A NOTE ON EQUATIONS OF TIME

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I should like to call attention to a serious limitation in Equation (5) of the paper entitled "Approximate Equations for Time of Batch Fractionations" by A. I. Johnson, Chen-Juang Huang, and F. D. F. Talbot(*1*), which contains several relationships which were derived for my course in distillation calculations at the Polytechnic Institute of Brooklyn. I had advised the students that I had no intention of publishing the work, which was distributed in mimeographed form, and that they were free to use the equations wherever they could be applied. This aforementioned limitation was not given in my original notes but was discussed and illustrated by problems in the accompanying lecture.

Equation (5) does not recognize the fact that at large values of x a large number of trays are squeezed into the upper right-hand corner of the xy diagram to produce substantially pure distillate. For example, an impossible result is obtained if the equation is used to calculate the amount of distillate produced at a reflux ratio of 3 from a feed consisting of equal moles of two components having a relative volatility of 4.0, up to the time when the instantaneous distillate is 90% of the light component. At this point the concentration x in the residue is obtained by solving the quadratic relationship derived by Smoker(*2*) for the intersection of the operating line and the equilibrium curve.

$$\frac{R}{R+1}(\alpha-1)\,x^2+\left[\frac{R}{R+1}+\frac{(\alpha-1)\,x_D}{R+1}-\alpha\right]x-\frac{x_D}{R+1}=0 \tag{1}$$

The value of x is 0.0945, and substituting in Equation (6) of reference *1* gives 71.5% of the initial batch remaining as residue. Since 90.55% of this is the less volatile component it contains 64.8% based on the original charge. This is 14.8% more than the 50% initially charged to the still.

The error lies in the initial product obtained from the still, which according to Johnson, Huang, and Talbot's Equation (3) is 170% light component (illustrated in Figure 1). Equation (5) in the previous paper(*1*) holds only when the concentration of light component in the initial charge is equal to $1/[(\alpha-1)R]$ or less. However, the equation can be used for other feed compositions if it is recognized that the distillate composition up to this point is substantially pure light component.

Thus in the previously cited problem the over-all material balance on the distillation when the residue concentration is equal to $1/(3\times 3)$, or 0.1111, mole fraction of light component is as follows:

	Charge to still moles	Residue Moles	Residue $m\%$	Distillate Moles	Distillate $m\%$
Light component	50	6.25	11.11	43.75	100
Heavy component	50	50.	88.89		
	100	56.25			

Using $W_i = 56.25$ and $x_i = 0.1111$ in Equation (5) gives a value for W of 55.1 for the final conditions, indicating that 44.9% of the batch will be distilled off when the distillate purity drops to 90%.

In this same course the relationships between residue quantity and composition were also derived from the same concept of a large number of plates in a system in which the equilibrium curve is substantially straight. The equation is

$$\ln\frac{W_i}{W}=\frac{1}{(R+1)\,(k-1)}\ln\frac{x_i}{x} \tag{2}$$

where k is the slope of the equilibrium curve.

This equation will hold only in the dilute region and is most useful in the calculation of systems at high reflux ratios, where the lower end of the operating line falls in this region. It also has the limitation that it cannot be applied directly if the initial charge concentration is greater than $1/[k+R(k-1)]$. By making the same assumption that the distillate is pure until the composition of the residue reaches this concentration, one can then apply the equation to the quantity at this time.

Thus in the previous problem the equilibrium curve can be assumed straight in the dilute region with a slope equal to the limiting slope of the constant relative volatility curve at zero concentration, namely $m = 4$. The distillate will be pure until the residue composition

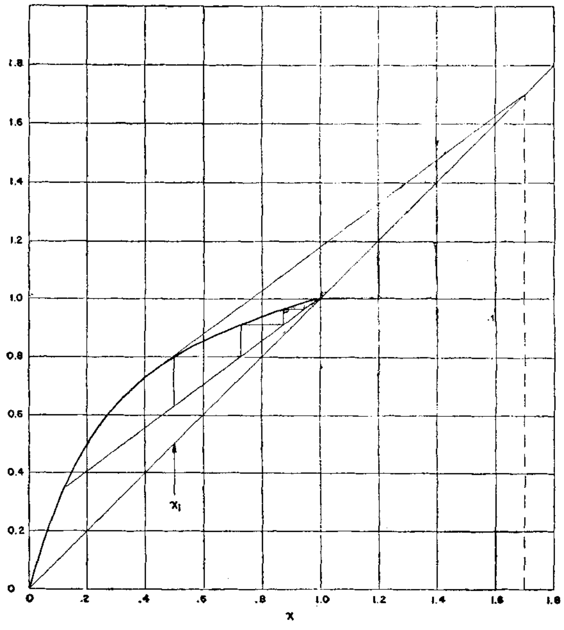

Fig. 1

is 7.7 mole % light component, when 45.8 moles of distillate will be obtained. When the overhead composition is 90%, the residue concentration x given by the equation

$$x = \frac{x_F}{k+R\,(k-1)} \tag{3}$$

is 0.069 mole fraction, and the total amount of distillate obtained up to this point can be calculated as 100 — 53.7, or 46.3, moles. The agreement between the two equations will be better at higher reflux ratios.

It is also interesting to recognize that when $R = 0$ both the authors' equation (5) and Equation (2) of this work reduce to the well-known equations derived from the integration of the Rayleigh equation without reflux for the respective cases of a constant relative volatility and a straight equilibrium curve.

The authors' Equation (34), based on a constant distillate composition, is also derived in my lecture notes for a number of trays sufficiently large so that the value of the residue composition a at total reflux will be substantially zero. In these notes I do not consider the case of a small number of trays. I have, however, also derived an alternate equation for the constant distillate composition operation. This equation can be more readily adapted for a small number of trays than the one selected by the authors of the present article for their development. It does not include the relative volatility of the components and therefore may be used for nonideal systems. The accuracy depends upon the degree to which the actual end of the operating line follows the parabolic curve.

If the slope of the operating line is assumed to vary linearly with the bottoms concentration from the initial feed concentration to a zero concentration at total reflux conditions, it may be shown that at any residue composition x the slope of the operating line is given by

$$\frac{L}{V} = \frac{x_D - y_i}{x_D - x_i} + \frac{x_i - x}{x_i}\left(1 - \frac{x_D - y_i}{x_D - x_i}\right) \tag{4}$$

where y_i is the vapor in equilibrium with the feed composition. Thus it may also be found that

$$1 - \frac{L}{V} = \frac{y_i - x_i}{x_i\,(x_D - x_i)}\,x \tag{5}$$

Substituting this value in the Bogart equation gives

$$\theta = \frac{W_i\,(x_D - x_i)^2 x_i}{V\,(y_i - x_i)} \int_x^{x_i} \frac{dx}{x(x_D - x)^2} \tag{6}$$

which upon integration between the indicated limits gives

$$\theta = \frac{W_i\,(x_D - x_i)^2 x_i}{V\,(y_i - x_i)\,x_D}\left[\frac{x_i - x}{(x_D - x_i)(x_D - x)} - \frac{1}{x_D}\ln\frac{(x_D - x_i)x}{(x_D - x)x_F}\right] \tag{7}$$

This equation can be rearranged in terms of the rate of product withdrawal from the still. Thus p_M, the maximum rate of product withdrawal, which occurs at zero time, is given as

$$p_M = \frac{V}{R_M + 1} = V\,\frac{y_i - x_i}{x_D - x_i} \tag{8}$$

where R_M is the usual minimum reflux ratio for the given feed composition x_i.

At any time θ when the residue composition is x, the instantaneous rate of product withdrawal is given as

$$p = \frac{p_M}{x_i}\,x \tag{9}$$

Eliminating y_i and x in Equation (7) by the use of relationships (8) and (9) yields the expression for the time required to reach a rate of product draw-off p

$$\theta = \frac{W_i\,x_i^2\,(p_M - p)}{p_M x_D\,(x_D p_M - x_i p)} + \frac{W_i\,x_i\,(x_D - x_i)}{p_M x_D}\ln\frac{x_D p_M - x_i p}{p\,(x_D - x_i)} \tag{10}$$

If a small number of trays are considered and so the lower end of the operating line does not approach the equilibrium curve, the value of y_i can be determined by a trial-and-error procedure, adjusting the reflux ratio until the given number of trays provide a concentration of x_i. The maximum rate of product withdrawal can thus be calculated from this reflux ratio according to Equation (8), considering this reflux ratio as the minimum for the given column.

The given number of trays can then be stepped off at total reflux on a McCabe-Thiele diagram to determine the value of a. When the equivalent assumption is made that the slope of the operating line varies linearly over the range of x_i and a from the minimum slope $R_M/(R_M + 1)$ to unity; Equations (4), (5), (6), (7), (9), and (10) became as follows:

$$\frac{L}{V} = \frac{x_D - y_i}{x_D - x_i} + \frac{x_i - x}{x_i - a}\left(1 - \frac{x_D - y_i}{x_D - x_i}\right) \tag{4a}$$

$$1 - \frac{L}{V} = \frac{(y_i - x_i)}{(x_D - x_i)}\,\frac{(x - a)}{(x_i - a)} \tag{5a}$$

$$\theta = \frac{W_i\,(x_D - x_i)^2\,(x_i - a)}{V\,(y_i - x_i)} \int_x^{x_i} \frac{dx}{(x - a)\,(x_D - x)^2} \tag{6a}$$

$$\theta = \frac{W_i\,(x_D - x_i)\,(x_i - a)}{V\,(y_i - x_i)\,(x_D - a)}\left[\frac{x_i - x}{(x_D - x_i)\,(x_D - x)} - \frac{1}{x_D - a}\ln\frac{(x_D - x_i)\,(x - a)}{(x_i - x)\,(x_F - a)}\right] \tag{7a}$$

$$p = p_M\,\frac{x - a}{x_i - a} \tag{9a}$$

$$\theta = \frac{W_i\,(x_i - a)^2\,(p_M - p)}{p_M\,(x_D - a)\,[(x_D - a)\,p_M - (x_i - a)p]} + \frac{W_i\,(x_i - a)\,(x_D - x_i)}{p_M\,(x_D - a)^2}\ln\frac{(x_D - a)\,p_M - (x_i - a)\,p}{p\,(x_D - x_i)} \tag{10a}$$

These equations are identical to the previous ones except that the origin has been moved to the point (a, a) and so all values of x are replaced by $x - a$.

It can be noted that the final equation includes only terms which are functions of the initial draw-off rate and total reflux conditions. It may thus be applied to nonideal

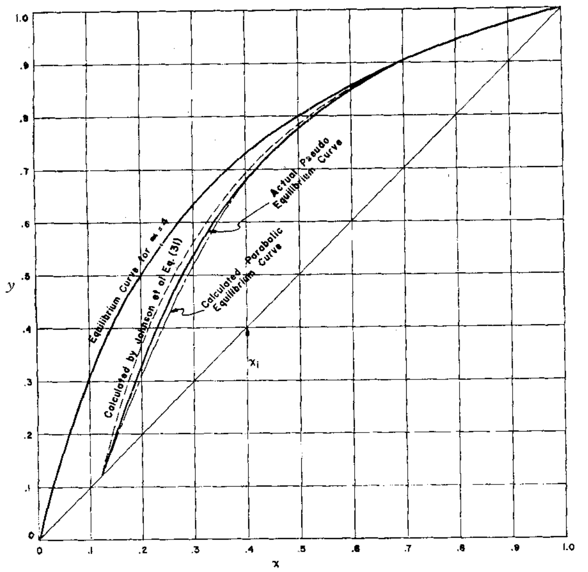

Fig. 2

systems and the agreement with the rigorous graphical technique will depend upon the deviation between the actual variation in the product draw-off rate with residue composition and the assumed linear variation. In all cases the equation can be used as a first approximation and for preliminary studies.

Calculation of the time for the distillation at constant product composition in the problem illustrated in Table 1 of the previous paper(*1*) gives a value of 8.38 by Equation (7) of this work, which compares with 8.10 calculated by Equation (34) of the previous paper. This is consistent with my experience in numerous other cases studied where the agreement was within 5% by the two equations.

In the problem given in Table 2 of the previous paper, involving two theoretical plates, the calculated time is very sensitive to the final reflux ratio. Thus calculating the final reflux ratio from Equation (9*a*) and substituting in Equation (10*a*) give a time of 1.94 hr. The trays at the corresponding reflux ratio of 7.5 were stepped off on a McCabe-Thiele diagram and the residue composition was 0.17; so this time corresponds to a somewhat greater recovery of distillate than anticipated in the authors' statement of the problem, since they specified a bottoms composition of 0.18. On the other hand, the authors' Equation (32) gives a reflux ratio of 4.4 at the final conditions. When the value of p calculated from this reflux ratio is used, the time given by the previous Equation (7) was in perfect agreement with the authors' calculated value of 1.48 hr. However, stepping this off on the McCabe-Thiele diagram gave a final residue composition of 0.20, which indicates poorer recovery than specified in the problem. On interpolation to a reflux ratio of 6.2 a residue composition of 0.18 was obtained, and at the corresponding product draw-off, Equation (7) gives a time of 1.74 hr. This latter value gives the best agreement with the previous authors' graphical integration and indicates that Equation (7) is the more readily adaptable to the problem when the final reflux ratio is properly established.

The relationship between both equations and the true value obtained by graphical integration of the Bogart equation can be readily seen from Figure 2, which has been constructed for the conditions of this problem. The pseudoequilibrium curve calculated by the authors' Equation (31) lies above the actual curve, and consequently the time required for a given change in the composition of the residue will be less than the true value. On the other hand, the parabolic equilibrium curve lies below the actual curve, and therefore a greater time will be calculated from Equations (9*a*) or (10*a*). The same relationship between the two forms of equations has also been found to hold in all the cases involving a large number of trays which I have calculated. No studies have been made, as yet to establish which equation more nearly represents the true condition encountered in practical systems.

LITERATURE CITED

1. Johnson, A. I., C. J. Huang, and F. D. F. Talbot, *A.I.Ch.E. Journal*, 51, No. 1, 111 (1955).
2. Smoker, E. H., *Trans. Am. Inst. Chem. Engrs.*, 34, 165 (1938).

REPLY

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In writing this paper(*1*) the authors were interested primarily in developing analytical expressions for treating constant reflux and constant overhead distillations for a small number of plates. The authors regret possible serious omission of references to previous work with large numbers of plates but believed this information to be generally known. While the integration of Rayleigh's equation leading to Equation (5) was first learned by one of the authors in Dr. Scheibel's excellent course, this work is treated in a very similar manner in Robinson and Gilliland's text(*2*). In this work the limitation discussed by Dr. Scheibel in his correspondence (that the overhead product cannot exceed 100%) is also treated. The authors chose their example of Table 1 so that this difficulty did not need to be considered.

In his correspondence Dr. Scheibel has proposed an alternative procedure for treating constant overhead distillation with a small number of plates. This appears to require some trial and error in its application and is quite different from the method proposed in the present authors' paper. It should be pointed out that the integration of Bogart's equation leading to Equation (34)(*1*) is uniquely different from the integration leading to Equation (10), which Dr. Scheibel covered in his course. The authors suggest that Dr. Scheibel's technique could form much of the material for a paper in this field.

The authors wish also to thank Dr. Scheibel for pointing out the following slide-rule calculation errors in Table 1:

Column 1

22.2 moles should be 19.5 moles
6.10 hr. should be 6.44 hr.

Column 2

7.11 hr. should be 8.10 hr.

There should not be so large a difference between the results by graphical analysis and those by the equations listed in the paper. This difference apparently was due to limitations in the graphical calculation.

LITERATURE CITED

1. Johnson, A. I., C. J. Huang, and F. D. F. Talbot, *A.I.Ch.E. Journal*, 51, No. 1, 111 (1955).
2. Robinson, C. S., and E. R. Gilliland, "Elements of Fractional Distillation," 4 ed., McGraw-Hill Book Company, Inc., New York (1950).