Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Grimma Jr., Galen A.(1985) 'Concentration Maxima in Ternary Distillation at Total Reflux', Separation Science and Technology, 20: 2, 85 — 99
To link to this Article: DOI: 10.1080/01496398508058352
URL: http://dx.doi.org/10.1080/01496398508058352

SEPARATION SCIENCE AND TECHNOLOGY, 20(2 & 3), pp. 85-99, 1985

Concentration Maxima in Ternary Distillation at Total Reflux

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Abstract

For a ternary fractionation system at total reflux, a procedure has been developed which predicts whether or not the component of intermediate volatility will achieve a concentration maximum at an intermediate location in the column rather than in the top or bottom product stream. Further, the value and location of any such maxima are analytically defined for a fixed feed and separation. Finally, the maximum value of the concentration maximum and its location are given for a fixed feed and column.

It is well-known that, in multicomponent distillation, components of intermediate volatility may or may not exhibit concentration maxima at intermediate points in a fractionation column rather than in the top or bottom product. Often these maxima are of little interest, but sometimes they are important to the design and operation of the column. For example, it may be necessary for the column to develop a liquid concentration profile of a component whose presence is required to enhance the relative volatility between the key components so that the desired separation between them can be achieved. Perhaps a trace component in the feed may react with other feed components if present in large concentration on the column trays. Such a component may also be corrosive, explosive, or otherwise hazardous. Examples include the potentially dangerous buildup of vinyl acetylene in C_4 hydrocarbons in the stripping section of a butadiene unit finishing column (*3*). Thus, in some cases it may be desirable to be able to predict whether or not a given component will display a concentration

0149-6395/85/2002-0085$3.50/0

maximum in a specific system and, if so, the value of that maximum and its location in the column.

There has apparently been little work done on this subject as useful literature references are surprisingly sparse. Asano and Fujita (*1*) presented a broad and general mathematical treatment for multicomponent systems at partial and total reflux, but, as its title suggests, the work to be presented here will be much narrower in scope.

At this point it is helpful to define several terms which will be needed in further discussion.

$S(\text{min})$ is the total number of equilibrium stages required (at total reflux) to achieve the specified separation of the key components.

$DR(I)$ is the distribution ratio of component I. It is the ratio of the moles of I in the top product (D) to the moles of I in the bottom product (B).

$$DR(I) = D(I)/B(I) \tag{1}$$

$R(I)$ is the recovery fraction of component I in the top product.

$$R(I) = D(I)/F(I) \tag{2}$$

Since

$$D(I) + B(I) = F(I) \tag{3}$$

$$R(I) = \frac{DR(I)}{DR(I) + 1} \quad \text{or} \quad DR(I) = \frac{R(I)}{1 - R(I)} \tag{4}$$

The Fenske (*2*) equation, derived for total reflux conditions, is then given by

$$S(\text{min}) = \frac{\ln\left[\dfrac{DR(I)}{DR(L)}\right]}{\ln\left[\alpha(I,L)\right]} \tag{5}$$

From Eq. (5) it follows that

$$DR(I) = DR(L) \cdot \alpha(I,L)^{S(\text{min})} \tag{6}$$

In this work only the liquid phase is considered, but we note that the equations which will be derived apply to the vapor phase as well. Stages will be counted from the bottom up, with the bottom stage designated as Stage

1. It is assumed that $X(I)$ and $K(I)$, the vapor–liquid equilibrium ratio, are continuous functions of stage number, not step functions as in stage-by-stage calculations. Stage number thus can take any positive value, rather than only integer numbers. The term "column" is taken to include any reboiler and/or condenser stages.

Consider a ternary system being fractionated at total reflux and whose components have constant volatility (α) relative to a reference component, taken here to be the heaviest, or least volatile, component. Arranging the components in order of decreasing volatility, Component (1) is the light key, (3) is the heavy key or volatility reference component, and (2) is the component of intermediate volatility which may or may not display a concentration maximum at some intermediate point in the column.

Also, the following terms are now defined. For a symmetrical feed,

$$X(1,F) = X(3,F) \tag{7}$$

For an equimolar feed,

$$X(1,F) = X(2,F) = X(3,F) = 1/3 \tag{8}$$

and, for a symmetrical separation,

$$R(1) = 1 - R(3) \tag{9}$$

or,

$$DR(1) = 1/DR(3) \tag{9a}$$

The Fenske (2) analysis is applied below to the liquid phase. At total reflux we may write

$$\left[\frac{X(1,N)}{X(2,N)}\right] = \alpha(1,2)^N \left[\frac{X(1,B)}{X(2,B)}\right] \tag{10}$$

and

$$\left[\frac{X(3,N)}{X(2,N)}\right] = \alpha(3,2)^N \left[\frac{X(3,B)}{X(2,B)}\right] \tag{11}$$

where N is the number of equilibrium stages and B refers to the bottom product composition.

Since the summation of the three mole fractions must equal unity, the following expression for $X(2,N)$ can be derived:

$$X(2,N) = \frac{X(2,B)}{X(2,B) + \alpha(1,2)^N \cdot X(1,B) + \alpha(3,2)^N \cdot X(3,B)} \tag{12}$$

Equation (12) may be differentiated with respect to N and the result set equal to zero to find J, that value of N which maximizes $X(2)$.

$$J = \frac{\ln\left[\left(\frac{X(3,B)}{X(1,B)}\right)\left(\frac{C}{1 - C}\right)\right]}{\ln\,[\alpha(1,3)]} \tag{13}$$

where

$$C = \frac{\ln\,[\alpha(2,3)]}{\ln\,[\alpha(1,3)]} \qquad (0 \leqq C \leqq 1) \tag{14}$$

Equation (13) is also given by Asano and Fujita (*1*).

If $0 < J < S(\text{min})$, then an $X(2,\text{max})$ greater than both $X(2,B)$ and $X(2,D)$ exists. If $J < 0$ or $J > S(\text{min})$, the $X(2,\text{max})$ calculated by Eq. (15), which follows, is physically unreal.

Substituting Eq. (13) into Eq. (12) with $N = J$:

$$X(2,\text{max}) = [1 + M \cdot X(1,B)^C \cdot X(3,B)^{1-C} \cdot X(2,B)^{-1}]^{-1} \tag{15}$$

where the mole fractions sum to unity and

$$M = \frac{(1 - C)^{C-1}}{C^C} \qquad (1 \leqq M \leqq 2) \tag{16}$$

Note that as Component (1) vanishes from the bottom product, $X(2,\text{max})$ approaches unity for $X(2,B)$ greater than zero.

Referring to Eqs. (10) and (11), we may also write, at $X(2) = X(2,\text{max})$,

$$\left[\frac{X(1,J)}{X(3,J)}\right] = \alpha(1,3)^J \cdot \left[\frac{X(1,B)}{X(3,B)}\right] \tag{17}$$

Substituting Eq. (13) into Eq. (17) yields the simple, interesting relation

$$\frac{X(1,J)}{X(3,J)} = \frac{C}{1 - C} \tag{18}$$

In addition, it can be shown from the above relations that, at J, the rate of change of Component (1) composition with stage number is the negative of the rate of change of Component (3) composition with stage number.

In a manner analogous to that by which Eq. (15) was derived, a companion equation to it may be written in terms of the top product compositions, $X(I,D)$:

$$X(2,\max) = [1 + M \cdot X(1,D)^{C} \cdot X(3,D)^{1-C} \cdot X(2,D)^{-1}]^{-1} \tag{19}$$

where the sum of the mole fractions equals unity and the other terms are the same as for Eq. (15). Note that as Component (3) vanishes from the top product, $X(2,\max)$ approaches unity for $X(2,D)$ greater than zero.

Indeed, equations of the form of (15) and (19) are found to hold for any set of stage compositions, $X(I,N)$.

Writing Eq. (5) for component pairs (1,3) and (2,3) and substituting into Eq. (14), we find that

$$C = \frac{\ln\left[\dfrac{DR(2)}{DR(3)}\right]}{\ln\left[\dfrac{DR(1)}{DR(3)}\right]} \qquad (0 \leqq C \leqq 1) \tag{20}$$

and

$$DR(2) = DR(1)^{C} \cdot DR(3)^{1-C} \tag{21}$$

Other equivalent forms of Eqs. (15) and (19) are then

$$X(2,\max) = \left\{1 + MQ\left[\frac{1 + DR(1)^{C} \cdot DR(3)^{1-C}}{(1 + DR(1))^{C} \cdot (1 + DR(3))^{1-C}}\right]\right\}^{-1} \tag{22}$$

where

$$Q = X(1,F)^{C} \cdot X(3,F)^{1-C} \cdot X(2,F)^{-1} \tag{22a}$$

where the $X(I,F)$ refer to feed composition, and, from Eq. (4),

$$X(2,\max) = \{1 + MQ[(1 - R(1))^{C}\cdot(1 - R(3))^{1-C} + R(1)^{C}\cdot R(3)^{1-C}]\}^{-1} \tag{23}$$

Simplified forms of Eqs. (15), (19), (22), and (23) result if Eqs. (7), (8), and/or (9) are assumed to hold.

Inspection of the above relations shows that, for a fixed value of C, the value of $X(2,\max)$ will increase (a) as the separation specifications are tightened, and (b) as the feed composition of either Component (1) or (3) becomes large relative to the other or if the feed composition of (2) is made larger. For very tight separations, buildups of $X(2)$ can sometimes be rather dramatic (see Table 1).

From Eqs. (5) and (13), the relative location of $X(2,\max)$ in the column can be found, for fixed $R(1)$ and $R(3)$, from

$$\frac{J}{S(\min)} = \frac{\ln\left[\left(\frac{X(3,B)}{X(1,B)}\right)\left(\frac{C}{1-C}\right)\right]}{\ln\left[\frac{DR(1)}{DR(3)}\right]} = \frac{\ln\left[\left(\frac{X(3,F)}{X(1,F)}\right)\left(\frac{1+DR(1)}{1+DR(3)}\right)\left(\frac{C}{1-C}\right)\right]}{\ln\left[\frac{DR(1)}{DR(3)}\right]} \tag{24}$$

Figure 1 shows, for an equimolar feed and symmetrical separation, how $X(2,\max)$ depends on C and parameter $R(1)$. Figure 2 overlays lines of constant $R(2)$ on Fig. 1, while Fig. 3 overlays lines of constant $J/S(\min)$ on Fig. 1. Physically unreal conditions are identified at the bottom of Fig. 1.

In the development of the equations presented here, $K(I)$ and $X(I)$ are taken as continuous functions of stage number. In equilibrium stage-by-stage calculations, however, stage number assumes only integer values, with the result that Eqs. (15), (19), (22), and (23) generally predict higher values of $X(2,\max)$ than are obtained from a corresponding stage-by-stage calculation. Table 1 gives a few illustrative comparisons between $X(2,\max)$

TABLE 1
Comparison of Eq. (23) with Stage-by-Stage Method

							Equation (23)			Stage-by-Stage		
Run	$X(1,F)$	$X(2,F)$	$R(1)$	$R(3)$	$\alpha(1,3)$	$\alpha(2,3)$	$X(2, \max)$	Stg[a]	$K(2,J)$[d]	$X(2,\max)$	Stg[a]	$K(2)$
1	0.49	0.02	.999	.001	9.0	3.0	0.2441	4.14	.6649	0.2418	4	.7421
2	0.49	0.02	.75	.25	2.0	1.1892	0.0252	1.00	.9525	0.0252	1	.9525
3	0.33	0.33	.90	.10	2.0	1.6818	0.4513	5.75	.9782	0.4507	6	.9688
4	0.40	0.20	.9999	.0001	4.0	2.0	0.9259	7.64	.9818	0.9238	8	.9682
5	0.49	0.10	.95	.00001	1.8	1.1	0.1982	3.00	.9788	0.1982	3	.9788
6	0.49	0.02	.959	.0001	16.0	3.1	0.0700	2.02	.4532	0.0700	2	.4645
7	0.01	0.01	.9999	.0001	1.8	1.39	0.7433	24.88	.9894	0.7432	25	.9869
8	0.01	0.10	.9999	.0001	1.2	1.1	0.9664	76.63	.9999	0.9664	77	.9998
9	0.49	0.02	.90	.0101	1.8	1.6	0.0450	7.25	.9769	0.0450	7	.9884
10	0.75	0.01	.998	.001	9.0	3.0	0.1338	3.31	.6339	0.1274	3	.8327
11	0.49	0.02	.999	.002	16.0	4.0	0.2111	3.49	.5298	0.1774	3	.9874
12	[c]	[c]	[c]	[c]	1.8	1.5	0.2015	2.49	.9731	0.2000	2	1.0
											3[b]	.949

[a] Stages numbered from the bottom, counting the bottom stage as 1; for Eq. (23), the value of J is the stage number minus unity, because of the material balance step.

[b] For stage-by-stage calculations, if $K(2,N) = 1.0$, then $X(2,N+1) = Y(2,N) = X(2,N)$ at total reflux.

[c] $X(2,\max)$ calculated from Eq. (15) with $X(1,B) = 0.3906$ and $X(3,B) = 0.4219$.

[d] Calculated from relative volatilities, Eqs. (15), (18), and the definition of the bubble point.

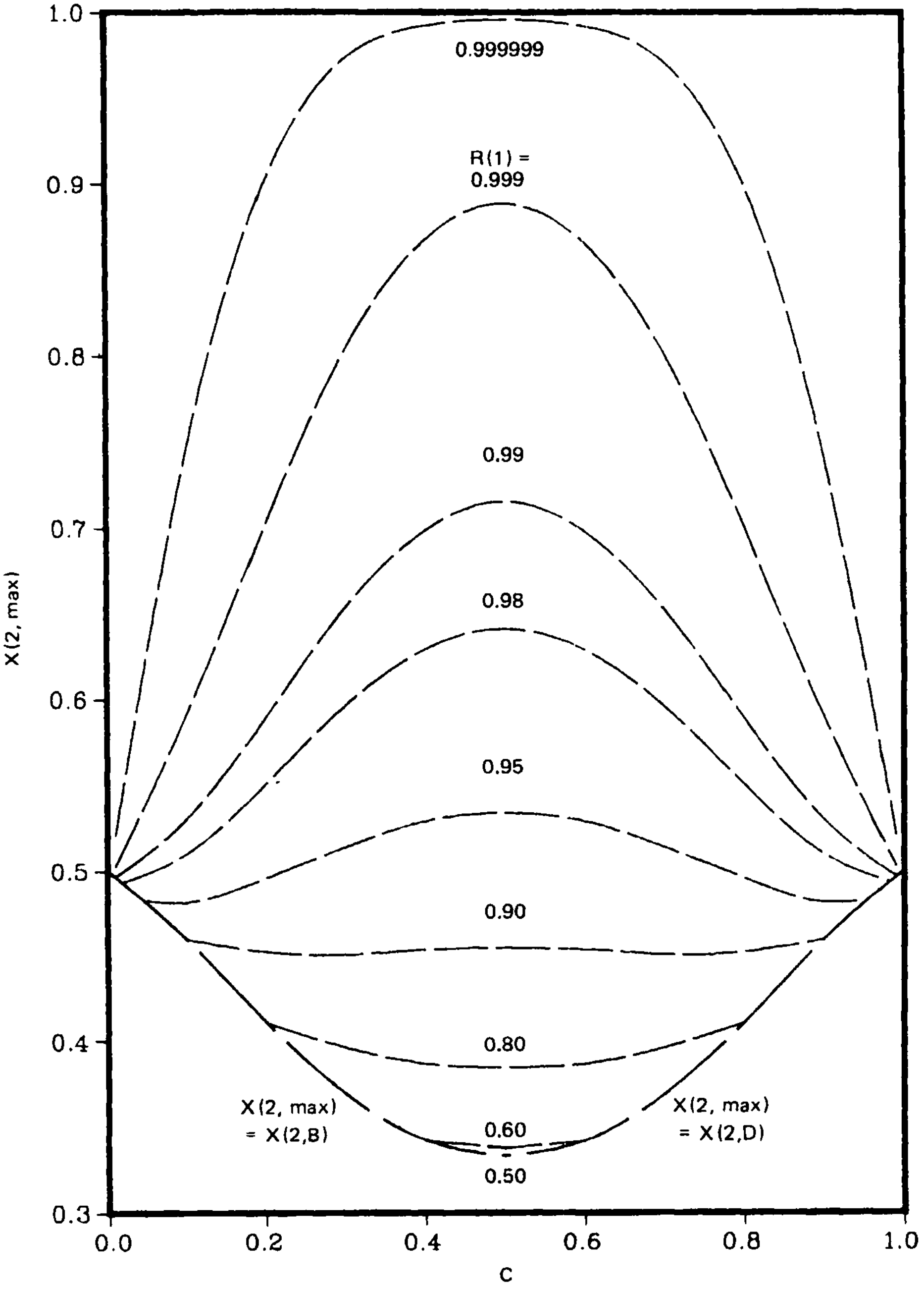

FIG. 1. Effect of C and $R(1)$ on $X(2,\mathrm{max})$ for symmetrical separations and equimolar feed.

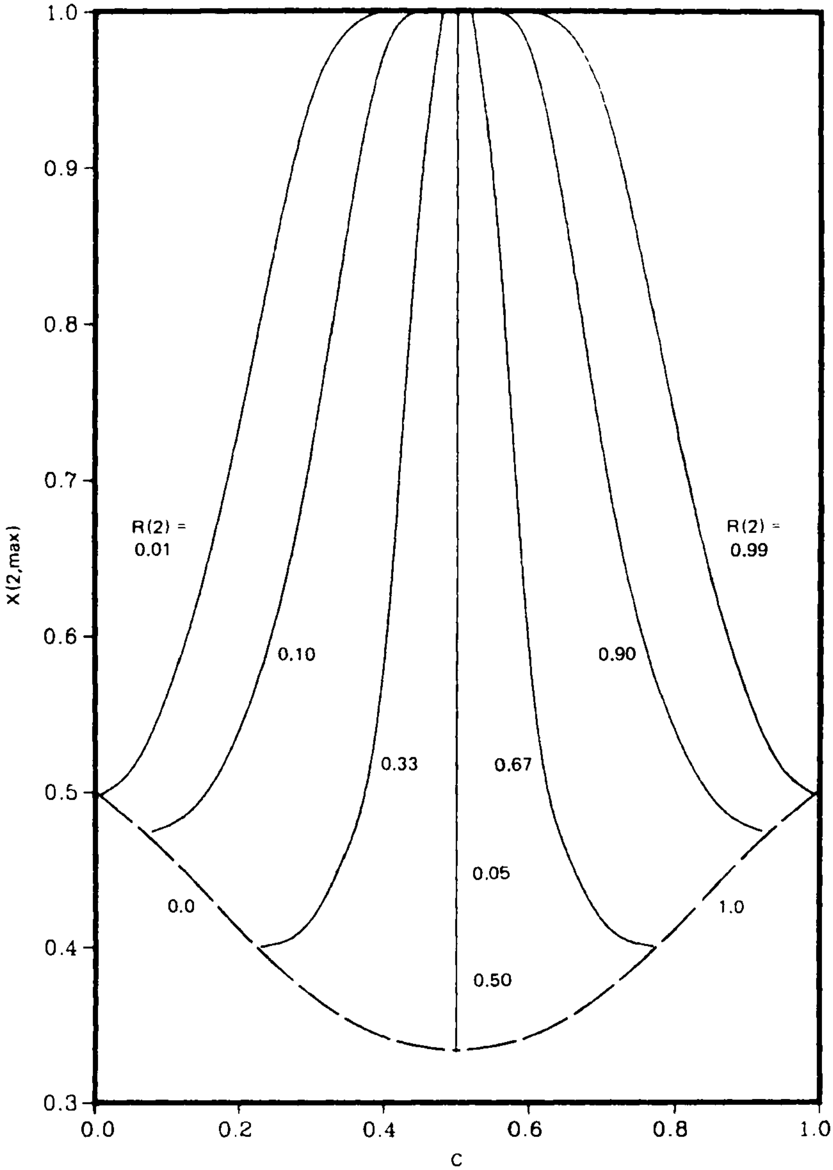

FIG. 2. Lines of constant $R(2)$ for conditions of Fig. 1.

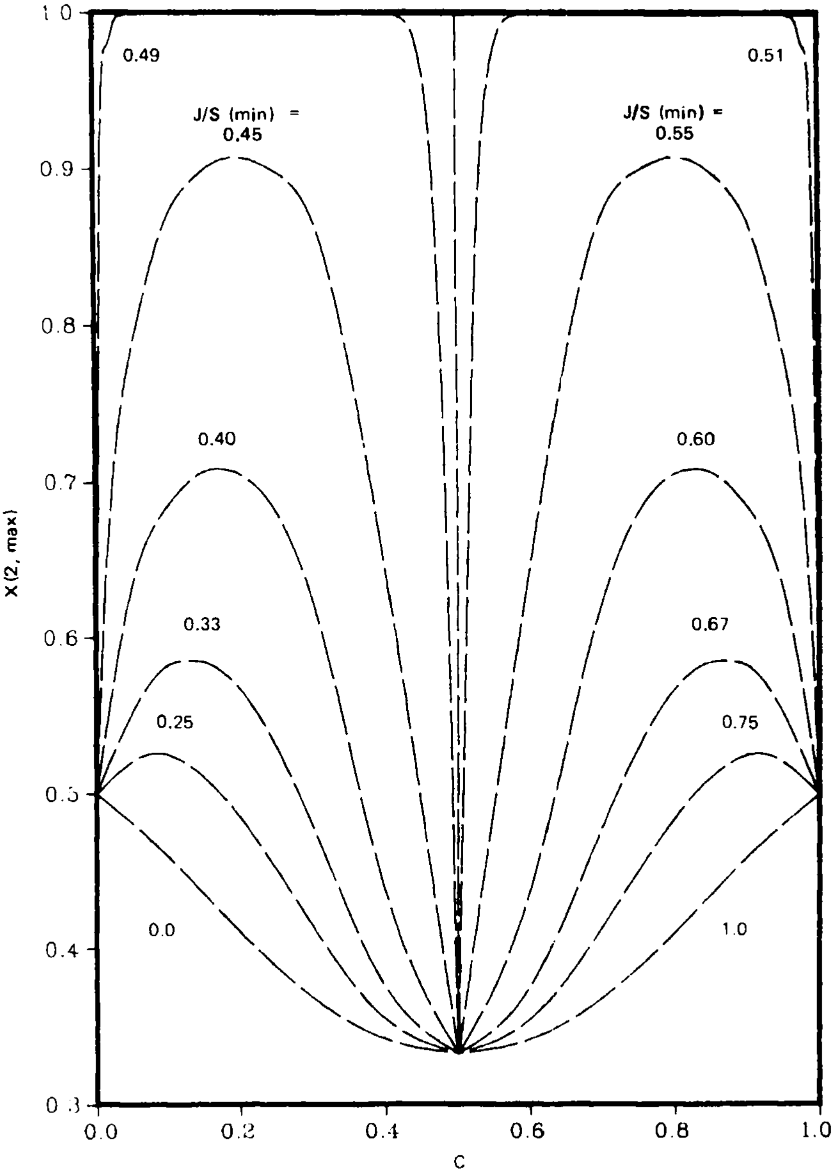

FIG. 3. Lines of constant J/S(min) for conditions of Fig. 1.

as calculated from Eq. (23) and $X(2,\max)$ found from equilibrium stage calculations. Exact agreement is obtained when J is calculated to be a whole number. If it is desired to reproduce exactly the stage-by-stage prediction of $X(2,\max)$, the following procedure is used:

1) Calculate J by Eq. (13)
2) If $0 < J < S(\min)$, then a physically real $X(2,\max)$ occurs; if so, round the value of J to the nearest whole number
3) Substitute this value of J into Eq. (12)

We now consider a specific column at total reflux fractionating, over fixed $S(\min)$ stages, a system with constant $\alpha(1,3)$ and $\alpha(2,3)$. From Eq. (6) we may write

$$P = DR(3)/DR(1) \qquad (0 \leqq P \leqq 1) \tag{25}$$

In Fig. 1, lines of constant $R(1)$ are also lines of constant P. At $P = 0$, $S(\min) =$ infinity and at $P = 1$, $S(\min) = 0$.

From Eqs. (21) and (25),

$$DR(2) = DR(1)\cdot P^{1-C} \tag{26}$$

Further, the system is not assumed to be symmetrical.

Combining Eqs. (4), (22), and (25), we get

$$X(2,\max) = \left\{1 + MQ\left[\frac{1 - R(1)(1 - P^{1-C})}{(1 - R(1)(1 - P))^{1-C}}\right]\right\}^{-1} \tag{27}$$

Equation (27) indicates that $X(2,\max)$ goes through a maximum as $R(1)$ changes at constant P, C, and feed composition. The value of $R(1)$ which gives this maximum value of $X(2,\max)$ is given by

$$\underset{\text{at } X(2,\max,\max)}{R(1)} = \frac{1}{C}\left[\frac{1}{1-P} - \frac{1-C}{1-P^{1-C}}\right] \tag{28}$$

The corresponding values for $R(2)$ and $R(3)$ are given by Eqs. (26) and (25), respectively, in conjunction with Eq. (4). The $R(I)$ are independent of feed composition.

For a column fractionating a system with $C = 0.5$, the maximum value of $X(2,\max)$ occurs for a symmetrical separation between Components (1) and (3) with Component (2), thus distributing half to the top product and half to the bottom product.

Substituting Eq. (28) into Eq. (27) yields

$$X(2,\text{max},\text{max}) = \left\{1 + M^2Q\left[\frac{(1 - P^{1-C})^{1-C} \cdot (P^{1-C} - P)^C}{1 - P}\right]\right\}^{-1} \tag{29}$$

Combining Eqs. (4), (24), and (28), we derive

$$\underset{\text{at } X(2,\text{max},\text{max})}{\frac{J}{S(\text{min})}} = \frac{\ln\left[\left(\frac{X(3,F)}{X(1,F)}\right)\left(\frac{C}{1 - C}\right)^2\left(\frac{1 - P^{1-C}}{P^{1-C} - P}\right)\right]}{-\ln (P)} \tag{30}$$

Figure 4 shows the relationships of $R(1)$, $R(2)$, and $R(3)$ at $X(2,\text{max}, \text{max})$ as a function of C and P. For clarity, only one line (for $P = 0$) is shown for $R(2)$. Some pertinent equations are:

At $P = 0$, $R(1) = 1$
$R(2) = C$
$R(3) = 0$
$X(2,\text{max},\text{max}) = 1$
At $P = 1$, $R(1) = R(2) = R(3) = 0.5$
Also, at a fixed value of P, $R(1)$ at C equals $(1 - R(3))$ at $(1 - C)$
and, $R(2)$ at C equals $(1 - R(2))$ at $(1 - C)$

As previously mentioned, the $R(I)$ on Fig. 4 are independent of feed composition. To indicate some illustrative limits of physical reality, lines of $J/S(\text{min})$ equal to zero and unity are obtained by trial-and-error from Eq. (30) and drawn in Fig. 4; these lines are valid only for a symmetrical feed.

From Eqs. (24) and (28) it is seen that the location of the Component 2 concentration maximum rises higher in the column as the $R(I)$ increase at fixed C, P, and feed composition.

The approach used in this paper does not appear to be easily extended theoretically to partial reflux conditions used in actual column design and operation. However, since the $DR(I)$ of nonkey components near typical optimum reflux ratios approximate the $DR(I)$ at total reflux (*4*), it may be useful, as a first approximation at least, to assume that such quantities as $X(2,\text{max})$, $X(2,\text{max},\text{max})$, and $J/S(\text{min})$ calculated at total reflux conditions

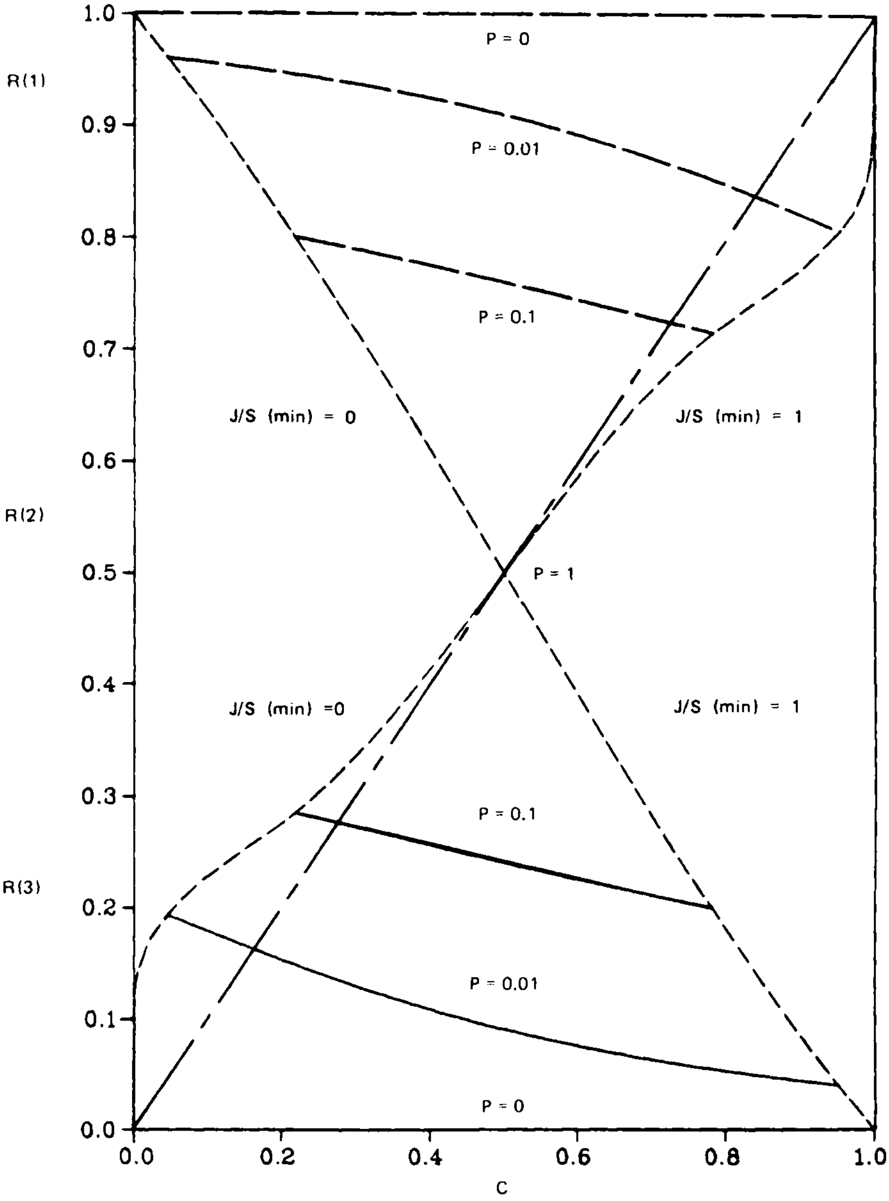

FIG. 4. Effect of C and P on $R(I)$ at X(2,max,max).

also apply at partial reflux. More specifically, we have had good success representing the results from rigorous computer calculations run on actual operating columns with Eq. (15). Even better correlations resulted when the constants "*C*" and "*M*" were not fixed by relative volatility data directly, but rather were calculated from computer results and then used in Eq. (15) to correlate concentration maxima. Assuming a bottoms composition of essentially pure Component (3) simplifies the calculations and graphical display of results. Also, the method of Asano and Fujita (*1*) may be appropriate for a particular problem.

An illustrative example will hopefully clarify some of the concepts developed in this paper.

A ternary system whose feed contains 75 mol% Component (1), 1 mol% Component (2), and 24 mol% Component (3) has relative volatilities of $\alpha(1,3) = 2.0$ and $\alpha(2,3) = 1.5$. It is desired to recover 99.9% of Component (1) in the tops and 99.8% of Component (3) in the bottoms. At total reflux, and with the above specifications, calculate

1) Whether or not a Component (2) liquid concentration maximum occurs
2) If so, what the maximum concentration is
3) Where in the column the maximum occurs
4) What the liquid concentrations are of the 2 key components at $X(2, \max)$
5) What the distribution ratio of Component (2) is
6) What the maximum value of $X(2,\max)$ is for this column with this feed
7) Where in the column this maximum occurs

From Eq. (14), $C = \ln(1.5)/\ln(2.0) = 0.585$ $R(1) = 0.999$ and $R(3) = 0.002$. From Eq. (4), $DR(1) = 999$ and $DR(3) = 0.002$. Then, from Eq. (24), $J/S(\min) = 0.466$, indicating that an $X(2,\max)$ does exist relative to both $X(2,D)$ and $X(2,B)$.

From Eq. (16), $M = 1.971$, and from Eq. (23), $X(2,\max) = 0.1042$.

From the value of $X(2,\max)$ and from Eq. (18), $X(1) = 0.5240$ and $X(3) = 0.3718$ at the point of maximum $X(2)$.

From Eq. (5), $S(\min) = 18.93$, and from Eq. (24), $J = 8.81$. As a practical consideration regarding relative column location, it should be noted that J includes any reboiler stage, while $S(\min)$ includes any reboiler and condenser stages.

From Eq. (21), $DR(2) = 4.313$ and $R(2) = 0.812$ from Eq. (4).

From Eq. (25), $P = 2.006\ E - 6$. Equation (28) then yields $R(1)$ at $X(2, \max, \max) = 0.9969$. Substituting this value in Eq. (27) gives the value of

X(2,max,max) as 0.1177. Equation (29) could have been used directly to give the same result. From Eqs. (26) and (4), $R(2) = 0.583$, which is approximately the value of C.

From Eq. (30), $J/S(\text{min}) = 0.380$. The same answer is obtained by using Eq. (25) to get $DR(3) = 0.00065$ and then substituting this value into Eq. (24).

SYMBOLS

B	bottom product
C	defined by Eq. (14)
D	top product
$DR(I)$	distribution ratio of Component I (Eq. 1)
F	feed
J	number of equilibrium stages, counting from the bottom, required to reach $X(2) = X$(2,max) or X(2, max,max)
$K(I) = Y(I)/X(I)$	vapor–liquid equilibrium ratio of Component I
M	defined by Eq. (16)
max	maximum value
min	minimum value
N	number of equilibrium stages, counting from the bottom
P	defined by Eq. (25)
Q	defined by Eq. (22a)
$R(I)$	recovery fraction of Component I in tops (Eq. 2)
S(min)	defined by Eq. (5)
$X(I)$	liquid mole fraction of Component I
$\alpha(I,L)$	volatility of Component I relative to Component L
(1), (2), (3), I, L	component designations

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Received by editor February 21, 1984
Revised May 3, 1984