An Analysis of the Equilibrium Stage Separations Problem — Formulation and Convergence

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The formulation of a solution method for the equilibrium stage model equations involves six major decisions. Each of these decisions is analyzed and the proper choices indicated. One major contribution of the analysis was a clearer understanding of why any one solution method is not convergent on both distillation and absorber types of problems. A correct solution method is formulated for absorption and extraction problems. This method when programed in parallel with a distillation method works all but a few unusual problems with a minimum of computer time. Another contribution was the development of a procedure for solving the concentration or component rate matrix equations which avoids the computational difficulties of the Lewis-Matheson and Thiele-Geddes methods; that is the procedure avoids truncation error build up, does not require mesh points, works equally well for any number of feeds and side streams, and handles nondistributed components in the same way as distributed ones.

The solution of the equilibrium stage model for separation problems is obtained by finding a set of temperatures, phase rates, and compositions which satisfies all the equations of the model. The model equations may be expressed as follows:

1. The equilibrium relationship

$$y_{i,n} = K_{i,n} x_{i,n} \qquad (1)$$

2. The component material balance around stage n

$$l_{i,n} + v_{i,n} - l_{i,n+1} - v_{i,n-1} - f_{i,n} = 0 \qquad (2)$$

3. The energy balance around stage n

$$L_n h_n + V_n H_n - L_{n+1} h_{n+1} - V_{n-1} H_{n-1} - F_n h_{Fn} - q_n = 0 \qquad (3)$$

4. The restriction on fractional concentrations

$$\sum_i x_{i,n} = 1.0 \text{ and } \sum_i y_{i,n} = 1.0 \qquad (4)$$

In addition enough specifications must be made to determine a unique operation. The number of specifications necessary has been systematically described by Smith (*18*).

Equation (1) can be used to eliminate the vapor or raffinate concentrations throughout the other three equations. Also the above equations imply the total rate material balance equation which can be used to eliminate one set of the phase rates, V_n or L_n. If all the L_n are eliminated, the remaining equations can be expressed in functional form as follows:

$$C_{i,n}(x_{i,n}, V_n, t_n) = 0 \qquad \text{all } i \text{ and } n \qquad (5)$$

$$E_n(x_{i,n}, V_n, t_n) = 0 \qquad \text{all } i \text{ and } n \qquad (6)$$

$$M_n(x_{i,n}, V_n, t_n) = 0 \qquad \text{all } i \text{ and } n \qquad (7)$$

The functions $C_{i,n}$ represent the left-hand side of Equation (2) after substitution for the $y_{i,n}$ with Equation (1). The functions E_n represent the left-hand side of Equation (3), and the functions M_n represent either $1.0 - \sum_i y_{i,n}$ or $1.0 - \sum_i K_{i,n} x_{i,n}$.

As denoted by Equation (5) the distribution coefficients $K_{i,n}$ will in general be functions of the $x_{i,n}$; that is Equation (5) will be nonlinear in the $x_{i,n}$. However in the iterative approach necessary in the solution of multicomponent, multistage separation problems Equation (5) is always solved for the $x_{i,n}$ with a given set of $K_{i,n}$, V_n, and t_n. In other words Equation (5) is always solved as though it were linear in the $x_{i,n}$ and had constant coefficients. Therefore it can be conveniently represented by matrix equations as follows (1):

$$C_i x_i = f_i$$

or

$$C_i l_i = f_i$$

The coefficient matrices are N by N (or $N + 1$ by $N + 1$ with a partial condenser). One equation or the other must be written for each component. Both equations will be referred to as the *C-matrix equations* since they represent the equations with concentrations or component rates as the unknowns.

If the $K_{i,n}$ are assumed to be functions of temperature only (the ideal solution case), Equation (5) becomes linear in the $x_{i,n}$ and could be solved explicitly for the $x_{i,n}$. Substitution for the $x_{i,n}$ in Equations (6) and (7) would then eliminate Equation (5) from the model set and permit representation of the remaining model equation as

$$E_n(V_n, t_n) \qquad \text{all } n \qquad (8)$$

$$M_n(V_n, t_n) \qquad \text{all } n \qquad (9)$$

However the algebraic manipulations involved in this reduction are too lengthy to be convenient, and Equations (8) and (9) are never expressed directly. So even in the ideal solution case Equation (5) is always used to provide numerical values for the $x_{i,n}$ or $l_{i,n}$. These values are then substituted in Equations (6) and (7). It can be seen that the only computational difference between the ideal and nonideal solution cases is the functional form which pro-

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vides a set of $K_{i,n}$ given sets of $x_{i,n}$ and t_n (assumed or calculated in the previous trial).

FORMULATION OF SOLUTION METHODS

Distillation, absorption, stripping, extraction, and washing processes can all be described by the above set of model equations. However experience has shown that the rate of convergence of a particular method of solving the model set will vary widely from problem to problem. For example computational procedures which are very efficient for close boiling distillation cases may require elaborate forcing procedures to attain convergence on wide boiling feeds and often will not converge at all on absorption and extraction problems. Conversely procedures that work well for absorption and extraction problems often fail on the ordinary close boiling distillation problems. The purpose of this paper is to analyze the reasons for this diverse convergence behavior in terms of well-known principles of numerical analyses and simple physical facts.

The formulation of a solution method involves six major decisions. In the case of the first, second, and fourth decision the correct choice does not depend upon the type of process being calculated. The proper way to handle some of the six decisions can be deduced from a study of the results of other investigators and consequently will be discussed only briefly. The conclusions presented are drawn from a detailed study by Friday (*6*).

First Decision

The first major decision to be made in the formulation of a solution method concerns the grouping of the model equations. All of the four types of restrictions, Equations (1) through (4), can be satisfied for each individual stage one stage at a time, or each individual type of restriction can be satisfied for all stages one restriction at a time. In other words the equations can be grouped by stages or by type. All modern computer methods with the exception of Greenstadt et al. (*8*) group the equations by type. Grouping by stages essentially restricts the solution method to single feed distillation problems, makes the method susceptible to build up of truncation errors, and requires the initial assumption of end compositions. Consequently grouping by type is preferable.

Second Decision

The second decision involves order of satisfaction of the four types of restrictions. The order (12) 43 for vapor-liquid processes is common. The 1 and 2 are put together in parentheses because they are always combined [as done in Equation (5)] and satisfied simultaneously when the *C*-matrix equations are solved for the concentrations or the component rates. All those permutations in which 4 or 3 precede the (12) would require the initial assumption of all the stage concentrations. Also 3 should follow 4 so that the stream enthalpies can be computed with normalized concentrations. Since 1 and 2 are satisfied simultaneously, the orders (12) and (21) are indistinguishable in practice. The analysis for extraction is slightly different because the energy balance restrictions (type 3 equations) are not involved in the solution of the model equations. The best order for extraction is obviously (12)4.

Third Decision

The third decision concerns the selection of the appropriate type of equation to provide a given variable. From a consideration of the number of variables and equations involved it is obvious that the *C*-matrix equation must be used to generate the $x_{i,n}$. This leaves Equations (3) and (4) to be matched in either of the two possible ways with the V_n and t_n variables. For any given set of $x_{i,n}$ (from the solution of the *C*-matrix equations) the energy balances can be used to provide the new V_n or they can be used to calculate the new t_n. Likewise the satisfaction of Equation (4) can be used to supply the new t_n (bubble or dew point calculations) or used to provide new V_n and L_n through the summations

$$V_n = \sum_i v_{i,n} \tag{10a}$$

and

$$L_n = \sum_i l_{i,n} \tag{10b}$$

All of the published distillation methods use Equation (4) to obtain the new t_n and Equation (3) to generate new V_n. This matching will hereafter be called the *bubble point* (BP) method. The reverse match [new V_n from Equation (10*a*) and new t_n from energy balances] will be called the *sum rates* (SR) method because the new rate profiles are obtained by simply summing the component rates obtained from the solution of the *C*-matrix equations. The (SR) method has been generally disregarded in the past but recently has been applied to absorbers by McNeese (*16*) and to absorbers and extractors by Smith (*19*). Two of the major purposes of this paper are to show why the proper assignment of duties to the type 3 and 4 restrictions may differ between processes, and to develop a criterion which will permit the selection of the correct assignment. The authors will proceed with these objectives after a discussion of the fourth, fifth, and sixth decisions.

Fourth Decision

The fourth decision is the selection of a method of solving the *C*-matrix equations for the new stage concentrations or phase rates. The matrices are too large to make inversion practical, and some numerical method (often stage-to-stage calculations) must be used. All the published distillation methods (excepting Greenstadt et al.) differ mainly in the method used to solve the *C*-matrix equations. The method of Greenstadt et al. is excepted because they grouped the equations by stage rather than by type. All bona fide solution methods would of course give identical sets of $x_{i,n}$ or $l_{i,n}$ if an unlimited number of digits could be carried. Since that is impractical, round off or truncation error is of vital importance. If the numerical procedure utilized to solve the *C*-matrix equations is based upon an improper rearrangement of Equation (5), the build up of truncation error may become acute whenever the feed material contains components whose *K* values differ widely in magnitude and whenever the process involves multiple feeds. One or both of these difficulties severely limits most of the published distillation methods.

The build up of truncation error in a Lewis-Matheson type of stage-to-stage calculation is shown by the following equation (*20*)

$$e_{x_n} = (S_1 \ldots S_{n-1} + S_2 \ldots S_{n-1} + \ldots + S_{n-2} S_{n-1} + S_{n-1} + 1) \frac{L_1}{L_n} e_{x_1} \tag{11}$$

which relates the calculated error in x_n for a given component to the error in x_1. Now assume that x_1 is exactly the correct value for the given *S* profile except for a truncation error of 1×10^{-9}. If the separation factors are of the order of 10, the e_{x_n} will be of the order 10 for $n = 11$. Obviously stage-to-stage procedures such as the Lewis-Matheson and the Greenstadt etal. methods which must generate stage compositions from assumed end compositions as the calculations pass through the stages will not be stable in such a case.

The rearrangement of the C-matrix equations utilized in the Thiele-Geddes method avoids the difficulty of the previous paragraph. However numerical instabilities arise as soon as the Thiele-Geddes stage-to-stage calculation

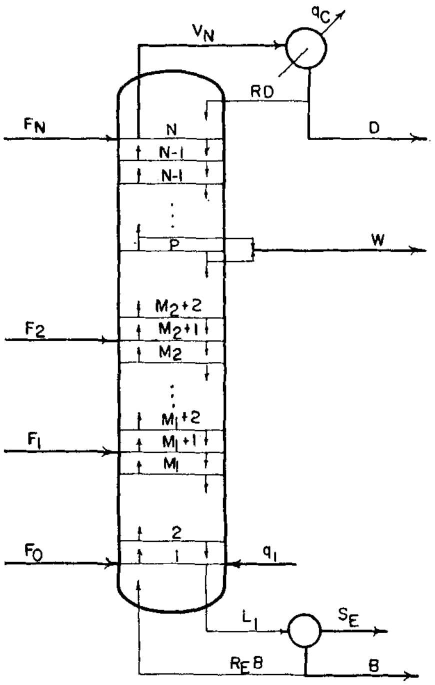

Fig. 1. Process for which Equations (14), (15), (16), (17), (18), (19), and (20) were derived.

crosses a feed stage because of a difference term which appears in the equations. This difference term is involved on all stages between feed stages and causes the Thiele-Geddes method to be basically unsuited for multiple feed columns. This of course includes absorption and extraction columns which have a feed at each end. The reader is referred to Holland *(12)* for a description of the procedures which are necessary to alleviate this deficiency.

All stage-by-stage solutions of the *C*-matrix equations (such as the Lewis-Matheson, Thiele-Geddes, and Greenstadt et al. methods) which work from both ends toward the middle suffer from two other disadvantages. First, the top down and bottom up calculations for each component must mesh somewhere in the column. Usually the mesh is accomplished at a feed stage, and if more than one feed stage exists, a choice of mesh point must be chosen for each component. As described above all components cannot mesh at the same feed stage if important build up of truncation error is to be prevented. Second, arbitrary procedures must be set up to handle nondistributed components since the concentrations of such components do not naturally take on nonzero values as the calculations proceed through the column.

A *C*-matrix solution method which is not susceptible to important truncation error, does not require mesh points, works equally well for any number of feeds and side streams, and handles nondistributed components in the same manner as distributed ones has been formulated by Friday *(6)*. Separation factor equations with the correct type of reduced coefficient matrix were derived for the column shown in Figure 1. For a liquid side stream above F_2 one has

$$l_1 = \frac{f_o\,(S\uparrow_2^N + R + S\uparrow_2^{P-2}\phi_P) + \phi_N + \phi_2 + \phi_1}{S_1S_2\ldots S_N + k(S\uparrow_2^N + R) + \phi_P\,(S_1S_2\ldots S_{P-2} + kS\uparrow_2^{P-2})} \qquad (12)$$

where

$$\phi_1 = f_1\,(S\uparrow_{M_1+2}^N + R + S\uparrow_{M_1+2}^{P-2}\phi_P) \qquad (13a)$$

$$\phi_2 = f_2\,(S\uparrow_{M_2+2}^N + R + S\uparrow_{M_2+2}^{P-2}\phi_P) \qquad (13b)$$

$$\phi_N = \begin{cases} f_N\,(1+R)\left(\dfrac{L_P - W}{L_p}\right) & \text{for } n < P \quad (14a) \\ f_N\,(1+R) & \text{for } n \geq P \quad (14b) \end{cases}$$

$$\phi_P = \frac{W}{L_P}\,S_{P-1}\,(S\uparrow_{P+1}^N + R) \qquad (15)$$

$$k = \left(1 + \frac{S_e\,x_{S_e}}{l_1}R_e\right)/(1 + R_e) \qquad (16)$$

and

$$S\uparrow_u^v = S_uS_{u+1}\ldots S_v + S_{u+1}S_{u+2}\ldots S_v + \ldots S_{v-1}S_v + S_v + 1 \qquad (17)$$

where u and v are any two stages. If $v = u$, then $S\uparrow_u^u = S_u + 1$. If $v = u - 1$, then $S\uparrow_u^{u-1} = 1.0$. The other symbols are evident from Figure 1. Note that Equation (12) contains no minus signs. Also note that it contains only one component rate. Therefore l_1 can be immediately calculated from the specified external stream component rates and the S profile obtained from the results of the previous trial (or *initially assumed*). *The* l_1 *obtained* is exactly (except for the single truncation) that value which corresponds to the given S profile and set of specifications. However if one attempts to obtain l_2, l_3, etc. by a stage-by-stage calculation up the column, the error build up described by Equation (11) occurs. This can be prevented by obtaining l_2 from

$$l_2 = \frac{v_1\,(S\uparrow_3^N + R + S\uparrow_3^{P-2}\phi_P) + \phi_N + \phi_2 + \phi_1}{S\uparrow_2^N + R + S\uparrow_2^{P-2}\phi_P} \qquad (18)$$

which is the equation obtained in the top down derivation if one stops one stage short of the bottom stage. The v_1 is obtained from l_1 by use of the general equilibrium expression

$$v_{i,n} = S_{i,n}\,l_{i,n} \qquad (19)$$

and contains the truncation error in l_1 multiplied by S_1. However note that in Equation (18) the contribution of the v_1 to the l_2 is essentially v_1/S_2, and this effectively cancels the multiplication of truncation error. This cancel*lation plus the absence of difference terms provides com*position profiles with negligible truncation error. No mesh points are needed, and multiple feeds and side streams place no strain on the method. Also any nondistributed component rate will appear naturally (that is become greater than the smallest permissible number in the computer) as the l's are calculated up the column. This is *possible* because the ϕ_N, ϕ_1, and ϕ_2 terms contain the component feed rates.

The normalized stage concentrations are provided by

$$x_{i,n} = \frac{l_{i,n}}{\sum_i l_{i,n}} \qquad (20a)$$

and

$$y_{i,in} = \frac{v_{i,n}}{\sum_i v_{i,n}} \qquad (20b)$$

Another method for reduction of the tridiagonal coefficient matrix is described by Grabbe et al. (*7*). The use of his recurrence formulas involve about the same arithmetic effort as the separation factor equations but are less cumbersome to derive. Ball (*3*) has indicated the use of the recurrence formulas is also essentially free of truncation difficulties.

Fifth Decision

The fifth major decision involves the selection of a method of calculating the new t_n for whichever choice was made in the third decision. If the BP assignment of restrictions is made, the new t_n can be calculated from the normalized stage concentrations by any of several well-known bubble point procedures. If the SR assignment is chosen, the new t_n can be obtained by a convenient procedure reported by Surjata (*22*) and developed independently by Friday (*6*). Briefly the procedure is as follows.

The solution of the C matrix has provided new $x_{i,n}$, V_n, and L_n. Newton's approximation is applied to Equation (6) to provide the new t_n. E_n involves three temperatures, t_{n-1}, t_n, and t_{n+1}. Newton's approximation is

$$E_n(t_{n-1}, t_n, t_{n+1})_{k+1} = E_n(t_{n-1}, t_n, t_{n+1})_k + \frac{\partial E_n}{\partial t_{n-1}} \Delta t_{n-1} + \frac{\partial E_n}{\partial t_n} \Delta t_n + \frac{\partial E_n}{\partial t_{n+1}} \Delta t_{n+1} \tag{21}$$

where the letter k represents the iteration number. Now define stream heat capacities as $c_n = \partial h_n/\partial t_n$ and $C_n = \partial H/\partial t_n$. If ideal solutions are assumed

$$h_n = \sum_i x_{i,n}\, h_{i,n} \text{ and } H_n = \sum_i y_{i,n}\, H_{i,n}$$

Evaluating the partials in Equation (21), setting the right side equal to zero, and rearranging one gets

$$(L_n c_n + V_n C_n)\Delta t_n - V_{n-1} C_{n-1} \Delta t_{n-1} - L_{n+1} c_{n+1} \Delta t_{n+1} = -E_{n,k} \tag{22a}$$

Equations (22) form a linear set of equations in the Δt's. The coefficient matrix is tridiagonal. Such a set is easily solved as follows. The n-th member can be expressed as

$$a_n \Delta t_n - b_{n-1} \Delta t_{n-1} - d_{n+1} \Delta t_{n+1} = -E_n \tag{22b}$$

The Δt_{n+1} can be eliminated from each to give the reduced set whose n-th member is

$$\Delta t_n = E'_n + b'_{n+1} \Delta t_{n-1} \tag{23}$$

The recurrence relationships for E'_n and b'_{n-1} are

$$E'_n = \frac{-E_n + d_{n+1} E'_{n+1}}{a_n - b'_n d_{n+1}} \tag{24}$$

and

$$b'_{n-1} = \frac{b_{n-1}}{a_n - b'_n d_{n+1}} \tag{25}$$

For stage N

$$E'_n = \frac{E_n}{a_n} \tag{26}$$

and

$$b'_{N-1} = \frac{b_{N-1}}{a_N} \tag{27}$$

Evaluation of the E'_n and b'_n from the trial values of the $x_{i,n}$, V_n, L_n, and t_n permits calculation of the Δt_n from Equation (23). The set of t_n which satisfy the linearized Equation (6) are then provided by

$$t_{n,k+1} = t_{n,k} + \Delta t_{n,k} \tag{28}$$

This method of establishing a new temperature profile after each trial has been used very successfully in several applications of the SR method.

Sixth Decision

This last decision concerns the method of obtaining the new V_n and L_n. Actually there is little choice here. In the SR method the new V_n and L_n are immediately available from Equations (*10a*) and (*10b*). In the BP method as practiced in this work the equations

$$V_n = \frac{F_n h_{F_n} + q_n + V_{n-1} H_{n-1} - L_n h_n + (L_n - F_n - V_{n-1})\, h_{n+1}}{H_n - h_{n+1}} \tag{29a}$$

and

$$L_{n+1} = V_n + L_n - F_n - V_{n-1} \tag{29b}$$

were used to compute new V_n and L_n in a stage-by-stage manner up the column starting with an L established by a combination of material and energy balances around one end of the column. This procedure allowed the BP and SR methods to be applied to different sections of the column in cases where neither the BP or SR methods alone were successful. However early work showed the use of both methods did not improve convergence to any great extent in the difficult problems. In all the convergence work described later the application of Equation (29*a*) started at the bottom stage.

One of the reasons why the BP method sometimes becomes instable on moderately wide boiling feeds is that the quantity $(H_n - h_{n+1})$ may go from a positive to a negative value as the boiling range of the material increases. When $(H_n - h_{n+1})$ is near zero, the V_n obtained from (29*a*) is of course very erratic and could even become indeterminate. One of the things done by Holland (*13*) and co-workers to extend the Thiele-Geddes method to systems where it is basically instable was to rearrange the energy balance so that the denominator term is always approximately equal to the latent heat of vaporization. For example below the lowest feed the conventional equation

$$V_n = \frac{q_1 + B(h_{n+1} - h_1)}{H_n - h_{n+1}} \tag{30}$$

was rearranged to the constant-composition form

$$V_n = \frac{B\left(\sum_{i=1}^{C} x_{i,B} h_{i,n+1} - h_1\right) - q_1}{H_n - \sum_{i=1}^{C} y_{i,n} h_{i,n+1}} \tag{31}$$

Equation (31) has no inherent advantage over (30) when $(H_n - h_{n+1})$ differs widely from zero but should be used if an attempt is made to apply the BP method to problems where $(H_n - h_{n+1})$ approaches zero.

BP VS. SR METHODS

Before the convergence of the BP and SR methods are investigated mathematically, the following qualitative discussion establishes an intuitive basis for both.

A logical basis for matching Equations (3) and (4) with the t_n and V_n variables is to use for each variable that restriction which physically determines the variable's value. Consider two extreme types of feed mixtures, close boiling and wide boiling, each of which is fed to an adiabatic flash stage which produces vapor and liquid product streams from a completely specified feed. For simplicity let the close boiling feed be the limiting case, a pure component. For such a feed the stage temperature is the boiling point of the component at the specified pressure. A change in the feed enthalpy will change the phase rates but not the stage temperature. Obviously the energy balances should be used to calculate V and L while the type 3 equations are satisfied by a bubble or dew point calculation (trivial in this extreme case). This assignment of duties for the type 3 and 4 equations is that used in all the distillation methods (*11*, *21*) for close boiling feeds.

Now let the wide boiling material be a mixture of two components, one very volatile and the other quite nonvolatile. For such a feed the amounts of each phase leaving the stage are almost completely determined by the distribution coefficients. Over a wide temperature range the volatile component will leave predominately in the vapor, while the heavy component leaves predominately in the liquid phase. Additional enthalpy in the feed will raise the stage temperature but have little effect on the V and L rates. Obviously in this case the energy balance (type 3) equation should be used to calculate the stage temperature. The type 4 equations can then be satisfied by summing the $l_{i,n}$ and $v_{i,n}$ provided by the solution of the C-matrix equations to give the new L_n and V_n. This is the basic procedure followed in the extraction (*19*) and absorption (*16*, *19*) methods for wide boiling feeds.

The SR method has worked easily all extraction and absorption problems tried to date. In extraction the SR method is simplified by the absence of the energy balance equations from the model set. All stage temperatures are specified a priori, and while energy balances are required eventually to calculate the heat transfer loads necessary to maintain the specified temperature profiles, the energy balances are not a part of the equilibrium stage model set of equations. Extraction problems are usually similar to absorption in that the range of distribution coefficient values is wide; that is the raffinate components have large K values compared with the solvent components. Even in those cases where all the K values are roughly of the same magnitude, convergence of extraction problems by the SR method is aided by the absence of the unsettling influence of changing stage temperatures from trial to trial. As far as the authors know the SR method works all extraction problems, but a complete check on the general validity of this statement is hindered by the scarcity of multicomponent equilibrium data.

One more simple illustration will be given to show why bubble points should not be used to establish new stage temperatures with wide boiling mixtures. Flash calculations were made on a close boiling (50-50 molar mixture of iC_5 and nC_5) feed and a wide boiling (53.05% C_2H_6 and 46.95% nC_8) feed. The exact (except for truncation) solutions are shown in Table 1. To illustrate the bubble point difficulty in wide boiling feeds a single iteration was made manually for each case. The correct temperatures (from Table 1) were assumed, but the assumed V's were 10% larger than the correct V's in Table 1. The assumed L's were lower than the correct L's by corresponding amounts. The classical flash equations $l_i = f_i/(1 + S_i)$ and $x_i = l_i/\Sigma\, l_i$ provided calculated liquid compositions. Values of 0.46 and 0.54 for the iC_5 and nC_5 were obtained for Case I. The corresponding bubble point temperature was 216.1°F., essentially unchanged from that in Table 1. For Case II the calculated x_i were 0.088 and 0.912 for the C_2H_6 and nC_8, and the corresponding bubble point was 220°F., a change of 24.5°F. from the Table 1 value. The bubble point (and dew point) temperature are extremely sensitive to small composition and phase rate changes in wide boiling mixtures and should not be used to determine new t_n in such cases.

TABLE 1.

Case I	Case II
$F =$ 100 moles/hr.	$F =$ 100 moles/hr.
$h_F =$ 20,900 Btu/mole	$F =$ 16,100 B.t.u./mole
$x_{F,iC5} =$ 0.5	$x_{F,C2H6} =$ 0.5305
$x_{F,nC5} =$ 0.5	$x_{F,nC8} =$ 0.4695
$t =$ 216°F.	$t =$ 195.5°F.
$V =$ 53.3	$V =$ 49.98
$L =$ 46.7	$L =$ 50.02
$x_{iC5} =$ 0.464	$x_{C2H6} =$ 0.104
$x_{nC5} =$ 0.536	$x_{nC8} =$ 0.896

The above discussion has given physical reasons for the observed instability of the BP method on wide boiling feeds. For analogous reasons the SR method is instable on close boiling feeds. The regions of convergence of any form of these two general approaches can be defined quantitatively as shown below.

CONVERGENCE OF THE BP AND SR METHODS

The BP and SR methods are convergent for close boiling and wide boiling mixtures, respectively. To apply the appropriate method to a given problem some means of characterizing the feed and defining the respective areas of convergence is needed. An obvious parameter for characterization of feed mixtures is the difference between the dew and bubble point temperatures. This difference will be denoted as Δ_{DB}. (Extraction systems will be omitted from this discussion since they can readily be handled by the SR method.)

A simple but laborious means of determining convergence over the range of possible mixtures which enter a stage would be to attempt a large number of problems and note whether convergence occurs or not. Initial assumptions would cloud the results however. A better way is to apply the condition for asymtotic stability to a selected group of problems which cover a suitable range of Δ_{DB}. Asymtotic stability means that if the initial assumptions are sufficiently good in any successive substitution procedure, the method will converge because each iteration reduces the error.

Early in this paper the possibility of reducing the model set of equations to Equations (8) and (9) was discussed. Although this is never done in any of the known solution methods, it will be convenient in this convergence discussion to represent all successive substitution procedures (both BP and SR methods) as the solution of the following system of equations:

$$\begin{aligned} V_n &= G_n\,(V_1 \ldots V_N, t_1 \ldots t_N) \\ t_n &= F_n\,(V_1 \ldots V_N, t_1 \ldots t_N) \end{aligned} \qquad (32)$$

where $n = 1, 2 \ldots N$. The G and F functions are not specific algebraic equations but rather procedures for generating new V_n and t_n values from the old V and t profiles. These procedures vary from one solution method to another. The criterion for asymptotic stability of any particular procedure is developed as follows.

Denote the correct set of $V_1 \ldots V_N$ as $a_1 \ldots a_N$ and the correct set of $t_1 \ldots t_N$ as $b_1 \ldots b_N$. Expansion around these correct values with a first-term Taylor's series gives the following approximations for the functions in the k-th iteration:

$$G_n(V_1 \ldots V_N, t_1 \ldots t_N)_k \doteq G_n(a_1 \ldots a_N, b_1 \ldots b_N) + \sum_{m=1}^{N} \frac{\partial G_n}{\partial V_m}\,(V_m - a_m)_k + \sum_{m=1}^{N} \frac{\partial G_n}{\partial t_m}\,(t_m - b_m)_k$$

$$F_n(V_1 \dots V_N, t_1 \dots t_N)\,(V_1 \dots V_n, t_2 \dots t_n)_k = F_n(a_1 \dots a_N, b_1 \dots b_N) + \sum_{m=1}^{N} \frac{\partial F_n}{\partial V_m}(V_m - a_m)_k + \sum_{m=1}^{N} \frac{\partial F_n}{\partial t_m}(t_m - b_m)_k$$

Noting from Equations (32) that

$$G_n(a_1 \dots a_N, b_1 \dots b_N) = a_n$$

$$F_n(a_1 \dots a_N, b_1 \dots b_N) = b_n$$

and

$$G_n(V_1 \dots V_N, t_1 \dots t_N)_k = V_{n,\,k+1}$$

$$F_n(V_1 \dots V_N, t_1 \dots t_N)_k = t_{n,\,k+1}$$

one gets the following approximate relations between the errors in successive iterations:

$$(a_n - V_n)_{k+1} \doteq \sum_{m=1}^{N} \left[\frac{\partial G_n}{\partial V_m}(a_m - V_m)_k + \frac{\partial G_n}{\partial t_m}(b_m - t_m)_k \right] \tag{33}$$

$$(b_n - t_n)_{k+1} \doteq \sum_{m=1}^{N} \left[\frac{\partial F_n}{\partial V_m}(a_m - V_m)_k + \frac{\partial F_n}{\partial t_m}(b_m - t_m)_k \right] \tag{34}$$

When one denotes all errors in both the V_n and t_n variables by e, all of these equations can be represented in vector notation as

$$e_{k+1} \doteq J\, e_k \tag{35}$$

where J represents the Jacobian matrix

$$\begin{bmatrix} \frac{\partial G_1}{\partial V_1} \cdots \frac{\partial G_1}{\partial V_N} & \frac{\partial G_1}{\partial t_1} \cdots \frac{\partial G_1}{\partial t_N} \\ \vdots & \\ \frac{\partial G_N}{\partial V_1} \cdots \frac{\partial G_N}{\partial V_N} & \frac{\partial G_N}{\partial t_1} \cdots \frac{\partial G_N}{\partial t_N} \\ \frac{\partial F_1}{\partial V_1} \cdots \frac{\partial F_1}{\partial V_N} & \frac{\partial F_1}{\partial t_1} \cdots \frac{\partial F_1}{\partial t_N} \\ \vdots & \vdots \\ \frac{\partial F_N}{\partial V_1} \cdots \frac{\partial F_N}{\partial V_N} & \frac{\partial F_N}{\partial t_1} \cdots \frac{\partial F_N}{\partial t_N} \end{bmatrix}$$

For any square matrix there are nontrivial row vectors u such that (2)

$$J\,u = \lambda\,u \tag{36}$$

The characteristic equation of J is

$$|J - \lambda I| = 0 \tag{37}$$

It represents a polynomial of N-th order in λ, and if any solution method represented by Equations (32) is to be convergent, all of the N roots λ_i must be less than unity in absolute value (9).

The largest root value can be found by the well-known power method. Associated with each root λ_i there is a latent vector w_i. In general the w_i are linearly independent (*10*). Therefore any vector in N space can be represented by a linear combination of the w_i. The vector u can be represented by

$$u = \sum_{i=1}^{N} c_i\, w_i \tag{38}$$

If Equation (38) is successively premultiplied by J, the result after k multiplications is from Equation (36)

$$J^k u = \sum_{i=1}^{N} c_i\, \lambda_i^k\, w_i \tag{39}$$

When k becomes sufficiently large, the only numerically important term in the summation will be the $\lambda_{\max}$ term, and

$$J^k u \doteq (c\,\lambda\,w)_{\max} \tag{40}$$

Since the vector $J^{k+1}u$ is then greater than $J^k u$ by the factor $\lambda_{\max}$, the $\lambda_{\max}$ is given by the ratio $|J^{k+1}u|/|J^k u|$ or more conveniently from the ratio of two corresponding elements of the two vectors

$$\lambda_{\max} \doteq \left(\frac{J^{k+1}u}{J^k u} \right)_{\text{element } i} \tag{41}$$

For any given J the $\lambda_{\max}$ was obtained by initially assuming $u = (1,1,1 \dots 1)$ and evaluating Equation (41) with successive k values until the λ obtained ceased to change with k. Between each trial it is helpful to normalize the vector $J^k u$ by dividing each element by the first element.

Since J is not symmetric, $\lambda_{\max}$ may be complex. If so the above iteration will not converge, and the solution for $\lambda_{\max}$ must be modified as indicated by Bodewig (*4*). The application of Bodewig's modification to the problem at hand is described by Friday (*6*).

The $\lambda_{\max}$ was calculated for both BP and SR solution methods on a series of test problems which covered a suitable range of number of stages and feed Δ_{DB}. The results obtained of course depended upon the particular formulation used in the BP and SR methods. In this work the C-matrix was solved in both methods by the stripping factor equations of which Equations (12) and (18) are examples. The SR method then generated new t_n by Equations (21) to (28) and new V_n and L_n from Equations (10*a*) and (10*b*). The BP method used obtained new t_n by bubble points and new V_n and L_n from Equations (29*a*) and (29*b*). It should be clearly understood that if either method is modified, the convergence behavior will change. For example substitution of the modified energy balances [Equation (31) is an example] for Equation (29*a*) would undoubtedly extend the convergence region for the BP method somewhat. Also it should be understood that the functions or procedures represented by the G_n and F_n in Equation (32) would include any extraneous convergence-forcing device such as the θ method of Lyster et al. (*15*).

The partial derivatives in J must be evaluated at the solution. The expression of these derivatives in explicit algebraic form is impractical in any general solution method formulation. Therefore it was necessary to evaluate the derivatives by a finite difference method. If the correct set of t_n and V_n are known

$$\frac{\partial G_n}{\partial t_m} = \frac{G_n(V_1 \dots V_N, t_1 \dots t_m + \delta \dots t_N) - G_n(V_1 \dots V_N, t_1 \dots t_N)}{\delta} \tag{42}$$

Each of the correct V_n and t_n were incremented separately, and the method being investigated (either the BP or the SR method) was used to find the corresponding new values for all the t_n and V_n. Equation (42) then supplied the partial derivatives. It was found that a δ of 1.0 was

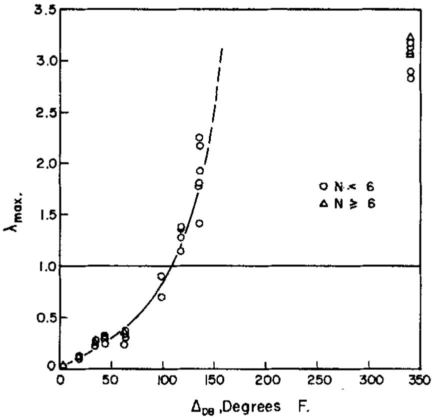

Fig. 2. Region of convergence for BP method without damping.

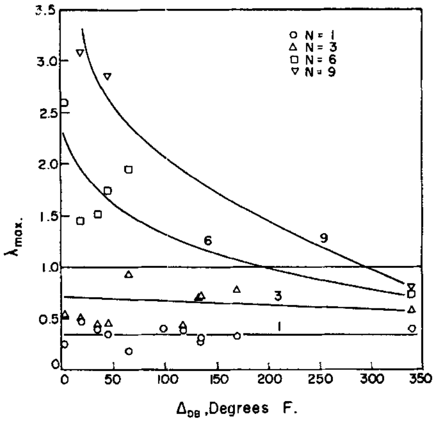

Fig. 3. Regions of convergence of SR method for various N values without damping

sufficiently small to provide accurate values of the derivatives. Reduction of δ below 1.0 had essentially no effect on the values obtained.

Test Problems

A special type of test problem was used to eliminate the necessity for a final solution in the evaluation of the partial derivatives. Each test problem involved an adiabatic section of equilibrium stages with a liquid feed to the top stage and a vapor feed to the bottom stage (simple absorber flow). The liquid and vapor feeds were the products from a single stage flash of the desired feed mixture. The temperature of the flash was adjusted to give approximately a 50-50 liquid-vapor split. The contacting of equilibrium streams in the adiabatic section of course produced no change in composition, rate, or temperature of either stream. Therefore the flash calculation results provided the final solution values of all the $x_{i,n}$, t_n, V_n, and L_n in the multistage test problem.

Eleven flash separator feeds composed of mixtures of the paraffin hydrocarbons C_2H_6 to C_8H_{18} were used. The Δ_{DB}'s ranged from zero for a pure iC_4 feed to 340°F. for a C_2H_6 — nC_8H_{18} feed. Seven of the feeds were binaries, while the other four contained five, six, seven, and nine components respectively.

Each set of flash products was fed to column sections which contained from two to nine stages. The λ_{max}'s obtained for the BP method for the various combinations of Δ_{DB}'s and number of stages is shown in Figure 2. The curve through the points was located by visual inspection. No attempt was made to define the curve at high Δ_{DB} because it was clear that no λ_{max} less than 1.0 occurred there. Apparently the curve goes through an undefined maximum near $\Delta_{DB} = 200$°F. because the $(H_n - h_{n+1})$ term in the denominator of the energy balance equations in the particular BP method used passes through zero in that region. Substitution of the constant-composition form of the energy balance would probably cause the curve in Figure 2 to rise less precipitously and go through the points in the upper right-hand corner without passing through a maximum. Once the region where $(H_n - h_{n+1})$ is close to zero is passed, either form of the energy balance is suitable. With either form the BP method used obviously is instable at high Δ_{DB}'s. The number of stages appears to have little effect in the convergent region. These results are in accordance with the long-standing experience of rapid convergence with BP methods on close boiling feed problems.

The λ_{max} curves for the SR method are shown in Figure 3. It can be seen that the SR method exhibits stability for very wide boiling feed mixtures. This agrees with the experience of rapid convergence for absorption and stripping problems. It can also be seen that increasing the number of stages decreases the region of applicability of the SR method. Experience has shown that the SR method will work all one-stage problems (Figure 3 indicates that all three-stage problems can be worked), but an increase in the number of stages introduces instabilities which increase the number of trials and finally causes nonconvergence above N of approximately 3 for relatively narrow boiling feeds.

The areas of convergence for the two methods did not overlap. There are some intermediate problems where evidently both the energy balance and the equilibrium relationships have nonnegligible effects on the stage temperature, that is neither effect predominates. In a distillation column with one or more wide boiling feeds there will be sections of stages containing close boiling material (toward the ends) and sections with wide boiling material. An attempt was made to work such problems by testing each stage for its Δ_{DB} value and then dividing the column into sections with the most appropriate method being used in each section. This procedure did not work any problems which could not be worked with either the BP or SR method alone. In the last section of the paper another approach (untried as yet) will be suggested for these now insolvable problems.

Damping

Holland and co-workers have shown that the area of convergence of a BP method (Thiele-Geddes) can be modified by damping the changes in the V_n and t_n from trial to trial (*15*). The calculated temperature profile was averaged with the last trial profile to provide the profile actually used in the next trial. A more elaborate averaging procedure was used on the rate profiles. These forcing procedures were carried to extremes in an attempt to handle wide boiling materials. On such problems they found it necessary to impose maximum and minimum limits on the rate profiles to keep the instable BP method from blowing up completely. As soon as the rate profiles hit one or the other arbitrarily imposed limit, it was necessary to assume a heat stream on each stage to close the energy balances, the so-called *Q-method.* If convergence was finally obtained, the heat stream vanished. That this did not occur in all cases has been shown by Holland (*14*).

Nevertheless there is no question that damping procedures permit convergence in some marginal problems where the unmodified BP or SR methods fail. Only one damping procedure was tried in this work, and since Holland and co-workers have demonstrated damping in BP methods, the damping factor chosen was aimed more toward the SR method. The λ_{max} were re-evaluated for the test problems with a damping factor of $N^{1/2}$ applied to each V_n

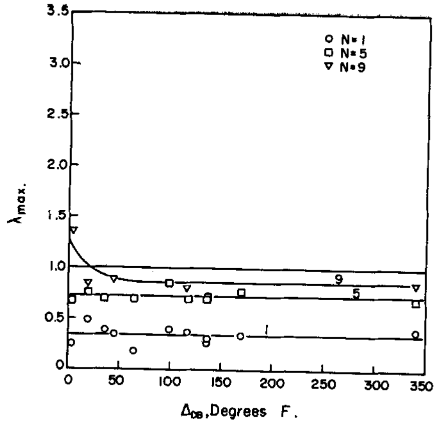

Fig. 4. Regions of convergence of SR method for various N values with damping.

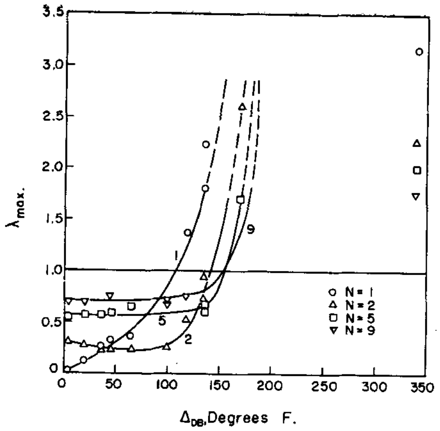

Fig. 5. Regions of convergence of BP method for various N values with damping.

and t_n correction. It was chosen arbitrarily for the single attempt along this line because the SR method showed decreasing stability with increased N. Figure 4 shows the λ_{max} for the SR method with damping. It can be seen that for $N < 9$ the area of convergence now overlaps that of the BP method. Unfortunately the troublesome intermediate problems involve distillation columns with $N > 9$. Also it was found that the convergence of absorber problems with large Δ_{DB}'s was slowed considerably by the damping factor.

Figure 5 shows the effect of the $N^{1/2}$ damping factor on the BP method λ_{max} curves. Since λ_{max} correlated well with the number of iterations required for a given problem, it is clear from a comparison of Figures 2 and 5 that the damping factor was deleterious for low Δ_{DB} and $N > 1$. The area of convergence at the higher N was extended slightly to the right.

INTERMEDIATE BOILING RANGES

There are certain distillation problems where there is no clear-cut reason for either of the two possible choices in matching the types 3 and 4 restrictions with the t_n and V_n variables. Since both restrictions seem to be involved strongly with both variables, a simultaneous solution of the two might handle these problems. This could be accomplished by a Newton-Raphson iteration on Equations (6) and (7). Equation (5) would not be included in the Newton-Raphson iteration, and the C-matrix equations would be solved as before in some correct manner to provide a set of $x_{i,n}$. For any given set of $x_{i,n}$, E_n and M_n can be considered to be functions of V_n and t_n only and Newton's approximation applied to give the following linearized sets of equations:

$$E_n(V_n, t_n) + \sum_{m=1}^{N} \frac{\partial E_n}{\partial V_m} \Delta V_m + \sum_{m=1}^{N} \frac{\partial E_n}{\partial t_m} \Delta t_m = 0 \quad (43a)$$

$$M_n(V_n, t_n) + \sum_{m=1}^{N} \frac{\partial M_n}{\partial V_m} \Delta V_m + \sum_{m=1}^{N} \frac{\partial M_n}{\partial t_m} \Delta t_m = 0 \quad (43b)$$

The partial derivatives would be evaluated by a finite difference approximation. The set (43) could then be solved for the corrections ΔV_n and Δt_n by any linear method. The amount of arithmetic involved in such a procedure would exceed that in the SR and BP methods by a wide margin, and therefore the latter two methods would be much faster where applicable.

The ultimate procedure of course would be to include Equation (5) also in the Newton-Raphson iteration. However this would further increase the arithmetic involved by a staggering amount, and until it has been shown that the simultaneous solution of Equations (6) and (7) for some given set of $x_{i,n}$ will not work, these intermediate problems such an approach can be deferred.

Convergence can sometimes be approached on these difficult problems by extensive forcing procedures such as averaging and limitation of temperature and rate profiles and devices such as the θ-method for the Thiele-Geddes method. See Canik (*5*) and McNeese (*17*) for efforts of this kind. However these forcing procedures are made necessary by deficiencies in the basic calculation method and represent a considerable amount of additional numerical computation. The desired successive substitution procedure would exhibit the kind of stability shown by the BP and SR methods on close boiling and wide boiling materials respectively.

GENERAL COMPUTER PROGRAM

A general computer program which would provide solutions for the maximum number of equilibrium stage separation problems would contain three main parts exclusive of equilibrium and enthalpy data routines. The first main part of the program would be the C-matrix solution section. The stripping factor equations of Friday (*6*) or the recurrence formulas described by Grabbe et al. (*7*) should be used to avoid the numerical difficulties inherent in the Lewis-Matheson, Thiele-Geddes, and Greenstadt et al. stage-by-stage procedures. Immediately after the C-matrix solution section the BP and SR methods would be programed as two parallel sections. The decision as to which path to follow could be made by the computer based on a calculated Δ_{DB}, or the decision could be imposed arbitrarily by the program user. All extraction, washing, absorber, and stripping problems plus wide boiling distillation problems with less than about ten stages would utilize the SR section. All other distillation problems would go to the BP section.

The use of the SR method on wide boiling materials saves considerable computer time, even though a solution might be obtained by a BP method. The SR method is basically faster because it eliminates the bubble point calculations which consume a major part of the BP calculation time. Also it converges much more rapidly on wide boiling feeds than does the BP method. Several examples of this are provided by Friday (*6*). Only one case will be presented here for the purposes of comparison to solutions by the Thiele-Geddes method as presented in Holland's examples 8-1 and 8-2 (*14*). The problem involves a simple absorber with a 70% methane, 15% ethane, 10% propane, 4% normal butane, 1% normal pentane feed, and a completely stripped lean oil of normal octane. The Δ_{DB}

TABLE 2. COMPARISON OF BP AND SR RESULTS ON AN ABSORBER EXAMPLE

Initial assumptions

		t	
Stage	*V*	Holland	Friday
1	98.1	170	90
2	96.2	180	90
3	94.3	190	90
4	92.5	200	90
5	90.6	210	90
6	88.7	220	90
7	86.8	230	90
8	85.0	240	90

Final results

	Convential			Constant Composition		SR	
Stage	*V*	*t*	*Q*	*V*	*t*	*V*	*t*
1	93	68.4	0	93.1	74.3	95.8	119.5
2	88	70.0	1.8×10^5	91.8	96.4	94.1	130.3
3	93	191.9	-3.0×10^5	91.2	105.8	94.1	133.8
4	88	93.6	2.8×10^5	90.9	110.2	93.8	134.2
5	93	195.6	-2.5×10^5	90.7	112.1	93.5	132.8
6	93	118.9	3.0×10^5	90.5	112.4	93.1	130.2
7	88	63.2	1.9×10^5	89.8	111.4	92.0	125.8
8	85	146.7	-1.4×10^5	85.0	107.6	85.0	117.5

for the combined feed and lean oil is too large to fall on Figures 2 to 5. The specifications are column pressure = 300 lb./sq. in. abs., $V_N = 85$, $N = 8$, and a lean oil temperature = 90°F. The initial assumptions and final results for Holland's conventional and Q method, Holland's constant-composition and Q methods, and Friday's SR solution are shown in Table 2. Direct comparison of solution results is always clouded by differences in physical data and in initial assumptions. However the rates of convergence differ by several orders of magnitude, enough to overshadow the effects of different data and initial assumptions. The SR results shown comprise an essentially exact solution in that the maximum changes in a t_n and a V_n were 0.002°F. and 0.0015 moles, respectively, between the seventh and eighth trials. These were undamped corrections, and no extraneous forcing or convergence methods were necessary or desirable. Also it is an exact solution in that Equations (1) through (4) are all satisfied to within the errors indicated. In comparison Holland's constant-composition method had reduced the Q's to zero after twenty-five trials but was still producing a damped temperature correction of the order of 0.05°F. and the results were still a considerable distance from the true solution.

The conventional method was divergent, and a narrow range of permissible V's (88 to 93) was necessary to keep the calculated stage temperatures within the range of the K-value equations used. (This sensitivity of stage temperature with respect to the phase rates was illustrated earlier in the paper.) After twenty-eight trials the calculated V's were still at one limit or the other. The tabulated Q's represent the errors in the energy balances after the twenty-eighth trial.

It is interesting to note that the different behavior of the conventional and constant-composition methods cannot be attributed to the denominator term $(H_n - h_{n+1})$ approaching zero in the conventional representation of the energy balance [Equation (32)]. The $(H_n - h_{n+1})$ values in this absorber example were of the order of −5,500 B.t.u./(lb.) (mole), and both forms of the energy balance are equally stable.

NOTATION

C_n = molar average heat capacity of the total vapor stream for stage n, B.t.u./(mole) (°F.)
c_n = molar average heat capacity of the total liquid stream for stage n, B.t.u./(mole) (°F.)
F = feed rate, lb./hr. or mole/hr., subscript denotes which feed
$f_{i,n}$ = component i feed rate, to stage n, lb./hr. or moles/hr.
H_n = total vapor stream enthalpy for stage n, B.t.u./mole
$H_{i,n}$ = molar enthalpy of component i in the vapor phase on stage n, B.t.u./mole
h_n = total liquid stream enthalpy for stage n, B.t.u./mole
$h_{i,n}$ = molar enthalpy of component i in the liquid phase on stage n, B.t.u./mole
$K_{i,n}$ = distribution coefficient for i in stage n
L_n = total liquid or extract phase rate for stage n, lb./hr. or moles/hr.
$l_{i,n}$ = component i liquid or extract phase rate for stage n, lb./hr. or moles/hr.
q_n = heat entering stage n, B.t.u./hr.
$S_{i,n}$ = $K_{i,n} V_n/L_n$ = separation factor for component i in stage n
t_n = temperature of stage n, °F.
V_n = total vapor or raffinate phase rate for stage n, lb./hr. or moles/hr.
$v_{i,n}$ = component i vapor or raffinate phase rate for stage n, lb./hr. or moles/hr.
$x_{i,n}$ = fractional concentration of i in liquid or extract phase in stage n
$y_{i,n}$ = fractional concentration of i in vapor or raffinate phase in stage n
$\lambda_{\max}$ = maximum root of the characteristic equation for the Jacobian matrix, Equation (37)
Δ_{DB} = dew point temperature minus bubble point temperature, °F., for the total material entering the stage or column

Subscripts

i = component number
k = iteration number
N = total number of stages, top stage
n = stage number
m = stage number also when two indices for stage number are needed

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Surface Combustion of Hydrogen: Part I. On Platinum-Coated Alumina

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It is well known that combustion of hydrogen, carbon monoxide, methane, and other gases can occur in the gas phase and on the surface of catalytic materials. The latter is referred to as *surface combustion.* Surface reactions are usually carried out industrially at temperatures high enough to obtain rapid rates of reaction. If the object of the reaction is the transformation of chemical species, to make a product or to destroy fumes, economy dictates high rates. If the object is heat generation, again, rates of reaction must be high to obtain a sufficiently rapid heat release. The surface combustion of hydrogen was chosen for this study as a representative reaction, without complications such as byproducts, hazards due to toxicity, or problems of chemical analysis.

The purpose of this investigation was to determine the rate behavior of surface combustion of hydrogen on the surfaces of a very active and a moderately active catalyst in the temperature range of industrial applications. To permit study of the rate of the surface reaction alone the homogeneous gas-phase reaction was suppressed with cold hydrogen-air feeds and dilute mixtures. To minimize the effects of boundary-layer diffusion on the rate measured high flow rates were used. A tubular reactor configuration was employed to simplify mathematical description of fluid and heat flow phenomena and to facilitate description of the active surface. The experimental setup was designed to permit maintenance of constant temperature and, in later phases of the work, constant total pressure for different flow rates. Gas samples were obtained through a movable water-cooled probe which also contained a high-velocity thermocouple. Sampling at various positions allowed separate study of sections of the reactor in which only surface reaction occurred.

BACKGROUND

Research on surface combustion started in 1817 when Sir Humphrey Davy (*5*) discovered that a warm spiral of platinum wire brought about the ignition of hydrogen. Later nineteenth-century investigators, such as Dulong and Thenard, William Henry, Graham, Faraday, Mendeleev, and De la Rive, studied the accelerating effect of surfaces on the combustion of hydrogen in an attempt to explain the phenomenon qualitatively. Bodenstein (*1*) attempted the experimental measurement of reaction velocities, and the complexity of the phenomenon was soon apparent from his work. In 1906 Bone and Wheeler (*3*) published the results of their rate studies on surfaces such as porous porcelain, silver, and nickel gauze. Bone's (*2*) work and that of his co-workers dealt with applications.

In the 1920's a group of chemists began to study the heterogeneous oxidation of hydrogen because of interest in the fundamentals of catalysis. The hydrogen-oxygen reaction appeared easy to study since its progress could be followed by observing the drop in pressure with time in a closed recirculating system. These investigators were interested in the rate law and not in the absolute values of the rate constants. Three reviews of their work are given in Advances in Catalysis (*6*), in Emmett's (*7*) and in Schwab's (*17*) books on catalysis. A recent review of the catalytic reaction on platinum or palladium in the pres-

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