Plate Efficiencies in Multicomponent Distillation

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A first approximation to the multicomponent plate-efficiency problem has been carried out with a film model combined with equations for steady state diffusion in a ternary gas mixture. Numerical integration of the equations through a plate yields the ternary efficiencies as functions of the binary efficiency.

The effects of diffusional interactions in a distillation column were studied by computing the efficiencies on each plate when a column is designed to separate a ternary mixture. In the example studied, the average column efficiency was 39% less than the binary efficiency.

Some criteria are suggested for comparing other multicomponent systems to the one studied in order to estimate the uncertainty in the use of binary correlations for these systems.

Plate efficiencies in distillation columns have been studied intensively and can be predicted adequately (2); however there is no information available on multicomponent systems, and the question arises as to how reliable the binary correlations may be when applied to a multicomponent system. In this paper a first approximation to the multicomponent problem will be carried out in order to explore the conditions under which a simple extrapolation of binary data is possible as well as the general magnitude of the error which may be caused by this extrapolation.

Mass transfer on a distillation plate is approached in a binary system by combining a rate equation for a single vapor bubble with a material balance on the bubble (4):

$$n_A = K_A(\bar{y}_A - y^*_A) = -\frac{m}{S}\frac{d\bar{y}_A}{d\theta} \quad (1)$$

m being constant for equimolal countercurrent transfer.

Although Equation (1) is rigorous in the sense that it merely defines the over-all mass transfer coefficient, it is usually integrated by assuming K_A, S, and y^*_A constant to yield

$$E_b = \frac{\bar{y}_{A1} - \bar{y}_{A11}}{\bar{y}_{A1} - y^*_A} = 1 - \exp\left(-\frac{K_A S}{m}\theta\right) \quad (2)$$

The assumptions made idealize the problem to one of complete liquid mixing in a vertical plane with a mass transfer mechanism such that $K_A S$ is independent of vertical position. When the above point efficiency is used as a plate efficiency, the constant K_A becomes some type of average across the plate. Notwithstanding the severe assumptions in Equation (2), its predictions on the additivity of resistances are found to be in reasonable accord with experiment (2).

Although the hydrodynamics in a multicomponent system would not be expected to differ from a binary one which has the same physical properties, the mass transfer process is considerably more complicated. For steady state, equimolal, countercurrent diffusion in a three-component system the flux of species A and B from points 1 to 2 is approximated by (6)

$$n_j = \frac{D_{jo}\rho}{x}\phi_c(\delta_m y_{j1} - y_{j2}) \quad (3)$$

where

$$\delta_m = \exp\left(1 - \frac{D_{AC}+D_{BC}}{2D_{AB}}\right)(y_{c1} - y_{c2}) \quad (4)$$

$$\phi_c = \frac{y_{c1} - y_{c2}}{(1 - y_{c2}) - \delta_m(1 - y_{c1})} \quad (5)$$

n_c is obtained from the equation

$$n_A + n_B + n_c = 0 \quad (6)$$

which is usually valid in distillation. In this approximation species C is chosen to minimize $(D_{AC} - D_{BC})^2$; that is, species C is the odd component, normally the lightest or heaviest. When $D_{AC} = D_{BC}$, the above equations are exact solutions to the Maxwell-Stefan equations.

The equations differ considerably from the equivalent binary equations where the diffusional interaction terms δ_m and ϕ_c are 1.0. Since δ_m and ϕ_c are positive numbers, in a ternary system the direction of diffusion depends upon the generalized driving force $(\delta_m y_{j1} - y_{j2})$ rather than upon the *binary* driving force $(y_{j1} - y_{j2})$. Consequently in a ternary system diffusion may take place in the direction opposite to the concentration gradient (reverse diffusion) when the concentration gradient is zero (osmotic diffusion), or in the presence of a gradient the flux may be zero (diffusion barrier).

Table 1. Diffusion Coefficients, Sq. Ft./Hr.

D_{AB}	D_{AC}	D_{BC}
0.422	0.7805	0.7805

In mass transfer, on a tray, of course, the flux is hardly likely to be controlled by steady state diffusion through a film. The transfer is undoubtedly complex with both convective and transient effects present. Furthermore generally there will be resistance in the liquid phase, and here even the diffusion problem has not been solved. (It would be expected however that the differences between binary and multicomponent transfer in the liquid phase are less marked than in the gas phase, since diffusional interactions appear to be less severe in liquids.)

Thus a complete solution to the mass transfer problem is not possible at present, but a first approximation can be obtained by resorting to the concept of steady state transfer through an effective gas film. It has been found recently that such a model does a surprisingly good job of predicting three-component mass transfer in a wetted-wall column (7). It will be assumed that the gas side is controlling. Since diffusional interactions in liquids and in turbulent fluids are expected to be relatively small, it appears probable that this approach will give the maximum deviation to be expected between binary and ternary transfer.

With this film viewpoint the mass transfer equations for A and B become

$$n_j = k_j\phi_c(\delta_m\bar{y}_j - y_{j\iota}) \quad (7)$$

The ϕ_c and δ_m are now given by Equations (4) and (5) with the compositions at point 1 taken as the mean composition and at point 2 as the interfacial composition. Combining with a material balance, one gets

$$-\frac{m}{S}\frac{d\bar{y}_j}{d\theta} = k_j\phi_c(\delta_m\bar{y}_j - y^*_j) \quad (8)$$

where $y_{j\iota}$ has been replaced by y^*_j, since the gas side is assumed to be controlling. If the binary Equation (2) is interpreted in terms of an effective

TABLE 2. DIFFUSION COEFFICIENTS AT 95°C. AND 1 ATM. AND ACTIVITY COEFFICIENTS

A = Methanol,	B = Isopropanol,	C = Water,
$D_{AB} = 0.422$	$D_{BC} = 0.623$	$D_{AC} = 0.938$

$$\ln\gamma_A = (1 - X_A)[0.13X_B + 0.9X_C - 4.2X_BX_C]$$
$$\ln\gamma_B = (1 - X_B)[0.13X_A + 1.6X_C - 0.5X_C(3X_B - X_C) - 1.05X_AX_C]$$
$$\ln\gamma_C = (1 - X_C)[0.9\ X_A + 1.6X_B - 0.5X_B(X_B - 3X_C)]$$

film, it can be written for each component as

$$E'_{bj} = \frac{\bar{y}_{jI} - \bar{y}_j}{\bar{y}_{jI} - y^*_j} = 1 - \exp\left(-\frac{k_jS}{m}\theta'\right) \quad (9)$$

where the subscript II has been removed so that E'_{bj} is the plate efficiency at a contact time θ' for component j in a binary system of j and c operating under the same hydrodynamics conditions as the ternary system. The gas side is assumed to be controlling here also. When θ' is θ, the contact time on the plate $\bar{y}_j$ becomes y_{jII}, and E'_{bj} becomes the actual binary plate efficiency.

Differentiating Equation (9) one obtains

$$d[\ln(1 - E'_{bj})] = -\frac{k_jS}{m}d\theta' = -dN'_j \quad (10)$$

and combining with (8) one gets

$$d\bar{y}_j = -\phi_c(\delta_m\bar{y}_j - y^*_j)\,dN'_j \quad (11)$$

It follows for the above equations that

$$\frac{dN'_A}{dN'_B} = \frac{N_A}{N_B} = \frac{k_A}{k_B} = \frac{D_{AC}}{D_{AB}} \quad (12)$$

But the ratio of the number of gas phase transfer units for two separate binary systems is not equal to the ratio of diffusion coefficients; rather it is found to be equal to the ratio of the square roots of the coefficients (2). This inconsistency is a result of the use of the present film model and will be avoided in later calculations by considering a ternary system in which there are two similar species, A and B, and one dissimilar one, C; so $D_{AC} = D_{BC} \neq D_{AB}$. The consequence of this restriction will be considered later, but it is interesting to note that these are the conditions under which Equation (3) is the exact solution of the Maxwell-Stefan equations.

Multicomponent plate efficiencies may be defined by

$$E = \frac{\bar{y}_{jI} - \bar{y}_{jII}}{\bar{y}_{jI} - y^*_j} \quad (13)$$

For a binary system the two efficiencies are equal, while in a multicomponent system there is one equation relating all the efficiencies (exclusive of the mass transfer relationships). The equation for a ternary system is

$$E_c = \frac{(\bar{y}_{AI} - y^*_A)\,E_A + (\bar{y}_{BI} - y^*_B)\,E_B}{(\bar{y}_{AI} - y^*_A) + (\bar{y}_{BI} - y^*_B)} \quad (14)$$

To compute the above plate efficiencies Equation (11) must be integrated from $N'_j = 0$ to $N'_j = N_j$.

If a system is considered in which $D_{AC} = D_{BC}$, $dN'_A = dN'_B = dN'$, Equation (11) becomes

$$d\bar{y}_j = -\phi_c(\delta_m\bar{y}_j - y^*_j)dN' \quad (15)$$

and, as the binary efficiencies of AC and BC mixtures are now the same, the integration is carried out from $N' = 0$ to $N' = N_A = N_B = N_b$. The binary efficiency is by definition the efficiency which would be measured, or predicted by standard correlations, for a binary system, in which the diffusivity is D_{AC}, operating on the same plate as the ternary system with all other physical properties, flow rates, and geometries the same as the ternary system.

Since, as far as species C is concerned, the AB mixture it is diffusing through is now a pure component, species C diffuses as if it were in a binary mixture. This means that species C will suffer no diffusional interactions and its efficiency will be equal to the binary efficiency.

CALCULATIONS OF PLATE EFFICIENCIES

Integration of Equation (15) necessitates the simultaneous integration of two nonlinear equations. Numerical integration was carried out on an IBM-650 digital computer by a modification of Newton's iteration method (1). With given values of y_{jI} and y^*_j calculations were carried out in increments of N' from $N' = 0$ to the value of N' corresponding to a binary plate efficiency of 99%. At each increment the multicomponent plate efficiencies were computed so that one integration yielded multicomponent efficiencies for each species in terms of the binary efficiency of the plate. The multicomponent efficiencies are shown as a function of the binary efficiency in Figure 1. The mole fractions used are also shown, and the diffusion coefficients used are given in Table 1.

TABLE 3. DESIGN CONDITIONS

Reflux ratio = 5	Total condenser	
Pressure = 1 atm.	Single feed, distillate and bottoms streams	
Saturated liquid feed		
	Methanol, %	Isopropanol, %	Water, %
Feed composition	40	20	40
Desired distillate	98		
Desired bottoms	5		

As species C suffers no interaction effects, its efficiency is the same as the binary efficiency, while species A shows minor interaction effects, and species B very strong interaction effects. (The fact that E_A and E_B are both less than E_b is not significant; other types of interactions could be obtained with other plate inlet conditions.) The difference between E_A and E_B depends mainly on how the generalized driving force in Equation (15) differs from the binary driving force, and it is clear that the smaller the absolute value of the binary driving force $(\bar{y}_j - y^*_j)$ the larger will be the effect of the interaction term δ_m. Thus the difference between E_A and E_B in the calculations is caused entirely by the choice of a relatively small absolute value of $(\bar{y}_{BI} - y^*_B)$ and a relatively large absolute value of $(\bar{y}_{AI} - y^*_A)$.

Although E_A is always less than E_b, E_B is not only always much less than E_b, but it is actually negative for all plates whose binary efficiencies are less than about 60%. This negative efficiency is caused by reverse diffusion.

At a binary efficiency of 60% E_B returns to zero, and as the binary efficiency increases, the effect of the reverse diffusion gets increasingly smaller. As the binary efficiency approaches 100%, all the efficiencies also approach 100%. This is, of course, quit a general characteristic, since a plate which brings a binary system to complete equilibrium will also bring any multicomponent system to complete equilibrium.

CALCULATION OF NUMBER OF PLATES

Because the diffusional interactions depend on so many factors, a plate-to-plate calculation was carried out to examine the cumulative effects of the interactions in a column. To carry out the calculations vapor-liquid equilibrium data must be available, and the best example is an actual system. The system methanol-isopropanal-water was chosen, and the reported equilibrium data (3) were smoothed, extrapolated, and set up in analytical equations. Table 2 shows the equations used for the activity coefficients. They are only thermodynamically consistent for the

binary pairs, since the available data as well as the requirements of this study do not justify further refinements.

The diffusivities for this system were calculated by Gilliland's method (5) and are given in Table 2 at an average temperature for the system. In the following work A refers to methanol, B refers to isopropanol, and C refers to water. The actual diffusivities used in the calculations below were not taken from Table 2 but rather from Table 1. (The values of D_{AC} and D_{BC} in Table 1 are the arithmetic average of D_{AC} and D_{BC} in Table 2.) This simplification means that a column design will be carried out for a hypothetical system which has the same equilibrium characteristics as methanol-isopropanol-water but has $D_{AC} = D_{BC}$. This procedure, while simplifying the problem, retains its essential characteristics. The design conditions used are given in Table 3.

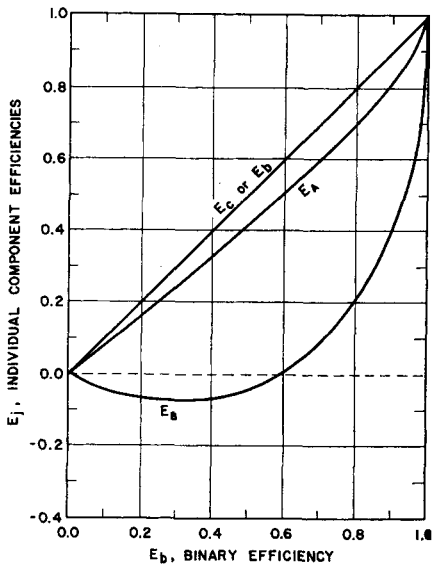

Fig. 1. Variation of efficiencies: $\bar{y}_{A1} = 0.1$, $y^*_A = 0.474$, $\bar{y}_{B1} = 0.3$, $y^*_B = 0.252$.

Plate-to-plate calculations were first carried out in the ordinary manner (4) with 100% efficiency assumed on each plate for all components. The usual operating lines and over-all balances hold (4) and constant molal overflow was assumed. Terminal compositions were assumed, and calculations were carried out on the computer. The feed-plate location was obtained by trial and error so as to minimize the total number of plates after first matching the ratio of the liquid mole fractions of the key components on the plate to the ratio in the feed. An iteration procedure was used to obtain the terminal compositions, which are given in Table 4. Figure 2 shows the variation of liquid composition throughout the column. Thirty-five ideal plates are required, with the feed on the twenty-fifth plate.

Since the single-plate calculations indicated that interaction effects were most pronounced at a binary efficiency of 40%, this value was chosen for the column calculations to maximize these effects. Thus it was assumed that every plate in the column had a binary efficiency of 40%.

Two methods of calculating real plates were used. In the first method it was assumed that all the diffusional interactions were negligible, $\delta_m = \phi_c = 1.0$, so that all the individual ternary efficiencies were 40%. The vapor leaving a plate was then not the vapor in equilibrium with the liquid but the value given by Equation (13) with $E_j = 40\%$. The results of this calculation are given by the dotted line in Figure 3 and in Table 4. Terminal compositions were essentially the same as in the ideal-plate calculation. Eighty-four plates are required with the feed on the fifty-ninth plate. If the over-all column efficiency is taken as 40%, then the ideal-plate calculations yield eighty eight real plates with the feed on the sixty third plate.

In the final method of calculation the normal plate-to-plate calculations were carried out, except that on each plate the numerical method of calculating individual plate efficiencies was used as a subroutine to obtain the vapor composition leaving the plate. The vapor rising from the still was assumed to be in equilibrium with the still liquid, so the y_{j1} for the first plate was known. The lower operating line gave the liquid composition on the plate, and equilibrium data yielded y^*_j. Equation (15) was then numerically integrated from $N' = 0$ to the value of N' corresponding to $E_b = 0.40$ to give the vapor composition leaving the plate. These calculations were repeated on each plate until the feed plate, at which point the upper operating line replaced the lower and calculations were continued until the desired methanol concentration in the distillate was obtained.

Figure 3 shows the resulting liquid compositions in the column, and Figure 4 gives the efficiencies on each plate. As before, the efficiency of component C is equal to the binary value. The efficiency of component A first drops slightly and then remains fairly constant at 28%, except for the slight discontinuity at the feed plate. The efficiency of component B jumps sharply to above 100% on the sixth plate, then drops to a negative 44% on the seventh plate before leveling off at 24%. This wild fluctuation has little effect on the total number of plates and is due to the sensitivity to composition of component B's very small generalized driving force. Thus component B's average efficiency throughout the column is 40% lower than the binary efficiency, while component A's average efficiency is 30% lower. The total number of plates needed to effect the separation is 117, equivalent to an over-all column efficiency of 30%. Thirty-three more plates are needed than would be required if all individual efficiencies were 40% and so the diffusional interactions can be said to have required an increase of 39% in the number of

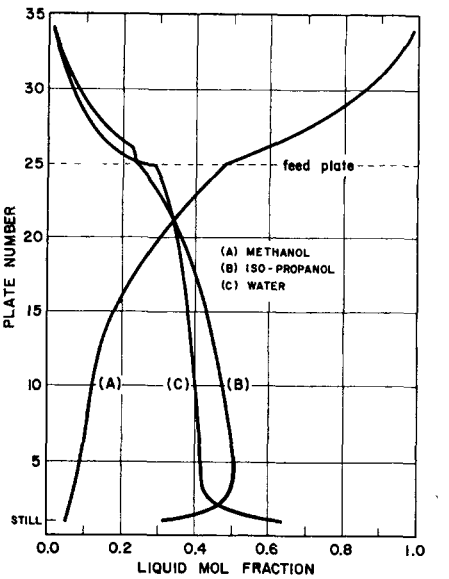

Fig. 2. Concentration profiles, ideal-plate column.

TABLE 4. RESULTS OF DESIGN CALCULATIONS

Type of calculation	Total plates	Feed-plate location: Plate	Feed-plate location: Distance up column, %	Over-all efficiency	Liquid terminal compositions: Bottoms X_A	Bottoms X_B	Bottoms X_C	Distillate X_A	Distillate X_B	Distillate X_C
Ideal	35	25	71	100	0.050	0.315	0.635	0.976	0.012	0.012
Over-all 40%	88	63	72	40						
Each component 40%	84	59	70	42	0.050	0.315	0.636	0.981	0.0094	0.0094
Calculated with interactions	117	82	70	30	0.050	0.309	0.641	0.982	0.012	0.006
Over-all 30%	117	83	71	30						

plates.

Since the individual efficiencies are roughly constant throughout the column, the relative feed-plate location is about the same for all methods of calculation, roughly 70% of the distance up the column. The results of the various calculations are given in Table 4.

As the individual efficiencies are relatively constant with position, the concentration profiles within the column are not greatly different for the three cases considered, Figures 2 and 3, although they would have been significantly different if the number of plates had been taken as equal in all examples.

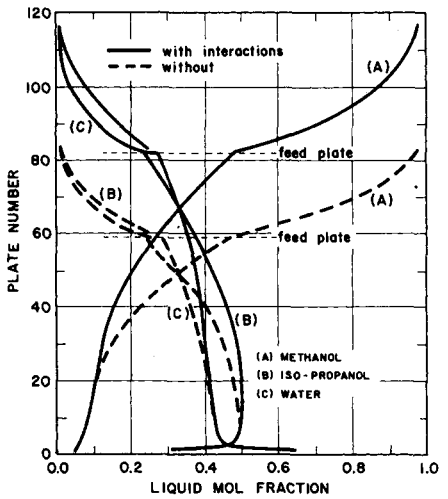

Fig. 3. Concentration profiles, column-design comparison.

It is clear that a column design which is carried out with all the individual column average efficiencies different from each other, as in the last calculation, will not yield the same terminal concentrations as a column designed with all the average efficiencies equal to each other, even though the terminal key component concentrations are equal in both designs. Thus in Table 4 the terminal compositions for the calculations with interactions differ from the results obtained when interactions were neglected. These differences could have been much larger if the terminal compositions had been chosen to be less pure. (The terminal compositions reported for the interaction case are not very accurate, since the iteration procedure used to calculate terminal compositions did not converge rapidly. Calculations were stopped before convergence, since the error had negligible effect on the other results and it was clear that the terminal compositions would not be the same as in the earlier calculations.)

In this example neglect of diffusional interactions in the design of a column would clearly lead to an underdesigned column (as compared to a design which included diffusional interactions). The rather surprising result is not that the over-all interactions were significant but rather that they were not larger, for a number of the conditions were chosen to emphasize the interaction effects. However it is not unlikely that in other systems or under other conditions the interactions may cause much more radical changes from ideal behavior than found here. If for example the wild fluctuation of the B efficiency persisted over a larger number of plates, and if a product of lower purity had been specified, then a product distribution very different from that predicted by an ideal-plate calculation could be obtained.

The above results are quite limited, and it is clear that there is a need for experimental work on multicomponent systems, especially in systems, where diffusion theory predicts strong interactions. For the time being a determination of the uncertainty in the extrapolation of binary correlations might be obtained by comparison of a system of interest with that studied here, with the results of the following section used.

GENERALIZATIONS

Unless stated otherwise the following comments would be expected to apply to any multicomponent system.

1. Highly efficient plates, that is plates which give high efficiencies for all the binary pairs, will tend to yield multicomponent efficiencies equal to each other and equal to the binary efficiencies.

2. As the fraction of the total transfer resistance in the liquid phase increases, the differences among the multicomponent efficiencies and between each multicomponent efficiency and the binary efficiency should generally tend to diminish.

3. If molecular diffusion in the gas phase plays a significant part in the transfer process, then the efficiency will in general be different for each component, and the differences among these efficiencies will increase as the differences between the diffusion coefficients of the binary pairs increase. If all the diffusion coefficients are equal, there will be no gas-side interactions (if, as is usual, equimolal countercurrent transfer takes place), and if there are also no liquid-side interactions, all the efficiencies will be equal to the binary efficiency.

4. In a ternary system where there are two similar species, and one dissimilar one, the dissimilar one will have an efficiency close to the binary value, and the efficiencies of the similar species will differ from each other and from the binary value. The restrictions in (3) above apply here also.

5. If one species in a ternary system is dilute in both the gas and liquid, its efficiency may differ from the binary value, but the efficiencies of the other two species would be expected to approach the binary efficiency. This can be extended to a four component system where two species are dilute, a five component where three are dilute, etc.

6. Diffusional interactions depend strongly on composition of the terminal points of the diffusion path. A

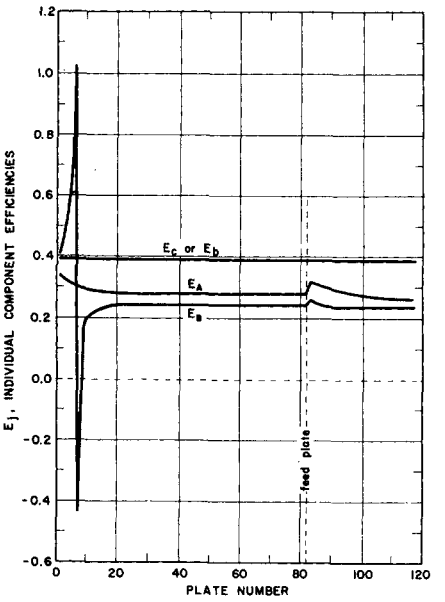

Fig. 4. Variation of efficiencies in column.

quick check of the possible magnitude of the interactions in a ternary system can be obtained by taking a few representative points in a column designed without inclusion of interactions and evaluating the ratio of the fluxes with and without interactions [Equations (1) and (7)]:

$$R = \phi_c \left[\frac{\delta_m \bar{y}_j - y^*_j}{\bar{y}_j - y^*_j} \right] \qquad (16)$$

If this ratio is close to 1, it is probable that the interactions are small and that the binary correlations can be used with some confidence. If the ratio differs significantly from 1, the correlations should be used with trepidation.

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NOTATION

D = binary diffusion coefficient, sq.ft./hr.
E = plate efficiency
k = gas-side mass transfer coefficient, lb.moles/(hr.)(sq.ft.)(mole fraction)
m = moles of vapor in bubble, lb. moles
n = flux, lb.moles/(hr.)(sq.ft.)
N = number of transfer units
R = ratio of fluxes with and without interactions
S = area, sq.ft.
x = effective film thickness, ft.
X_j, X_c = mole fraction in liquid
y = mole fraction in gas

Greek Letters

γ = activity coefficient
δ_m = diffusional interaction term defined by Equation (4)
θ = time, hr.
ρ = molar density, lb.moles/cu.ft.
ϕ_o = diffusional interaction term defined by Equation (5)

Subscripts

A, B, C = species A, B, and C, respectively
b = binary value
i = interface
j = index which refers to species A or B
1, 2 = terminal points of diffusion path
I, II = entering and leaving plate, respectively

Superscripts

* = equilibrium value
$\bar{}$ = bulk mean value
$'$ = values at any vertical position on plate

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Critical Temperatures and Pressures of Organic Compounds

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The approach presented for the prediction of critical temperatures and pressures for hydrocarbons from the van der Waals' constants *a* and *b* (1) has been extended to permit the estimation of these constants for other organic compounds. Analogously, contribution values for a number of functional groups have been established, and the majority were found to depend on the size of the organic molecule. Information presently available in the literature (4) has permitted the establishment of values for functional groups in organic compounds of the following types: alcohols, phenols, ethers, ketones, carboxylic acids and esters, amines, nitriles, and halides. These functional group contributions, in conjunction with the values previously developed for the hydrocarbons, now make possible the calculation of both van der Waals' constants from only structural considerations. Once these van der Waals' constants have been established, the critical temperature and pressure are readily calculated.

With the approach developed in this investigation critical temperatures and pressures for eighty-one organic compounds have been calculated and when compared with literature values produced average absolute deviations of 1.36% for the critical temperature and 2.82% for the critical pressure.

The use of van der Waals' constants has been presented at length for the calculation of the critical temperatures and pressures of hydrocarbons (*1, 5, 6, 7, 8*). The most recent investigation (*1*) is concerned with the establishment of the van der Waals' constants *a* and *b* for hydrocarbons of all classes. These earlier studies permit the calculation of these constants from structural considerations alone, without the necessity of utilizing any physical properties. The original work (*5, 6, 7, 8*) involves the successive building up of the molecular structure through the replacement of hydrogen by methyl groups along a definite prescribed pattern of substitution. The dependence upon a definite substitution pattern was later eliminated (*1*) through the introduction of structural group contributions, which when added together in any manner produced the van der Waals' constants directly. The latter approach has been selected for the extension of this method beyond the hydrocarbons to include organic compounds of other classes.

For a pure substance the critical temperature and pressure are related to the van der Waals' constants *a* and *b* by the relationships

$$T_c = \frac{8a}{27Rb} \tag{1}$$

$$p_c = \frac{a}{27b^2} \tag{2}$$

Conversely Equations (1) and (2) enable the calculation of the van der Waals' constants from available critical temperatures and pressures:

$$a = \frac{27R^2T_c^2}{64p_c} \tag{3}$$

$$b = \frac{RT_c}{8p_c} \tag{4}$$

Critical values found in the litera-

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