1=((Z/2.0D0)*(PR1-QQ1))-(PR1-1.0D0)
       TL2=((Z/2.0D0)*(PR2-QQ2))-(PR2-1.0D0)
       TL3=((Z/2.0D0)*(PR3-QQ3))-(PR3-1.0D0)
       C1=DLOG(PHI1/X1)
       C2=DLOG(THETA1/PHI1)
       C3=(X1*TL1)+(X2*TL2)+(X3*TL3)
       C11=DLOG(PHI2/X2)
       C22=DLOG(THETA2/PHI2)
       C111=DLOG(PHI3/X3)
       C222=DLOG(THETA3/PHI3)
       COMBI1=C1+(Z/2.0D0)*QQ1*C2+TL1-(PHI1/X1)*C3
       COMBI2=C11+(Z/2.0D0)*QQ2*C22+TL2-(PHI2/X2)*C3
       COMBI3=C111+(Z/2.0D0)*QQ3*C222+TL3-(PHI3/X3)*C3
C
C

       DO 11 I=1,6
       DO 12 J=1,6
       PSI(I,J)=DEXP(-A(I,J)/T)
   12 CONTINUE
   11 CONTINUE
C
C
C
C      FOR PURE M-XYLENE XACH=4/6, XACCH3=2/6
C      FOR PURE TOLUENE XACH=5/6, XACCH3=1/6
C      FOR PURE BENZENE XACH=6/6
C
C
C
       F=Q1(1)*4.D0/6.D0+Q1(2)*2.D0/6.D0
       THET11=(Q1(1)*(4.D0/6.D0))/F
       H11=(Q1(2)*(2.D0/6.D0))/F
       B=THET11*PSI(1,1)+H11*PSI(2,1)
       BC=THET11*PSI(1,2)+H11*PSI(2,2)
       PGR1A=Q1(1)*(1.D0-DLOG(B)-(THET11/B+(H11*PSI(1,2))/BC))
       PGR1B=Q1(2)*(1.D0-DLOG(BC)-((THET11*PSI(2,1))/B+H11/BC))
C
       A1=Q2(1)*(5.D0/6.D0)+Q2(2)*(1.D0/6.D0)
       THET21=(Q2(1)*(5.D0/6.D0))/A1
       H22=(Q2(2)*(1.D0/6.D0))/A1
       B1=THET21*PSI(3,3)+H22*PSI(4,3)
       BC1=THET21*PSI(3,4)+H22*PSI(4,4)
       PGR2A=Q2(1)*(1.D0-DLOG(B1)-((THET21*PSI(3,3))/B1+
      1(H22*PSI(3,4))/BC1))
       PGR2B=Q2(2)*(1.D0-DLOG(BC1)-((THET21*PSI(4,3))/B1+
      1(H22*PSI(4,4))/BC1))
C
       A2=Q3(1)*(6.D0/6.D0)+Q3(2)*(0.D0/6.D0)
       THET31=(Q3(1)*(6.D0/6.D0))/A2
       H33=(Q3(2)*(0.D0/6.D0))/A2
       B11=THET31*PSI(5,5)+H33*PSI(6,5)
       BC11=THET31*PSI(5,6)+H33*PSI(6,6)
       PGR3A=Q3(1)*(1.D0-DLOG(B11)-((THET31*PSI(5,5))/B11
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#+(H33*PSI(5,6))/BC11))
 PGR3B=Q3(2)*(1.DO-DLOG(BC11)-((THET31*PSI(6,5))/B11
#+(H33*PSI(6,6))/BC11))
C
C
C     FOR THE MIXTURE OF A TERNARY SYSTEM
C     FOR X1- M-XYLENE (4ACH-1A,2ACCH3-2A)
C     FOR X2- TOLUENE (5ACH-3A, 1ACCH3-4A)
C     FOR X3- BENZENE (6ACH-5A)
C
C     1A,3A,5A ARE THE SAME GROUP OF ACH
C     2A,4A ARE THE SAME GROUP OF ACCH3
C
C     THERE ARE TWO CASES :
C     (1) WITHOUT ANY SAME FUNCTIONAL GROUPS IN THESE
C         THREE COMPOUNDS, THEN AMN(I,J) = SAME SIZE
C         XM = NUM(1)*X1/SUM(NUM1(K)*X1+NUM2(K)*X2)
C     (2) WITH SAME FUNCTIONAL GROUPS IN THESE THREE
C         COMPOUNDS, THEN RECALCULATE NUM(K)
C         ALSO AMN(I,J) WILL BE SMALLER SIZE
C         XM = NUM1(K)*X1+NUM(K)*X2/SUM(NUM1(K)*X1+NUM2(K)*X2
C
C      THERE ARE ONLY TWO GROUPS IN THIS TERNARY SYSTEM
C      WHICH ARE ACH AND ACCH3 GROUPS
C
C           A1=ACH          A2=ACCH3
C           ------------------------------------
C      A1     0.0             167.0
C      A2    -146.8            0.0
C
C
      U=(X1*6.DO)+(X2*6.DO)+(X3*6.DO)
      XACH=(4.0DO*X1+5.0DO*X2+6.0DO*X3)/U
      XACCH3=(2.0DO*X1+1.0DO*X2+0.0DO*X3)/U
      D=Q1(1)*XACH+Q1(2)*XACCH3
      THEACH=Q1(1)*XACH/D
      THACH3=Q1(2)*XACCH3/D
      EACH=THEACH*PSI(1,1)+THACH3*PSI(2,1)
      EAC3=THEACH*PSI(1,2)+THACH3*PSI(2,2)
      GROACH=1.DO-DLOG(EACH)-(((THEACH*PSI(1,1))/EACH)+
     *((THACH3*PSI(1,2))/EAC3))
      GRACH3=1.DO-DLOG(EAC3)-(((THEACH*PSI(2,1))/EACH)+
     *((THACH3*PSI(2,2))/EAC3))
      FACH=Q1(1)*GROACH
      FACH3=Q1(2)*GRACH3
      GR1A=FACH
      GR2A=FACH3
      GR3A=GR1A
      GR5A=GR1A
      GR4A=GR2A
      GR6A=GR2A
      REST1=NU1(1)*(GR1A-PGR1A)+NU1(2)*(GR2A-PGR1B)
      REST2=NU2(1)*(GR3A-PGR2A)+NU2(2)*(GR4A-PGR2B)
      REST3=NU3(1)*(GR5A-PGR3A)+NU3(2)*(GR6A-PGR3B)
      TOT1=REST1+COMBI1
```

```
      TOT2=REST2+COMBI2
      TOT3=REST3+COMBI3
      ACT1=DEXP(TOT1)
      ACT2=DEXP(TOT2)
      ACT3=DEXP(TOT3)
      P=(X1*ACT1*P1S)+(ACT2*X2*P2S)+(ACT3*X3*P3S)
      Y1=(X1*P1S*ACT1)/P
      Y2=(X2*P2S*ACT2)/P
      Y3=1.D0-Y1-Y2
      VOLTY1=Y1/X1
      VOLTY2=Y2/X2
      VOLTY3=Y3/X3
      WRITE (6,3322)
3322  FORMAT(//,10X,'%%% REPORT EQUILIBRIUM RELATIONSHIP %%%')
      WRITE (6,4434) T
4434  FORMAT(/,10X,'CURRENT TEMPERATURE OF PLATE IS ',F16.6)
      WRITE (6,4433) X1,Y1,ACT1
4433  FORMAT(//,10X,'INLET HEAVIEST LIQUID COMPOSITION = ',
     1F8.4,/,10X,'EQUILIBRIUM GAS COMPOSITION = ',F8.4,
     15X,'ACTIVITY COEFFICIENT = ',F8.4)
      WRITE (6,3344) VOLTY1,VOLTY2,VOLTY3
3344  FORMAT(/,10X,'EQUILIBRIUM CONSTANTS ARE ',
     *'(1) = ',F11.6,3X,'(2) = ',F11.6,3X,'(3) = ',F11.6)
      YAEQ=Y1
      YBEQ=Y2
  144 WRITE (6,143) X2,Y2,ACT2
  143 FORMAT(/,5X,'X2 = ',F7.4,5X,'Y2 = ',F7.4,
     15X,'ACT2 = ',F7.4)
  244 WRITE (6,243) X3,Y3,ACT3
  243 FORMAT(/,5X,'X3 = ',F7.4,5X,'Y3 = ',F7.4,
     15X,'ACT3 = ',F7.4)
      WRITE (6,4435)
4435  FORMAT(//,10X,'%%% END OF REPORTING EQUILIBRIUM %%%')
      RETURN
      END
```

```
          SUBROUTINE PROPER(XAIN,XBIN,YAIN,YBIN,TPLATE,RELATA,
         1RELATB,RELATC,QGIN,HRINA,HRINB,GA,GB,QMOLEV,D11,
         1D12,D22,D21,SG1,SG2)
          IMPLICIT REAL*8(A-H,O-Z)
C*****************************************************************
C
C
C         THIS PROGRAM IS TO CALCULATE ALL THE PROPERTIES
C         NECESSARY TO PROCED THE CALCULATIONS FOR DISTILLATION
C
C
C*****************************************************************
C
C
C         THE PLATE TEMPERATURE,AND COMPOSITION HAVE TO BE
C         INTRODUCED INTO THIS PROGRAM
C         THE TEMPERATURE IN DEGREE K
          DIMENSION BETA(20)
          DIMENSION TC(3),WM(3),VC(3),TB(3),PC(3)
          DIMENSION ZC(3),V(3),ROHL(3),DA(3),DB(3)
          DIMENSION TBR(3),TR(3),Q(3),A(3),SIG(3)
          DIMENSION PR(3)
          DIMENSION ETAG(3),FETA(3),FEP(3),ETAPUR(3)
          DIMENSION VLA(3),ETAL(3),VISB(3),VISTO(3)
          DIMENSION GUMV(3),DCO(3,3),DC(3,3),DLO(3,3)
          DIMENSION CAPSG(2),TTUM(2)
          DIMENSION CLQSG(2),EQLQ(2),CKKF(2)
C
C         TC,PC,VC ARE THE CRITICAL PROPERTIES FOR TEM. PRESSURE,
C         AND VOLUME
C         WM IS MOLECULAR WEIGHT, TB IS BOILING POINT
C
          DATA TC(1),PC(1),VC(1)/617.0D0,35.0D0,376.D0/
          DATA TC(2),PC(2),VC(2)/591.7D0,40.6D0,316.D0/
          DATA TC(3),PC(3),VC(3)/562.1D0,48.3D0,259.D0/
          DATA TB(1),WM(1)/412.3D0,106.168D0/
          DATA TB(2),WM(2)/383.8D0,92.141D0/
          DATA TB(3),WM(3)/353.3D0,78.114D0/
          DATA ZC(1),ZC(2),ZC(3)/0.260D0,0.264D0,0.271D0/
          DATA VISB(1),VISTO(1)/453.42D0,257.18D0/
          DATA VISB(2),VISTO(2)/467.33D0,255.24D0/
          DATA VISB(3),VISTO(3)/545.64D0,265.34D0/
          DATA SUMVA,SUMVB,SUMVC/131.6D0,111.14D0,90.68D0/
C         SUMVA,SUMVB,SUMVC ARE FOR GAS PHASE DAB,PAGE 554 IN REID
          WRITE (6,7755)
7755      FORMAT(///,10X,'### THIS SECTION REPORTS PROPERTIES ###')
C         COLUMN PRESSURE IS CONSTANT
          DATA PCLMN/760.D0/
          P=PCLMN/760.D0
          T=TPLATE
          XA=XAIN
          YA=YAIN
          XB=XBIN
          YB=YBIN
```

```
       Q1=QGIN
       YC=1.DO-YA-YB
       XC=1.DO-XA-XB
C
       DO 10 I=1,3
       TBR(I)=TB(I)/TC(I)
       TR(I)=T/TC(I)
       PR(I)=P/PC(I)
C
C       THIS SECTION CALCULATE SURFACE TENSION
C       PAGE 604 IN REID
C
       Q(I)=0.1207DO*(1.DO+((TBR(I)*DLOG(PC(I)))/(1.DO-TBR(I))
      1))-0.281DO
       AA=2.DO/3.DO
       BB=1.DO/3.DO
       CC=11.DO/9.DO
C
       SIG(I)=(PC(I)**AA)*(TC(I)**BB)*Q(I)*((1.DO-TR(I))**CC)
       WRITE (6,22) I,SIG(I)
22     FORMAT(/,10X,'SURFACE TENSION FOR PURE COMPONENT (',
      *I2,' ) IS ',F11.6,' DYNE/CM')
C
C        THE ABOVE EQUATION FOR SIG IS FOR NON-HYDROGEN BONDED
C
       V(I)=0.285DO*(VC(I)**1.048DO)
C       V(I) PAGE 59 IN REID
       A(I)=(V(I)**AA)*((6.023D23)**BB)
C
C       THIS SECTION CALCULATE LIQUID DENSITY
C       PAGE 3-230 IN PERRY HANDBOOK
C
       ROHL(I)=(PC(I)*WM(I)/TC(I))*((0.065DO/(ZC(I)**0.773))-
      *0.09DO*TR(I))
       WRITE (6,222) I,ROHL(I)
222    FORMAT(/,10X,'DENSITY OF PURE LIQUID ',I2,' IS ',F11.6)
C
C       THIS SECTION CALCULATE CONSTANTS FOR GAS DENSITY
C       PAGE 270-277 IN SMITH&VAN NESS
C       REDLICH-KWONG EQUATION OF STATE IS USED
C
       DB(I)=(0.0867DO*82.05DO*TC(I)/PC(I))
       DA(I)=(0.4278DO*82.05DO*(TC(I)**2.5))/PC(I)
C
C       THIS SECTION CALCULATES GAS PHASE VISCOSITY
C       PAGE 3-247 IN PERRY HANDBOOK
C
       ETAG(I)=(33.3DO*DSQRT(WM(I)*TC(I)))/(VC(I)**AA)
       FEP(I)=0.91DO*DLOG10(1.9DO*TR(I))
       FETA(I)=1.058DO*(TR(I)**0.645)-0.261DO/((1.9DO*TR(I))**
      1FEP(I))
       ETAPUR(I)=ETAG(I)*FETA(I)*1.D-4
       WRITE (6,330) I,ETAPUR(I)
330    FORMAT(/,10X,'VISCOSITY,PURE GAS  COMPONENT ',I2,' IS ',
```

```
     *F11.6,'  CENTIPOISE')
C
C        THIS SECTION CALCULATES LIQUID VISCOSITY
C        PAGE 629 IN REID
C
       VLA(I)=VISB(I)*((1.D0/T)-(1.D0/VISTO(I)))
       ETAL(I)=10.D0**(VLA(I))
       WRITE (6,335) I,ETAL(I)
335    FORMAT(/,10X,'VISCOSITY FOR PURE LIQUID COMPONENT',I2,
     *' IS ',F11.6,'  CENTIPOSE')
10     CONTINUE
       AM=(A(1)+A(2)+A(3))/3.D0
       BM=AM/(3.D0*8.314D7*T)
       SIGM=XA*SIG(1)+XB*SIG(2)+XC*SIG(3)-BM*((SIG(1)-SIG(2))**
     12)*XA*XB-BM*((SIG(1)-SIG(3))**2)*XA*XC-BM*((SIG(2)-SIG(3
     1))**2)*XB*XC
       WRITE (6,110) SIGM
110    FORMAT(/,10X,'SURFACE TENSION FOR THE MIXTURE IS ',
     *F11.6,' DYNE/CM')
C
C        THIS SECTION CALCULATE DENSITY FOR GAS MIXTURE
C        PAGE 270-277 IN SMITH&VAN NESS
C
       TC12=DSQRT(TC(1)*TC(2))
       TC13=DSQRT(TC(1)*TC(3))
       TC23=DSQRT(TC(2)*TC(3))
       VC12=((VC(1)**BB+VC(2)**BB)/2.D0)**3
       VC13=((VC(1)**BB+VC(3)**BB)/2.D0)**3
       VC23=((VC(2)**BB+VC(3)**BB)/2.D0)**3
       ZC12=(ZC(1)+ZC(2))/2.D0
       ZC13=(ZC(1)*ZC(3))/2.D0
       ZC23=(ZC(2)*ZC(3))/2.D0
       PC12=(ZC12*82.05D0*TC12)/VC12
       PC13=(ZC13*82.05D0*TC13)/VC13
       PC23=(ZC23*82.05D0*TC23)/VC23
       DA12=(0.4278D0*82.05D0*82.05D0*(TC12**2.5))/PC12
       DA13=(0.4278D0*82.05D0*82.05D0*(TC13**2.5))/PC13
       DA23=(0.4278D0*82.05D0*82.05D0*(TC23**2.5))/PC23
       DBM=YA*DB(1)+YB*DB(2)+YC*DB(3)
       DAM=YA*YA*DA(1)+2.D0*YA*YB*DA12+YB*YB*DA(2)+
     1YC*YC*DA(3)+2.D0*YA*YC*DA13+2.D0*YB*YC*DA23
C
       ZNEW=1.D0
       DO 100 J=1,100
       ZOLD=ZNEW
       H=(DBM*P)/(ZOLD*82.05D0*T)
       ZNEW=(1.D0/(1.D0-H))-(DAM/(DBM*82.05D0*(T**1.5)))*(H/(1.
     1D0+H))
       WRITE (6,2222) J,ZNEW
2222   FORMAT(/,10X,'COMPRESBILITY FACTOR IS  ON TERMS ',I3,
     *' IS ',F11.7)
       IF (DABS((ZNEW-ZOLD)/ZOLD) .LT. 1.D-4) GO TO 101
100    CONTINUE
C
```

```
101    VGM=ZNEW*82.05D0*T/P
       WMAVG=(YA*WM(1)+YB*WM(2)+YC*WM(3))
       WMAVL=(XA*WM(1)+XB*WM(2)+XC*WM(3))
       ROHGM=WMAVG/VGM
       ROHLM=XA*ROHL(1)+XB*ROHL(2)+XC*ROHL(3)
       WRITE (6,111) ROHGM,ROHLM
111    FORMAT(/,10X,'DENSITY OF MIXTURE FOR GAS IS ',F11.6,
      */,10X,'    FOR LIQUID IS ',F11.6,' G/ CM**3')
C
C       THIS SECTION CALCULATES VISCOSITY FOR GAS MIXTURE
C       PAGE 411 IN REID
C
       ETM1=YA*DSQRT(WM(1))
       ETM2=YB*DSQRT(WM(2))
       ETM3=YC*DSQRT(WM(3))
       ETAM=(ETAPUR(1)*ETM1+ETAPUR(2)*ETM2+ETAPUR(3)*ETM3)/
      1(ETM1+ETM2+ETM3)
       WRITE (6,331) ETAM
331    FORMAT(/,10X,' VISCOSITY FOR GAS MIXTURE IS ',F11.6,
      *' CENTIPOISE')
C
C       THIS SECTION CALCULATE VISCOSITY FOR LIQUID MIXTURE
C       PAGE 3-247 IN PERRY HANDBOOK
C
       VISCOL=(XA*(ETAL(1)**BB)+XB*(ETAL(2)**BB)+XC*(ETAL(3)**
      1BB))**3
       WRITE (6,336) VISCOL
336    FORMAT(/,10X,'VISCOSITY FOR LIQUID MIXTURE IS',F11.6,
      *' CENTIPOSE')
C
C       THIS SECTION CALCULATE DIFFUSIVITY COEFFICIENT IN
C       GAS PHASE, PAGE 554 IN REID
C
       GUMV(1)=SUMVA
       GUMV(2)=SUMVB
       GUMV(3)=SUMVC
       DO 3530 IDF=1,3
       DO 3540 JDF=1,3
       DCO(IDF,JDF)=DSQRT((WM(IDF)+WM(JDF))/(WM(IDF)*WM(JDF)))
       DCO22=(1.D-3)*(T**1.75)*DCO(IDF,JDF)
       DCO33=P*((GUMV(IDF)**BB+GUMV(JDF)**BB)**2)
       DC(IDF,JDF)=DCO22/DCO33
3540   CONTINUE
3530   CONTINUE
       D11=DC(1,1)
       D12=DC(1,2)
       D13=DC(1,3)
       D22=DC(2,2)
       D23=DC(2,3)
       D21=DC(2,1)
       D33=DC(3,3)
       D32=DC(3,2)
       D31=DC(3,1)
       WRITE (6,338) D11,D12,D13,D22,D21,D23,D33,D31,D32
```

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```
338     FORMAT(/,10X,'GAS PHASE DIFFUSIVITY COEFFICIENTS ARE :',
      1/,10X,'D11 = ',F11.6,5X,'D12 = ',F11.6,5X,'D13 = ',F11.6,
      1/,10X,'D22 = ',F11.6,5X,'D21 = ',F11.6,5X,'D23 = ',F11.6
      1/,10X,'D33 = ',F11.6,5X,'D31 = ',F11.6,5X,'D32 = ',
      1F11.6)
C
C       THIS SECTION CALCULATE LIQUID PHASE DIFFUSIVITY
C       COEFFICIENT,PAGE 557 IN REID
C
        DATA HIP/2.6D0/
C
C       HIP DEPENDS ON THE SYSTEM, PAGE 568 IN REID
C
        DO 1112 ILL=1,3
        DO 1113 JLL=1,3
        DLO(ILL,JLL)=(7.4D-8)*((DSQRT(HIP*WM(JLL))*T)/
      *(ETAL(JLL)*(V(JLL)**0.6)))
1113    CONTINUE
1112    CONTINUE
        DL11=(DLO(1,1)**XA)*(DLO(1,1)**XA)
        DL12=(DLO(1,2)**XB)*(DLO(2,1)**XA)
        DL13=(DLO(1,3)**XC)*(DLO(3,1)**XA)
        DL22=(DLO(2,2)**XB)*(DLO(2,2)**XB)
        DL21=(DLO(2,1)**XA)*(DLO(1,2)**XB)
        DL23=(DLO(2,3)**XC)*(DLO(3,2)**XB)
        DL33=(DLO(3,3)**XC)*(DLO(3,3)**XC)
        DL32=(DLO(3,2)**XB)*(DLO(2,3)**XC)
        DL31=(DLO(3,1)**XA)*(DLO(1,3)**XC)
        WRITE (6,348) DL11,DL12,DL13,DL22,DL21,DL23,
      *DL33,DL31,DL32
348     FORMAT(/,10X,'LIQUID PHASE DIFFUSIVITY COEFFICIENTS ARE:'
      *,/,10X,'DL11 = ',F11.6,5X,'DL12 = ',F11.6,5X,'DL13 = ',
      *F11.6,5X,/,10X,'DL22 = ',F11.6,5X,'DL21 = ',F11.6,5X,
      *'DL23 = ',F11.6,/,10X,'DL33 = ',F11.6,5X,'DL31 = ',
      *F11.6,5X,'DL32 = ',F11.6)
C
C       THIS SECTION CALCULATE THE BUBBLE DIAMETER,
C       RISING VELOCITY,  CONTACT AREA, CONTACT TIME
C
C       Q1=GAS FLOW RATE IN FT**3/HR PER INCH WIDTH OF SLOT
C
C       WIDTH OF SLOT IS 1/4 INCHES, 12 SLOTS PER CAP, TOTAL
C       3 INCHES
C       QFLOWG IS THE VOLUMETRIC FLOW RATE OF VAPOR FLOW
C
        DATA NSLOT/12/
        QGAS=Q1*4.D0/16.D0
        QFLOWG=Q1*3.0D0
C
C       ETAM = GAS MIXTURE VISCOSITY IN CENTIPOISE
C       UETAM = VISCOSITY IN LB/FT HR, 1 CP = 2.42 LB/FT HR
C
        UETAM=ETAM*2.42D0
C
```

```
C       DIAMETER OF SLOT IN FT = 1/4 INCHES
C       DEPTH OF LIQUID SEAL IS 1 INCHES, IN FT
C
        DSLOT=(4.D0/16.D0)*(1.D0/12.D0)
        HSEAL=(1.0D0)*(1.D0/12.D0)
        DBUBL=0.222D0*(DSLOT**0.33)*(QGAS**0.125)*(UETAM**0.02)+
       *(3.02D-4)*(QGAS**1.09)
C       DBUBL IN FT
        DCMBL=DBUBL*30.48D0
C       DCMBL IN CM
        WRITE (6,5010) DCMBL
5010    FORMAT(/,10X,'THE BUBBLE DIAMETER IS ',F11.6,
       *'      CM')
        VBUBL=(4.1D3)*(QGAS**0.16)
C       VBUBL IN FT/HR
        VCMBL=VBUBL*(30.48D0/3600.D0)
C       VCMBL IN CM/SEC
        WRITE (6,5011) VCMBL
5011    FORMAT(/,10X,'RISING VELOCITY IS ',F11.6,'    CM/SEC')
        ACNTAT=(1.46D-3)*(QGAS**0.84)/DBUBL
C       ACNTAT IS CONTACT AREA OF BUBBLES IN FT*FT PER FT OF
C       LIQUID SEAL
        ATAT=ACNTAT*HSEAL*30.48D0*30.48D0
C.      ATAT CONTACT AREA IN CM*CM
        WRITE (6,5012) ATAT
5012    FORMAT(/,10X,'THE CONTACT AREA IS ',F11.6,'    CM*CM')
        TCNTAT=HSEAL/VBUBL
C       TCNTAT CONTACT TIME THROUGH THE LIQUID SEAL IN HOUR
        TCAT=TCNTAT*3600.D0
C       TCAT CONTACT TIME IN SECOND
        WRITE (6,5013) TCAT
5013    FORMAT(/,10X,'THE CONTACT TIME IS ',F11.6,'    SECOND')
        RCMBL=DCMBL/2.D0
C
C        THIS SECTION CALCULATE TERNARY RISING FUNCTION
C        BY USING TOOR'S METHOD
C
        D55=YA*D23+YB*D13+YC*D12
        CAPD11=(D13*((D23*YA)+(D12*(YB+YC))))/D55
        CAPD12=(YA*D13*(D23-D12))/D55
        CAPD21=(YB*D13*(D23-D12))/D55
        CAPD22=(D23*((D13*YB)+(D21*(YA+YC))))/D55
        CAPSG(1)=0.5D0*(CAPD11+CAPD22+DSQRT(((CAPD11-CAPD22)**
       12)+(4.D0*CAPD12*CAPD21)))
        CAPSG(2)=0.5D0*(CAPD11+CAPD22-DSQRT(((CAPD11-CAPD22)**
       12)+(4.D0*CAPD12*CAPD21)))
        DATA (BETA(I),I=1,10)/4.4934094D0,7.7252517D0,
       110.9041216D0,14.0661938D0,17.2207549D0,20.371303D0,
       123.5194525D0,26.6660542D0,29.8115988D0,32.956389D0/
        DATA EPS/1.D-10/
C        THIS SECTION CALCULATE SHERWOOD NUMBER
C
        DO 7765 IMA=1,2
        DITCAT=TCAT*CAPSG(IMA)/(RCMBL*RCMBL)
```

```
         WRITE (6,5025) DITCAT
5025     FORMAT(/,10X,'THE DIMENSIONLESS TIME = ',F11.6)
         DRE=(DCMBL*VCMBL*ROHGM)/ETAM
         DSC=(ETAM/(CAPSG(IMA)*ROHGM))
         SHRWOD=2.DO+0.76DO*DSQRT(DRE)*(DSC**BB)
         WRITE (6,5035) IMA,SHRWOD
5035     FORMAT(/,10X,'SHERWOOD NUMBER FOR ',I2,' IS ',F11.6)
C
C        THIS SECTION CALCULATE PART OF MASS TRANSFER
C        DURING BUBBLE RISING
C
C         MASS TRANSFER FROM A SINGLE BUBBLE
C         CONSIDER BOTH LIQUID AND GAS FILM RESISTANCE
C
         SH=SHRWOD
         TIME=DITCAT
         SUM=0.DO
         DO 1000 I=1,10
         ZZ=-(BETA(I)**2)
         Z=ZZ*TIME
         ZZ1=DEXP(Z)
         YY1=BETA(I)*DCOS(BETA(I))
         Y1=DSIN(BETA(I))
         Y2=(3.DO*SH)-(BETA(I)**2)
         YY2=(2.DO*SH*RCMBL)
         SU=(YY2*(YY1-Y1)*(1.DO-ZZ1))/(Y2*Y1*BETA(I)*BETA(I))
         SSUM=SUM+SU
         TT=SSUM-SUM
         TO1=DABS(TT)
         IF (TO1-EPS) 3,3,5
5        SUM=SSUM
1000     CONTINUE
         TSUM=SUM
         GO TO 6
3        TSUM=SSUM
6        TY4=RCMBL/3.DO
         TY11=3.DO*SH*TIME
         TY2=DEXP(-TY11)
         TY6=TY4*(1.DO-TY2)
         TTUM(IMA)=TY6+TSUM
7765     CONTINUE
C
C        THIS SECTION CONVERT THE VOLUMETRIC FLOW RATE OF VAPOR
C        TO MOLAR FLOW RATE IN G MOLE / HR
C
         QMOLEG=QFLOWG*(30.48DO**3)
         QMOLEV=QMOLEG*ROHGM/WMAVG
         WRITE (6,5099) QMOLEV
5099     FORMAT(/,10X,'THE MOLAR FLOW RATE FOR GAS IS ',
        1F11.6,'  G MOLE/HR')
         HRINA=ATAT*TTUM(1)
         HRINB=ATAT*TTUM(2)
C
C        THIS SECTION CALCULATE THE PART OF MASS TRANSFER
```

```
C       DURING BUBBLE FORMATION
C
        DLQ55=XA*DL23+XB*DL13+XC*DL12
        CADL11=(DL13*((DL23*XA)+(DL12*(XB+XC))))/DLQ55
        CADL12=(XA*DL13*(DL23-DL12))/DLQ55
        CADL21=(XB*DL13*(DL23-DL12))/DLQ55
        CADL22=(DL23*((DL13*XB)+(DL21*(XA+XC))))/DLQ55
        CLQSG(1)=0.5D0*(CADL11+CADL22+DSQRT(((CADL11-CADL22)
       1**2)+(4.D0*CADL12*CADL21)))
        CLQSG(2)=0.5D0*(CADL11+CADL22-DSQRT(((CADL11-CADL22)
       1**2)+(4.D0*CADL12*CADL21)))
        EQLQ(1)=RELATA
        EQLQ(2)=RELATB
        DO 8842 ILQ=1,2
        TF=(2.D0/3.D0)*((DCMBL**3)/((DSLOT*30.48D0)**2)*VCMBL)
        AF=(3.D0/5.D0)*NSLOT*3.1415968D0*DCMBL*DCMBL
        CKF0=DCMBL/TF
        CKF1=((ROHGM+ROHLM)/2.D0)/WMAVG
        CKF2=(VCMBL*VCMBL)/(DCMBL*980.66D0)
        CKF3=DCMBL*DCMBL/(TF*CAPSG(ILQ))
        CKF4=ETAM/DSQRT(ROHGM*DCMBL*SIGM)
        CKDF=0.0432D0*CKF0*CKF1*(CKF2**0.089)*(CKF3**(-0.334))*
       1(CKF4**(-0.601))
        CKF5=CLQSG(ILQ)/TF
        CKF6=(ROHLM*SIGM)/((DABS(ROHGM-ROHLM))*980.66D0*TF*
       1VISCOL)
        CKF7=980.66D0*TF*TF/DCMBL
        CKF8=((ROHGM+ROHLM)/2.D0)/WMAVL
        CKCF=0.386D0*CKF0*CKF8*(CKF5**0.5)*(CKF6**0.407)*(CKF7**
       10.148)
        CKKF(ILQ)=(CKCF*CKDF)/(CKCF+EQLQ(ILQ)*CKDF)
8842    CONTINUE
        GA=CKKF(1)*AF*3600.D0
        GB=CKKF(2)*AF*3600.D0
        WRITE (6,646)
646     FORMAT(/,10X,'#### END OF PROPERTIES REPORTING ####')
        D11=CAPD11
        D12=CAPD12
        D22=CAPD22
        D21=CAPD21
        SG1=CAPSG(1)
        SG2=CAPSG(2)
        RETURN
        END
```

```fortran
      SUBROUTINE ENTHPY(TPLATE,XA,XB,YA,YB,ENTHVM,ENTHLM)
      IMPLICIT REAL*8(A-H,O-Z)
C
C     THIS SECTION CALCULATE THE ENTHALPIES FOR LIQUID PHASE
C     AND GAS PHASE, ALSO LATENT HEAT IS ESTIMATED
C     CP DATA FROM REID, PAGE 629
C     LATENT HEAT FROM PAGE 201 IN REID
C
      DIMENSION CPGA(3),CPGB(3),CPGC(3),CPGD(3)
      DIMENSION ENTHLV(3),ENTHLL(3)
      DIMENSION OMEGA(3)
      DIMENSION TC(3)
      DATA CPGA(1),CPGB(1),CPGC(1),CPGD(1)/-6.966D0,1.504D-1,
     1-8.950D-5,2.025D-8/
      DATA CPGA(2),CPGB(2),CPGC(2),CPGD(2)/-5.817D0,1.224D-1,
     1-6.605D-5,1.173D-8/
      DATA CPGA(3),CPGB(3),CPGC(3),CPGD(3)/-8.101D0,1.133D-1,
     1-7.206D-5,1.703D-8/
      DATA OMEGA(1),OMEGA(2),OMEGA(3)/0.331D0,0.257D0,0.212D0/
      DATA TC(1),TC(2),TC(3)/617.0D0,591.7D0,562.1D0/
      T=TPLATE
      XC=1.D0-XA-XB
      YC=1.D0-YA-YB
C
      DO 303 NL=1,3
      PP1=CPGA(NL)*(T-298.D0)
      PP2=(CPGB(NL)/2.D0)*((T**2)-(298.D0**2))
      PP3=(CPGC(NL)/3.D0)*((T**3)-(298.D0**3))
      PP4=(CPGD(NL)/4.D0)*((T**4)-(298.D0**4))
      ENTHLV(NL)=PP1+PP2+PP3+PP4
C     ENTHLV IS IN CALORIES/G MOLE
C
      TR=T/TC(NL)
      CH=7.08D0*((1.D0-TR)**0.354)
      CG=10.95D0*OMEGA(NL)*((1.D0-TR)**0.456)
      CLAMDA=1.987D0*TC(NL)*(CH+CG)
      ENTHLL(NL)=ENTHLV(NL)-CLAMDA
303   CONTINUE
      ENTHVM=YA*ENTHLV(1)+YB*ENTHLV(2)+YC*ENTHLV(3)
      ENTHLM=XA*ENTHLL(1)+XB*ENTHLL(2)+XC*ENTHLL(3)
      RETURN
      END
```

```
      SUBROUTINE TEMP(XA,XB,E,TNXT)
      IMPLICIT REAL*8(A-H,O-Z)
C
C     THIS ROUTINE USE NEWTON-RAPHSON'S METHOD
C     TO ESTIMATE THE NEXT PLATE TEMPERATURE
C
      DIMENSION CPGA(3),CPGB(3),CPGC(3),CPGD(3)
      DIMENSION ENTHLL(3),ENTHLV(3),DENTHL(3)
      DIMENSION OMEGA(3)
      DIMENSION TC(3)
      DATA CPGA(1),CPGB(1),CPGC(1),CPGD(1)/-6.966D0,1.504D-1,
     1-8.950D-5,2.025D-8/
      DATA CPGA(2),CPGB(2),CPGC(2),CPGD(2)/-5.817D0,1.224D-1,
     1-6.605D-5,1.173D-8/
      DATA CPGA(3),CPGB(3),CPGC(3),CPGD(3)/-8.101D0,1.133D-1,
     1-7.206D-5,1.703D-8/
      DATA OMEGA(1),OMEGA(2),OMEGA(3)/0.331D0,0.257D0,0.212D0/
      DATA TC(1),TC(2),TC(3)/617.0D0,591.7D0,562.1D0/
      T=TNXT
      XC=1.D0-XA-XB
      DO 404 I=1,100
      DO 303 NL=1,3
      PP1=CPGA(NL)*(T-298.D0)
      PP2=(CPGB(NL)/2.D0)*((T**2)-(298.D0**2))
      PP3=(CPGC(NL)/3.D0)*((T**3)-(298.D0**3))
      PP4=(CPGD(NL)/4.D0)*((T**4)-(298.D0**4))
      ENTHLV(NL)=PP1+PP2+PP3+PP4
C     ENTHLV IS IN CALORIES/G MOLE
C
      TR=T/TC(NL)
      CH=7.08D0*((1.D0-TR)**0.354)
      CG=10.95D0*OMEGA(NL)*((1.D0-TR)**0.456)
      CLAMDA=1.987D0*TC(NL)*(CH+CG)
      ENTHLL(NL)=ENTHLV(NL)-CLAMDA
      DPP1=CPGA(NL)
      DPP2=CPGB(NL)*T
      DPP3=CPGC(NL)*(T**2)
      DPP4=CPGD(NL)*(T**3)
      DCH=-7.08D0*0.354D0*((1.D0-TR)**(-0.646))
      DCG=-10.95D0*OMEGA(NL)*0.456D0*((1.D0-TR)**(-0.544))
      DENTHL(NL)=DPP1+DPP2+DPP3+DPP4-1.987D0*(DCH+DCG)
303   CONTINUE
      F1=XA*ENTHLL(1)+XB*ENTHLL(2)+XC*ENTHLL(3)-E
      DF1=XA*DENTHL(1)+XB*DENTHL(2)+XC*DENTHL(3)
      TNEW=T-(F1/DF1)
      IF((DABS(TNEW-T)/T) .LE. 1.D-5) GO TO 40
      T=TNEW
404   CONTINUE
      TNXT=T
      GO TO 50
40    TNXT=TNEW
50    WRITE (6,555) TNXT
555   FORMAT(/,10X,'THE NEXT PLATE TEMPERATURE = ',F11.5)
      RETURN
      END
```

NOMENCLATURE

| | | |
|---|---|---|
| Aeff | = | effective contact area of all the bubbles |
| $(C)$ | = | the concentration vector |
| $\overline{C}_A$ | = | average concentration of A inside the sphere |
| $C_{Agl}$ | = | the gas phase concentration which is in equilibrium with the existing liquid phase concentration |
| d, D | = | diffusivity coefficient |
| $(D)$ | = | diffusion coefficient matrix |
| $E_G$ | = | gas phase Murphree efficiency |
| $E_{local}$ | = | local efficiency on the plate |
| $K_G$ | = | overall gas phase mass transfer coefficient |
| $(K_G')$ | = | overall mass transfer coefficient matrix |
| $N_{sh}$ | = | Sherwood number $= K_G R/D$ |
| $Q_r$ | = | overall mass-transfer up to time t during bubble rising |
| $Q_f$ | = | overall mass transfer rate during bubble formation |
| R | = | the radius of the bubble |
| $(t)$ | = | a non-singular matrix which can diagonalize $(D)$ |
| $Y_{AN}$ | = | vapor concentration from the plate N |
| $Y_{AN}^{*}$ | = | vapor concentration in equilibrium with liquid |
| $Y_{AN-1}$ | = | vapor concentration to the plate N |
| $\alpha_n$ | = | eigenvalues of function X = TAN X |
| $\Theta$ | = | dimensionless concentration $= (C_{A0}-C_A)/(C_{A0}-C_{Agl})$ |
| $\Theta_1$ | = | dimensionless concentration $= \left[(\psi_0)-(\psi)\right]/\left[(\psi_0)-(\psi_{gl})\right]$ |

$\eta$ = dimensionless radius = $r/R$

$\tau$ = dimensionless time = $Dt/R^2$

$\tau_i$ = dimensionless time = $(\sigma) t/R^2$

$(\sigma)$ = the diagonal matrix of the eigenvalues of $(D)$

$(\psi)$ = as defined in equation (2-38)

# REFERENCES

1.  Abrams, D.S., Prausnitz, J.M., AIChE J., 21, 116, (1975).

2.  Antoine, C., Compt. rend., 107, 681, 836, (1888).

3.  Boublikova, L., Lu, B.C.Y., J. Appl. Chem., 19, 89, (1969).

4.  Bromley, Wilke, Ind. Eng. Chem., 43, 1641, (1951).

5.  Carey, J.S., Griswold, J., Lewis, W.K., McAdams, W.H., Trans. Amer. Inst. Chem. Engrs., 30, 504, (1934).

6.  Carruth, G.F., Kobayashi, R., Ind. Eng. Chem. Fundam., 11, 509, (1972).

7.  Chaudhry, M.M., Van Ness, H.C., Abbott, M.M., J. Chem. Eng. Data., 25, 254, (1980).

8.  Cussler, E.L., "Multicomponent Diffusion", New York, Elsevier Scientific, (1975).

9.  Davidson, L., Amick, E.H., AIChE J., 2, 337, (1956).

10. Drickmer, H.H., Bradford, J.R., Trans. AIChE, 39, 319, (1943).

11. Fredendlund, A., Jones, R.L., Prausnitz, J.M., AIChE J., 21, 1086, (1975).

12. Fredenslund, A., Gmehling, J., Michelden, J.M., Rasmussen, P., Prausnitz, J., Ind. Eng. Chem. Process Des. Dev., 16, 450, (1977).

13. Fuller, E.N., Schettler, P.D., Giddings, J.G., Ind. Eng. Chem., 58, 18, (1966).

14. Gmehling, J., Rasmussen, P., Fredenslund, A., Ind. Eng. Chem. Process Des. Dev., 21, 118, (1982).

15. Goyal, Doraiswamy, Hydrocarbon Proc. and Petrol. Ref., 45, 200, (1966).

16. Griswold, J., Wong, S.Y., Chem. Eng. Progr. Symp. Ser. 48, 18, (1952).

17.  Guggenheim, E.A., "Mixtures", Clarendon Press, Oxford, (1952).

18.  Herning, Zipperer, Gas-U. Wasserfach, 79, 49, (1936).

19.  Huffman, J.R., Treybal, R.E., Ind. Eng. Chem. Ana. Ed., 12, 745, (1940).

20.  Kendall, Monroe, J. Am. Chem. Soc., 43, 115, (1921).

21.  Kind, R., Kahnt, G., Schmidt, D., Schumann, J., Bittrich, H.J., Phys. Chem., 238, 277, (1968).

22.  Kretchmer, C.B., Wiebe, R., J. Am. Chem. Soc., 71, 1793, (1949).

23.  Maxwell, J.C., Scientific Papers, Vol. II, New York, Dover, (1952).

24.  Miller, D.G., Ind. Eng. Chem. Fundam., 2, 78, (1965).

25.  Nord, M., Trans. AIChE, 42, 863, (1946).

26.  O'Connel, H.E., Trans. AIChE, 42, 741, (1946).

27.  Onsager, L., Ann. N.Y. Acad. Sci., 46, 241, (1945).

28.  Pemberton, R.C., Mash, C.J., J. Chem. Thermodyn., 10, 867, (1978).

29.  Quigely, C.J., Johnson, A.I., Harris, B.S., Chem. Eng. Progress Symp. Ser. 16, 31, (1955).

30.  Redlich, O., Kwong, J.N.S., Chem. Rev., 44, 233, (1949).

31.  Reid, R.C., Prausnitz, J.M., Sherwood, T.K., "The Properties of Gases and Liquids", 3d ed., New York, McGraw-Hill, (1977).

32.  Rowe, P.N., Claxton, K.T., Lewis, J.B., Trans. Inst. Chem. Eng., 43, 14, (1965).

33.  Scheibel, Ind. Eng. Chem., 46, 1574, (1954).

34.  Schmidt, G.C., Z. Phys. Chem., 121, 221, (1926).

35.  Shilling, G.D., Beyer, G.H., Watson, C.C., Chem. Eng. Progress, 128, (1953).

36.  Skelland, A.H.P., "Diffusional Mass Transfer", New York, John Wiley & Sons, (1974).

37. Skelland, A.H.P., Hemler, C.C., unpublished work at the University Notre Dame, (1969).

38. Skelland, A.H.P., Minhas, S.S., AIChE J., 17, 1316, (1971).

39. Skjold-Jorgensne, S., Kolbe, B., Gmehling, J., Rasmussen, P., Ind. Eng. Chem. Progress Des. Dev., 18, 714, (1979).

40. Sprow, F.B., Prausnitz, J.M., Trans. Faraday Soc., 62, 1097, (1966).

41. Tamir, A., Appelblat, A., Wagner, M., Fluid Phase Equilibria, 6, 113, (1981).

42. Toor, H.L., AIChE J., 10, 460, (1964).

43. van Velzen, D., Cardozo, R.L., Laugenkamp, H., Ind. Eng. Chem. Fundam., 11, 20, (1972).

44. Wilke, C.R., Chang, P., AIChE J., 1, 264, (1955).

45. Williams, B., Begley, J.W., Wu, C., "Tray Efficiencies in Distillation Columns", AIChE Research Committee, (1960).