Convergence Properties of Systems of Algebraic Equations—Explicit Loops

Techniques are developed for using the structural information contained in algebraic equation sets to aid in the study of convergence properties of iterative equation loops.

The concept of inverse mapping is applied directly in order to study convergence properties of sequences. For problems in which there exist both a direct and inverse path for the computation of iterative loops, direct substitution techniques will converge via one path and diverge via the other path. When an inverse path existed, the direct substitution method was superior to simultaneous solution techniques for the problems studied. Not all iterative loops have an inverse path. For problems in which inverse paths do not originally exist, rearrangement of the equations of an iterative loop can result in a modified loop for which an inverse path does exist. The digraph representation of an iterative loop aids in deciding whether rearrangements are feasible for a particular problem. When inverse paths cannot conveniently be obtained, direct substitution cannot be successfully used and simultaneous solution techniques such as quasi-linearization are recommended.

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SCOPE

Particularly in the mathematical description of design problems, it is necessary to solve a large set of algebraic equations. Recently much has been published on how the structural information contained in equation sets can be used to develop algorithms for minimizing and simplifying iterative loops (Ramirez and Vestal, 1972). However, little has been published on how this structural information influences the convergence properties of systems of algebraic equations. Structural information is important in the study of convergence properties. In this paper we present a direct method for applying the mapping concepts of functional analysis in order to show how structural information relates to, and aids in the study of, solution strategies for algebraic equation sets. The method presented is easy to use and should be of use to practicing engineers.

CONCLUSIONS AND SIGNIFICANCE

Our proposed method of analysis is illustrated with three different examples of increasing complexity in order to show how mapping concepts of functional analysis are advantageous in the solution of sets of algebraic equations. Example one contains a single simple iterative loop with only two equations in the loop (that is, there are no intermediate equations within the loop). Forward and reciprocal mappings (computational paths) exist for this example. Therefore, from the structural information alone we can tell that direct substitution convergence will be obtained along one of the paths. Example two is a case of an easily decomposable single iterative loop. This loop contains intermediate equations which do not contain the iterative variable explicitly. A biunique inverse path may not exist for this type of problem, and therefore, rearrangements within the iterative loop might be necessary in order to obtain a biunique inverse path so that convergence will be guaranteed via direct substitution. A digraph representation of the iterative loop aids in deciding whether rearrangements are feasible. The third example involves nested loops and contains a nondecomposable iterative loop. Three iterative loops exist for this problem (that is, an outside loop and two successive inside loops). Direct substitution convergence loses many of its advantages when nested loops appear and a quasi-linearization solution seems superior.

A system of algebraic equations can be expressed in vector form as

$$\mathbf{f}(\mathbf{x}) = \mathbf{0} \qquad (1)$$

where $\mathbf{x}$ is the unknown vector and $\mathbf{f}$ is a functional operator. If it is possible to find a sequence $(\mathbf{x}_0, \mathbf{x}_1, \ldots \mathbf{x}_n)$ with $\mathbf{x}_0$ assumed, so that for all ϵ arbitrarily small and > 0 and with $|x_n - x_{n-1}| < \epsilon$, we then have defined a convergent iterative scheme of solution for the system of equations. Many iterative methods of solutions are used to solve algebraic equations. We shall consider only two of them: direct substitution and the Newton-Raphson technique. Most other techniques, however, involve perturbations upon these two basic methods.

Direct substitution rearranges the original system equations into the following form:

$$\mathbf{x} = \mathbf{g}(\mathbf{x}) \qquad (2)$$

where the left-hand side is the image of the right-hand side (transformed by the operator g). Assuming the vector $\mathbf{x}_0$, Equation (2) gives

$$\mathbf{x}_1 = \mathbf{g}(\mathbf{x}_0) \tag{3}$$

If an error criterion is set as ϵ, then the system has converged to its solution when

$$|x_1 - x_0| < \epsilon \tag{4}$$

Otherwise the new guess to be operated by g is chosen as $\mathbf{x} = \mathbf{x}_1$. This is repeated until convergence is obtained.

Explicit iterative loops are defined as iterative equation solution strategies for which the last equation of the loop gives directly a new value for the iterative variable. This means an explicit check can be made between the initial guess and the new value of the iterative variable.

Building on the initial work of Rudd and Watson (1968), recent work (Ramirez and Vestal, 1972), has shown how structural information contained in equation sets can be used to develop algorithms for minimizing and simplifying iterative loops. It is the interest of this paper to develop techniques for using this same structural information to aid in the study of convergence properties of iterative loops. What we present is a direct method for applying the mapping concepts of functional analysis to convergence associated with the iterative solution of nonlinear algebraic equations. The traditional attack (Ortega and Rheinbolt, 1970) has been an indirect application that is virtually useless for engineering problems. In order to develop the direct method we make use of the following two mathematical properties.

Property I. If a recurring sequence, f

$$\mathbf{x}_n = \mathbf{f}(\mathbf{x}_{n+1}),$$

has a limit r, the sequence will either diverge or converge toward r. Assuming that the mapping operator f has a biunique (one-to-one) reciprocal operator $\mathbf{f}^{-1}$, then, if f is a diverging operator, $\mathbf{f}^{-1}$ is a converging operator and vice versa.

A graphical representation of the sequence

$$x_n = f(x_{n+1}) \tag{5}$$

is given in Figure 1. Let us assume that curve (I) is monotonically increasing. For an initial value x_0, the image of x_0 by the mapping operator f is

$$x_1 = f(x_0) \tag{6}$$

Using the main diagonal it is easy to see that x_1 is the abscissa of the point M_1 on the graph. In the same way, $x_2 = f(x_1)$ is the abscissa of M_2. Then a geometric interpretation of the recurring sequence, $x_n = f(x_{n-1})$, is the staircase line which takes support on the curve (I) for an upper bound and on the main diagonal for a lower bound. If we consider only strictly concave or strictly convex functions, then a geometric criterion for convergence is given by the comparison of the lengths of two consecutive segments N_iM_i. For the curve (I) of Figure 1 regardless of the initial guess x_0, the sequence $x_{n+1} = f(x_n)$ will diverge since consecutive segments N_iM_i increase in length. This sequence does have a limit r, but unless the initial guess is exactly r, it is impossible to converge to that limit through the sequential path considered.

However, since $y = f(x)$ is a monotonic continuous function, that is, f is a biunique mapping operator, a reciprocal transformation $x = f^{-1}(y)$ exists. The graph of $x = f^{-1}(y)$ is symmetrical to the graph of $y = f(x)$ with respect to the main diagonal.

In Figure 1 if we apply a direct substitution technique

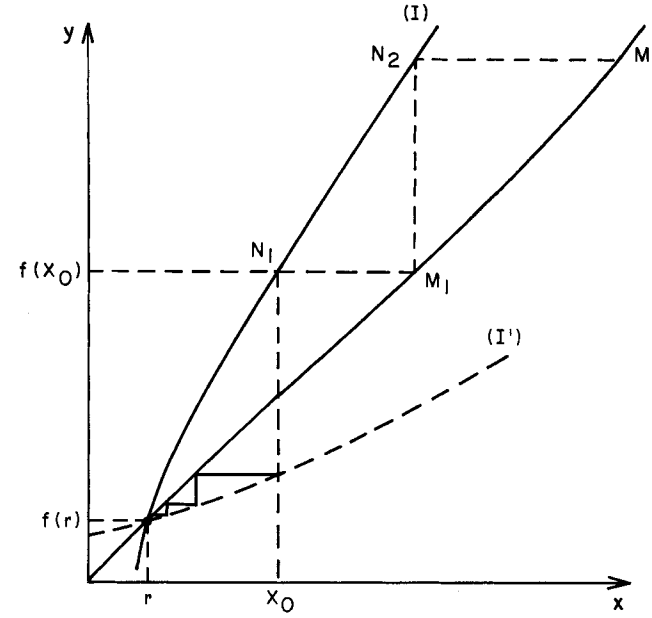


Fig. 1. Convergence-divergence graph study.

to the reciprocal operator, graph (I'), we see that $x_{n+1} = f^{-1}(x_n)$ converges toward r whatever the initial guess for x_0.

Property II. If the number of members (edges) of the input set A for each vertex of a digraph representation of the recurring sequence $x_n = f(x_{n+1})$ equals the number of edges of the output set B, then the mapping equator f has a biunique reciprocal operator $\mathbf{f}^{-1}$. Therefore, if f is the diverging path, $\mathbf{f}^{-1}$ is the converging path and vice versa. The inverse path is obtained by simply reversing the flow of the digraph.

Besides the classical algebraic approach to the mathematical theory of equations, another approach for large scale systems has been introduced in the last decade. This alternate approach is based on the theory of graphs as developed in Maxwell (1971) and Harary (1967) and has been applied to chemical engineering problems by Himmelblau (1966).

A graph is defined as a collection of vertices V (nodes, points) and lines joining the verticies called edges. A directed graph also contains orientation properties. A directed graph (digraph) is a graph in which the edges are directed. Since the concept of a digraph is associated with the idea of flow, it is easy to understand that it is possible to define an inverse flow.

Let's apply the theory of graphs to a representation of the solution of a set of algebraic equations. Consider the equation set:

$$f_1(x_1, x_2) = 0 \tag{7}$$

$$f_2(x_1, x_3) = 0 \tag{8}$$

$$f_3(x_2, x_3) = 0 \tag{9}$$

Application of the iterative variable selection and computational structuring algorithm of Ramirez and Vestal (1972) shows that there is one essential iterative variable. The computational sequence is: with x_2 assumed, compute x_1 from Equation (7); now with x_1 known, compute x_3 from Equation (8); and finally a new guess for x_2 is obtained from Equation (9). A digraph representation of this iterative loop is shown in Figure 2. Here each equation is a vertex or node of the graph and each variable an edge. We see that there is a direct correspondence between the strategy of solving the system and the associated digraph of the iterative loop. Since for each vertex

the number of members (edges) of the input set A equals the number of members of the output set B we know from Property II that the mapping operator f for the recurring sequence

$$\mathbf{x}_n = \mathbf{f}(\mathbf{x}_{n+1}) \tag{10}$$

has a biunique reciprocal operator $\mathbf{f}^{-1}$. The inverse operator $\mathbf{f}^{-1}$ can be obtained by simply reversing the flow of the digraph. Therefore, either the forward path or the reverse path will converge.

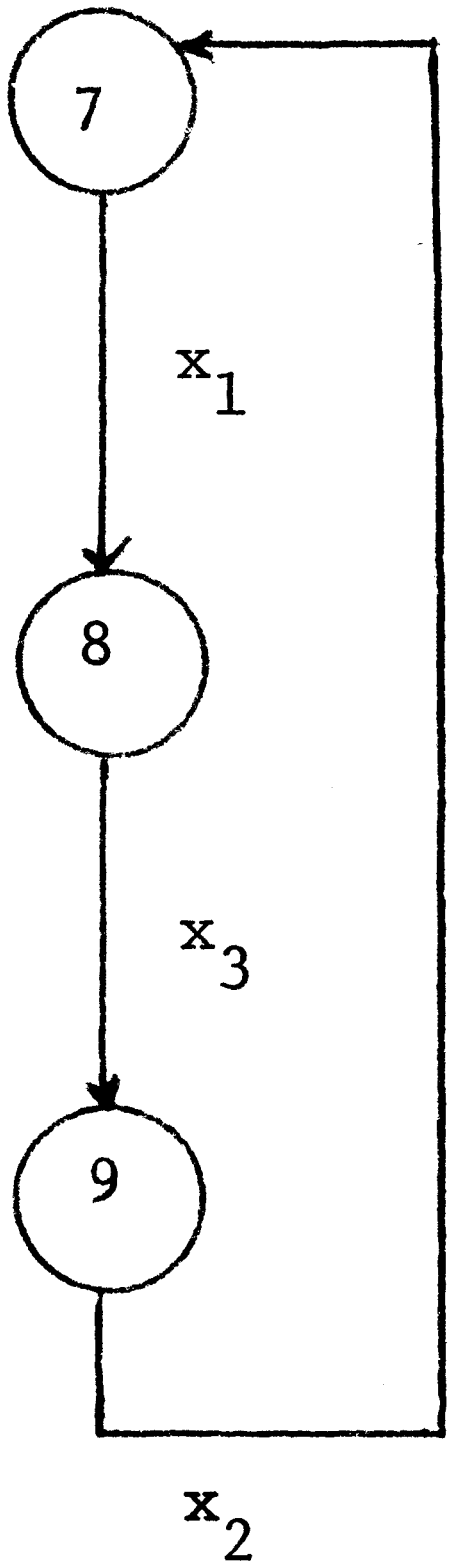


Fig. 2. Digraph representation of Equations.

The Newton-Raphson convergence techniques (Lee, 1968) is based on the idea of obtaining a new guess for the root by extropolation of a linear (that is, tangent) function. To solve the equation set

$$\mathbf{f}(\mathbf{x}) = 0$$

we linearize the vectorial equation as

$$f(\mathbf{x}) = \mathbf{f}(\mathbf{x}_n) + \underline{\mathbf{J}}(\mathbf{x}_n)(\mathbf{x} - \mathbf{x}_n)$$

about an initial guess to the solution $\mathbf{x}_n$. The matrix $\underline{\mathbf{J}}(\mathbf{x}_n)$ is the Jacobian matrix. A new value for the root is then

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \underline{\mathbf{J}}(\mathbf{x}_n)^{-1}\mathbf{f}(\mathbf{x}_n)$$

It has been shown that the sequence $\mathbf{x}_n$ converges to the solution of the original nonlinear equation if the initial guess is close enough to the solution. If there is convergence at all, the convergence is quadratic.

In this paper we consider three different examples of increasing complexity which illustrates how structural information aids in the development of a solution strategy for the solution of sets of algebraic equations. Optimal tearing is obtained via the algorithm of Ramirez and Vestal. Convergence properties of the iterative loops are analyzed with the use of Properties I and II. Example one contains a single simple iterative loop with only two equations (that is, there are no intermediate equations). Example two is a case of an easily decomposable single iterative loop. This iterative loop contains intermediate equations which do not contain the iterative variable explicity. The third example involves nested loops and contains a nondecomposable iterative loop. Here three iterative loops exist (that is, three iterative variables one with an outside loop and two successive inside loops). Any really large set of algebraic equations will simply consist of combinations of these classes of iterative loops.

EXAMPLE 1: AN ADIABATIC CFSTR (A SIMPLE ITERATIVE LOOP PROBLEM)

An adiabatic continuous flow stirred tank reactor is used to conduct the first order chemical reaction $A \rightarrow B$. The equations describing the system are

Material balances:

$$F_0 C_{A0} = F_0 C_{A1} + V C_{A1} k_0 e^{-E/RT_1} \tag{11}$$

$$C_{A0} - C_{A1} = C_{B1} - C_{B0} \tag{12}$$

Energy balance:

$$F_0 c_p T_0 = V k_0 (\Delta H) e^{-E/RT_1} C_{A1} + F_0 c_p T_1 \tag{13}$$

Data on the following parameters are known:

ΔH	$= -700$ cal/g	T_0	$= 280$°K
c_p	$= 1$ cal/g °K	C_{A0}	$= 0.4$ g/l
V	$= 50$ l	C_{B0}	$= 0$ g/l
E	$= 1 \times 10^4$ cal/g mole		
k_0	$= 3 \times 10^7$ min^{-1}		

The mathematical description of this problem therefore involves three equations [Equations (11), (12), and (13)] and four variables (C_{A1}, C_{B1}, T_1 and F_0). This means that there is one degree of freedom, or equivalently, that there is one design variable to be chosen. Ramirez and Vestal (1972) have presented algorithms for the selection of design variables and the determination of a computational sequence for solving the system of equations. Their work is based on the dual objective of decomposing the system in order to minimize the number of iterative variables necessary for solution and to minimize the number of nested iterative calculations. The plant structural matrix for the CFSTR is given in

	C_{A1}	C_{B1}	T_1	F_o
Equation 11	1	0	1	1
Equation 12	1	1	0	0
Equation 13	1	0	1	1

Fig. 3. Plant structural matrix for CFSTR.

TABLE 1. COMPUTATIONAL SEQUENCES FOR A CSTR: CASE 1.1

Possibility 1-A

Sequence no.	Equation no.	Variable to be solved for	Hierarchy level
1	11	C_{A1}	1
2	13	T_1	1
3	12	C_{B1}	0

Possibility 1-B

Sequence no.	Equation no.	Variable to be solved for	Hierarchy level
1	13	C_{A1}	1
2	11	T_1	1
3	12	C_{B1}	0

Figure 3. The result of applying the Elimination Algorithm of Ramirez and Vestal (1972) is

Hierarchy level	Variable not eliminated	Interpretation
0	none	—
1	T_1, F_0	one iterative variable one design variable

There are two different computational sequences possible, corresponding to whether T_1 or F_0 is chosen as the design variable. We will investigate both cases.

Case 1.1: F_0 as Design Variable and T_1 as Iterative Variable

With the choice of F_0 as the design variable we now use the structuring algorithm of Ramirez and Vestal (1972) to determine the computational sequence for the CFSTR whose plant structural matrix is given in Figure 3. Starting at hierarchy level 1, there are no equations with a minimum frequency of one. We therefore temporarily set the iterative variable associated with this hierarchy level, T_1, to zero. Equation (11) and (13) then both have a minimum frequency of one, and therefore there are two possible ways of continuing the algorithm. These are

1. Eliminate Equation (11) and variable C_{A1}, and then get a new guess for T_1 with Equation (13).
2. Eliminate Equation (13) and variable C_{A1}, and then get a new guess for T_1 with Equation (11).

The two possible computational sequences (1-A and 1-B) are shown in Table 1. In both cases Equation (12) gives a value of C_{B1}.

The digraphs associated with the two possible computational sequences are shown in Figure 4. The iterative loop of path 1-A is just the reverse of the path 1-B. Therefore from Principle II, the two calculational sequences are a direct path and a biunique inverse path since the number of edges of the input set equals the number of edges of the output set for each node. Convergence is guaranteed via one of the paths. A graph of both the forward path (1-A) and the reciprocal path (1-B) is shown in Figure 5. From the digraph representation of the iterative loop (Figure 4), we know that the two paths are symmetrical and we therefore will converge via one path and diverge via the other path. The convergence path for this problem is the inverse path 1-B as shown in Figure 5. Convergence is independent of the initial guess.

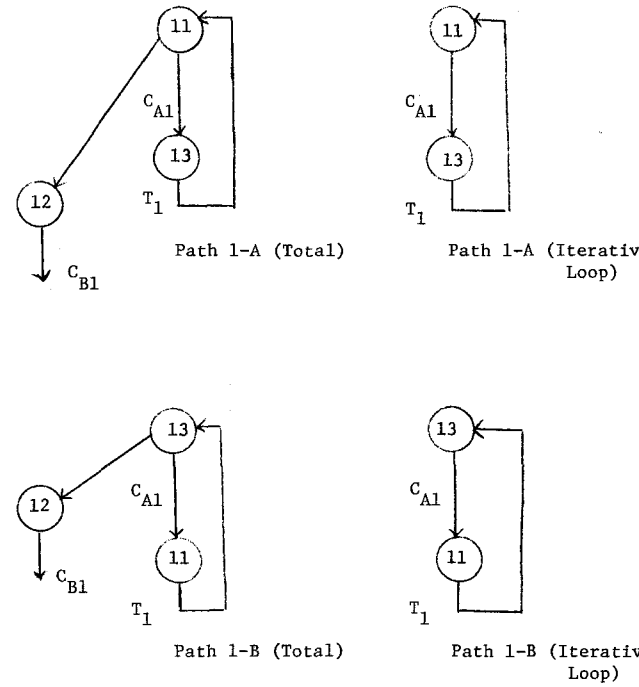


Fig. 4. Digraph representation of computational paths 1-A and 1-B.

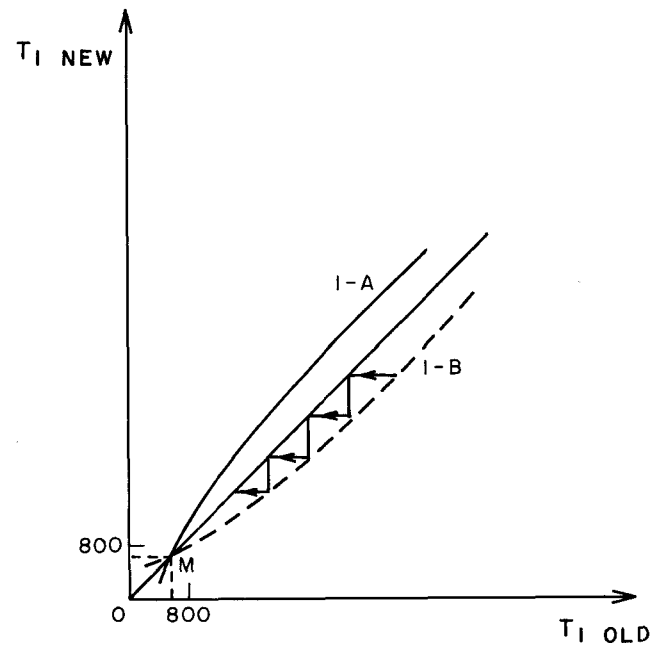


Fig. 5. Direct substitution convergence for reactor temperature T_1.

Case 1.2: T_1 as Design Variable and F_0 as Iterative Variable

The other possible choice for the iterative variable is the flow rate F_0. Again we use the structuring algorithm of Ramirez and Vestal (1972) to determine the computational sequence. The digraph associated with computation of the iterative loop is given in Figure 6. Using Principle II we know that convergence is guaranteed via either the direct path shown in Figure 6 or via the inverse path which is obtained by reversing the flow of the digraph.

CONCLUSIONS FROM EXAMPLE 1

Several conclusions can be drawn. First, for each choice of the iterative variable, the order of the computations, (that is, the path followed) is of prime importance. Forward and reciprocal paths exist for this example. Therefore, from only the structural information it is possible to know that direct substitution convergence will be obtained along one of the paths.

The second conclusion is that the convergence rate is a function of the choice for the iterative variable. A faster rate of convergence is obtained when the reactor temperature T_1 is the iterative variable. There are mathematical reasons for this (the value of the slope of the recurring sequence at the root), but it is important to notice that, for this problem, the right mathematical choice does not always correspond to the right engineering choice. If we are dealing with a product which is degradable outside of a certain range of temperature, then the reactor temperature has to be the design variable. However, if this is not the case, then the intuitive choice is the reactor flow since it is easier to control properly.

EXAMPLE 2: A SINGLE STAGE FLASH SEPARATOR (AN EASILY DECOMPOSED ITERATIVE LOOP PROBLEM)

A flash separator is used to separate a mixture of three components, H_2, C_2H_4, and C_2H_6. H_2 corresponds to component numer 1, C_2H_4 is component number 2, C_2H_6 is component number 3. The mathematical equations for the system are

Mole fraction relations:

$$y_1 + y_2 + y_3 = 1 \tag{14}$$

$$x_1 + x_2 + x_3 = 1 \tag{15}$$

Overall material balance:

$$W_0 + W_B = W_F \tag{16}$$

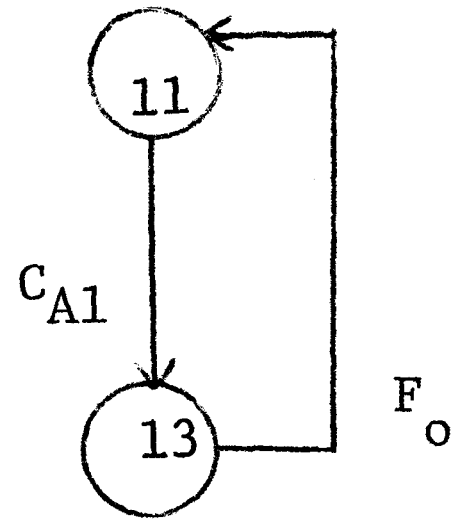


Fig. 6. Digraph representaiton of the iterative loop using F_0 as the iterative variable in Example 1.

Component material balance: (2 relations)

$$x_1W_B + y_1W_0 = x_{1F}W_F \tag{17}$$

$$x_2W_B + y_2W_0 = x_{2F}W_F \tag{18}$$

Energy balance:

$$W_FC_{pF}T_F + Q_S = C_{pB}W_BT_B + C_{p0}W_0T_0 + W_0\Delta H_{u0} \tag{19}$$

Equilibrium relations:

$$T_0 = T_B \tag{20}$$

$$T_{\text{still}} = T_0 \tag{21}$$

$$P_{\text{still}} = P_0 \tag{22}$$

$$y_1 = K_1x_1 \tag{23}$$

$$y_2 = K_2x_2 \tag{24}$$

Equipment size calculation: (based on Souders-Brown analysis)

$$D = 0.22\sqrt{W_0} \tag{25}$$

All quantities with a subscript F are known quantities

W_F = 300 lb min^{-1}
x_{1F} = 0.2
x_{2F} = 0.5
T_F = 300°K

	T_0	P_0	W_0	y_1	y_2	y_3	T_B	P_B	W_B	x_1	x_2	x_3	T_{still}	P_{still}	Q_s	D
14	0	0	0	1	1	1	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	1	1	1	0	0	0	0
16	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0
17	0	0	1	1	0	0	0	0	1	1	0	0	0	0	0	0
18	0	0	1	0	1	0	0	0	1	0	1	0	0	0	0	0
19	1	0	1	1	1	1	1	0	1	1	1	1	0	0	1	0
20	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
21	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
22	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0
23	0	0	0	1	0	0	0	0	0	1	0	0	1	1	0	0
24	0	0	0	0	1	0	0	0	0	0	1	0	1	1	0	0
25	0	0	1	1	1	1	0	0	0	0	0	0	1	1	0	1

Fig. 7. Plant structural matrix for flash separator.

Moreover, the heat capacities are assumed to be independent from the temperature.

$$C_{pF} = \sum_{i=1}^{3} x_{Fi} C_{pi}$$

$$C_{pB} = \sum_{i=1}^{3} x_{Bi} C_{pi}$$

$$C_{p0} = \sum_{i=1}^{3} y_{0i} C_{pi}$$

The pressure of the bottoms P_B is assumed to be 300 lb./sq.in.abs. Therefore, the K values correlations are at 300 lb./sq.in.abs.

$$K_1 = (41.91 - 0.2089\, T_{\text{still}} + 6.53\, 10^{-4}\, T^2_{\text{still}})$$

$$K_2 = (1.296 + 0.01345\, T_{\text{still}} + 3.29\, 10^{-5}\, T^2_{\text{still}})$$

The plant structural matrix is given in Figure 7.

Applying the Ramirez and Vestal (1972) design variable selection algorithm yields:

Known variable	Iterative or design variables	Hierarchy level
P_B	$x_1, P_{\text{still}}, x_2, W_B$	1

Since there are four degrees of freedom for this problem and P_B is known, the results of the selection algorithm tells us that we have to specify three design variables and also that there will be one iterative variable for this problem. Since variables x_1 and x_2 have similar roles in the equation set as well as W_B and P_{still}, only the two cases of choosing either x_2 or W_B as the iterative variable will be considered.

Case 2.1: W_B as Design Variable and x_2 as Iterative Variable

The structuring algorithm of Ramirez and Vestal (1972) was again used to determine the computational sequence. The digraph associated with computation of the iterative loop is given in Figure 8. Again this is a simple loop for which both a forward and an inverse path exist. Therefore direct substitution convergence is guaranteed via one of the paths. For the numerical examples studied the forward path was the convergent path.

Case 2.2: x_2 as Design Variable and W_B as Iterative Variable

For the case when the flow rate of the bottoms W_B was chosen as the iterative variable the digraph of the iterative loop obtained from the structuring algorithm of Ramirez and Vestal (1972) is given in Figure 9. Some parallel branches of the loop can be temporarily neglected, that is, some of the equations can be solved outside of the loop. Neglecting these parallel branches gives the reduced digraph of Figure 9. By analyzing this reduced digraph we observe that there are three nodes [Equations (16), (17), and (18)] which have unequal input and output sets. For example, node 17 has two inputs and one output. This means from Principle II that as the problem is presently formulated it is impossible to determine a reciprocal path which is a biunique transformation. This result has many consequences. If the direct path is the diverging path, then, there is no way to obtain the inverse path by reversing the order of the computations. However, if the loop can be rearranged so that a biunique mapping exists, then it will be possible to find a reciprocal path. This can be done by deleting Equation (16) from the iterative loop by algebraic manipulations. Namely Equation (16) can be directly substituted into both Equation (17) and (18) to give two new equations which do not explicitly contain the variable W_0:

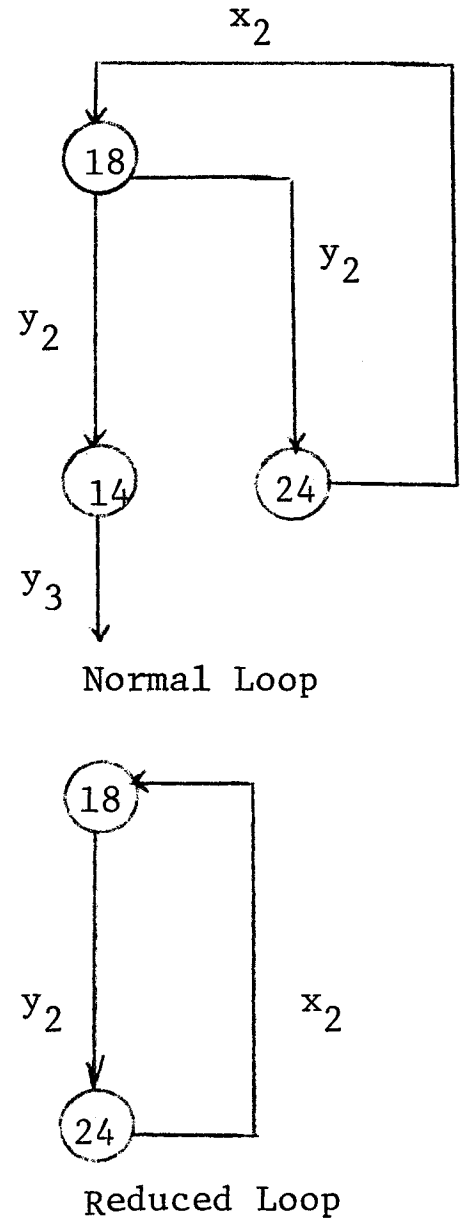


Fig. 8. Case 2.1 x_2 as iterative variable.

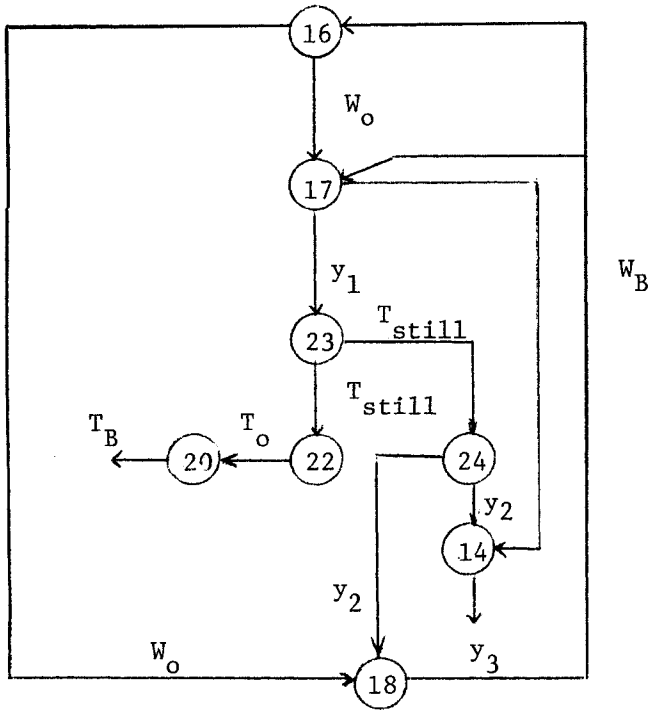
$$x_1 W_B + y_1(W_F - W_B) = x_{1F} W_F \qquad (17')$$

$$x_2 W_B + y_2(W_F - W_B) = x_{2F} W_F \qquad (18')$$

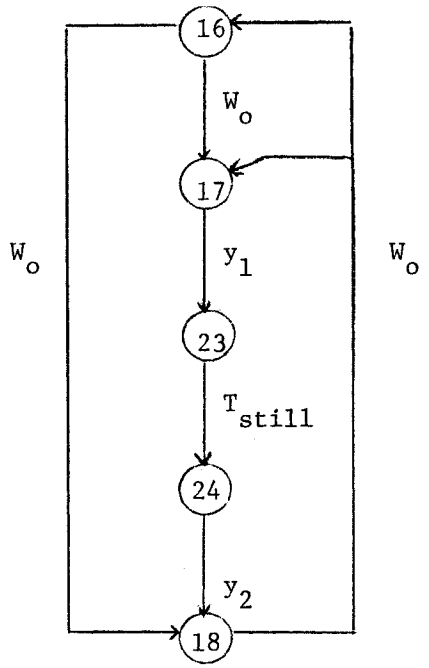
The completely reduced digraph representation of the loop is given in Figure 10. Now the input and output sets for this completely reduced digraph are equal for all the nodes, and therefore it is now possible to find a biunique inverse path. Convergence is assured on one of the paths. For the numerical case studied convergence was obtained on the inverse path.

Case 2.3: Solution by Quasilinearization

A simultaneous solution was also carried out for this problem. Since several of the describing equations are nonlinear, quasilinearization, using truncated Taylor series expansions, was used. The linearized system of equations were solved by matrix inversion techniques. Besides a total simultaneous solution to the problem a partial simultaneous solution was obtained. From the structuring algorithm and the resulting digraph of Figure 9 we know that only the iterative loop need be solved



Original Digraph



Reduced Digraph

Fig. 9. Case 2.2 W_B as iterative variable.

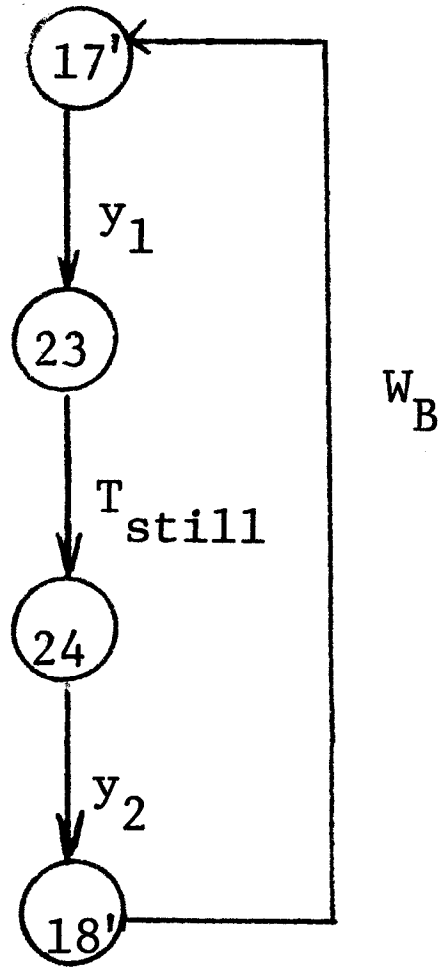


Fig. 10. Case 2.2 completely reduced diagraph.

TABLE 2. ITERATIVE COMPUTATIONAL SCHEME FOR EXAMPLE 3

Sequence no.		Variable	Equation no.	Hierarchy level
	Assume x_3			
1		x_1	27	3
	Assume T			
2		y_1	28	2
3	B	y_2	29	2
4	B	y_3	26	2
5	A	T	30	2
	Assume D			
6	C	B	31	1
7	C	D	32	1
8	A	x_3	33	0

simultaneously via quasilinearization. This reduces the size of the linear algebra to be solved and therefore reduces the time and effort required to obtain a solution.

Conclusions for Example 2

If we plot the computer time required for solution on a CDC 6400 versus the solution method used (Figure 11), we see that the two shortest methods of solution are by direct substitution. Also it is important to note that for the direct substitution case with W_B as the iterative variable, it was necessary to rearrange the iterative loop in order to obtain a biunique inverse path. The digraph representation of the iterative loop aided in this reduction.

EXAMPLE 3: A NESTED LOOP (A NONDECOMPOSABLE ITERATIVE LOOP PROBLEM)

Let us consider the system of equations given below:

$$y_1 + y_2 + y_3 = 1 \tag{26}$$

$$x_1 + x_2 + x_3 = 1 \tag{27}$$

$$y_1 = K_1 x_1 \tag{28}$$

$$y_2 = K_2 x_2 \tag{29}$$

$$y_3 = K_3 x_3 \tag{30}$$

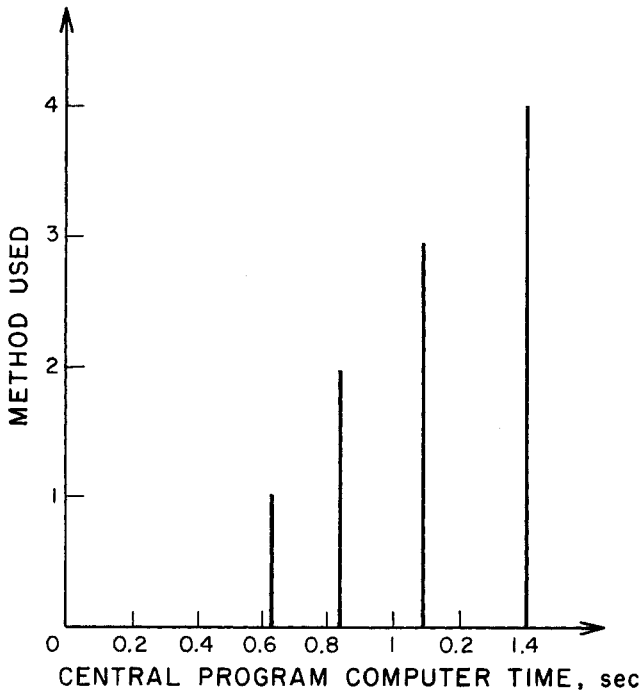


Fig. 11. Time required by different methods for example 2: 1 = dir. substitute (x_2 iterative variable), 2 = direct substitute (W_B iterative variable), 3 = partial quasilinearization, and 4 = total quasilinearization.

$$x_1B + y_1D = 5 \quad (31)$$

$$x_2B + y_2D = 30 \quad (32)$$

$$x_3B + y_3D = 65 \quad (33)$$

The equilibrium constants have the following temperature dependency:

$$K_1 = 41.91 - 0.2089\ T$$
$$K_2 = 1.296 + 0.01345\ T$$
$$K_3 = 0.815 + 0.00952\ T$$

This system does not represent a mathematical model of any real plant. However, it has certain characteristics of the plant studied in Example 2.

The result of applying the Ramirez and Vestal (1972) design variable selection algorithm is

Hierarchy level	Variables not eliminated	Interpretation
0	none	—
1	none	—
2	none	—
3	T, D, x_2, x_3	3 iterative variables (one associated with each hierarchy) and 1 design variable.

We will choose x_2 to be the design variable. The iterative computational scheme is given in Table 2. There is one outside loop (A) associated with hierarchy level 3 and two inside loops (B and C) associated with hierarchy levels 2 and 1.

The simplest of the three loops is loop C associated with the iterative variable D. The digraph of loop C is given in Figure 12a. This graph corresponds to a biunique mapping which means that there exists an inverse path for the loop by reversing the flow direction of the digraph.

The digraph of loop B is given in Figure 12b. In order to get a loop which will eventually have a reciprocal path, some transformations must be made in the original loop.

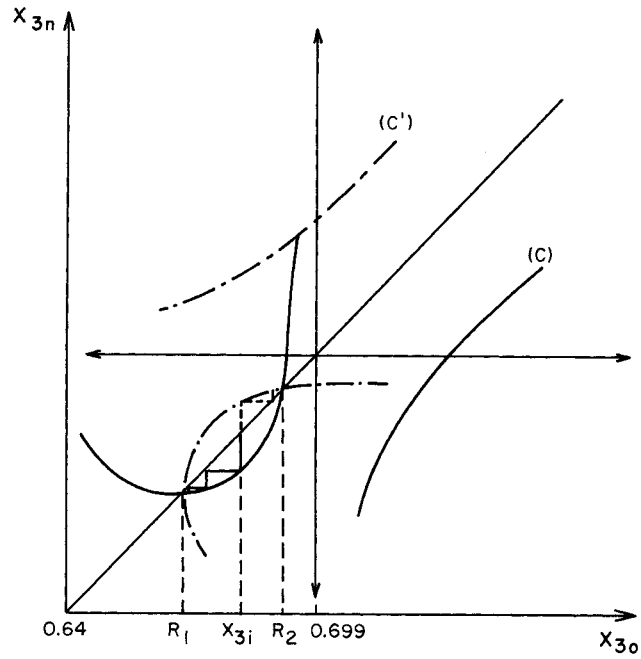
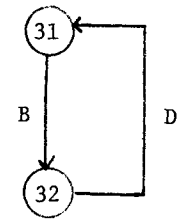
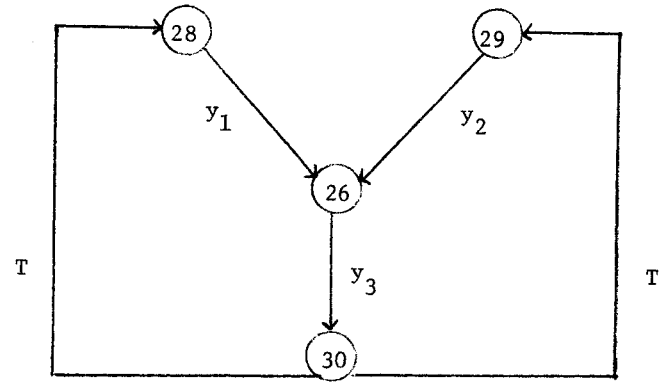


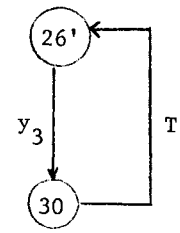
Fig. 13. Convergence paths associated with loop A for Problem 3.



12-A - Loop C



12-B - Loop B



12-C - Loop B modified

Fig. 12. Digraphs for example 3.

We can see from Table 2 that if both $y_1 = f_1(T)$ and $y_2 = f_2(T)$ are replaced algebraically in Equation (26) by their respective values as a function of T, the resulting loop will then be represented by Figure 12c. This is a simple loop for which there exists a reciprocal path.

There are no easy manipulations which one can make in order to get a reciprocal path for loop A. Therefore direct substitution techniques for this problem become useless. A graphical representation of

$$x_{3N} = f(x_{30}) \tag{34}$$

has been obtained from a digital computer and is shown in Figure 13. The curve is not monotonic and there is a discontinuity at $x_{30} = 0.699$. There are two values R_1 and R_2 for which $x_{30} = x_{3N}$. On the forward path C convergence is always at R_1. Unfortunately, the solution to the system corresponding to $x_3 = R_1$ has no physical meaning. The reciprocal path is shown as C′ but cannot be realized via iterative computation since inverse flow is not possible for loop A.

A quasilinearization solution of this problem has been carried out. The system has eight nonlinear terms. Depending upon the initial guess for the nonlinear variables, convergence has been obtained on either the real root R_2 or the nonreal root R_1.

As we can see from the study of the last example, a solution by direct substitution loses many of its advantages when nested loops appear. However, the algorithm of Ramirez and Vestal (1972) tends to minimize the number of nested loops required to solve a problem, and therefore nested loops are fairly rare in actual design computations. If they cannot be avoided, the engineer must be very careful when he tries to get an actual solution to his problem. For this type of problem quasilinearization is recommended.

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Determination of Liquid-Mixture Solubility Parameters and Interaction Energy Densities

Integral, isothermal heat-of-condensation values for continuously generated vapors of various constant-composition mixtures, along with the isothermal densities of the condensates, enable the calculation of the cohesive energy densities of solutions. Data for the complete range of composition of the chloroform-acetone system and for a major portion of the chloroform-diethyl ether system at 35°C are reported. From these data, the specific-interaction-energy density for each system is calculated, based upon an extension of the Scatchard-Hildebrand Regular Solution Theory.

The essential equality of the specific-interaction energy-density values for the two systems indicates a preponderance of the same kind of hydrogen bonding (CH- - -O) in each.

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SCOPE

Despite many proposals, no comprehensive theory has evolved to explain the behavior and predict the properties of many classes of solutions. Moreover, testing of various theories has been generally limited because sufficient experimental data to establish valid parameters are not available.

The simplest theory, the Scatchard-Hildebrand Regular Solution Theory, is especially notable for its successful correlation and prediction of nonpolar solution properties. This theory predicts the molar energy of mixing of a two-component, additive-volume system by means of the equation:

$$\Delta U_{\text{mixing}} = \phi_1\phi_2(C_{11} + C_{22} - 2C_{12})V_{\text{mixt.}} \tag{1}$$

The ϕ's represent molal-average volume fractions of the components while C_{11} and C_{22} are their cohesive energy densities (C.E.D.'s) as defined by Hildebrand (1919). Evaluation of the energy density of interaction between the dissimilar molecules C_{12} presents the major difficulty in using this equation. Scatchard (1931) and Hildebrand (1929) made the basic assumptions that solutions in which the molecules are randomly oriented and the volumes are

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