THE MATHEMATICAL SIMULATION OF A THREE-FEED DEMETHANIZER-ABSORBER

THE MATHEMATICAL SIMULATION OF A THREE-FEED DEMETHANIZER-ABSORBER

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SCOPE AND CONTENTS: The steady state and dynamic behaviour of a demethanizer-absorber have been studied using the IBM 7040 computer. The model considers as many as 10 components and 30 ideal trays, and three feeds to the column are permitted; this allows comparison with a real column in the Polymer Corporation plant in Sarnia.

The steady state solution is obtained using the Thiele-Geddes calculational procedure and the Θ-method of inducing convergence. In addition other means of ensuring convergence have been extended and tested.

The transient model was studied using a third-order Runge-Kutta process. Although successful, this method was extremely slow.

Equilibrium constant data in numerical form based on the Braun charts have been presented and tested. The enthalpy correlations of Yen and Alexander have also been examined and used.

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NOMENCLATURE

a_i', b_i', c_i', d_i'	coefficients of regressed equations
a_i'', b_i'', c_i''	coefficients of regressed equations
$A_{i,j}$	absorption factor for component i on tray j is defined by equation (20)
b_i	moles of component i in bottoms product and $b_i = l_{i,NR}$
B	total bottoms product $B = \sum_i (b_i)$
C	constant defined in equation (44)
C_{p_i}	heat capacity
d_i	moles of component i in the overhead
D	total overhead product $D = \sum_i (d_i)$
E	total flow entering column (moles/U.T.)
f, f'	function and function derivative designation
F, F_o, F_1, F_2	feed flow rates (lb. moles/U.T.)
G_j	term defined by equation (54)
h_j	molar enthalpy of liquid leaving tray j $\left(\frac{B.T.U.}{Lb.mole}\right)$
$\bar{h}_f$	molar enthalpy of feed stream f. (B.T.U./Lb.mole)
H	molar enthalpy of mixture

H_j	molar enthalpy of vapour leaving tray j (B.T.U./Lb.mole)
$\overline{H}_{v_f}$	molar enthalpy of vapour portion of feed stream f (B.T.U./Lb. mole)
$I_{i,j}$	term defined by equation (53)
k	tray counter
k_r	the Runge-Kutta intermediate estimates of $x_{i,j}$
$K_{i,j}$	equilibrium ratio for component i on tray j
$l_{i,j}$	moles of component i in liquid leaving tray j
$\overline{L}_f$	moles of liquid in feed f at feed tray temperature T_f
L_j	total liquid flow leaving tray j (Lb. moles/ unit time) and $L_o = F_o$
m	factor in $\theta_{max} - \theta_{min}$ restriction
M	factor is defined in equation (29b)
p	factor defined by equation (44)
P	column pressure
P_c, T_c, Z_c	critical temperature, pressure and compressibility factor, respectively
P_c', T_c', Z_c'	pseudocritical constants for mixtures
q	factor in temperature restriction equation (48)
Q_k	intercooler-interheater heat duty
Q_{NR}	reboiler heat duty
R_j	term defined by equations (45)

s	standard error of estimate
S_j	term defined by equations (46)
t, t^+	time variable and time variable with $t^+ = 0$ at step change
T, T_j	temperature and tray temperature respectively
U_j	holdup on tray j
$v_{i,j}$	moles of component i in vapour leaving tray j
$\overline{V}_f$	moles of vapour in feed f at feed tray temperature T_f
$\overline{V}_j$	total vapour flow leaving tray j (Lb.moles/U.T.)
W_j	term defined by equations (22)
$x_{i,j}$	liquid mole fraction
$X_{i,f}$	mole fraction of component i in feedstream f
$y_{i,j}$	vapour mole fraction
Y_j	term defined by equations (23)
ψ_f	the liquid to feed ratio of feedstream f or $\psi_f = (\overline{L}_f/F_f)$
τ_j, τ_o	tray and overall time constants defined in equations (61) and (60) respectively.

Subscripts

conv	convergence
ca, co	calculated and corrected values respectively

f	number of feed stream $f = 0$ absorption stream $f = 1$ liquid feed $f = 2$ mixed feed
form	represents the formula calculation of $\left(\frac{b_i}{d_i}\right)$ ratio
i	refers to component
j	refers to tray and is numbered from the top of the tower
k	refers to tray in intercooler heat duty expression
N	iteration number
10	datum of 10 p.s.i.a.
N1, N2, N3, N4, N5, NR	tray numbers defined in Figure 1
o	as a superscript this represents the ideal gas state
t	tray - to - tray calculations in equations (27) and (28)
v	refers to vapour in feed stream f

NOTE: U.T.- Time units; i.e. 10 U.T. = 1 Hr.

1. INTRODUCTION

With the advent of the high-speed digital computer, rigorous calculations resulting from the mathematical analysis of complex unit operations have been successfully executed. Not only have efficient techniques been derived for the steady state situation, but the chemical engineer can now investigate the transient situation in the most complex unit operations.

The sophistication of the mathematical models derived to describe the behaviour of these unit operations may however be restricted;

(1) by the lack of plant data to confirm the model.

(2) by the lack of physical property data.

(3) by the economics of the simulation, i.e. the savings to be gained from a computational look at the process.

and (4) by the size and speed of the computer available.

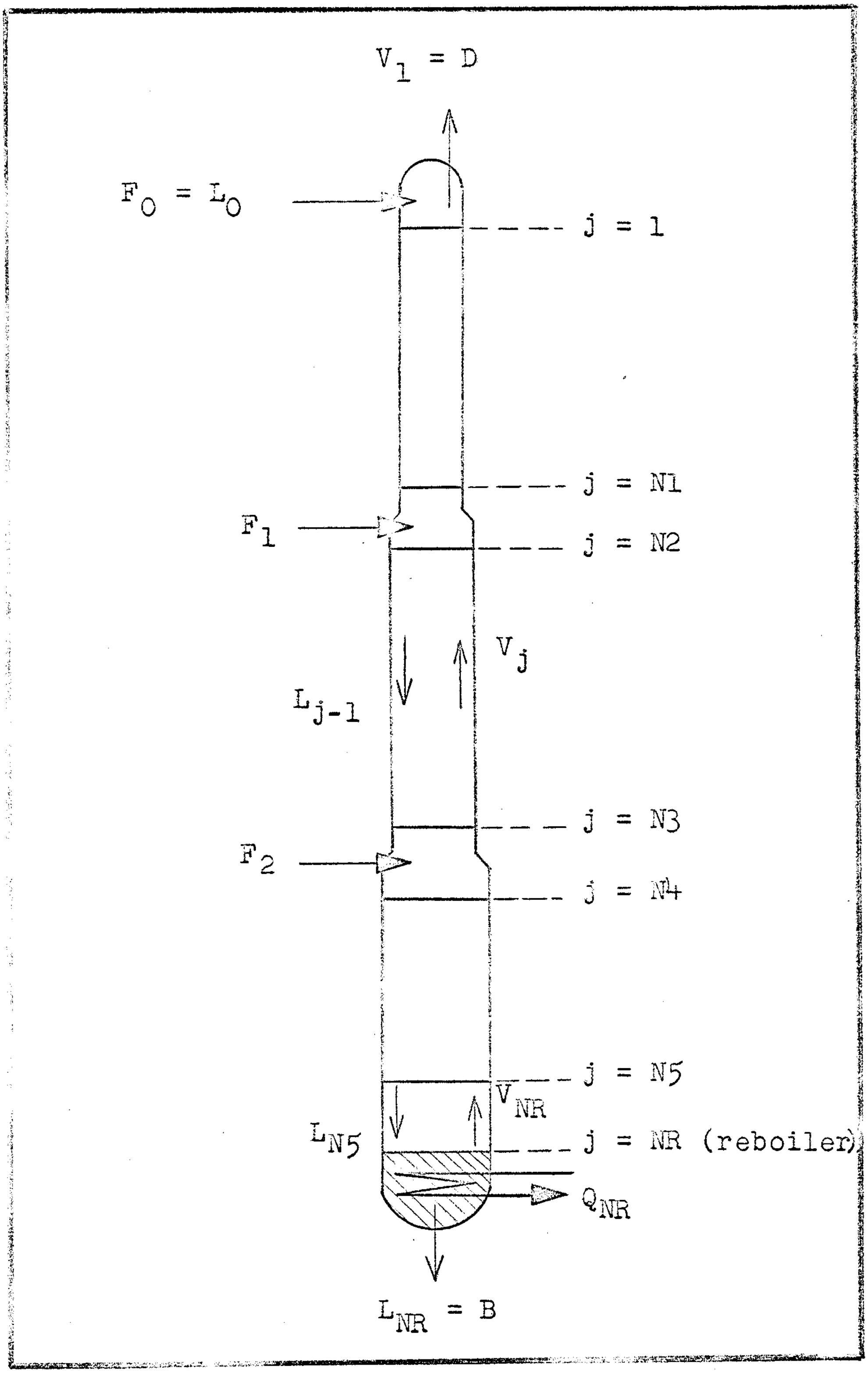
Simplifications are normally applied to parameters having a small or negligible effect on overall plant behaviour.

The complex distillation column under consideration is a 42-tray demethanizer-absorber in which methane plus some hydrogen and nitrogen are removed from heavier hydrocarbons. This column is the first in a train which handles the refinery feedstock streams at Polymer Corporation Ltd., Sarnia. The feedstocks are eventually converted to butadiene and other monomers used in the polymerization reaction producing synthetic rubber.

Referring to Figure 1, two separate raw feeds plus an absorption or "sponge-oil" stream form the multi-feed input to the demethanizer-absorber. The sponge-oil is an internal recycle stream composed primarily of the butanes, butylenes, and pentanes. This stream enters at 0°F. to -5°F. at the top tray of the tower. A liquid refinery feed containing minor quantities of methane and at 0°F. enters at tray 17, the trays being numbered from the top of the column. A mixed gas-liquid refinery feed containing approximately 25% by volume of methane enters at 0°F. at tray 31. The column is constructed in three distinct sections which are divided at the feed trays. The top section, center section and bottom section are 3½, 5 and 6½ feet in diameter respectively. The trays are all bubble-cap in design but vary in specification from a single cross-flow or rim down-flow type in the top section to split-flow or double-pass type in the other two sections. The details of the column internals are presented in Appendix II. The column has an overall height of 106 feet. The reboiler operates on the thermosyphon principle to recycle part of the flow from tray N5 up the column as vapour.

The difficulty of operating and controlling the column is the specification of "essentially zero" methane in the bottoms product and a minimum of ethylene in the overhead product. Control action taken to maintain the former is, of course, detrimental to the retention of the latter stipulation. There are two means employed to maintain column

Figure 1: SCHEMATIC DIAGRAM OF A MULTI-FEED DEMETHANIZER-ABSORBER



control. Where "excessive" ethylene is being lost in the overhead, the sponge-oil flow is raised to increase the absorption effect in the top section of the column. When the methane content of the bottoms product becomes appreciable, steam to the reboiler is increased. The steam is controlled by a signal from an infra-red analyzer located in the bottom section of the column (28).

The feeds entering the demethanizer-absorber continually vary in composition and flow rates. This is especially true of the raw refinery feedstock streams F_1 and F_2. The investigation of the column was prompted by these continually varying conditions. The ethylene currently lost overhead is directed to use as fuel gas. This component should preferably be directed to use in the production of the styrene monomer. There is therefore an economic incentive to reduce the ethylene content of the overhead without increasing the methane content of the bottoms product.

2. LITERATURE SURVEY

2.1. Literature on the Steady State Situation

Various calculational techniques have been proposed for solving steady state distillation problems (9), (17), (23), (26), (27), (30), (37), (39), (48), (50). In recent years, the digital computer has revolutionized the approach to the solving of the steady state situation. There has been a determined effort to solve the problem in a rigorous manner and to apply the calculational procedures to even the most "complex" column. This effort has resulted in a condensation of techniques to variations of

(1) the relaxation method (48)

(2) the Lewis and Matheson proposal (37)

(3) the Thiele and Geddes proposal (51)

The relaxation method proposed by Rose et al (48) utilizes the unsteady state equations to make gradual changes in tray and product compositions until steady state is reached. This method suffers from the disadvantage of long, and therefore expensive, computation times when compared to the other more conventional methods. However the relaxation method is of particular advantage where complex columns and multiple columns are being studied since it is not subject to wide fluctuations of plate compositions when small perturbations of terminal compositions occur. These wide fluctuations lead to instabilities in the conventional methods which rely on forcing functions to ensure convergence to the steady state solution. Ball (3), (30) has proposed modifications to the relaxation method to increase the rate of convergence.

The Lewis and Matheson proposal requires the selection of the distribution of each component between the top and bottom products as the independent variable (37), (30). This technique involves the alternate solution of material balance and bubble point relationships from tray to tray. The match is made at the feed tray; calculations being carried out from the top and from the bottom of the column. This iterative procedure was found by Holland (30) to be competitive with the Thiele and Geddes technique in the rate of convergence. The comparison is made when the θ-method of convergence is applied to both techniques.

The Thiele and Geddes proposal selects the tray temperatures throughout the column as the independent variable (50), (30). This choice requires the prespecification of the number of trays in each column section, the thermal and flow conditions of the feeds and the total overhead flow. Holland (30) has presented a rigorous appraisal of this calculational procedure as applied to both simple and complex distillation columns. Canik (9) has applied the Thiele and Geddes approach along with the θ-method to the analysis of a two feed reboiler-absorber. It is this particular combination that has been used by the author to solve for the steady state situation of the three-feed demethanizer-absorber.

The latter two methods were originally used with a "direct-iteration" approach to the ultimate steady state solution. This "direct-iteration" consists of taking the calculated values of the variables in trial N as the assumed values for the next iteration (N + 1). For complex multi-feed columns (9) and situations where there are "wide-boiling" feeds (17), the "direct-iteration" approach has proven inadequate due to divergence and when convergence is obtained, computational time is excessive. This inadequacy has resulted in the introduction of convergence methods (9), (27), (30) of which the aforementioned Θ-method is one. These techniques select a "better" value of the independent variable to be used for the calculation of the (N + 1)th trial than was used for the (N)th trial.

2.2. Literature on Dynamic Behaviour Situations

It is only recently, with the increase in adequate computational facilities, that the transient behaviour of distillation columns has been studied. The current effort on this aspect of chemical engineering has been directed towards batch distillation where the nature of the problem demands an unsteady state analysis. Some effort has also been expended on simple two-component distillation columns. The progress in this field is exemplified by Meadows (43) and Bowman (8) who have applied themselves to the batch problem while Baber (1), (2), Gilliland (21) and Huckaba (32) have studied continuous distillation. These papers are reviewed in some detail in Appendix I.

Numerical methods for the solution of differential equations are adequately presented in several texts (16), (34), (35). Specific reference to the equations representing the dynamic behaviour of multicomponent, multi-stage systems and their solutions is made by Mah et al (40) in their paper. The third order Runge-Kutta procedure is used by the author in the solution of the set of first order, non-linear differential equations describing the behaviour of the demethanizer-absorber model. This technique has the advantage of being self starting. It is also readily adapted to digital computation. The disadvantages of the Runge-Kutta procedure include the lack of a mathematical estimate of the inherent error and its apparent "computational slowness".

3. SCOPE

It is the purpose of this investigation of the multi-component, multi-feed demethanizer-absorber

(i) to obtain, in analytic form, expressions describing the equilibrium vapour-liquid relationships at the column pressure.

(ii) to evaluate and apply a numerical solution of the non-linear algebraic equations describing the steady-state behaviour of this column.

(iii) to evaluate and apply a numerical solution of the non-linear differential equations describing the dynamic behaviour of this column.

(iv) to compare the calculated results with actual column performance with the object of proposing recommendations for improving this performance.

(v) to obtain column response to variations in the external parameters, feed flows and reboiler heat load.

4. TREATMENT OF EQUILIBRIUM AND ENTHALPY INFORMATION

In the past, engineering data have normally been presented in tabular or graphical form. The intention of representing these data was to facilitate the manual calculations carried out on the unit operations and processes. The conversion of these calculations to "automatic" computer methods has created a need for analytic expressions to relate a dependent variable as a function of the significant parameters. This form of representation has the advantage of simplicity and speed when compared to the alternative of data storage and data lookup. The latter technique is more attractive where only few physical properties and correspondingly few components are to be considered.

4.1. Calculation of Vapour-Liquid Equilibrium Ratios

The equilibrium relationship expressing the vapour mole fraction as a function of liquid mole fraction, temperature and pressure is

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

This relationship for component i on tray j can be rearranged and the equilibrium ratio expressed as a function of temperature, pressure, and composition.

$$K_{i,j} = \frac{y_{i,j}}{x_{i,j}} = f_1(T,P,i) \qquad (2)$$

There are many graphical correlations of component equilibrium ratio (25), (36), (44), (49) expressed in terms of the above variables. In some cases these correlations are quite general and relatively simple to use (25), (49) while at the other extreme in excess of 325 graphs for the 12 light hydrocarbons are required to represent this relationship (44). These plotted values have as their basis, binary and ternary data as well as computed values from available P-V-T data for pure components. The Braun charts (10) were used as the basis for the analytic expressions which were obtained by multiple linear regression. These charts consider the effect of composition on the equilibrium ratios by choosing the "convergence pressure" as a correlating parameter (36). This is more important at higher pressures where deviations from ideality are, of course, more pronounced. The demethanizer-absorber operates at a pressure of 475 p.s.i.a. thereby requiring the consideration of non-ideal equilibrium. The basic assertion involved in this method is

$$K = f_2(i,T,P,P_{conv}) \qquad (3)$$

where P_{conv} is the convergence pressure, the pressure at which the equilibrium ratio is unity. The Braun charts are composed of 12 graphs expressing

$$K_{10} = f_3(i,T)\Big|_{P = 10} \qquad (4)$$

where the subscript refers to P = 10 p.s.i.a. These graphs cover a temperature range from -220°F. to 980°F. and consider paraffinic, olefinic, naphthenic, aromatic and heavy oil hydrocarbons. In addition two nomographs are employed to express

$$K = f_4(K_{10}, P, P_{conv}) \tag{5}$$

It was from these nomographs that the regressed relationships for the equilibrium ratios used in the demethanizer-absorber model were obtained.

Reference (36) presents graphical methods for predicting the convergence pressure for multicomponent mixtures. Where the convergence pressure varies little over the extremes of column compositions, the K can be regressed against temperature at the column pressure. Further sophistication would be required where P_{conv} has a wide range over the length of the column.

Three types of curve fits were attempted, the Antoine equation

$$\ln(K_i) = a_i' + \frac{b_i'}{T + 460.0} \tag{6}$$

a quadratic fit

$$K_i = a_i' + b_i'.T + c_i'.T^2 \tag{7}$$

and a cubic fit

$$K_i = a_i' + b_i'.T + c_i'.T^2 + d_i'.T^3 \tag{8}$$

Table 1 summarizes the coefficients used in equation (8). Figure 2 compares the use of P_{conv} = 1000 p.s.i.a. with P_{conv} = 1500 p.s.i.a. to indicate the variation in composition resulting from this change.

Appendix III·1 summarizes the regression and indicates

Table 1: EQUILIBRIUM RATIO REGRESSIONS

P = 475 p.s.i.a. T is in °F.

$$K_i = a_i' + b_i'T + c_i'T^2 + d_iT^3$$

valid over range - $40 \leq T \leq 240$

P_{conv} = 1500 p.s.i.a.

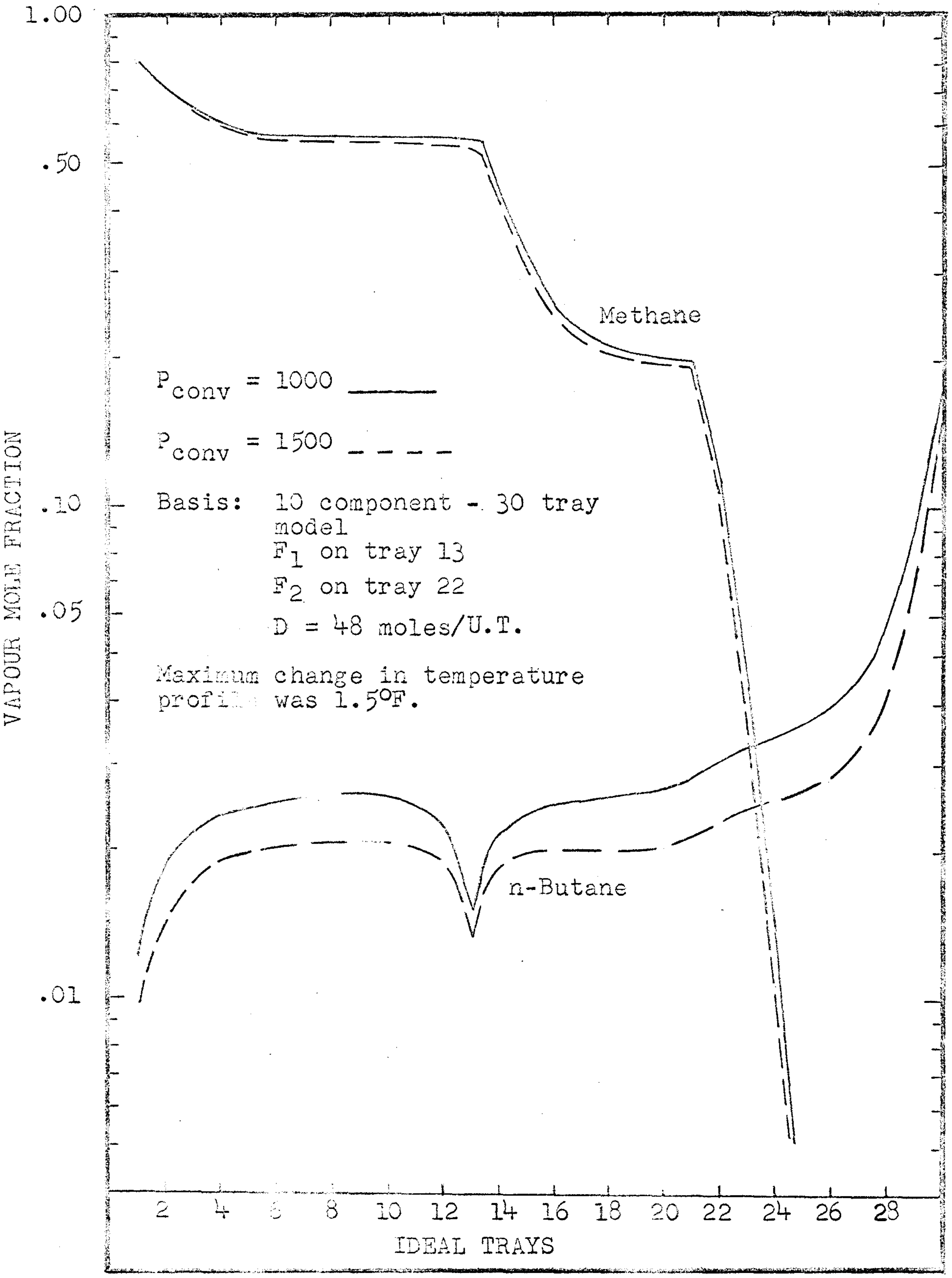
Component	a_i'	$b_i' \times 10^3$	$c_i' \times 10^5$	$d_i' \times 10^8$
Methane	4.0112	22.325	-4.8979	7.0899
Ethylene	.88377	7.2166	2.8217	1.4034
Ethane	.56412	6.8113	.45843	3.1325
Propylene	.18231	2.6766	1.4937	-1.4939
Propane	.15712	2.0996	1.5374	-1.0029
Isobutylene	.051048	1.0488	.55619	1.1980
N-Butane	.041062	.82358	.64406	.72920
Butene-2	.036037	.50236	1.1830	-1.2915
Pentane	.011103	.27875	.27425	1.0569
Heptane	.0010751	.038833	.0058433	.66929

P_{conv} = 1000 p.s.i.a.

Methane	3.8529	18.866	-1.9479	-11.170
Ethylene	.88557	7.4336	3.1244	-4.3543
Ethane	.61695	6.4084	1.1501	-0.74454
Propylene	.21477	3.0372	1.2907	-1.5637
Propane	.18283	2.3040	1.6833	-2.6304
Isobutylene	.064514	1.1052	.90072	-0.32859
N-Butane	.053794	1.0077	.68095	.39174
Butene-2	.048575	.90670	.76748	-0.012943
Pentane	.015777	.35573	.37287	.72536
Heptane	.0017439	.060248	.023171	.73507

Source: Graphical data in Reference (10).

Figure 2: EFFECT OF CONVERGENCE PRESSURE ON COMPOSITION PROFILE



the reasons for choosing equation (8) to express the equilibrium ratio for component i.

4.2. Calculation of Liquid and Vapour Enthalpies

The enthalpy of a single, pure component is a function of both temperature and pressure. Charts for the paraffinic and olefinic hydrocarbons are found in references (15), (42), (45). For mixtures at elevated pressures, the mixture enthalpy relative to the corresponding ideal gas enthalpy can be calculated from the P-V-T data by using thermodynamic relationships and an equation of state. Generalized correlations have been offered by Lydersen et al (38) in the form of tables and charts expressing

$$\frac{H^{o} - H}{T_c} = f_5(T_r, P_r, Z_c) \qquad (9)$$

These charts were improved and converted to analytical expressions by Yen and Alexander (51). Equations of the form of (9) are presented for the four physical states

(i) subcooled liquid
(ii) saturated liquid
(iii) saturated vapour
(iv) superheated vapour and for compressibility factors Z_c = 0.29, 0.27, 0.25, 0.23.

To use these relationships for mixtures of non-polar compounds, pseudo-critical constants are calculated using Kay's rule

$$T_c' = \sum_i x_i . T_{c,i} \tag{10}$$

$$P_c' = \sum_i x_i . P_{c,i} \tag{11}$$

$$Z_c' = \sum_i x_i . Z_{c,i} \tag{12}$$

The component critical constants are weighted according to mole fraction to yield the pseudo-critical values.

In the lower section of the demethanizer-absorber, methane, ethylene and ethane appear in liquid solution above their respective critical points. Using equations (10), (11) and (12) eliminates the alternative necessity of extrapolating the saturated liquid line beyond the critical point. This extrapolation would be necessary if each component were dealt with individually and then weighted to provide a final result (51).

To evaluate the explicit enthalpy of the mixture, the ideal gas state enthalpy must be calculated and inserted in equation (9). Since the pressure is assumed constant in the demethanizer-absorber, the ideal gas state enthalpy is given by

$$H^o_{2,i} - H^o_{1,i} = \int_{T_1}^{T_2} c^o_{p_i} . dT \tag{13}$$

Heat capacity ($c^o_{p_i}$) data are available for most light hydrocarbons in reference (15). These data are in tabular form with temperature the parameter. A quadratic curve fit was applied to these data, i.e.

$$c^o_{p_i} = a''_i + b''_i.T + c''_i.T^2 \qquad (14)$$

which when substituted into (13) and upon integration yields the desired enthalpy. Since the choice of the datum T_1 is arbitrary, (13) can be further simplified by setting $T_1 = 0^oF$.

$$H^o_{2,i} = \int_0^{T_2} c^o_{p_i}.dT \qquad (15)$$

To calculate the mixture enthalpy at zero pressure, the following relationship is used

$$H^o = \sum_i x_i.H^o_i = \sum_i \left(x_i . \int_0^{T_2} c^o_{p_i}.dT \right) \qquad (16)$$

Substitution of (16) into (9) accompanied by the reduced temperature and pressure and the pseudo-critical constants yields the required mixture enthalpy H.

Tables 2 and 3 contain the regressed relationship for equation (14) and Yen's correlations for equation (9) respectively. Since the superheated vapour situation is not encountered in the demethanizer-absorber under consideration, the correlations describing this specific region have been omitted here but are readily available in reference (51).

Table 2: IDEAL GAS STATE HEAT CAPACITY REGRESSIONS

P = 0 T is in °F.

valid over range - 100.0≤T≤240.0

$$c^{o}_{p_i} = a''_i + b''_i . T + c''_i . T^2$$

	a''_i	$b''_i \times 10^2$	$c''_i \times 10^5$
Methane	8.2280	0.32005	1.0119
Ethylene	9.3813	1.2295	0.61924
Ethane	11.459	1.3965	0.91570
Propylene	13.771	1.8575	0.91157
Propane	15.647	2.4190	1.0007
Isobutylene	18.929	3.0839	-0.58362
N-Butane	21.165	2.8756	1.4171
Butene-2	18.036	3.0787	0.077777
Pentane	25.227	4.5541	-0.75878
Heptane	35.115	5.9477	-0.19890

Source: Tabular Values in Reference (15).

Table 3: LIQUID AND VAPOUR ENTHALPY CORRELATIONS

H^o, H in B.T.U./lb. mole

A. Saturated Vapour Line: for $0.01<P_R<1.0$

$Z_c = 0.29$

$$\frac{H^o - H}{T_c} = \frac{5.4\ P_R^{0.6747}}{1.0 + 1.227\ (-\mathrm{Ln}\ P_R)^{0.503}}$$

$Z_c = 0.27$

$$\frac{H^o - H}{T_c} = \frac{5.8\ P_R^{0.63163}}{1.0 + 1.229\ (-\mathrm{Ln}\ P_R)^{0.55456}}$$

B. Subcooled Liquid Region: for $0.01<P_R<30$ and $0.5<T_R<1.0$

$Z_c = 0.29$

$$\begin{aligned}\frac{H^o - H}{T_c} = {} & -0.09572107(P_R - 4.2) - 9.501235(T_R - 0.77) \\ & -17.30389(T_R - 0.77)^2 - 0.3195707(P_R - 4.2)(T_R - 0.77) \\ & +1.368092\ \mathrm{Ln}P_R + 4.227096.(\mathrm{Ln}P_R)(\mathrm{Ln}T_R) + 3.181639 \\ & (\mathrm{Ln}P_R)(\mathrm{Ln}T_R)^2 + 9.707447\end{aligned}$$

$Z_c = 0.27$

$$\frac{H^o - H}{T_c} = -0.1368774(P_R-4.664) - 14.56975(T_R-0.79749) -7.812724(T_R-0.79749)^2 - 0.1642482(T_R-0.79749)(P_R-4.664) + 1.036851\ \mathrm{Ln}P_R + 4.463472(\mathrm{Ln}P_R)(\mathrm{Ln}T_R) +4.525831(\mathrm{Ln}P_R)(\mathrm{Ln}T_R)^2 + 10.86085$$

C. Saturated Liquid Line: for $0.01<P_R<1.0$

$Z_c = 0.29$

$$\frac{H^o - H}{T_c} = \frac{5.4 + 3.6485(-\mathrm{Ln}P_R)^{0.33464}}{1.0 - 0.0056942(\mathrm{Ln}P_R)}$$

$Z_c = 0.27$

$$\frac{H^o - H}{T_c} = \frac{5.8 + 5.19(-\mathrm{Ln}P_R)^{0.4963}}{1.0 - 0.1(\mathrm{Ln}P_R)}$$

Source: Reference (51)

Ln - is the base "e" logarithm

5. STEADY STATE SOLUTION

To find the steady state solution of the demethanizer-absorber, the general conservation law

$$\text{INPUT} - \text{OUTPUT} = 0 \tag{17}$$

is applied to the tray and overall material balances and to the tray and overall heat balances. The kinetic and potential energy changes are neglected. Further, all stages are considered ideal trays. These simplifications result in a family of non-linear equations, the non-linearity being due to the equilibrium relationship described by equation (1). The following concerns itself with the specification of this set of equations and the Thiele and Geddes calculational procedure used with the θ-method convergence technique to solve the system.

5.1. Mathematical Model

This model considers the reboiler as a "partial-reboiler" where the vapour rising from the reboiler is in equilibrium with the liquid leaving the column.

5.1.1. Component Material Balances

Two sets of equations represent the tray material relationships (Figure 1). The two sets are distinguished by the choice of liquid or vapour compositions as the dependent variables and are related through the equilibrium relationship (1). To derive the equations in which the vapour compositions are the dependent variables, consider an envelope about the top of the column and enclosing tray j-1. A component material balance yields (in the top section)

$$L_o.X_{i,o} + V_j.y_{i,j} = L_{j-1}.x_{i,j-1} + D.y_{i,1} \tag{18}$$

for the steady state situation. The trays are numbered from the top. Rearrangement of, and substitution of (1) into (18) results in

$$V_j.y_{i,j} = \frac{L_{j-1}}{K_{i,j-1}}.y_{i,j-1} + D.y_{i,1} - L_o.X_{i,o} \tag{18a}$$

Further simplification can be achieved by introducing

$$v_{i,j} = V_j.y_{i,j} \tag{19}$$

$$A_{i,j-1} = \frac{L_{j-1}}{K_{i,j-1}.V_{j-1}} \tag{20}$$

$$d_i = D.y_{i,1} \tag{21}$$

into (18a). Therefore

$$v_{i,j} = A_{i,j-1}.v_{i,j-1} + d_i - L_o.X_{i,o} \tag{18b}$$

which when expressed as a ratio of the moles of component i in the vapour leaving tray j to the moles of component i in the overhead product becomes

$$\frac{v_{i,j}}{d_i} = A_{i,j-1}.\left(\frac{v_{i,j-1}}{d_i}\right) + 1.0 - W_j \tag{22}$$

where if $\Psi_1 = \frac{\bar{L}_1}{F_1}$ and $\Psi_2 = \frac{\bar{L}_2}{F_2}$ the following holds,

$$W_j = \frac{L_o . X_{i,o}}{d_i} \qquad 1 \leq j \leq N1 \qquad (22a)$$

$$W_j = \frac{L_o . X_{i,o} + (1.0 - \Psi_1) . F_1 . X_{i,1}}{d_i} \qquad j = N2 \qquad (22b)$$

$$W_j = \frac{L_o . X_{i,o} + F_1 . X_{i,1}}{d_i} \qquad N2+1 \leq j \leq N3 \qquad (22c)$$

$$W_j = \frac{L_o . X_{i,o} + F_1 . X_{i,1} + (1.0 - \Psi_2) . F_2 . X_{i,2}}{d_i} \qquad j = N4 \qquad (22d)$$

and

$$W_j = \frac{L_o . X_{i,o} + F_1 . X_{i,1} + F_2 . X_{i,2}}{d_i} \qquad N4+1 \leq j \leq NR \qquad (22e)$$

By considering an envelope about the bottom section and tray j+1, the liquid relationship can similarly be derived.

$$\frac{\ell_{i,j}}{b_i} = \frac{1}{A_{i,j+1}} . \frac{\ell_{i,j+1}}{b_i} + 1.0 - Y_j \qquad (23)$$

where $Y_j = 0$ and $b_i = \ell_{i,j+1}$ $\qquad j = N5 \qquad (23a)$

$$Y_j = 0 \qquad N4 \leq j \leq N5-1 \qquad (23b)$$

$$Y_j = \frac{\Psi_2 . F_2 . X_{i,2}}{b_i} \qquad j = N3 \qquad (23c)$$

$$Y_j = \frac{F_2 . X_{i,2}}{b_i} \qquad N2 \leq j \leq N3-1 \quad (23d)$$

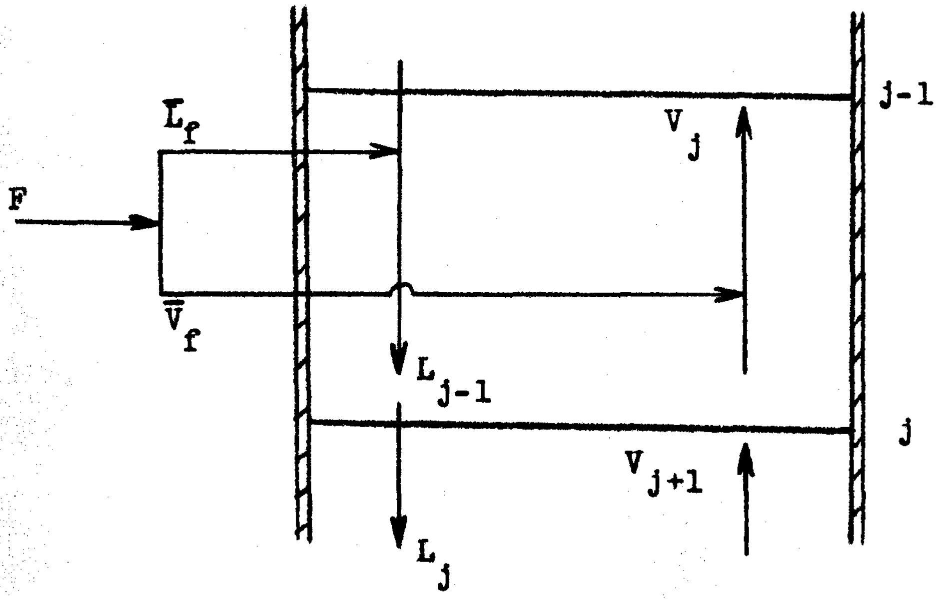
$$Y_j = \frac{\psi_1 . F_1 . X_{i,1} + F_2 . X_{i,2}}{f\ b_i} \qquad j=N1 \quad (23e)$$

$$\text{and } Y_j = \frac{F_1 . X_{i,1} + F_2 . X_{i,2}}{b_i} \qquad 1 \leq j \leq N1-1 \quad (23f)$$

5.1.2. Feed Tray Representation

The mathematical representation at a feed tray is sketched in Figure 3 below.

Figure 3



where for a bubble-point or subcooled feed

$$\bar{L}_f = F \qquad \bar{V}_f = 0 \qquad (24)$$

The enthalpy and heat balance relationships (9) and (45) respectively, consider the degree of subcooling of the feed stream. Normally L_o and F_1 enter the column as subcooled feeds.

For a dew-point or superheated feed

$$\bar{L}_f = 0 \qquad \bar{V}_f = F \tag{25}$$

This particular feed condition is not normally realized in the demethanizer-absorber being considered.

For a partially vaporized feed

$$\bar{V}_f + \bar{L}_f = F \tag{26}$$

The feed F_2 which enters the column at tray N4 is a gas-liquid mixture at the normal tray temperature and column pressure.

5.1.3. Round-Off Error

The Θ-method of convergence involves the bottoms to distillate ratio $\left(\frac{b_i}{d_i}\right)$. This term must be evaluated at each iteration of the calculational procedure with a minimum of round-off error. This ratio can be calculated by using either equation (22) successively from the top down or equation (23) in the opposite direction. For a three-feed column, there are several alternatives available at this point. Equation (22) could be used for the full length of the column $1 \leq j \leq NR$ or only to $j=N4$ and could even be cut off at $j=N2$ while (23) could be used for the remainder of the column. Similar alternatives are available in the application of relationship (23) to the tray-to-tray calculation from the reboiler up. It was found that to avoid the very low concentrations of methane which occur in the bottom of the column, equation (22) was applied over the range $1 \leq j \leq N4$ to obtain $\left(\frac{v_{i,N4}}{d_i}\right)_t$. By applying identity (20) and equation (23), the desired ratio is obtained

$$\left(\frac{b_i}{d_i}\right)_t = \left(\frac{v_{i,N4}}{d_i}\right)_t \cdot A_{i,N4} \Bigg/ \left(\frac{\ell_{i,N4}}{b_i}\right)_t \qquad (27)$$

Further, application of equation (23) over the range $1 \leq j \leq N5$ yields an alternative calculation of the ratio.

$$\left(\frac{b_i}{d_i}\right)_t = A_{i,1} \Bigg/ \left(\frac{\ell_{i,1}}{b_i}\right)_t \qquad (28)$$

In using either equation (22) or (23), the $(j+1)^{th}$ calculation is a function of the $(j)^{th}$ calculation, thereby propogating and amplifying any round-off error. The magnitude of the error is a function of the number of trays and relative magnitudes of b_i and d_i. To minimize this error, successive substitution of the $(j-1)^{th}$ relationship into the $(j)^{th}$ equation of (22) yields the following formula which is essentially free of round-off error.

$$\left(\frac{b_i}{d_i}\right)_{form} = \frac{M}{\bar{F}\cdot\left(1.0 + \alpha\cdot\gamma + \gamma + \alpha\cdot\beta\cdot\left(\frac{v_{i,N4}}{b_i}\right)\right) - M} \tag{29}$$

where, $\bar{F} = L_o\cdot X_{i,o} + F_1\cdot X_{i,1} + F_2\cdot X_{i,2}$ (29a)

$$M = L_o\cdot X_{i,o} - \alpha\cdot\beta\cdot(1.0-\psi_2)\cdot F_2\cdot X_{i,2} - \alpha\cdot(1.0-\psi_1)\cdot F_1\cdot X_{i,1} + (1.0+\delta)\cdot(F_1\cdot X_{i,1} + F_2\cdot X_{i,2}) + \alpha\cdot\gamma\cdot F_2\cdot X_{i,2} \tag{29b}$$

$$\alpha = (A_{i,1}\cdot A_{i,2} \cdots\cdots A_{i,N1-1}\cdot A_{i,N1})^{-1} \tag{29c}$$

$$\beta = (A_{i,N2}\cdot A_{i,N2+1} \cdots\cdots A_{i,N3-1}\cdot A_{i,N3})^{-1} \tag{29d}$$

$$\gamma = (A_{i,N2} \cdots\cdots A_{i,N3})^{-1} + (A_{i,N2} \cdots\cdots A_{i,N3-1})^{-1} + \cdots\cdots + (A_{i,N2}\cdot A_{i,N2+1})^{-1} + (A_{i,N2})^{-1} \tag{29e}$$

$$\delta = (A_{i,1} \cdots\cdots A_{i,N1})^{-1} + (A_{i,1} \cdots\cdots A_{i,N1-1})^{-1} + \cdots\cdots + (A_{i,1}\cdot A_{i,2})^{-1} + (A_{i,1})^{-1} \tag{29f}$$

Dividing the ratios obtained from equations (27) and (28) by the ratio calculated by formula (29) should yield 1.0 in both cases. Almost invariably and depending upon which component is under consideration, one of these divisions will not be 1.0 due to the round-off error in the tray-to-tray calculation. The values calculated by the alternative equation will then be used to represent the compositional variation from tray-to-tray. Normally for the light components, the calculation is carried out from the top of the tower while for the heavy hydrocarbons the calculation is in the opposite direction.

5.1.4. The Θ-method of Convergence

References (9), (27), (30) give excellent detailed accounts of the Θ-method as applied to both simple and complex distillation columns and to a two-feed reboiled-absorber (9). A short summary of this technique as applied to the three-feed demethanizer-absorber with single bottoms draw-off follows.

Consider a set of "calculated" overhead flows $(d_i)_{ca}$ and bottom flows $(b_i)_{ca}$ which do not necessarily add up to the specified overhead product D or bottoms product B respectively. A set of corrected values $(d_i)_{co}$, $(b_i)_{co}$ are required which will satisfy the overall material balance

$$L_o . X_{i,o} + F_1 . X_{1,1} + F_2 . X_{1,2} = (b_i)_{co} + (d_i)_{co} \qquad (30)$$

and the overhead specification

$$D = \sum_i (d_i)_{co} \qquad (31)$$

simultaneously. The θ-method is a technique used to select the set of θ_i's which satisfies

$$\left(\frac{b_i}{d_i}\right)_{co} = \theta_i \cdot \left(\frac{b_i}{d_i}\right)_{ca} \qquad (32)$$

Since the correct set of θ_i's can be calculated only when the final solution is obtained, a first approximation of the corrected ratios is given by

$$\left(\frac{b_i}{d_i}\right)_{co} = \theta . \left(\frac{b_i}{d_i}\right)_{ca} \qquad (33)$$

To calculate θ, it is necessary to eliminate $(b_i)_{co}$ from (30) and (33). Upon rearranging the substitution yields

$$(d_i)_{co} = \frac{L_o.X_{i,o} + F_1.X_{i,1} + F_2.X_{i,2}}{1.0 + \theta.\left(\frac{b_i}{d_i}\right)_{ca}} \qquad (34)$$

Substitution of (34) into (31) results in the functional relation

$$f(\theta) = \sum_i \left(\frac{L_o.X_{i,o} + F_1.X_{i,1} + F_2.X_{i,2}}{1.0 + \theta.\left(\frac{b_i}{d_i}\right)_{ca}} \right) - D \qquad (35)$$

The desired value of θ is the positive root of (35) for which $f(\theta) = 0$. The steady state programme utilizes the Newton tangent technique to seek out the correct root. This iterative technique requirès the derivative of (35) which is

$$f'(\theta) = -\sum_{i} \frac{(L_o.X_{i,o} + F_1.X_{i,1} + F_2.X_{i,2}).\left(\frac{b_i}{d_i}\right)_{ca}}{\left[1.0 + \theta.\left(\frac{b_i}{d_i}\right)_{ca}\right]^2} \tag{36}$$

The final solution to the steady state problem is obtained when $(1-\Delta\theta)\leq\theta\leq(1+\Delta\theta)$ (37) where $\Delta\theta$ is the tolerance and is a specified value in keeping with the differences between successive composition and temperature estimates. Experience has indicated that to obtain four significant figure precision in the tray composition $0.0002\leq\Delta\theta\leq0.0005$. Continued calculation would yield more precise results but at the expense of considerable computation time. This criterion specification will be discussed and a comparison of criteria is presented in a succeeding section. (See Table 4).

5.1.5. Calculation of Corrected Liquid Mole Fractions

Once the θ-root has been obtained from the functional relation (35), the corrected values of the overhead and bottoms are obtained from equations (34) and (33) respectively, i.e. equation (33) rearranges to

$$(b_i)_{co} = \theta.\left(\frac{b_i}{d_i}\right)_{ca}.(d_i)_{co} \tag{33a}$$

It is readily seen that the corrected liquid mole fractions are

$$x_{i,j} = \frac{\left(\frac{l_{i,j}}{b_i}\right)_{ca} \cdot (b_i)_{co}}{\sum_i \left(\frac{l_{i,j}}{b_i}\right)_{ca} \cdot (b_i)_{co}} \tag{38}$$

and the corrected vapour mole fractions are

$$y_{i,j} = \frac{\left(\frac{v_{i,j}}{d_i}\right)_{ca} \cdot (d_i)_{co}}{\sum_i \left(\frac{v_{i,j}}{d_i}\right)_{ca} \cdot (d_i)_{co}} \tag{39}$$

Equations (38) and (39) are definitions of the mole fractions. It is from these corrected liquid mole fractions that the new temperature profile is calculated.

5.1.6. Heat Balance Relationships

Assuming constant molal overflow and constant molal vaporization leads to the solution indicated in Appendix VII. The temperature in the center section is sufficiently high to vaporize F_2 and thereby supply the bulk of the overhead specification D. A decrease of D causes even lower vapour flows in the bottom section until ultimately the vaporization of the gas feed supplies the total overhead vapour. This situation bears no relation to the real situation in the demethanizer-absorber being considered. To improve the model, the energy balances at each tray must be considered.

To derive the familiar heat balance equations, consider the top envelope of Figure 1 and apply the general conservation law (17).

$$L_o.\bar{h}_o + V_{j+1}.H_{j+1} = D.H_D + L_j.h_j \qquad (40)$$

and $$V_{j+1} = L_j + D - L_o \qquad (41)$$

Substituting (41) into (40) and solving for L_j yields

$$L_j = \frac{L_o.(\bar{h}_o - H_{j+1}) + D.(H_{j+1} - H_D)}{(h_j - H_{j+1})} \qquad (42)$$

Where methane-rich systems or wide-boiling range feeds are concerned, the Θ-method using the bubble-point as a definition of tray temperature has a tendency towards over-correction for successive estimates of the column profiles. This leads to wide fluctuations in flow rates between iterations. To dampen this effect, the author has taken Canik's (9) suggestion to control the change with the following criteria

$$\frac{L_{j,N}}{p} \leq L_{j,N+1} \leq L_{j,N}.(p) \qquad (43)$$

However the calculation of p from iteration to iteration obeys

$$p = 1.0 + e^{-N/C} \qquad (44)$$

Equation (44) is an improvement over Canik's technique since the dampening factor p approaches the final desired value of 1.0 as the number of iterations N increases. The constant C attenuates the rate of approach toward 1.0 and is related to the number of components and trays, i.e. experience has indicated that as the model increases in the number of variables, C correspondingly increases. For a 10 component-10 tray system $N_{final} \rightarrow 50$, $C = 10$ while for a 10 component-30 tray model $N_{final} \rightarrow 120$ and C correspondingly increases to about 15. This factor is a continuous function and is to be compared to a similar discontinuous step relationship employed by Canik for the two-feed reboiled-absorber.

Such a forcing procedure will create heat imbalances at the trays where there are wide flow variations from iteration to iteration. In the demethanizer-absorber this effect is most pronounced at the top of the column where the vapour is rich in methane. To compensate for the heat imbalance, an "intercooler-interheater" is introduced at each tray (9). The heating load (or cooling load) at steady state should ideally be zero in each of these artificial heat exchangers. Thus equation (42) becomes

$$L_j = \frac{L_o.(\bar{h}_o - H_{j+1}) + D.(H_{j+1} - H_D) + R_j - \sum_{k=1}^{j-1} Q_k}{(h_j - H_{j+1})} \qquad (45)$$

where Q_k is the interstage heat imbalance caused by restriction (43)

$$\text{and } V_{j+1} = L_j + D - L_o - S_j \qquad (46)$$

also

$$S_j = 0 \tag{46a}$$

$$1 \leq j \leq N1-1$$

$$R_j = 0 \tag{45a}$$

$$S_j = F_1.(1.0-\Psi_1) \tag{46b}$$

$$j=N1$$

$$R_j = S_j.(\bar{H}_{v_1}-H_{j+1}) \tag{45b}$$

$$S_j = F_1 \tag{46c}$$

$$N2 \leq j \leq N3-1$$

$$R_j = S_j.(\bar{h}_1-H_{j+1}) \tag{45c}$$

$$S_j = F_2.(1.0-\Psi_2) + F_1 \tag{46d}$$

$$j=N3$$

$$R_j = F_2.(1.0-\Psi_2).(\bar{H}_{v_2}-H_{j+1})+ F_1.(\bar{h}_1-H_{j+1}) \tag{45d}$$

$$S_j = F_2 + F_1 \tag{46e}$$

$$N4 \leq j \leq N5$$

$$R_j = F_2.(\bar{h}_2-H_{j+1}) + F_1.(\bar{h}_1-H_{j+1}) \tag{45e}$$

After the liquid flow is calculated from equation (45), the vapour flow is obtained from the material balance (46).

5.2. Forcing Procedures

Along with the introduction of restrictions on maximum flow variation between successive iterations, there are restrictions imposed upon successive tray temperature estimates and boundary values imposed on the value of Θ. Hardy (27), Canik (9) and Holland (30) recommend the dampening of successive tray temperature estimates to speed the rate of convergence for the Θ-method. The author in addition found it necessary to limit the upper and lower boundaries of the Θ-value. The latter restriction proved most valuable for the first few (<10) iterations and was more significant as an aid to computation stability as the number of trays increased.

5.2.1. Temperature Restriction

All tray temperature bubble point calculations are accomplished using the Newton-Raphson method to solve

$$f(T_j) = \sum_i (K_{i,j} x_{i,j}) - 1.0 = 0 \qquad (47)$$

The technique is presented in detail in Appendix III.1. The bubble point determination has the undesirable characteristic of over-estimating successive temperature estimates when large quantities of methane or when wide-boiling mixtures are encountered. The following weighting of successive trials dampens this effect.

$$T_{j,N+1} = T_{j,N} + q \cdot \left(T_{j,calc(N+1)} - T_{j,N} \right) \qquad (48)$$

where $0 < q \leq 1$ (49)

Applying a stringent value of q to (48) will not necessarily lengthen the iterative calculation as indicated by Figure 4. Figure 5 shows the comparative trial to trial temperature variations for the key trays.

The tray temperature is also bounded to lie within the range of the data curve fit for the equilibrium ratios and the ideal gas state heat capacities.

Figure 4: Θ - VARIATION UPON APPROACHING SOLUTION

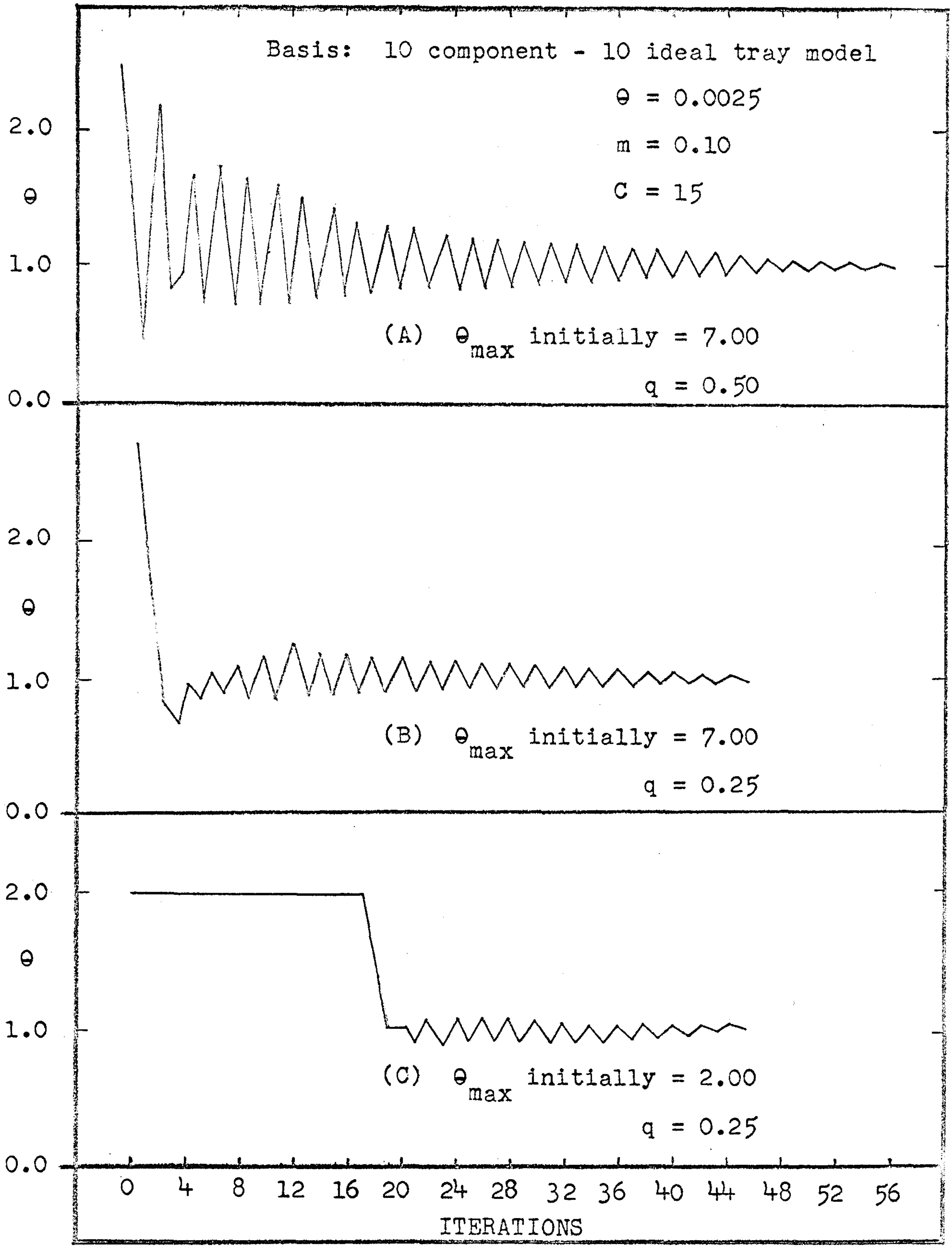
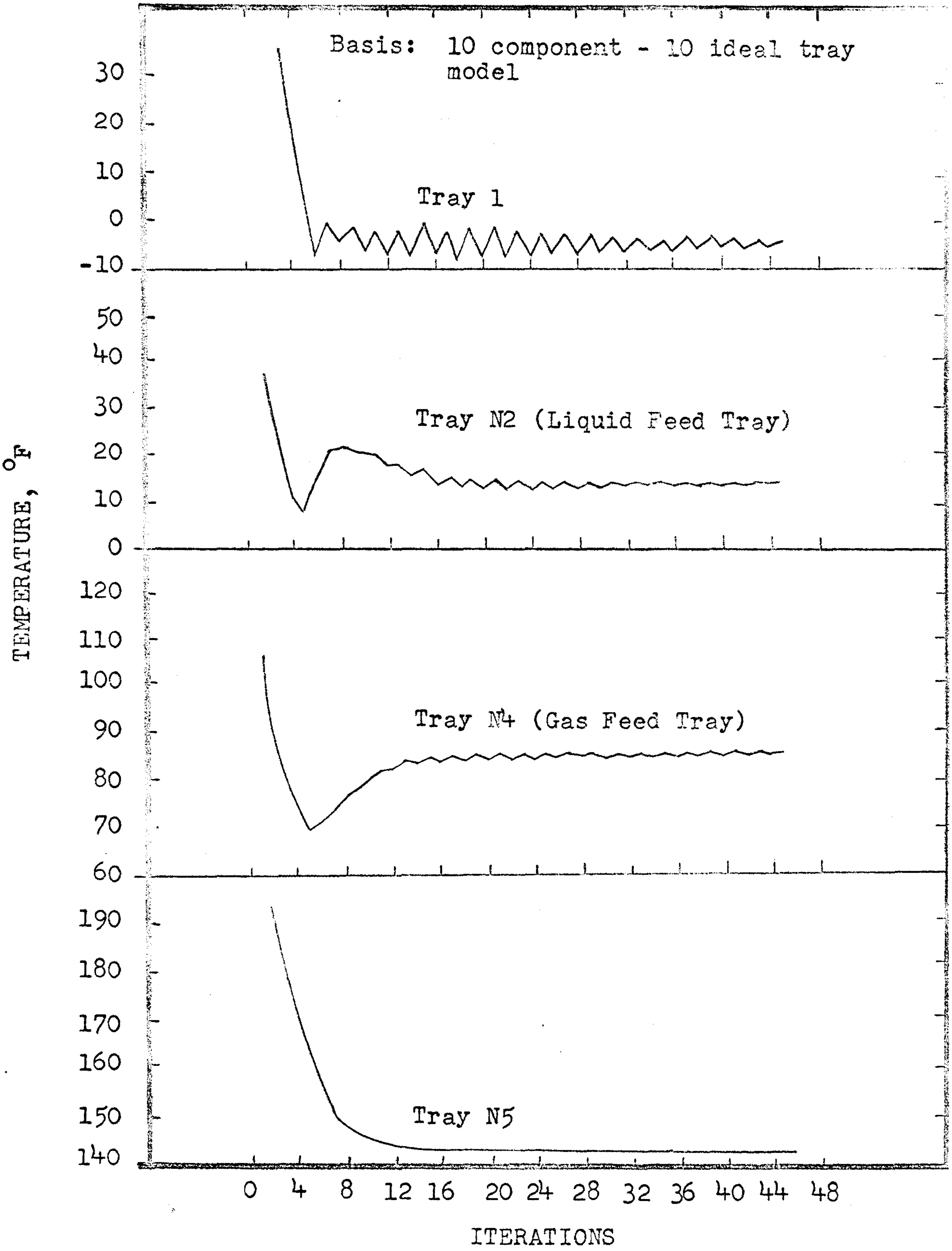


Figure 5: TRAY TEMPERATURE VARIATION UPON APPROACHING SOLUTION



5.2.2. The Θ-Restriction

To further maintain a stable iterative search for $\left(\frac{b_i}{d_i}\right)_{co}$, the Θ-root was itself bounded. The tendency towards instability in the search technique was most pronounced for cases where the overhead was approaching pure methane (i.e. >90% by volume).

The maximum-minimum boundary values for Θ can also be suitably adjusted to approach $\Theta = 1.0$ as the iterations proceed. The following formulae govern this change

$$\Theta_{max,N+1} = \Theta_{max,N} - m.(\Theta_{max,N} - 1.0) \qquad (50)$$

$$\Theta_{min,N+1} = \Theta_{min,N} - m.(\Theta_{min,N} - 1.0) \qquad (51)$$

It should be noted that these equations are employed only when the Θ-value for (N + 1) falls between the boundary limits for iteration (N).

The "normal" factor values applied when seeking the steady state solution were

$0.2 \leq q \leq 0.5$

$0.05 \leq m \leq 0.2$

$10 \leq C \leq 15$

$4.0 \leq \Theta_{max} \leq 10.0$ for initial trials

$0.1 \leq \Theta_{min} \leq 0.2$

5.3. Calculation Sequence

Appendix V contains the detailed Fortran listing for the steady-state calculation as well as the data input listing. The following general procedure was employed for the cases cited in this dissertation. The flow diagram in Appendix V is a schematic representation of these steps.

(1) A temperature profile, normally linear with tray number and covering the range $0^{\circ}F. < T_j < 200^{\circ}F.$ was assumed for the first trial.

(2) The column flows necessary for the first iteration are calculated using constant molal overflow and adjusted to ensure sufficient vapour flow throughout the column.

(3) The enthalpies of the individual feeds were calculated.

(4) Equilibrium ratios and absorption factors were calculated for each tray at the assumed temperatures and flow rates.

(5) Equations (27) and (28) were used to obtain the $\left(\frac{b_i}{d_i}\right)_t$ ratio. Comparison of this result with that obtained from the formula calculation (29) determined the direction of calculation with the least round-off error. Either equation (27) or (28) was then used to calculate the $\left(\frac{v_{i,j}}{d_i}\right)$ and $\left(\frac{l_{i,j}}{b_i}\right)$ ratios.

(6) Using these calculated ratios, the appropriate θ-value was computed. At this point a test of $1-\Delta\theta \leq \theta \leq 1 + \Delta\theta$ was carried out. If the θ-value satisfied this criterion the iterative procedure was terminated.

(7) The corrected $\left(\frac{b_i}{d_i}\right)_{co}$ ratio was then computed using equation (33). Equation (38) yielded the required liquid mole fractions.

(8) At the end of the second and subsequent trials, the temperature profile was adjusted using equation (48). During the first trial, the restriction is bypassed.

(9) For the first two trials, the original flow rates are maintained constant. In subsequent trials, the liquid flow rates were calculated using the heat balance relationship (45) and equation (43). The vapour flow rates were calculated from the material balances (46).

(10) The iterative search recycles to item (4).

5.4. Presentation and Discussion of Results

It has been previously mentioned that the criterion of an acceptable solution is the satisfaction of

$$(1 - \Delta\theta) \leq \theta \leq (1 + \Delta\theta) \qquad (37)$$

Table 4 indicates the variation in the overhead and bottoms concentrations for the final and successive iterations at the acceptable level.

Table 4: COMPARISON OF OVERHEAD FLOWS FOR SUCCESSIVE ITERATIONS AT AN ACCEPTABLE SOLUTION

Case A			**Case B**	
10-tray model		Component	30-tray model	
$\Delta\theta=0.0025$	$D=45.0\ \frac{\text{Moles}}{\text{U.T.}^*}$		$\Delta\theta=0.0003$	$D=45.0\ \frac{\text{Moles}}{\text{U.T.}^*}$
$(d_i)_{ca}$	$(d_i)_{co}$		$(d_i)_{ca}$	$(d_i)_{co}$
37.804	37.804	Methane	39.687	39.687
5.7259	5.7288	Ethylene	4.3457	4.3466
.53946	.53983	Ethane	.015098	.015103
.016522	.016533	Propylene	$.42051\times10^{-6}$	$.42063\times10^{-6}$
.068859	.068906	Propane	.063533	.063552
.13510	.13520	Isobutylene	.14303	.14308
.43075	.43104	Butane	.45491	.45505
.22769	.22785	Butene-2	.23892	.23899
.046976	.047009	Pentane	.049751	.049729
$.56448\times10^{-3}$	$.56487\times10^{-3}$	Hexane	$.60536\times10^{-3}$	$.60554\times10^{-3}$

*U.T. is the unit of time and is equivalent to 0.1 HR.

It is evident from a comparison of successive estimates of (d_i) for ethane, propane and butane that the variation in case A exceeds that in case B by a substantial margin. The tolerance in case A was $\Delta\theta = 0.0025$ while that in case B was $\Delta\theta = 0.0003$. The latter specification ensures 4 significant figure precision but is not recommended since such a tolerance undoubtedly exceeds the accuracy of the equilibrium data. A decrease in $\Delta\theta$ also entails more computation time and is therefore unattractive from an economic point of view.

At the acceptable solution, it has been found that there is still some heat imbalance. The imbalance is most pronounced at tray 1 and occurs to a lesser extent at the other two feed trays. However, successive flow estimates do not vary outside the limits imposed by flow restriction (43). The p-factor value is normally within 1% of 1.0 at the acceptable solution. These considerations, along with the fact that successive composition profiles and temperature profiles agree to well within the error of the physical data indicate that the heat imbalance does not invalidate the claim that steady state was obtained.

To test the reproducibility of a steady state solution for a specified overhead D, alternative initial temperature and flow profiles were used. The results of this investigation are tabulated in Appendix X. The final solution is reproducible to three significant figures for a solution criteria of $\Delta\theta = 0.0015$. This point is further strengthened by the comparison in Tables 8 and 9 of the steady state solution by the Θ-method and by the integration of the differential equations describing the dynamic behaviour of the demethanizer-absorber.

5.4.1. Comparison of the Model with the Real Demethanizer-Absorber

The feedstock flows to the tower, under normal operating conditions, are continually fluctuating in rate and composition. An infra-red analyzer monitors the methane content at the 37th tray. If the methane content exceeds a prescribed maximum, the steam flow to the reboiler is increased and the vapour flow rate in the column is increased. To map the column operating conditions, spot samples and blended samples of the feedstocks and exit streams are periodically analyzed. The temperatures at 5 points on the column are continually recorded. The composition of the feedstock samples is determined by mass spectrometer and 31 peaks are picked. The analysis is reported as weight % of the following components.

Hydrogen
Nitrogen
Carbon Monoxide
Methane
Ethylene
Ethane
Propylene
Propane
Butadiene
combined-Butylenes
Isobutane
n-Butane

and C5+

Polymer Corporation has submitted data concerning the feedstocks, operating conditions and the temperature profile given by the five points. Complete known internal and external physical details of the column are available (See Appendix II). There is current activity to obtain a more detailed composition mapping throughout the demethanizer-absorber.

The assumptions included in the model are

(i) hydrogen, carbon monoxide and butadiene are present in sufficiently small concentrations as to be neglected.

(ii) the nitrogen has a negligible effect on the equilibrium relationships amongst the hydrocarbons in the column and can be treated as a non-distributed component.

(iii) the recycle vapour from the partial reboiler is in equilibrium with the bottoms product.

(iv) only ideal equilibrium stages are considered and the mathematical model treats each section in terms of equivalent equilibrium stages.

(v) the remaining 26 components can be represented by the hydrocarbons

1. Methane
2. Ethylene
3. Ethane
4. Propylene
5. Propane
6. Isobutylene (+ Butene-1)
7. n-Butane (+ Isobutane)
8. Butene-2
9. Pentane (+ Isopentane)
10. Heptanes

Of these assumptions, (ii) offers the greatest opportunity for improving the model. Although nitrogen appears to the extent of approximately 2-3% of the total column input, its concentration increases to over 15% in the overhead vapours. The other neglected components are present in only trace quantities and should have a negligible influence on the column operation.

Table 5: TYPICAL FEED COMPOSITIONS

Flows in lb./U.T.

	Absorption	Liquid Feed	Mixed Gas-Liquid Feed	Totals
Methane	0.0	25.0	610.0	635.0
Ethylene	0.0	20.0	450.0	470.0
Ethane	0.0	70.0	535.0	605.0
Propylene	0.0	625.0	1290.0	1915.0
Propane	27.9	450.0	470.0	947.9
Isobutylene	276.2	1000.0	800.0	2076.2
N-Butane	1132.7	1900.0	600.0	3632.7
Butene-2	625.0	350.0	145.0	1120.0
Pentane	600.0	380.0	460.0	1440.0
Heptane	117.0	50.0	50.0	217.0
TOTALS	2778.8	4870.0	5410.0	13058.8

Without detailed composition data from every tray, it would be difficult to determine a variation of tray efficiency throughout the column. To discuss the available plant data, a section efficiency is defined as

$$\frac{\text{number of theoretical trays}}{\text{number of actual trays}} \times 100$$

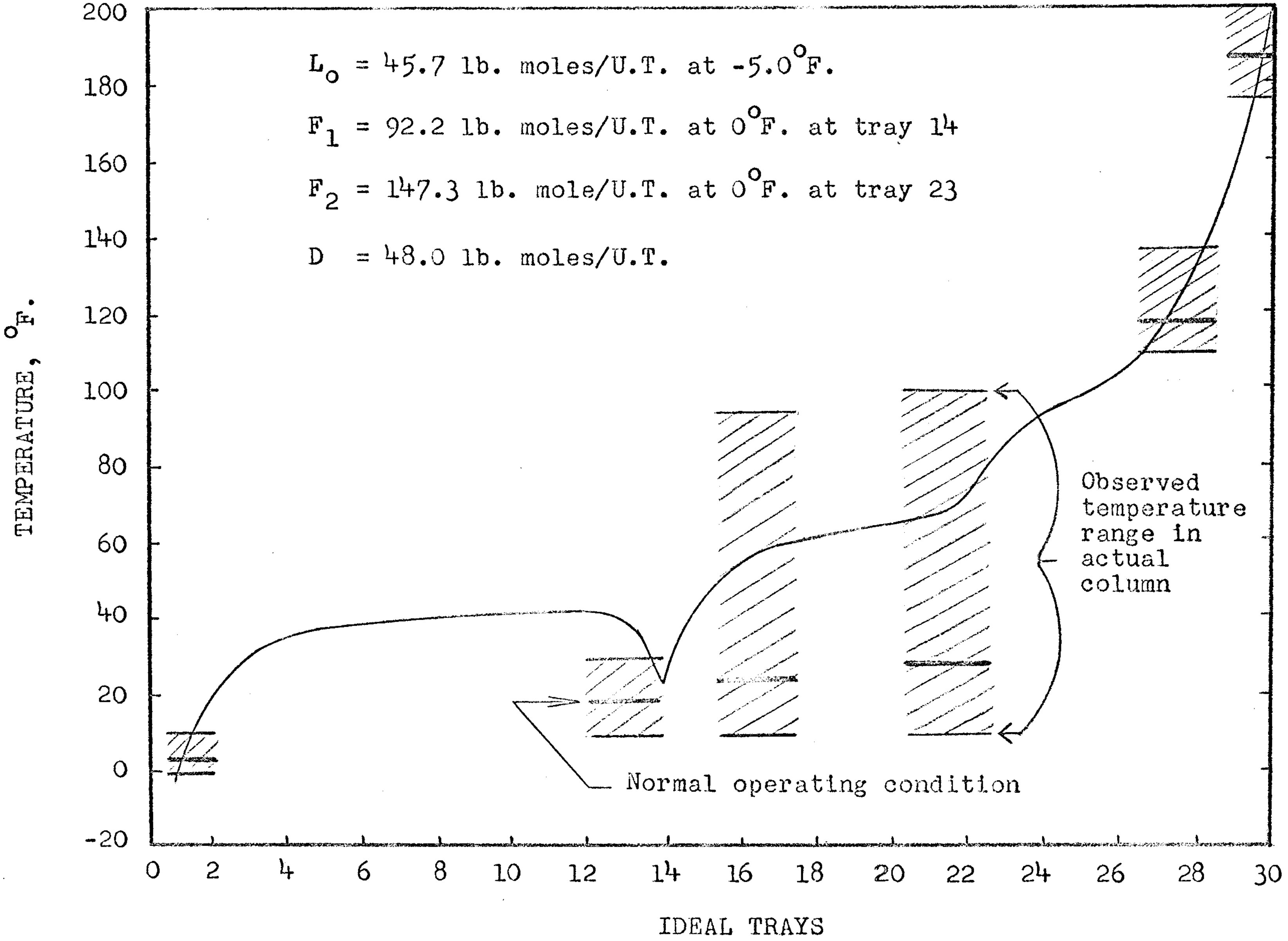
The preliminary model contains 14 trays in the absorbing section, 9 trays in the center section and 7 trays in the stripping section for a total of 30 ideal trays. These correspond to efficiencies of 87.5%, 75% and 54% respectively. These are rather arbitrary estimates based on the temperature data available from Polymer Corporation as indicated in Figure 6 and Table 6. Figure 6 presents a comparison of the calculated temperature profile and the actual known temperatures. The actual column temperatures are indicated as shaded bands with wide ranges in the center section of the column. The "normal" or "average" operating temperature profile is indicated by a solid line. These temperature points are at the following real locations:

1. the overhead
2. tray 14
3. tray 23
4. tray 28
5. tray 39
6. reboiler recycle vapour

A detailed variation of these temperatures over a 24 hour period of slight upset is presented in Appendix IX.

Table 6 summarizes the calculated overhead and bottoms

Figure 6: COMPARISON OF CALCULATED AND REAL TEMPERATURE PROFILES



L_o = 45.7 lb. moles/U.T. at -5.0°F.

F_1 = 92.2 lb. moles/U.T. at 0°F. at tray 14

F_2 = 147.3 lb. mole/U.T. at 0°F. at tray 23

D = 48.0 lb. moles/U.T.

Observed temperature range in actual column

Normal operating condition

Table 6: COMPARISONS OF CALCULATED RESULTS WITH ACTUAL COLUMN

weight %

	Overhead Product			Bottoms Product		
	Calculated		Actual*	Calculated		Actual*
	D = 48	D = 45		D = 48	D = 45	
Methane	70.0	78.5	77.0	trace	trace	trace
Ethylene	21.4	14.9	3.2	2.3	2.9	6.1
Ethane	.3	.1	.7	5.0	4.8	7.0
Propylene	trace	trace	.3	15.9	15.8	15.6
Propane	.4	.3	1.0	7.8	7.7	11.6
Isobutylene	1.2	1.0	16.8	17.0	16.9	44.3
N-Butane	4.0	3.2		29.4	29.4	
Butene-2	2.0	1.7		9.0	9.0	
Pentane	.6	.4	1.0	11.8	11.7	15.4
Heptane	trace	trace		1.8	1.8	

D is expressed in moles/U.T.

* The numbers reported are average figures for a four day test run and are on a nitrogen-free basis.

product and compares the result to the actual situation. The latter figures represent a 4 day average for actual demethanizer-absorber operation. The largest discrepancies of observed versus calculated occur between the ethylenes and the C_4 hydrocarbons. It is difficult to make a comparison of a single calculated steady state situation with a 4-day average which is made up of many "almost" steady state situations. The above differences can be partially explained in this manner. With additional data the "instantaneous" plant operation will be observed and should lead to a more precise determination of the section efficiencies.

Figure 7 presents the variation of liquid and vapour flow rates leaving each ideal tray. This flow map is to be compared to the map resulting from the assumptions of constant molal overflow and constant molal vaporization which is presented in Appendix VII. The heat balances correct the flow rates and adequately take into account the degree of subcooling in each of feedstreams L_o and F_1. It is noteworthy that over each section the flow rates are essentially constant suggesting that a section heat balance might be applied with due consideration at the feed trays for the indicated differences. Figures 8 and 9 present the calculated variations of liquid and vapour mole fractions for the three key components, methane, ethylene and n-butane throughout the column. The objective of future calculations and column studies should be the maximization of the divergence of vapour curves for methane

Figure 7: CALCULATED FLOW RATE PROFILE

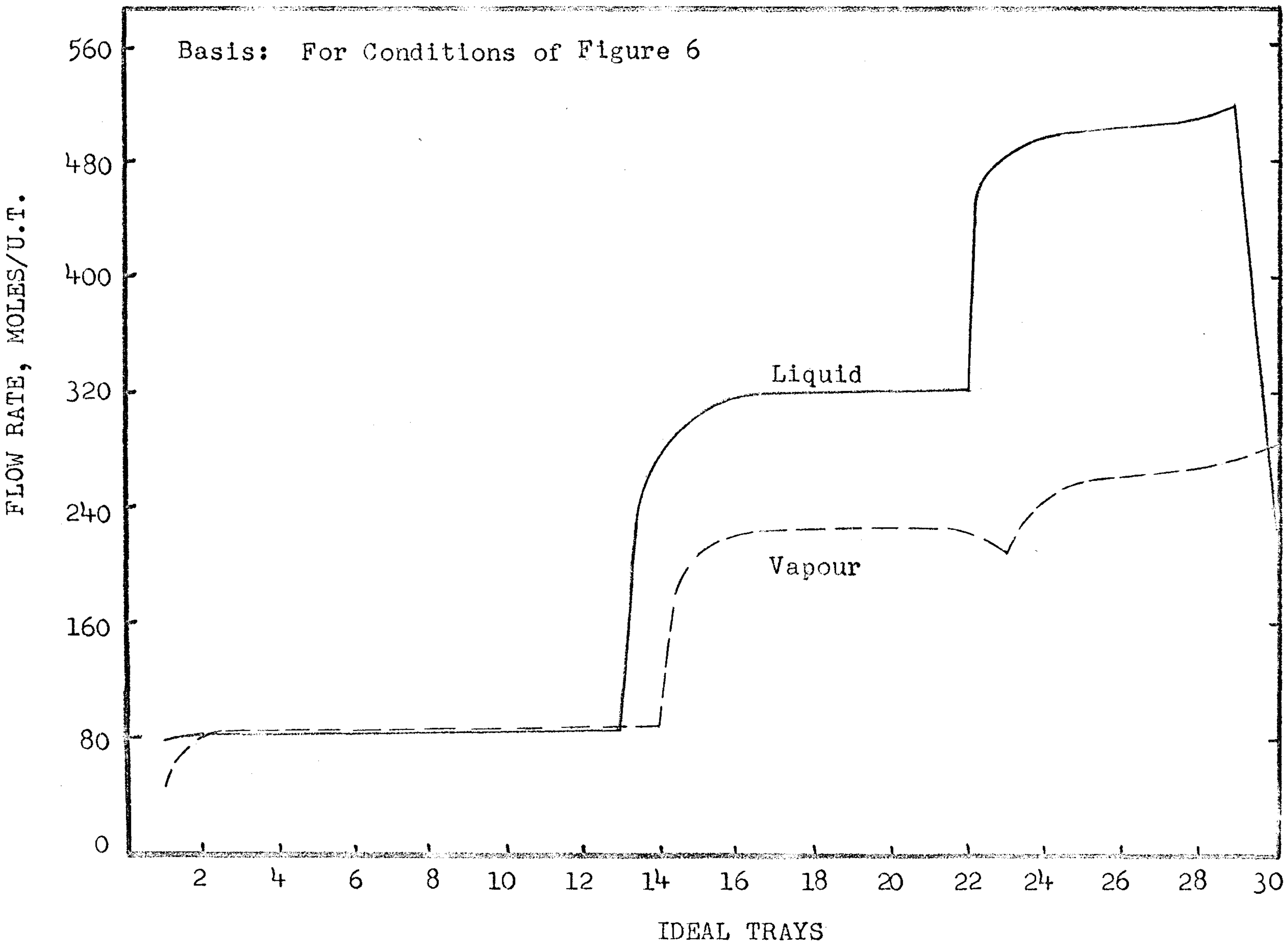


Figure 8: CALCULATED LIQUID COMPOSITION PROFILE

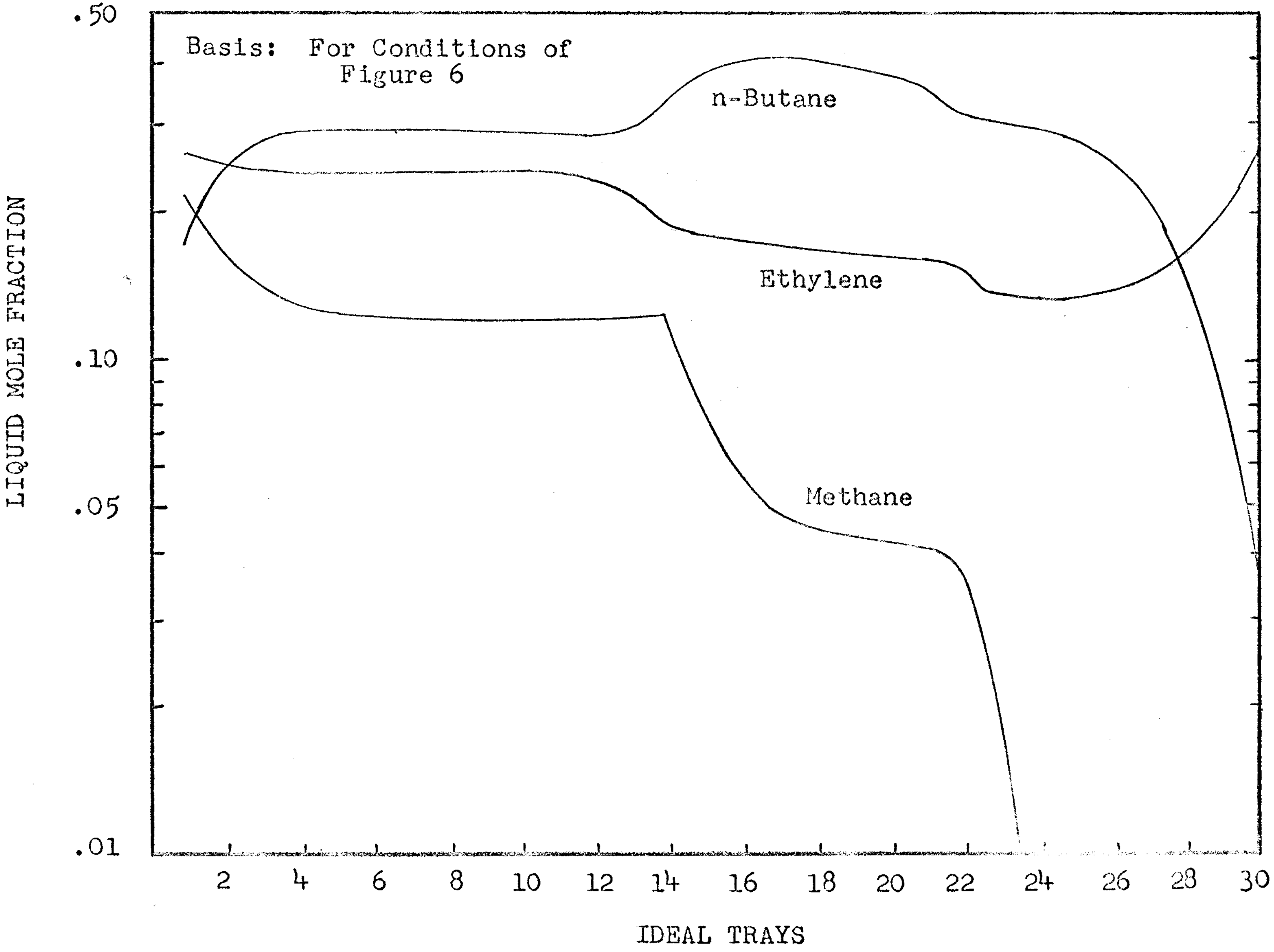
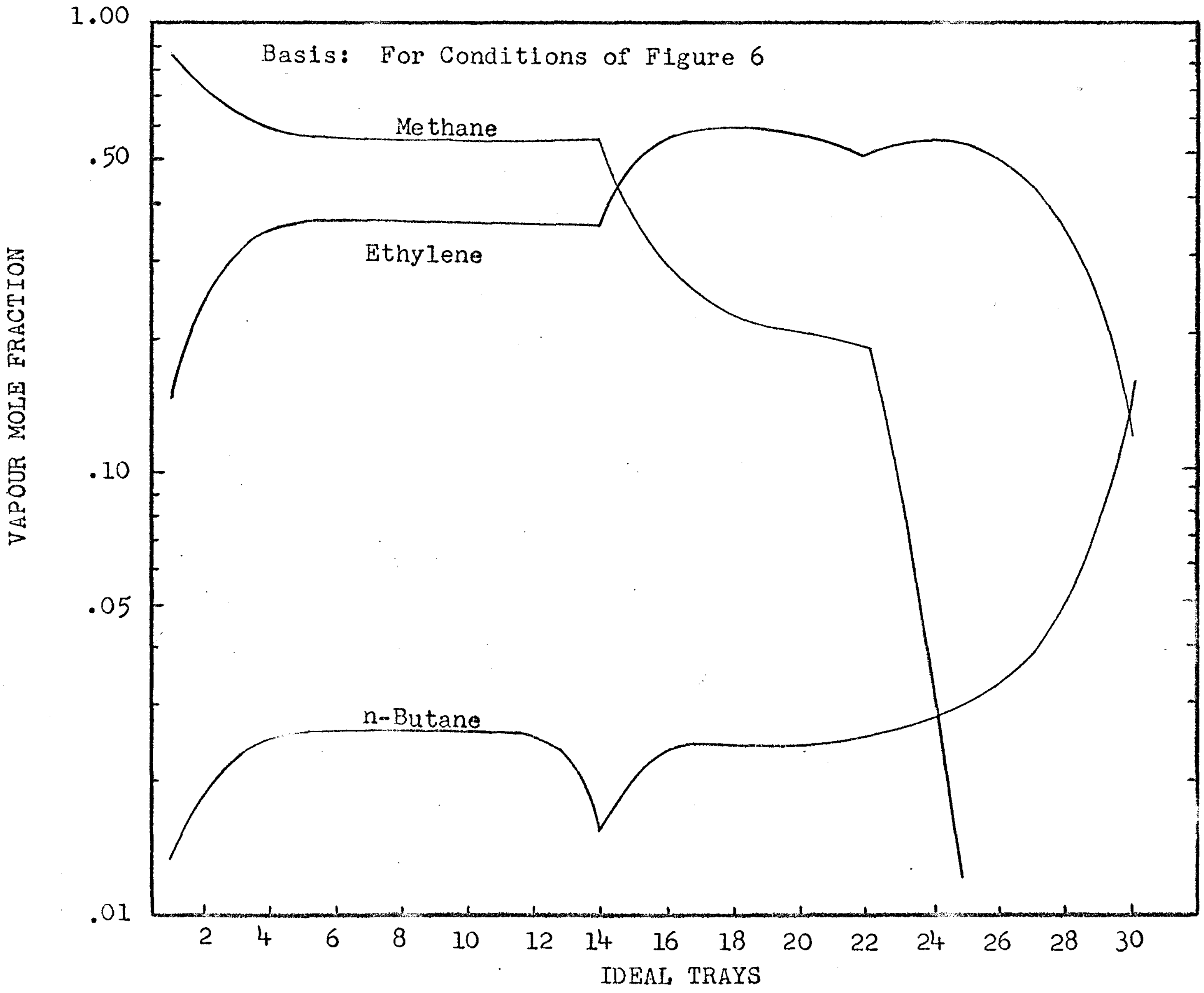


Figure 9: CALCULATED VAPOUR COMPOSITION PROFILE



and ethylene on the top tray. Some recommendations for any investigations along these lines are

(1) to increase the sponge-oil flow.

(2) to use essentially pure C_4 hydrocarbons or C_5 + hydrocarbons as the sponge-oil.

and (3) to vary the number of trays in the absorption section.

Many of the components indicated by the mass spectrometer analysis as contained in the feedstocks, are in very low concentration or in trace quantities. The grouping and reducing of these to 10 components of significant concentrations has reduced the duration of the calculation and increased the stability of the iterative search. Although computer runs were not made to quantitatively determine this effect, some comparison is available with Canik's (9) work. His studies involved a two-feed tower of 10 trays and 5 components. Using the θ-method this example converged to an acceptable solution in 27 iterations. This is to be compared with the 10 component-30 tray model discussed here which took 120 iterations to converge to within a tolerance of $\Delta\theta = 0.0003$.

5.5. Duration of Computer Runs

For a 10 component-10 tray calculation approximately 50 iterations are required for satisfactory convergence (Figure 4). Each iteration averages about 4.5 seconds. The 10 component-30 tray model takes 5.4 seconds per iteration and in excess of 100-120 iterations are necessary to obtain the steady state solution.

These computing times are quoted for the IBM 7040 digital computer with all subroutines located in the main 16K memory. The program, including subroutines occupies approximately 9K words. The model has been modified to accept a given solution as the initial estimate for a successive case. No appreciable increase in the rate of convergence was thereby obtained. The approach to the steady state solution was, in all respects, almost identical with an arbitrary initial estimate of temperatures and the assumed flow rates. This is probably caused by the relaxation of the p-factor to its initial value and since a new heat balance applies to the successive case, the new flow rate estimates will be quite different from the previous case during these first few iterations.

5.6. Conclusions and Recommendations

(1). The θ-method has been applied to a 10 component-30 tray demethanizer-absorber. Difficulty in convergence is encountered when the overhead vapours tend to pure methane. Otherwise the θ-method and accompanying restrictions do lead to successful solutions. The former situation is of no practical interest.

(2) A 10 component-30 tray model normally converges in approximately 120 iterations or about 12 minutes of IBM 7040 computation time.

(3) Heat balances must be included in an absorption-

type column. Assumption of constant molal overflow and vaporization leads to erroneous temperature and composition profiles.

(4) The actual temperature profile is a necessary but not sufficient corroboration of the mathematical model. Composition data at several points within the column are necessary to validate the simulation.

(5) To include Murphree type efficiencies rather than section efficiencies, liquid and vapour composition data are necessary at several locations in the actual column.

(6) The nitrogen, which has been neglected, should be included in any future investigation.

(7) The sum-rates method (S-R) proposed by Friday and Smith (17) should be evaluated.

(8) Section heat balances should be utilized to estimate the section flow rates and thereby speed up the computation.

6. SIMULATION OF THE TRANSIENT BEHAVIOUR

As has been previously mentioned, the feedstocks F_1 and F_2 are subject to continual perturbations both in flow rates and in compositions. Appendix IX indicates some of the fluctuations occurring in these streams.

To solve the differential equations describing this behaviour, a 3rd order Runge-Kutta technique was utilized. This represents a preliminary investigation into the dynamic behaviour and does not necessarily constitute the final integration. The Runge-Kutta technique (16), (34), (35) is both simple to understand and simple to adapt to the 110 differential equations involved in the 10 component-10 tray model. It is also relatively simple to programme for the digital computer.

6.1. Mathematical Model

As in the case of the steady state behaviour, this model considers the reboiler as a "partial reboiler" and all stages as ideal trays. There are additional simplifications which were not necessary in the steady state study, namely, the assumptions of constant liquid holdup and negligible vapour holdup on each tray. The former simplification was based on a calculation which indicated that a 50% change in tray liquid flow rate caused a 16% change in holdup. Appendix VI deals with this calculation. It was originally considered that a 50% change in flow rate was a rare occurrence. Figure (21) in Appendix IX indicates the flow situation when one of the refinery supplies was cut off. This represents a severe situation where a 35% change in column input was experienced.

6.1.1. Component Material Balances

Consider an envelope about tray j of the demethanizer-absorber depicted in Figure 1. The general conservation law states that for an unsteady state situation

$$\text{INPUT} - \text{OUTPUT} = \text{ACCUMULATION} \tag{52}$$

Consider component i and apply (52) to obtain

$$L_{j-1}.x_{i,j-1} + V_{j+1}.y_{i,j+1} - (L_j.x_{i,j} + V_j.y_{i,j}) = U_j.\frac{dx_{i,j}}{dt} \tag{53}$$

which has the general form

$$\frac{dx_{i,j}}{dt} = \frac{1}{U_j}\left(L_{j-1}.x_{i,j-1} + V_{j+1}.y_{i,j+1} + I_{i,j} - L_j.x_{i,j} - V_j.y_{i,j}\right) \tag{53a}$$

where $I_{i,j} = 0$ $\qquad 1 \le j \le N5, j \ne N2, j \ne N4$ (53b)

$I_{i,j} = F_1.X_{i,1}$ $\qquad j=N2$ (53c)

$I_{i,j} = F_2.X_{i,2}$ $\qquad j=N4$ (53d)

and for the reboiler j=NR

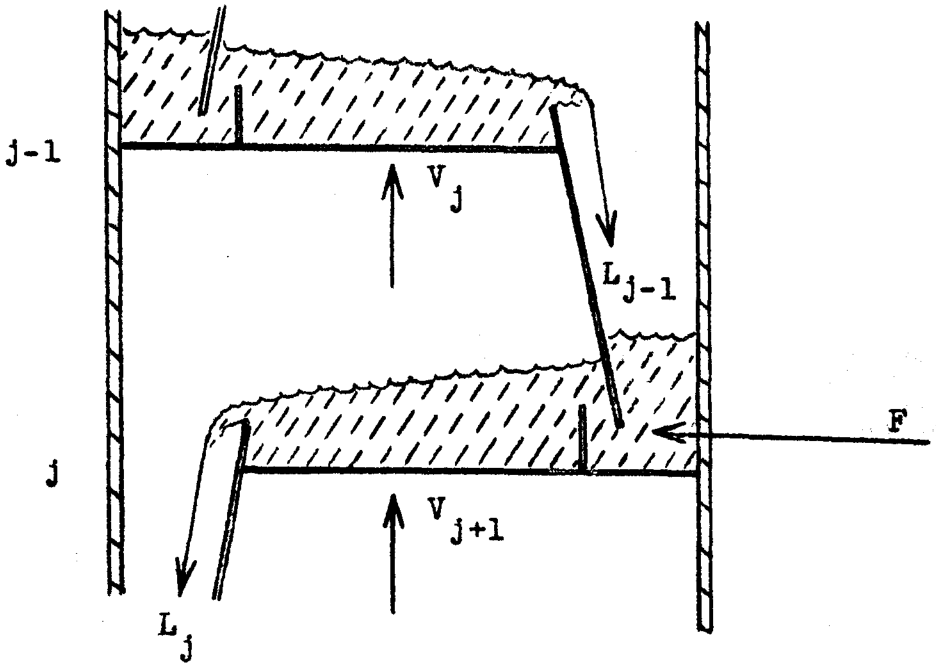
$$\frac{dx_{i,NR}}{dt} = \frac{1}{U_{NR}}\left(L_{N5}.x_{i,N5} - L_{NR}.x_{i,NR} - V_{NR}.y_{i,NR}\right) \tag{53e}$$

Equations (53) represent ideal stages. The equilibrium relationship defined by equation (1) eliminates the vapour mole fraction $y_{i,j}$ from (53) thereby expressing the rate of change of the liquid mole fractions as a function of temperature, liquid composition and flow rates. These relations are non-linear differential equations with variable coefficients. The non-linearity is introduced by the equilibrium relation equation (1).

6.1.2. Feed Tray Representation

For the transient situation, the following schematic diagram, Figure 10, indicates the mathematical model assumed for the feed trays.

Figure 10



The feed stream is assumed to be completely mixed with the liquid on the tray and the vapour V_j is assumed to be in equilibrium with the liquid L_j. An alternative would be to introduce the feed stream F_1 into the vapour space between trays j and j-1. This model would have involved an additional temperature and an additional differential equation to describe it. It was considered that for a preliminary study this addition was not warranted. The real situation likely lies between these two configurations.

6.1.3. Heat Balance Relationships

Application of (52) to an envelope about tray j yields

$$L_{j-1}.h_{j-1} + V_{j+1}.H_{j+1} - (L_j.h_j + V_j.H_j) = U_j.\frac{dh_j}{dt} \qquad (54)$$

The assumption of constant liquid holdup U_j on each tray allows the use of the material balance

$$V_j = L_{j-1} + V_{j+1} - L_j \qquad (55)$$

Substitution of (55) into (54) and rearrangement yields

$$L_j = \frac{L_{j-1}.(H_j-h_{j-1}) + V_{j+1}.(H_j-H_{j+1}) + U_j.\frac{dh_j}{dt}}{(H_j - h_j)} \qquad (54a)$$

The general form of (54a) is

$$L_j = \frac{L_{j-1}.(H_j-h_{j-1}) + V_{j+1}.(H_j-H_{j+1}) - G_j + U_j.\frac{dh_j}{dt}}{(H_j - h_j)} \qquad (54b)$$

where

$$G_j = 0 \qquad j \neq NR, j \neq N2, j \neq N4 \qquad (54c)$$

$$G_j = F_1 . (\bar{h}_1 - H_{N2}) \qquad j = N2 \qquad (54d)$$

$$G_j = F_2 . (\bar{h}_2 - H_{N4}) \qquad j = N4 \qquad (54e)$$

$$V_{j+1} = 0 \qquad j = NR \qquad (54f)$$

To maintain consistency, the subscript j when equated to zero refers to the absorption stream L_o. Equations (54) and (55) then apply to tray 1.

The derivative is located on the right hand side of equation (54b). This equation is used to solve for the liquid flow from tray j and is applied only after equations (53) have been integrated over the step length Δt for the tray concerned. This technique therefore requires an independent equation to solve for $\frac{dh_j}{dt}$. Since $h_j\Big|_{t+\Delta t}$ can be calculated from the analytical expressions represented by equation (9) and $h_j\Big|_t$ is known from the previous iteration, one can approximate the true change in liquid molar enthalpy by

$$h_j\Big|_{t+\Delta t} - h_j\Big|_t \doteq dh_j \qquad (55)$$

and also assume $\Delta t \doteq dt$ (56)

Division of (55) by (56) allows the explicit determination of the liquid flow from equation (54). The vapour flow is then calculated using equation (55).

In applying the Runge-Kutta integration technique (16), (34), (35) to the solution of equations (53), each tray was treated individually, starting at the reboiler. The time variable was incremented after the equations describing tray 1 behaviour were integrated for the previous interval.

The Runge-Kutta integration is discussed in more detail in Appendix V.2.

6.2. Restrictions

It has been previously mentioned that there were slight heat imbalances incurred at the feed trays in the steady state solution using the Θ-method of convergence. This steady state situation was used for the initial values of the transient situation. These imbalances cause unstable integration of the differential equations (53). This was especially pronounced when integration was attempted starting at tray 1. To circumvent this difficulty, the integration was begun at the reboiler where no detectable heat imbalance occurred and in addition it was found necessary to impose restrictions and dampening on successive flow calculations for the first few integrating increments. The restriction is described by

$$L_{j,N} - \Delta L \leq L_{j,N+1} \leq L_{j,N} + \Delta L \qquad (57)$$

When $L_{j,N+1}$ was outside the imposed limits, the following dampening was applied

$$L_{j,N+1} = L_{j,N} + n.(L_{j,N+1} - L_{j,N}) \tag{58}$$

Equation (58) was only applied for the first 10 time increments after which the integration proceeded normally. It should be noted that originally a maximum-minimum restricting procedure was employed on the flow rate determination. This upper and lower bounding of L_j led to complete instability and has since been removed. Restricting the flow estimates in this rigid manner causes material imbalances on each tray through the successive use of equations (54) and (53). The restriction defined by equation (58) has the advantage that any imbalance will be corrected in the desired direction and will be balanced by the calculation of vapour flow rate by equation (55).

6.3. Calculation Sequence

Appendix V contains the detailed Fortran listing for the transient calculation as well as the data input listing. The following general procedure was employed for the integration of the cases cited in the succeeding chapter.

(1) The steady state solution from the Θ-method was employed as the initial condition in the column.

(2) The perturbation to the steady state is read.

(3) The integration starts at the reboiler.

(4) The 3rd order Runge-Kutta technique calculates

3 estimates of the component mole fractions with the corresponding estimates of tray temperature. These variables are then calculated at end of the time increment Δt by weighting the three estimates.

(5) The molar enthalpy of the liquid at $t + \Delta t$ is calculated using the new mole fractions and tray temperature in equation (9).

(6) The liquid flow rate is then calculated using equation (54) and the vapour flow rate is calculated from the material balance (55).

(7) The integration proceeds from tray to tray until the tray 1 variables are updated to time $t + \Delta t$.

(8) The time variable is then increased by Δt and the iterative procedure returns to item (3).

6.4. Presentation and Discussion of Results

The 3rd order Runge-Kutta technique calculates three separate estimates of $x_{i,j}$ within the time interval Δt then does a fourth calculation to arrive at a final estimate of the variable at the end of the interval. As a result the integration consumes considerable computation time when 100 equations of the form of (53) and 10 equations of the form of (54) are solved for each time increment. This is the number of equations which result from considering a 10 component-10 tray model.

6.4.1. Increment Size

The increment size was varied in an attempt to speed up this integration procedure. The holdup on the trays in the 10 component-10 tray model was (on a per tray basis)

2.5 moles - top section
3.6 moles - center section
4.7 moles - bottom section
5.0 moles - reboiler

These tray holdups were calculated knowing the individual tray dimensions with the exception of the reboiler which is an estimated value. The calculation of the holdup is presented in Appendix VI.

In the steady-state solution where D = 45 moles/U.T. was the specification, the highest liquid flow rate of 498.1 moles/U.T. occurred on tray 9. It was discovered that for stable integration the step length lay between the limits

$$0.00005 < \Delta t < 0.0004 \qquad (59)$$

These limits are equivalent to 0.2 moles of liquid displacement per step (approximately 4% of the tray holdup) and 0.025 moles of liquid displacement per time increment (approximately 0.5% of the tray holdup) respectively. These values are to be compared to the recommendation of Rose et al (48) of displacing approximately 10% to 20% of the plate holdup for a stable approach to the steady state solution using the relaxation method.

It is considered that the lower boundary of $\Delta t > 0.00005$ U.T.

is due to the approximations which are equations (55) and (56). The enthalpy change Δh_j is analytically determined by evaluating $h_j\big|_t$ and $h_j\big|_{t+\Delta t}$ assuming only changes in composition and temperature on tray j during the time increment Δt. Any errors resulting from this simplification will be amplified in the expression $\frac{\Delta h_j}{\Delta t}$ as $\Delta t \rightarrow 0$. Since this ratio expression is used in equation (54) to determine the liquid flow rate from tray j, any errors will be transferred to the flow values. The column flow rates are thereby affected not only by the errors inherent in the rate of change of liquid enthalpy on each tray but by the slopes calculated for the two adjacent trays. There would be a cumulative and amplification effect of the initial error as the integration proceeded unless the error were of a purely random nature. Since the integration was carried out from the reboiler to the top of the demethanizer-absorber model, a cumulative error would cause the strongest instability to occur on tray 1. This situation did in fact occur whenever there was instability in the integration of the differential equations.

Table 7 gives a comparison of the integration using step lengths $\Delta t = 0.0001$ and $\Delta t = 0.0002$.

Table 7: VARIATION IN INCREMENT SIZE

	Δt = 0.0001 U.T.		Δt = 0.0002 U.T.	
Tray j	L_j	V_j	L_j	V_j
1	126.0	120.5	125.7	118.9
2	143.4	200.8	143.7	199.0
3	364.7	218.3	363.6	217.1
4	370.2	349.0	368.9	346.6
5	368.8	354.6	367.9	352.3
6	505.8	353.2	506.1	351.4
7	509.7	348.9	510.6	348.4
8	507.3	353.0	508.7	353.1
9	514.0	350.7	515.1	351.5
10	156.3	357.5	156.6	358.2
	Results for t^+=0.0313 or 313 iterations from step change		Results for t^+= 0.0312 or 156 iterations from step change	

6.4.2. Transient Response to Step Change in Reboiler Duty

To study the dynamic behaviour of the 10 component-10 tray model, step changes to the external model parameters were imposed on a steady-state situation. The initial step change was an increase in reboiler heat load by 33% to $Q_{NR} = 2.0 \times 10^6$ B.T.U./U.T. This response was allowed to attain essentially the new steady state whereupon the reboiler heat load was reduced to 1.7×10^6 B.T.U./U.T. in three successive steps 0.1 U.T. apart.

Figures 11, 12, 13 and 14 present a graphical display of the approach to steady state in response to the three step changes. Figure 11 shows the vapour flow rate variation in response to the reboiler heat load reductions. The vapour flow rate reductions were 26% on tray 10 and 38% on tray 1 for an overall 15% reduction in heat load. There was a distinct drop in these vapour flow rates at the instant the step changes were applied, i.e. at $t^+ = 0$, 0.1 and 0.2 U.T. respectively. The amplitude of the deviations from a "smoothed" curve of the calculated response varied from ±2 moles/U.T. on tray 10 to ±4 moles/U.T. on tray 1, i.e. the fluctuations are most severe on tray 1.

These oscillations are absent in the temperature plot, Figure 12, where the variations on tray 10 and tray 1 are not nearly as pronounced as in the case of Figure 11. The slopes $\frac{dT_j}{dt}$ increase as the step changes occur but $\frac{dT_j}{dt} \rightarrow 0$

Figure 11: DYNAMIC BEHAVIOUR OF 10-TRAY MODEL

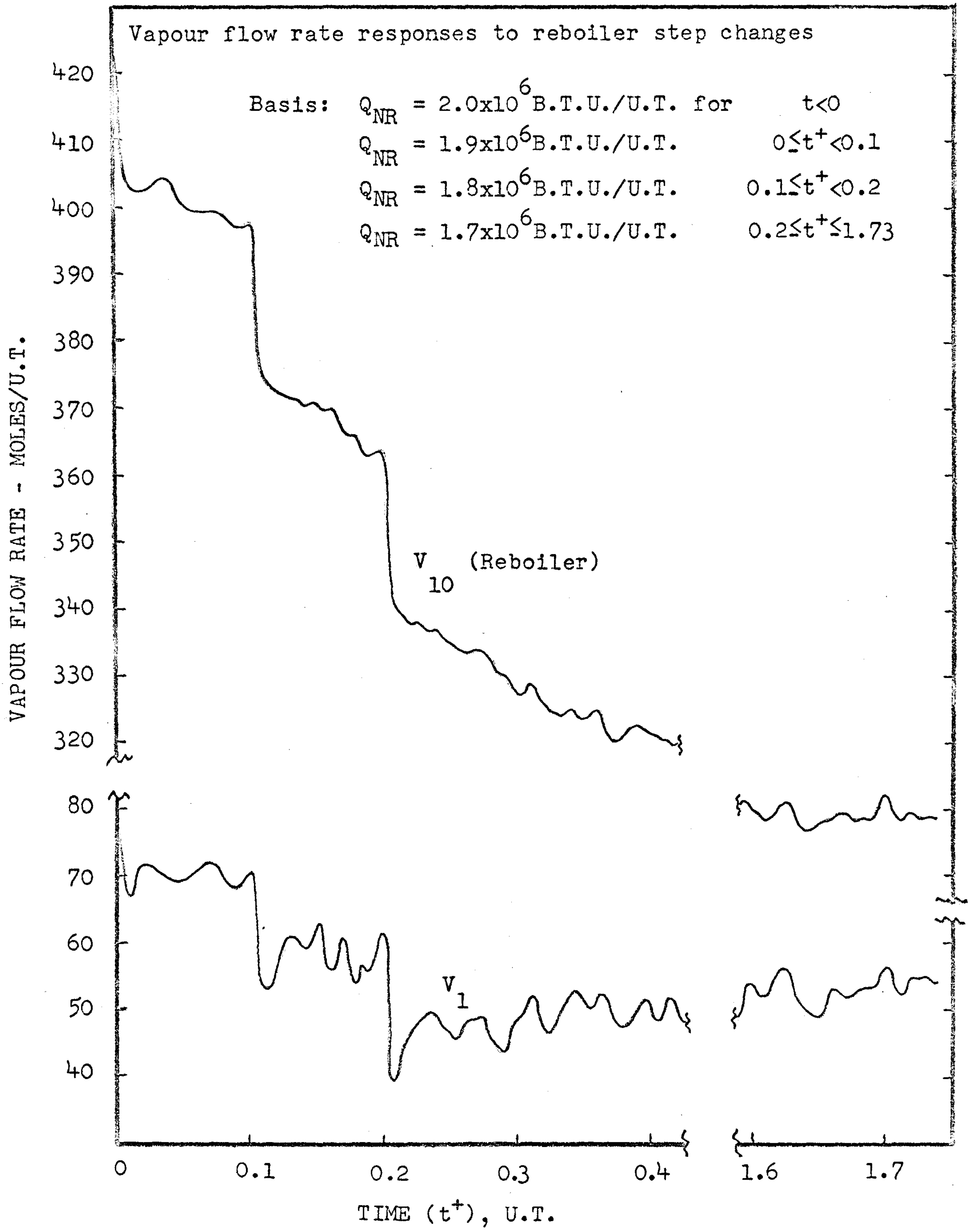
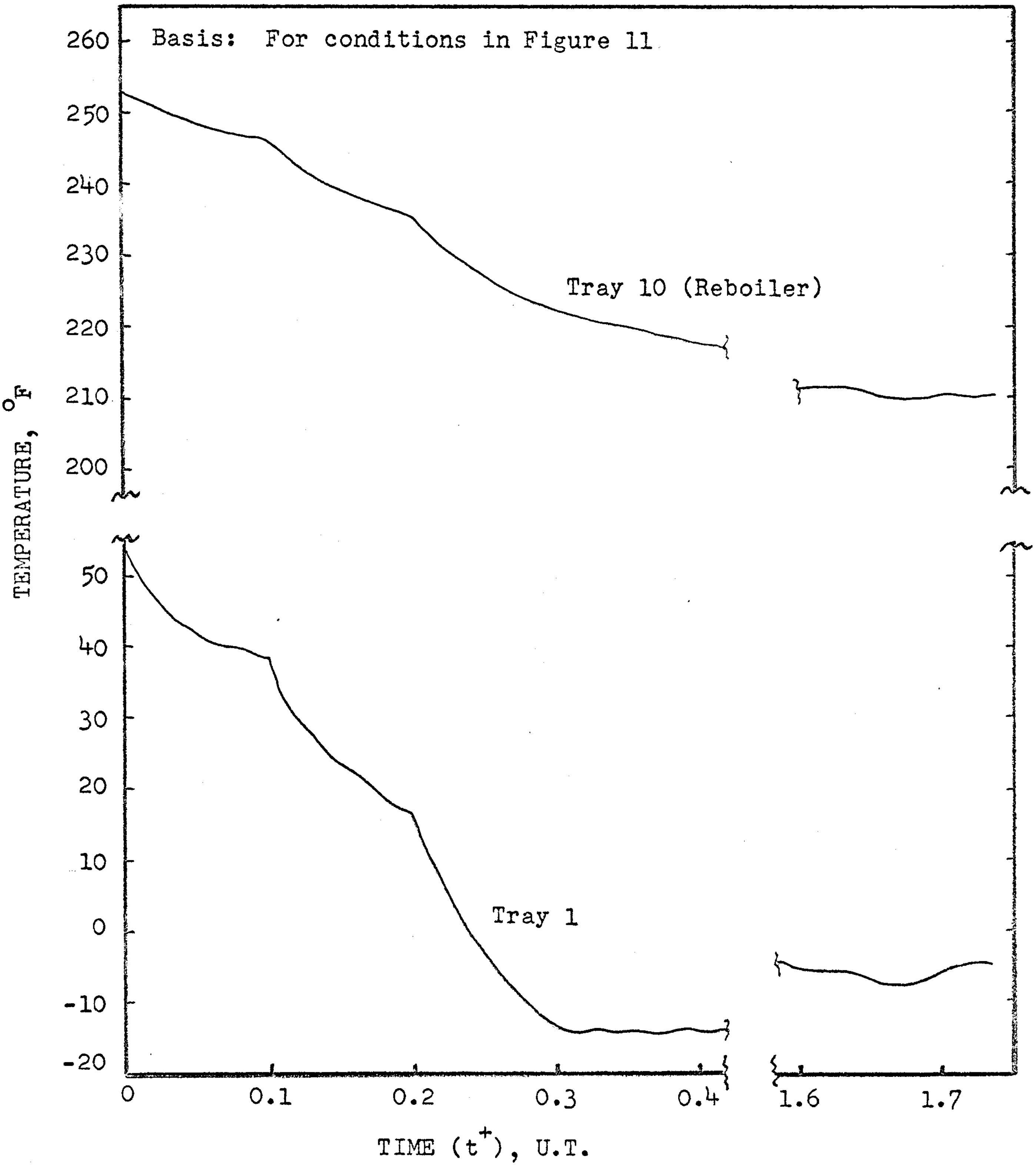


Figure 12: TRAY TEMPERATURE RESPONSE



within 0.1 U.T. after the last step change occurs. Since the temperature changes are quite gradual after $t^+ = 0.4$ U.T., another parameter must be chosen which more precisely indicates the steady state behaviour. There are essentially two independent alternatives available

(i) the component compositions

or (ii) the column overall heat imbalance

Since the former involves 10 variables on each of 10 trays, considerable scanning of the $x_{i,j}$'s would be required to determine whether the steady state situation had been achieved. The latter alternative, however, has the distinct advantage of being a single number. The heat imbalance is a function of temperature, composition and flow rates and therefore is a sensitive variable to any unsteady state behaviour in the column model.

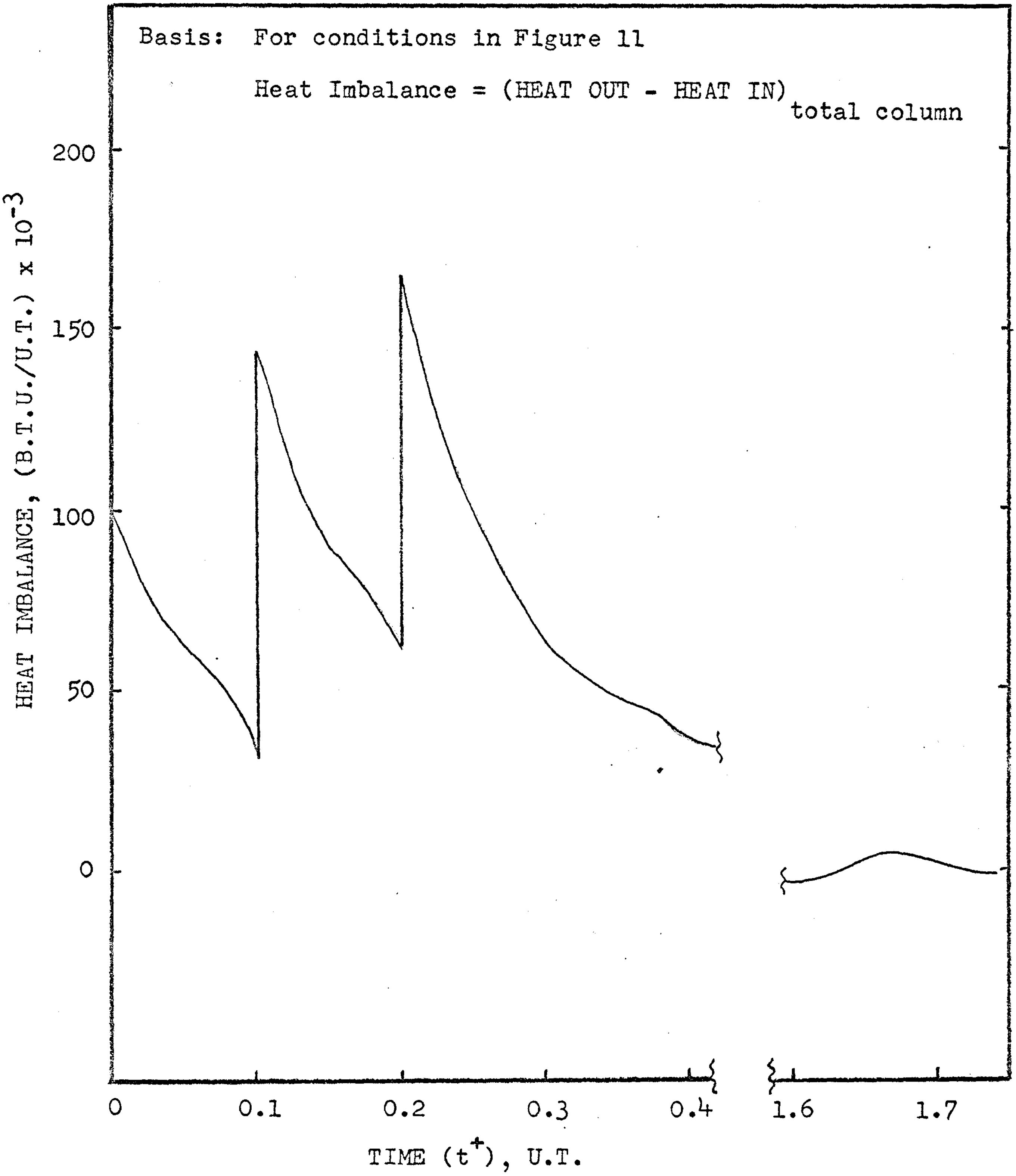
Figure 13 is a plot of the overall column heat imbalance (ΔH) resulting from the aforementioned reboiler heat load step changes. The criteria for attainment of steady state are

$$(1)\quad \Delta H \rightarrow 0$$

$$(2)\quad \frac{d(\Delta H)}{dt} \rightarrow 0$$

Figure 13 indicates that after 1.73 U.T. of column model operation from the initial step change, $\Delta H \triangleq \pm 5{,}000$ B.T.U./U.T. which is less than 2% of the total change in reboiler heat load. This duration of column operation corresponds to over

Figure 13: OVERALL COLUMN HEAT IMBALANCE



Basis: For conditions in Figure 11

Heat Imbalance = $(\text{HEAT OUT} - \text{HEAT IN})_{\text{total column}}$

12 complete tower volume displacements, i.e. the model demethanizer-absorber time constant (τ_o) is 0.14 U.T. The real column has a time constant of approximately 0.5 U.T. In this analysis, the time constant is defined as

$$\tau_o = \frac{\sum_j U_j}{\sum_f F_f} \qquad (60)$$

for consistent units. Additional time constants could be defined for the individual stages and would have the form

$$\tau_j = \frac{U_j}{L_j} \qquad (61)$$

For the case under consideration, the time constants for tray 1 vary from .016 U.T.$\Big|_{t^+=0}$ to 0.024 $\Big|_{t^+=1.73}$ and for tray 9 vary from .0075 U.T.$\Big|_{t^+=0}$ to 0.0088 $\Big|_{t^+=1.73}$. During this run, the tray 1 contents were displaced approximately 70 times while tray 9 contents were displaced approximately 200 times.

A comparison of the flow and temperature profiles from this calculation at $t^+ = 1.73$ U.T. with the steady state solution obtained using the θ-method is made in Tables 8, 9 and 10. The vapour flow deviations about the mean were still pronounced and varied from ±7% on tray 1 to ±0.7% on tray 10

Table 8: COMPARISON OF STEADY-STATE SOLUTIONS
COLUMN PROFILES

Tray	Θ-method			Transient*			Θ-method		
	D=54 Moles/U.T.			$Q_{NR}=1.7\times10^{6}$ B.T.U./U.T.			D=53 Moles/U.T.		
j	T_j	V_j	L_j	T_j	V_j	L_j	T_j	V_j	L_j
1	0.7	54.0	99.5	-5.4	53.6	103.9	0.4	53.0	97.6
2	31.2	107.8	108.2	31.0	111.8	114.0	30.4	104.9	106.4
3	38.5	116.5	323.8	43.0	121.6	332.0	36.9	113.7	320.8
4	61.1	241.6	339.5	64.2	248.8	349.0	60.2	237.6	337.2
5	74.9	257.2	345.8	75.0	265.5	357.5	74.1	254.0	343.8
6	92.6	244.4	514.8	81.3	273.9	506.0	91.6	241.5	512.6
7	107.3	291.0	523.0	102.4	280.7	522.7	105.9	287.8	520.8
8	127.1	299.3	526.2	124.4	297.3	529.0	125.3	296.0	523.5
9	160.1	302.4	531.4	158.3	303.5	534.1	158.0	298.7	528.0
10	211.8	307.6	223.8	210.8	308.5	225.6	210.2	303.3	224.8

* Transient solution after t^{+} = 1.73 U.T.

Table 9: COMPARISON OF COMPOSITION PROFILES

Tray j	METHANE $x_{1,j}$			ETHYLENE $x_{2,j}$		
	Θ-method $D=54 \frac{\text{Moles}}{\text{U.T.}}$	Transient* $Q_{NR}=1.7\text{x}10^6 \frac{\text{B.T.U.}}{\text{U.T.}}$	Θ-method $D=53 \frac{\text{Moles}}{\text{U.T.}}$	Θ-method $D=54 \frac{\text{Moles}}{\text{U.T.}}$	Transient* $Q_{NR}=1.7\text{x}10^6 \frac{\text{B.T.U.}}{\text{U.T.}}$	Θ-method $D=53 \frac{\text{Moles}}{\text{U.T.}}$
1	.1691	.1826	.1720	.2663	.2826	.2553
2	.1086	.1093	.1124	.3202	.3336	.3120
3	.0885	.0848	.0926	.3386	.3376	.3369
4	.0493	.0491	.0513	.3422	.3393	.3447
5	.0349	.0368	.0360	.3021	.3083	.3067
6	.0140	.0325	.0146	.2734	.2675	.2802
7	.0042	.0100	.0044	.2304	.2340	.2394
8	.0012	.0028	.0013	.1660	.1704	.1754
9	.0003	.0007	.0003	.0939	.0966	.1010
10	.0001	.0002	.0001	.0360	.0370	.0393

* Transient situation after $t^+ = 1.73$ U.T.

Table 10: COMPARISON OF PRODUCT COMPOSITIONS

	Θ-method		Transient		Θ-method	
Component i	$D=\sum_i d_i=54\frac{\text{Moles}}{\text{U.T.}}$		$Q_{NR}=1.70\times10^6\frac{\text{B.T.U.}}{\text{U.T.}}$ $t^+ = 1.73$ U.T.		$D=\sum_i d_i=53\frac{\text{Moles}}{\text{U.T.}}$	
	d_i	b_i	d_i	b_i	d_i	b_i
1	37.822	.015	38.041	.035	37.821	.017
2	13.103	8.051	12.801	8.341	12.331	8.823
3	2.011	19.823	1.827	20.289	1.785	20.049
4	.045	34.332	.041	34.481	.042	34.336
5	.091	25.122	.079	25.237	.089	25.124
6	.152	14.919	.124	15.007	.153	14.918
7	.481	60.089	.393	60.425	.483	60.087
8	.240	33.719	.203	33.899	.242	33.717
9	.053	22.138	.042	22.256	.054	22.138
10	.001	5.568	.001	5.603	.001	5.568
TOTALS	54.0	223.8	53.6	225.6	53.0	224.8

Units for b_i, d_i are Moles/U.T.

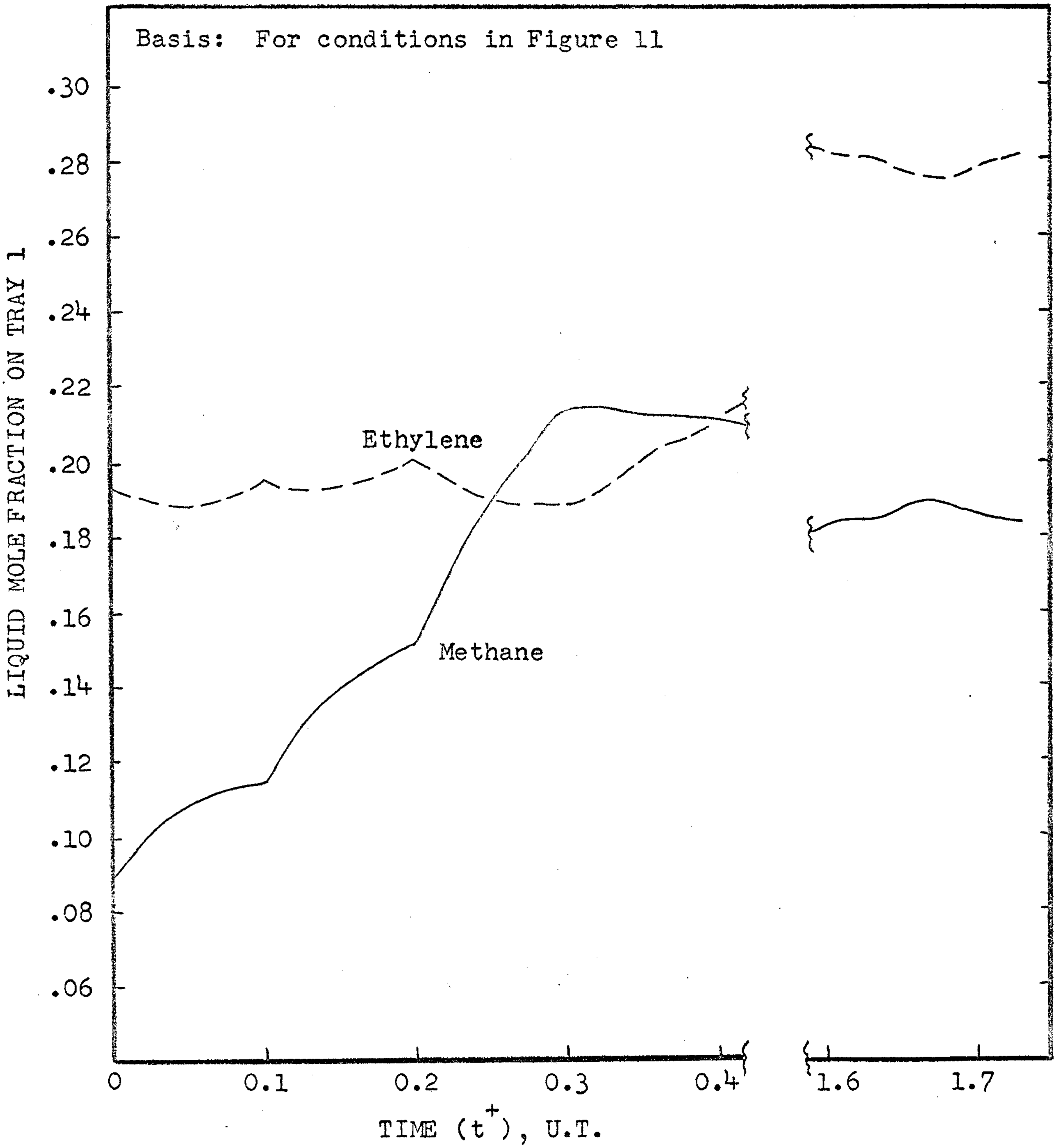
during the final 0.1 U.T. of operation. These percentages are based on the average vapour flow on the tray during the time duration considered. The relative liquid flow deviations are somewhat smaller due to the proportionately higher tray flows.

Tables 8 and 9 indicate the difference in feed tray models between the Θ-method steady state solution and the integration of the differential equations describing the dynamic behaviour of the model. At tray 6, the F_2 feed tray, the deviation between the two models is most pronounced. The vapour flow rate differs by approximately 30 moles/U.T. between the two solutions. Table 9 indicates the difference in methane and ethylene liquid concentrations on tray 6 between the two models. Since F_2 is methane rich, it is understandable that the feed tray representation in Figure 10 would increase the methane concentration on the feed tray over the alternative offered in Figure 3, i.e. the feed stream is completely mixed with the liquid on the tray in the former situation.

The product compositions, however, do not appear to be markedly affected by the choice of feed tray model as is indicated by the comparison made in Table 10. Both the overhead vapour and the bottoms liquid compositions resulting from the transient solution seem to lie between the two steady state solutions from the Θ-method.

Figure 14 shows the variations in the liquid mole fraction of methane and ethylene on tray 1. It is evident

Figure 14: LIQUID MOLE FRACTION RESPONSE



from this figure and from the previously tabulated results that 12 column displacements after a significant step change in an external parameter are not adequate to achieve the new steady-state. This would correspond to approximately 40 minutes of actual column operation. At $t^+ = 1.73$ U.T. the heat imbalance was 2400 B.T.U./U.T. or 0.8% of the change in reboiler heat load. Over the interval $1.6<t<1.73$, the methane concentration on tray 1 varied up to ±2.5% from the mean and the ethylene concentration varied up to ±1.8% from the mean. These variations plus the heat imbalance criteria indicate that the transient solution at $t^+ = 1.73$ has covered approximately 98% of the path towards the true steady state solution.

From Figure 12, the minimum tray 1 temperature reached was -16°F. A further step reduction of reboiler heat load to $Q_{NR} = 1.6 \times 10^6$ B.T.U./U.T. at $t^+ = 0.3$ leads to a limiting situation where the temperature $T_1 < -40^{\circ}F$. This temperature limit is, however, imposed on all trays since the regression of the equilibrium ratios is not valid for $T < -40^{\circ}F$. Once the limit is imposed the integration becomes unstable and must be curtailed. To reduce the reboiler heat load, smaller step reductions would have had to be used.

6.4.3. Transient Response to Step Changes in Feed Stream Flows

After the 10 component-10 tray model was subjected to the 3-step reduction in reboiler duty and allowed to settle out for 12 tower volume displacements, flow changes were imposed.

The two feedstream flows and the absorption oil flow were individually increased by 25% with the respective composition breakdowns maintained constant. The tower model was subjected to each of these step increases while the other two streams were maintained at the lower flow values.

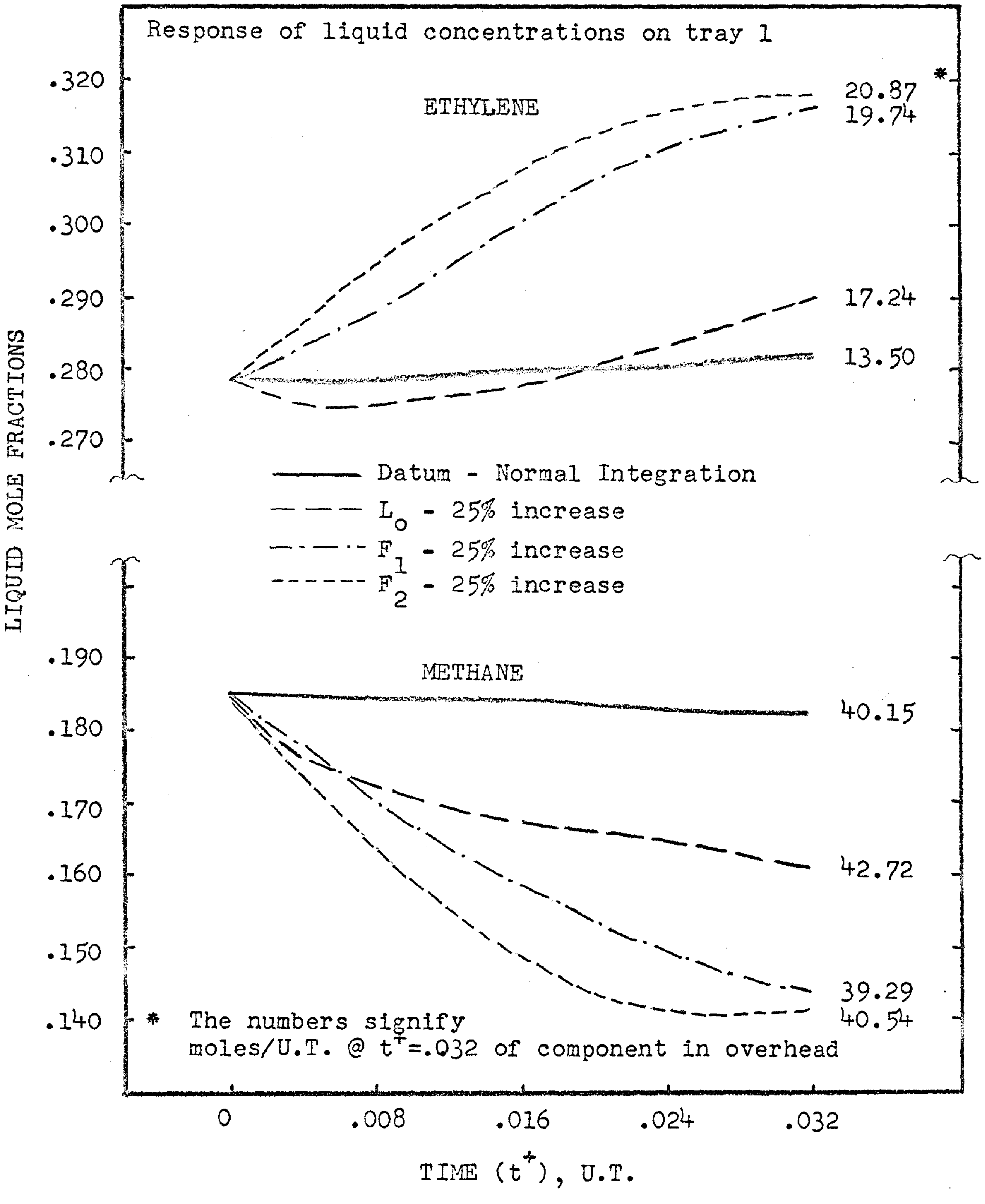
Figure 15 indicates the response experienced by the methane and ethylene in the liquid on tray 1. In all three step changes, the ethylene content on the tray increased and ethylene losses in the overhead increased. The largest losses occurred when the major ethylene supplier F_2 was stepped up by 25%. The methane concentration in the liquid on tray 1 decreased in all three instances but the overhead methane flow was only marginally affected by the variations.

It should be recalled that this is the response to a 10 tray model with only 2 trays in the top absorption section and bears no specific relation to the actual plant. On the other hand, the above observation is unusual for one would expect less ethylene overhead losses when the absorption stream (L_o) is increased in flow.

6.5. Duration of Computation Runs

The 10 component-10 tray model involved 100 differential equations for component concentration variations of the form of (53) and 10 tray flow equations of the form of (54). To displace the column volume approximately 12 times ($t^+ = 1.73$ U.T.), 6.35 hours of IBM 7040 time were required. The third order Runge-Kutta technique was used with integration increments as

Figure 15: STEP CHANGES TO FEEDS



follows.

$$t = 0.0001 \text{ for the interval } 0 \leq t \leq 0.6$$

$$\text{and } t = 0.0002 \text{ for the interval } 0.6 \leq t \leq 1.73$$

Each complete pass through the column averaged 2.65 seconds.

6.6. Conclusions and Recommendations

(1) More than twelve column volume displacements are required to obtain a steady state solution to three significant figures for a reboiler duty reduction of 15%. In the real column, this is equivalent to approximately 40 minutes of operation.

(2) The transient solution agreed with the steady state solution obtained by the Θ-method.

(3) The tray temperatures are less sensitive to the unsteady state situation than are the tray flow rates or the heat balances.

(4) The approximations which are relations (55) and (56) are crude and lead to instability in the integration procedure. These approximations should be improved in any future investigations.

(5) The 3rd order Runge-Kutta integration technique is inefficient with respect to computation time. Other methods should be investigated.

(6) The integration should be applied to the 10 component-30 tray model when a faster integration method proves successful.

(7) The temperature range of the equilibrium ratio regressions should be extended to include the boiling point of methane.

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Appendix I - Details of Literature Search

The literature review can be divided into three distinct phases, namely

(1) Vapour-Liquid Thermodynamics

(2) Steady state calculations

and (3) Transient calculations

The papers reviewed in this appendix are the ones considered by the author to be pertinent to the simulation of the demethanizer-absorber.

I.1. Vapour-Liquid Thermodynamics

Simple nomographical techniques of obtaining equilibrium ratios are presented by Scheibel (49) and Hadden (25). Schiebel's nomograph presents the equilibrium ratios for the normal paraffins from methane to tetradecane and also for ethylene, propylane, isobutane and isopentane. These ratios are functions of pressure and temperature and "the nomograph was developed empirically by calibrating the temperature scale according to the logarithm of the liquid fugacity of n-pentane and calibrating the pressure scale according to the logarithm of vapour fugacity of n-pentane". Scheibel also presents a simplified chart for enthalpies of light hydrocarbons plotted as a function of temperature, pressure and average molecular weight. The correlation of enthalpy with molecular weight is simple but is recommended as "of sufficient accuracy for most process-design calculations". A third nomogram of petroleum fractions' enthalpies is offered by Schiebel where the specific gravity of the liquid replaces the density as a correlating parameter.

Hadden's nomographs use convergence pressure as a composition parameter and apply to light hydrocarbons and petroleum fractions at temperatures from -260°F. to 800°F. and pressures to 10000 p.s.i.a. These nomographs have the versatility of applying to mixtures of aromatics, special mixtures of methane, hydrogen, hydrogen fluoride, carbon dioxide, hydrogen sulphide, methyl mercaptan, and water over specified ranges of temperatures and pressures. In addition, this paper indicates a short method for approximating the convergence pressure. Graphs are used which present P_{conv} as function of typical refinery streams and temperatures.

Lenoir and White (36) present a more rigorous method for the determination of P_{conv}. Their method can be used for paraffinic, olefinic, naphthenic and aromatic hydrocarbon mixtures. This technique considers a multicomponent mixture as a fictitious binary which is constructed from the boiling points of the components. This conversion involves the calculation of effective boiling points (EBP) for the "light" and "heavy" components in the mixture. Lenoir also suggests a short cut method of converting to the fictitious binary namely, "estimate the EBP_L as the molal average of the EBP values for the components making up the lightest 7% of the mixture. The estimate of EBP_H is the molal average of the heaviest 40% in the mixture". This 7-40 rule is recommended for operating pressures lower than 60% of the convergence pressure.

Cajander et al (10) present "a Nomogram of Improved Accuracy" for the determination of equilibrium ratios. Their work is the result of the correlation of published data for 58 systems including binary, ternary and some multicomponent mixtures. It is claimed that the average prediction error has been reduced by 2% from a previous nomogram published by Meyers and Lenoir in 1957. This nomographical technique asserts that the equilibrium ratio is a function of composition, temperature, pressure and convergence pressure. Twelve graphs and two nomographs are used to convey the relationships over a temperature range -200°F. to 980°F. and pressures from 10 p.s.i.a. to 10000 p.s.i.a.

Howerton (31) presents "a thermodynamically rigorous procedure for calculating component fugacities in liquid-phase solutions entirely on the basis of experimental P-V-T data plus solution heat capacity measurements at a single supercritical pressure". Where direct experimental data or a suitable equation of state are not available for a system being considered, Howerton suggests that reliable estimates can be based on available compressibility factor data. Calculations for multicomponent systems are illustrated and compared with experimental vapour-liquid equilibrium for ethane-pentane mixtures.

Gordon et al (22) use the correlations proposal by Edmister and Ruby (14) for adaption to machine computation. This composition-dependent correlation was used because of its compactness (only six graphs), its accuracy (equivalent to other proposals) and its "relatively sound theoretical basis". The equilibrium ratios were described by three independent variables in each phase, boiling point ratio, reduced pressure, and reduced temperature. Gordon proceeds to define a regression equation with 20 distinct terms in it and 26 coefficients. A table of these coefficients is presented in the paper.

Cobb (12) treats the regression of equilibrium data by considering Raoult's law

$$\frac{y}{x} = \frac{\text{Vapour Pressure (V.P.)}}{\text{System Pressure (P)}}$$

as a basis. The regression has the form

$$\log K = f(T,P).\log \frac{(V.P.)}{P}$$

where f(T,P) is a 10 term fit in reduced temperature and reduced pressure. Cobb mentions that the basis is not particularly useful for system pressures over 1000 p.s.i.a. No actual regressions are tabulated in the paper.

Grieves and Thodos (24) discuss the "critical pressures of hydrocarbon mixtures. The abstract for the paper reads "A method of predicting the critical pressures of multicomponent hydrocarbon mixtures of known composition has been developed. These mixtures include ternary, quaternary and quinary systems consisting of normal and isoparaffins, olefins, acetylenes, naphthenes and aromatics. The method, based upon the mole fraction of the low-boiling component in the mixture, graphically presents the ratio of the actual critical pressure to the pseudocritical pressure as a function of a boiling parameter. For mixtures of more than two components the pseudocritical pressure is based on the critical pressure of the pure low-boiling component and on the actual critical pressure of the mixture consisting of all the remaining higher-boiling components". Grieves also presents a method for calculating critical densities for binary hydrocarbon mixtures which is of no particular interest in this discussion. The former method provides an alternative to the Kay rule used in determining the pseudocritical pressures for the enthalpy correlation of Yen and Alexander (51).

Yen and Alexander have improved upon and proceeded to regress the enthalpy correlations of Lydersen et al (38). Enthalpy data for 28 compounds were collected from the literature and classified into four critical compressibility factor groups, namely Z_c = 0.29, 0.27, 0.25, 0.23 respectively. The regression was expressed as

$$\frac{H^o - H}{T_c} = f(T_r, P_r, Z_c)$$

with an analytic expression for each of

(1) the superheated vapour region

(2) the subcooled liquid region

(3) the saturated vapour line

(4) the saturated liquid line

The process of curve-fitting the tabulated results was done by trial and error with the aid of a computer program on non-linear estimation. The equations represent the charts from which they were derived to within 3%. This paper also contains a list of 50 references from which the data was drawn and the 4 charts representing the aforementioned expression at the four critical compressibility factors.

Organick et al (46) extends "the methods of determining the Benedict-Webb-Rubin equation of state coefficients for pure hydrocarbons to utilize experimental equilibrium ratio data for the hydrocarbon in a wide-boiling two phase binary mixture. The resulting equation of state coefficients are found to improve the prediction of phase behaviour when this same hydrocarbon is present in multicomponent mixtures over a whole range of conditions, but particularly at high reduced pressures and at low reduced temperature for the heavy component where the BWR equation of state had been found generally to be in substantial error". The technique utilizes a modified form of the equation of state and resolves itself to a curve-fitting problem.

I.2. Steady State Calculations

The many manual methods for absorption and fractionation calculations are extensively reviewed by a series of papers appearing in the Petroleum Engineer from May, 1947 to March, 1949. W. C. Edmister is the author of these articles and presents in this series an excellent background of the graphical and short cut techniques available up to the late 1940's for the design of distillation equipment.

A basic review of the literature concerning multicomponent distillation is covered by Maddox (39). He divides the review into three categories

(i) those techniques which years of use have proved of great value.

(ii) newer methods which seem to have promise

and (iii) a few methods whose unique approaches made them worthy of consideration.

Maddox reviews the determination of the number of variables that must be fixed in defining a distillation system and the typical choices for standard distillation calculations. Total reflux operation and the minimum reflux ratio of multicomponent distillation operation are discussed briefly. The shortcut methods of Underwood, Brown, Gilliland, Mason and Maddox are also briefly reviewed with accompanying graphs. These techniques are oriented towards manual design methods but some extension to complex fractionators is made. Sample calculations from part of the paper to summarize and compare several methods of calculating the minimum number of trays to achieve a specified separation. Maddox also briefly reviews the Lewis and Matheson rigorous calculational procedure.

Graven (23) proposes a "rapid convergence" method for use on all tower arrangements including absorbers, strippers and complex fractionating towers. His method utilizes fractionation equations of the form proposed by Edmister with the extension to the definition of a fractionation factor (which is the reciprocal of the absorption factor $A_{i,j}$ used in this dissertation) and to the concept of the equilibrium feed tray. Graven presents the generalized fractionation equation and outlines the steps in the calculational procedure. He further presents an example where six components are considered in a single feed column with reboiler and overhead condenser. Graven further suggests that with a few simplifications such as the use of the equations of Franklin to calculate tray temperatures and vapour-liquid flow profiles, this technique is adaptable to lean oil absorption and steam stripping towers.

Rose et al (48) utilize the unsteady state equations to solve for the steady state situation. The basic equation expresses the change in moles of a component present in the holdup on a particular plate during any brief interval during the distillation operation. Once the compositions and flows are known for some initial state, the relaxation method iteratively applies the unsteady state equations to achieve the new steady state. Rose suggests some precautions to maintain stability. The flow rates V and L should be one fifth to one tenth of the plate holdup H and the compositions should be normalized after each set is calculated. Rose presents the relaxation solution to a three component side stream problem in a graphical form. The calculation was carried out on an IBM-650 with 160 intervals necessary to reach the steady state solution. There is no comment as to the duration of the calculation.

The paper by Hardy et al (27) concerns itself with the application of the Θ-method and the Thiele and Geddes calculational procedure to absorbers with reboilers. Canik (9) in his thesis extends Hardy's work and presents a more detailed version of the Θ-method. In both works there is discussion of round-off error, of the treatment of separated and single-phase components, of enthalpy balances and the use of the Q-method for applying the latter. The Q-method is the term used to describe the intercooler-interheater arrangement mentioned in this thesis which resulted from the restrictions of successive flow rate profile estimates. Hardy and Canik present illustrated examples of several problems. These are a comparison of the Q-method solution with that obtained by a "constant-composition" method. The latter is discussed in detail by Holland (30). Canik was mainly concerned with speeding up the rate of convergence of the Θ-method as applied to this particular type of column.

More recently Friday and Smith (17) compare their sum-rates (SR) method with the bubble-point (BP) method of determining tray temperatures. This paper presents the six major decisions involved in formulating a solution method for the equilibrium stage model equations. There are four basic model equations

(i) equilibrium relationship

(ii) component material balance on each tray

(iii) energy balance on each tray

(iv) the moles fractions in the vapour and liquid phases must add up to 1.

The first decision, Friday claims, concerns the grouping of equations (i) to (iv). They can be grouped by stage or by type, the former being the less desirable due to buildup of truncation errors. The second decision involves the order of satisfying equations (i) to (iv). The third decision concerns the selection of the appropriate equation to provide the value of the specific variables. The bubble point method is defined as the technique which uses (iv) to provide the tray temperatures and equations (iii) to generate the flow rate variable. The reverse, where the temperature results from the energy balances and the flow rates are the sums of the individual flow rates from equations (ii), is termed the sum-rates method. The fourth decision involves the selection of a method to solve the component concentration matrix equations. The fifth and sixth decisions involve the selection of either the BP or SR method to determine the new tray temperatures and the new flow rates. Friday compares the convergence range of the SR and BP methods for a variety of column configurations. He further discusses the damping applied by Holland and co-workers and indicates that the convergence range of the BP method can be expanded by using such techniques. A serious consideration of the SR method is warranted if one is interested in expanding the convergence range of his calculational technique.

I.3. Dynamic Behaviour Calculations

Meadows (43) derives "a set of differential equations to represent the distillation of a multicomponent mixture in a tray type batch still. The equations include enthalpy balances on all trays and assume constant volume holdup on the trays and condenser". Meadows used a finite difference method to solve the equations numerically on an IBM 7070. He further developed an empirical relationship to vary the size of the time increment during the course of the calculation. The finite difference method is outlined in detail for a 4 component mixture in a 5 tray column with a 5:1 reflux ratio.

Huckaba et al (32) outline a mathematical model representing the dynamic behaviour of a simple distillation column with overhead condenser and reboiler. Empirical equations are used to represent the equilibrium relation, the enthalpy and heat capacity data, as well as the plate efficiency data. The analysis is applied to a mixture of methanol and t-butyl alcohol in a 12 plate bubble-cap column. The comparisons of the model response and the actual column response agree amazingly well. Huckaba subjected the column to reflux ratio changes only in making these comparisons. The Runge-Kutta-Gill procedure was used to start the Modified Adams predictor-corrector integration procedure.

Bowman and Clark (8) analyze a batch distillation column using an analog computer. The equations and simplifications are standard with the exception that a Murphree-type efficiency is included. The abstract reads "analog simulation of 20 and 30 plate batch distillation columns with plate holdup indicates that the analysis of the column performance can be divided into two independent parts - the period on total reflux and the period when distillate is withdrawn. A procedure is given for determining the stillpot composition at any time when the column is on total reflux and the performance during the distillate withdrawal is related to the stillpot composition at the end of total reflux". Bowman presents the analog wiring diagram used for the simulation as well as a graphical summary of the calculated results.

Baber et al (1), (2) deals with experimental transient behaviour in a pilot plant distillation column. The column has 5 trays and is 2 feet in diameter. The acetone-benzene system is considered. (1) deals with step changes in the reflux stream to the top tray while (2) concerns itself with step changes in the liquid or vapour rate to the column. The first paper showed "that in the absence of rate perturbations, the experimental composition-time behaviour of the tray liquids could be predicted quite well by equations developed by Lamb, Pigford and Rippen for characterizing the transient behaviour of distillation columns". Baber employed a analogue circuit to predict the transient behaviour. The magnitude of the Murphree efficiencies varied from 70% to 85%, increasing with increasing liquid rate and decreasing with increasing gas rate. The use of the Lamb et al equations in the analysis of the second step perturbation also proved successful. The technique is however not recommended for cold reflux or cold feed to a tray as in the case of the demethanizer-absorber.

Gilliland and Mohr (21) investigate the rate of response of a standard distillation column containing a binary mixture to a step change in feed composition. Again the mathematical model is simplified by making the standard assumptions

(i) constant relative volatility

(ii) flow rates are constant in each column section

(iii) negligible holdup in overhead condenser

(iv) liquid holdup on each tray is constant, vapour holdup is negligible

(v) reboiler holdup is identical to that on each tray

(vi) feed enters the column at the boiling point

(vii) the liquid on each tray is well mixed and all plate efficiencies are equal to unity.

Gilliland concluded from this work that "there is a pronounced increase of the major time constants with the degree of curvature of the equilibrium relationship". He further suggests that "the general method of attack can be used successfully to predict dynamic characteristics of simple distillation systems from steady state operating data". The method involves the fitting of the transient compositions of the product streams to a two-time constant expression with variable coefficients.

Several runs at various column configurations were made to provide data for the curve fit.

Mah et al (40) review the standard numerical integration procedures such as the Runge-Kutta and predictor-corrector techniques. In addition, some effort was expended in determining the range of stability of Kutta-Simpsons rule. The step length was varied over a wide range and the results of the integrations are presented in graphical form. Mah proceeds to propose a method of integrating the non-linear differential equations involved in step-wise separation process which in some instances can have a step length 128 times greater than the largest stable step length used in the Kutta-Simpson process. This new proposal is described by Mah as "a stepwise linear approximation" and "an exponential quadrative formula". The proposed method however suffers from the disadvantage that the computation is proportional to the square of the number of stages whereas in the Kutta-Simpson process, computation is directly proportional to the number of stages. Thus Mah's proposal is limited to small or at most intermediate-sized separation problems for the increased step length advantage is soon lost to the increased computation.

Appendix II.1. Internal Column Details

Trays 1-16: 3' - 6" diameter.

26 - 4" diameter bubble caps, 5" triangular spacing.

Trays are spaced 1' - 8" apart.

Rim-downflow type

Trays 17-30: 5' - 0" diameter

38 - 4" diameter bubble caps, 5" triangular spacing

Trays are spaced 2' - 0" apart

Cross-flow type

Trays 31-42: 6' - 6" diameter

42 - 4" diameter bubble caps, 6" triangular spacing

Exceptions are trays 31, 32 which have 3" diameter bubble caps on 6" triangular spacing

Cross-flow type

Table 11: TRAY DETAILS

Part 1

	Trays			
Areas[†] of	1 - 16	17 - 30	31, 32	33 - 42
Riser	.874	1.274	.79	1.41
Annular	1.055	1.544	.86	1.706
Slot	.968	1.414	.823	1.563
Tower	9.62	19.635	33.18	33.18
Vapour	6.36*	10.0	14.84	14.84

*Tray 16 has a vapour area of 6.2 ft^2.

[†] All area units are in $(ft.)^2$

Part 2

	Trays											
Areas† of	1-15	16	Odd* 17-29	23	Even* 18-28	30	31	32	Odd* 33-37	39,41	Even* 34-38	40,42
Top downflow	1.63	1.63	4.935	4.935	4.74	4.74	9.14	9.2	9.14	9.14	9.2	9.2
Bottom downflow	.657	.625	1.98	1.98	1.94	1.45	3.92	3.66	3.92	3.92	3.66	3.66
Under downflow	.785	.728	1.98	1.98	2.35	2.11	3.7	3.69	3.7	3.7	3.69	3.69
Inlet to Deck below	.835	-	2.67	2.7	2.03	-	4.74	5.20	4.74	4.8	5.2	5.27
Outlet weir lengthǂ	35	35	95	95	117	117	124	152	124	124	152	152

ǂ in inches

† all areas in (ft.)^2

* odd numbered trays are rim downflow, even numbered trays are center downflow excepting "top" section of the demethanizer-absorber.

Appendix II.2. Reboiler Details

The reboiler is composed of two shell-and-tube heat exchangers. The absorption oil transfers excess heat to the shell side of the first exchanger while steam is used as a heating medium and a control device in the second exchanger.

Table 12: REBOILER DETAILS

		Exchanger 1		Exchanger 2	
		Shell	Tube	Shell	Tube
Surface area			12350		14924
Shells		1		1	
Operating pressure p.s.i.a.		475		475	
TUBES	O.D.		¾ in.		¾ in.
	No. per Shell		456		554
	Length		16.0 ft.		16.0 ft.
	Pitch		1 in.sq.		1 in.sq.
No. of passes		2	8	2	2
Shell diameter		31 in.		30 in.	

Note: The demethanizer-absorber bottoms are split into two parallel streams to pass through the shell side of the above two heat exchangers.

Appendix III.1. Equilibrium Ratio Regressions

The equilibrium ratios obtained from the Braun charts were regressed in the form of the Antoine equation, a quadratic fit and a cubic polynomial in temperature. The results of these regressions are tabulated below. It was from these results that it was decided to use the cubic polynomial expression in representing the data for digital computation use. The decisions considered not only the precision of the reproducibility of the data but the speed of computation. The Antoine type equation lacks in the latter specification relative to the other two fits for it involves both a log function and a division; the former being a truncated series solution and taking approximately 60 times longer to calculate than squaring a number. The calculation below indicates the variance of the Antoine equation compared to the cubic polynomial. Here too the Antoine equation performs poorly.

Consider propane at 100°F.

1. Antoine equation: $s^2 = 6.65 \times 10^{-4}$

$\ln K = -0.6731$ or $K = 0.51$

$3.s = 3 \times 0.0258 = .0774$

0.99 probability that the result is within $0.471 \leq K \leq 0.551$

2. Cubic polynomial: $s^2 = 0.56 \times 10^{-4}$

$K = 0.504$

$3.s = 0.0225$

0.99 probability that the result is within $0.481 \leq K \leq 0.526$

The chart value for K(propane) is 0.490.

Table 13: REGRESSION ANALYSIS OF EQUILIBRIUM RATIOS

$$\ln K_i = a_i' + \frac{b_i'}{T+460.0} \qquad\qquad K_i = a_i'' + b_i''.T + c_i''.T^2$$

	a_i'	b_i	$s^2 \times 10^5$	D.F.	a_i''	$b_i'' \times 10^2$	$c_i'' \times 10^4$	$s^2 \times 10^5$	D.F.
Methane	3.4223	-932.38	50.3	16	4.0017	2.2774	.43905	517.	15
Ethylene	4.2000	-1992.0	93.1	16	.88369	.75762	.25927	101.	15
Ethane	4.2145	-2202.2	42.4	16	.56286	.65136	.11307	6.78	15
Propylene	4.7311	-2954.5	55.0	16	.18251	.28727	.11307	5.16	15
Propane	4.6819	-3002.5	66.5	16	.15791	.22159	.12820	6.47	15
Isobutylene	5.2399	-3775.3	76.0	16	.050385	.098178	.076658	.537	15
n-Butane	5.4320	-3961.3	70.9	16	.040750	.077572	.077664	.927	15
Butene-2	5.6504	-4108.5	70.4	16	.036910	.067529	.083095	1.17	15
Pentane	6.2438	-4937.0	14.8	16	.010719	.018865	.048727	.315	15
Heptane	7.13473	-6462.3	239.5	16	.00080791	-.0014436	.013747	.0539	15

Table 13: Continued

$$K_i = a_i' + b_i'.T + c_i'.T^2 + d_i.T^3$$

	a_i'	$b_i' x10^2$	$c_i' x10^4$	$d_i' x10^6$	$s^2 x10^5$	D.F.
Methane	3.9837	1.9154	.46009	.46110	236.	14
Ethylene	.88707	.82559	.084142	.086576	97.5	14
Ethane	.56375	.66925	.068623	.022791	6.55	14
Propylene	.18123	.26151	.17707	-.032823	3.93	14
Propane	.15909	.24526	.069393	.030157	5.57	14
Isobutylene	.050185	.094138	.086692	-.0051457	.538	14
n-Butane	.040987	.082331	.065840	.0060633	.941	14
Butene-2	.037671	.082842	.045055	.019507	.683	14
Pentane	.011192	.028395	.025053	.012140	.118	14
Heptane	.0010450	.0033283	.0018932	.0060788	.00249	14

s - standard error of estimate
T - temperature in °F.
D.F. - degrees of freedom
Source: Braun charts
Note: Only 18 data points were used in the above comparison

Appendix III.2. Critical properties of the Hydrocarbons

Table 14: CRITICAL PROPERTIES OF HYDROCARBONS

	Mol.Wt.	P_c	T_c	Z_c
Methane	16.0	45.8	343.7	.29
Ethylene	28.0	51.0	510.0	.27
Ethane	30.1	48.2	550.1	.285
Propylene	42.1	45.4	656.5	.279
Propane	44.1	42.0	666.3	.277
Butene	56.1	39.5	753.5	.277
Butane	58.1	37.4	766.0	.274
Butene	56.1	37.0	773.0	.275
Pentane	72.1	32.6	846.5	.269
Heptane	100.2	26.8	972.5	.260

Sources: References (15), (47), (51).

The subroutine which calculates the critical properties of mixtures solves equations (10), (11), and (12) and is presented in this appendix as a Fortran listing.

XX(I).....is the vector of component mole fractions making up the mixture

PC(I).....is the vector containing the pure component P_c

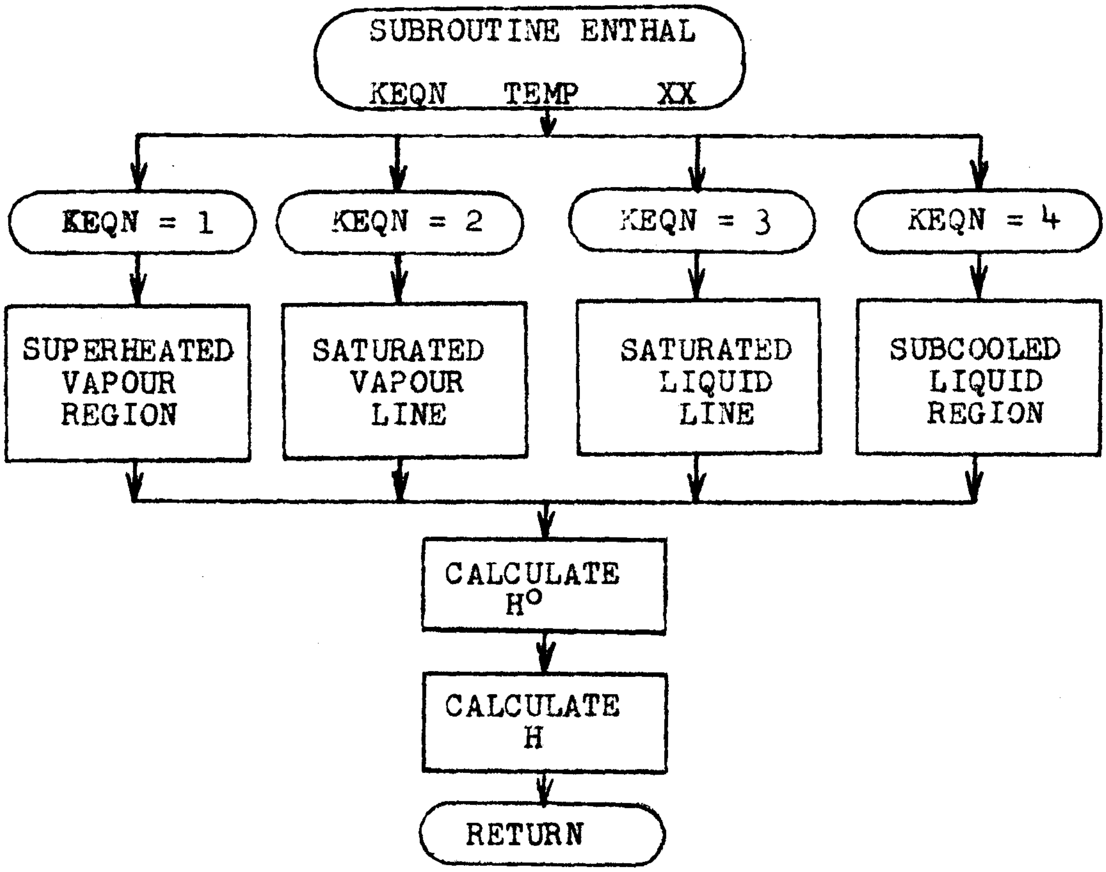
TC(I).....is the vector containing the pure component T_c

ZC(I).....is the vector containing the pure component Z_c

Appendix III.3. Calculation of Mixture Enthalpies

The Fortran listing for the ENTHAL subroutine is included in this appendix. This subroutine solves for the appropriate molar enthalpy based on a specification of the fixed point variable KEQN. The equations solved by this subroutine are included in Table 3. In addition the ideal gas state enthalpy is calculated to arrive at the required value of H. The following flow diagram illustrates the general steps in the calculation procedure.

ENTHAL Flow Diagram



The flow diagram shows only one of the two parallel branches which occur in ENTHAL. The two branches correspond to the two situations

(i) $Z_c^{\prime}>0.28$

and (ii) $0.28>Z_c^{\prime}$

It should be noted that the CRITIC subroutine must precede ENTHAL since the critical properties of the mixture are used in the regressed correlations of Table 3.

TEMP.......is the temperature of the stream

```
      SUBROUTINE  CRITIC(  XX)
C
C  ZCMIX......PSEUDOCRITICAL COMPRESSIBILITY FACTOR OF THE MIXTURE
C  PCMIX......PSEUDOCRITICAL          PRESSURE       OF THE MIXTURE
C  TCMIX......PSEUDOCRITICAL      TEMPERATURE        OF THE MIXTURE
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),PC(10),
     1           TC(10),ZC(10),TEMPX(10),XX(10)
      COMMON  A,B,C,D,AE,BE,CE,PC,TC,ZC,TT,PSI,TOL1,ZZ,HTCON,PRESS,
     1        TCMIX,PCMIX,ZCMIX ,NC
      PCMIX = 0.0
      ZCMIX = 0.0
      TCMIX = 0.0
      DO   800          I=1,NC
      PCMIX = PCMIX + XX(I)*PC(I)
      TCMIX = TCMIX + XX(I)*TC(I)
  800 ZCMIX = ZCMIX + XX(I)*ZC(I)
      RETURN
      END
```

……

```
      SUBROUTINE  ENTHAL(KEQN,TEMP,XX)
C
C  KEQN=1.....SUPERHEATED VAPOUR REGION
C      =2.....SATURATED VAPOUR LINE
C      =3.....SATURATED LIQUID LINE
C      =4.....SUBCOOLED LIQUID REGION
C  DELH.......(H*-H)  AS CALCULATED FROM THE RELATION--(H*-H)/TC =
C                                       F(TR,PR,ZC)    BTU/LB.MOLE
C  TOTEMP.....IS THE MIXTURE MOLAR HEAT CONTENT AT THE IDEAL GAS STATE
C  HTCON......IS THE  H  IN THE ABOVE RELATION
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),PC(10),
     1           TC(10),ZC(10),TEMPX(10),XX(10)
      COMMON  A,B,C,D,AE,BE,CE,PC,TC,ZC,TT,PSI,TOL1,ZZ,HTCON,PRESS,
     1        TCMIX,PCMIX,ZCMIX ,NC
      CT = TCMIX
      CP = PCMIX
      CZ = ZCMIX
      TR = (TEMP+460.0)/CT
      PR = PRESS/CP
      IF(CZ - 0.280)   898,   898,   899
C
```

```
C                              FOR CZ .GT.0.280
C
  899 GO TO (801,802,803,804),KEQN
  801 IF (TR - 0.8)    897,    897,    810
  810 IF (TR - 8.0)    811,    813,    813
  811 C1 = (166.0/EXP(5.16*TR)) + 0.017
      C2 = (0.62/EXP(18.4*(TR-1.0))) + 0.05
      C3 = EXP((38.8/TR) - 34.2)
      C4 = 0.989*((TR-0.75)**1.63)/EXP(0.3175*(TR-0.75))
      C5 = 0.215/EXP(0.1045*(TR**4.935))
      C6 = 0.0564*((TR-0.5)**4.67)/EXP(2.869*(TR-0.50))
      XO = 1.15 - (0.314*((TR-8.0)**3))
      XM = (1.0 - ((0.0001499*(TR**9.17))/EXP(1.297*TR)))/(0.1879 +
     1     (1.0826*((TR-0.65)**1.1726)))
  812 AB = 1.0 - C2 - C4 - (C5*PR) + (C2*(((ATAN(C3-(C3*PR))/3.1415925)
     1     +0.50)**2))
      DELH = XM*PR*(1.0 - (PR/XO))/((AB/EXP(C1*(PR**2))) + C4 + C5*PR +
     1     C6*(PR**2))
      DELH = DELH*CT
      GO TO   895
  813 DELH = CT*((0.053*TR) - (0.00341*(TR**2)) + (0.13*PR - (0.00176
     1     *(PR**2)))- (0.02725*TR*PR) + (0.000128*TR*(PR**2)) +
     2     (0.000508*(TR**2)*PR) + (0.0000634*(TR**3)) + (0.0000258*
     3     (PR**3)) - 0.2078)
      GO TO   895
  802 DELH = (5.4*(PR**0.6747)/(1.0 + 1.227*((-ALOG(PR))**0.503)))*CT
      GO TO   895
  803 DELH = ((5.4+ 3.6485*((-ALOG(PR))**0.33464))/(1.0 - (0.0056942*
     1     ALOG(PR))))*CT
      GO TO   895
  804 DELH = CT*((-0.09572107*(PR-4.2)) - (9.501235*(TR-0.77)) -
     1     (17.30389*((TR-0.77)**2)) - (0.3195707*(PR - 4.2)*(TR-0.77))
     2     + (1.368092*ALOG(PR)) + (4.227096*ALOG(PR)*ALOG(TR))
     3     + (3.181639*ALOG(PR)*(ALOG(TR)**2)) + 9.707447)
      GO TO   895
C
C                              FOR CZ .LT. 0.280
C
  898 GO TO (821,822,823,824),KEQN
  821 IF (TR - 0.90)    897,    897,    830
  830 C1 = (40.0/(EXP(5.7*TR)*(TR-0.81))) + 0.01
      C2 = (0.35/(EXP(26.2*(TR-1.0))*TR)) + 0.31
      C3 = (17.25/EXP(16.7*(TR-1.0))) + 2.75
      C4 = (0.444*(TR-2.0)) - (0.0215*(TR-2.0)**2) + (0.061*(TR-2.0)**3)
     1     - (0.0404*(TR-2.0)**4) + 0.6564
      IF (TR - 2.25)    831,    831,    832
```

```
  831 C5 = -(0.0697*(TR-2.0)) + (0.0734*(TR-2.0)**2) - (0.0533*(TR-2.0)
     1     **5) + 0.0125
      GO TO 833
  832 C5 = 0.0
  833 C6 = 0.00301*(TR-0.80)/EXP(0.87*((TR-0.80)**2))
      XO = 8.5 + (10.5*((TR-4.0)**2))
      XM = 1.0/(0.1052 + (1.2044*((TR-0.4429)**2.135)))
      GO TO 812
  822 DELH = CT* 5.8*(PR**.63163)/(1.0 + (1.229*((-ALOG(PR))**0.55456)))
      GO TO   895
  823 DELH = CT*((5.8 + (5.19*(-ALOG(PR))**0.4963))/(1.0 - (0.1*ALOG(PR)
     1     )))
      GO TO   895
  824 DELH = CT*(-(0.1368774*(PR-4.664))    - (14.56975*(TR-0.79749))
     1     - (7.812724*((TR-0.79749)**2)) - (0.1642482*(TR-0.79749)
     2     *(PR-4.664)) + (1.036851*ALOG(PR)) + (4.463472*ALOG(PR)*
     3     ALOG(TR)) + (4.525831*ALOG(PR)*(ALOG(TR)**2)) + 10.86085)
C
C                CALCULATE THE ENTHALPY AT THE IDEAL GAS STATE
C
  895 TOTEMP = 0.0
      DO   841          I=1,NC
      TEMPX(I) = XX(I)*((AE(I)*(TEMP      )) + (BE(I)*((TEMP      )**2)/
     1           2.0) + (CE(I)*((TEMP      )**3)/3.0))
  841 TOTEMP = TOTEMP + TEMPX(I)
      HTCON = TOTEMP - DELH
      RETURN
  897 WRITE(6,896)
      STOP
  896 FORMAT(47X,38HENTHALPY DATA BOUNDS HAS BEEN EXCEEDED)
      END
```

Appendix IV. Subroutines to Main Programs

The BUBLPT, DEWPT, FLASH, CRITIC, and ENTHAL subroutines are shared by both the steady state solution program and the transient behaviour program. The DIMENSION and COMMON statements differ for the two main programs. The listings included in Appendix III and IV are compatible in this respect with the transient listing. For use with the steady state solution the dimensioned variables should appear in the DIMENSION statement and the three COMMON statements duplicated from the main listing.

The TEST subroutine is used in the steady state solution to ensure that any specified variable does not lie outside specific limits. If the value exceeds a limit, it is set equal to the particular limit concerned. The DIMENSION and COMMON statements do not appear in this subroutine.

Appendix IV.1. Bubble Point Temperature Calculation

When the composition of a liquid and the total pressure are known as in the case of the equilibrium stages used in the mathematical models described in the body of this report, it is only necessary to apply Henry's Law (equation (1)) and stipulate that the sum of the vapour mole fractions must equal unity or

$$\sum_{i=1}^{NC} y_i = \sum_{i=1}^{NC} K_{i,j} . x_{i,j} = 1 \tag{62}$$

for NC components and tray j and the equilibrium ratio is expressed as a function of temperature and pressure by (8). The problem resolves itself into finding the temperature T_j such that equation (62) is satisfied.

To use the Newton-Raphson technique (35), (30) to solve for T_j, equation (62) can be rearranged into functional form or

$$f_5(T_j) = \sum_{i=1}^{NC} K_{i,j} . x_{i,j} - 1 \tag{63}$$

The required value of T_j is the positive root of $f(T_j) = 0$.

Newton's formula states

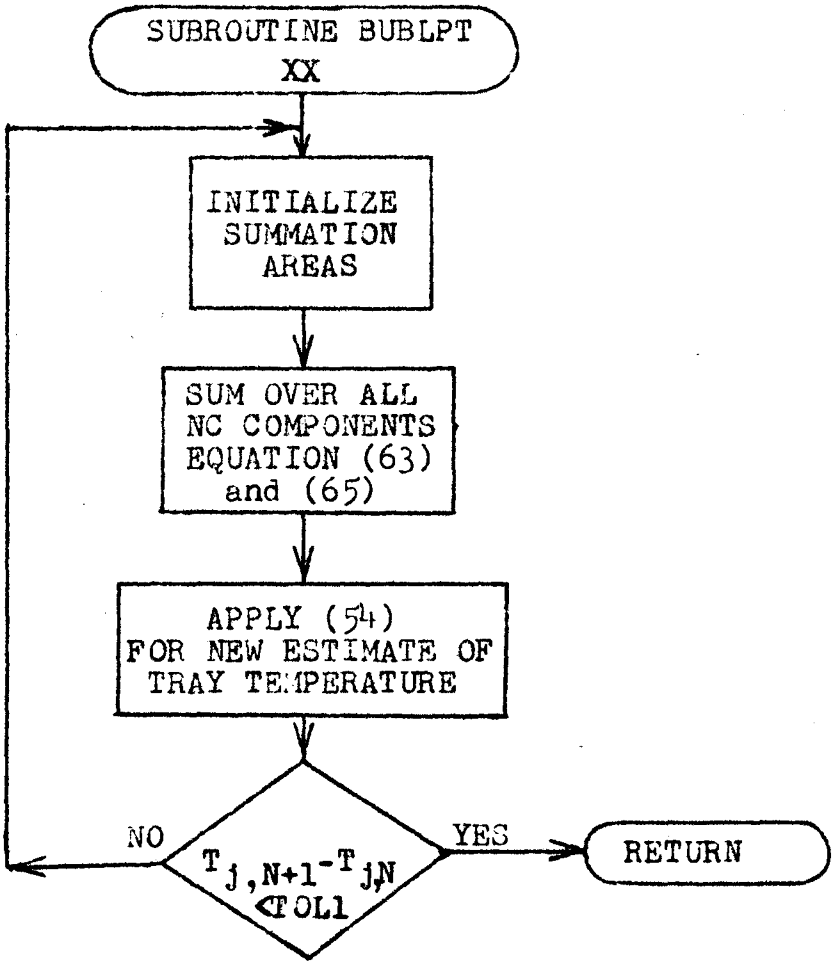
$$T_{j,N+1} = T_{j,N} - \frac{f_5(T_{j,N})}{f_5'(T_{j,N})} \tag{64}$$

where $$f_5'(T_{j,N}) = \sum_{i=1}^{NC} x_{i,j} . \left(\frac{dK_{i,j}}{dT_j}\right)_N \tag{65}$$

where the (N+1)th estimate is closer to the required root than estimate N.

Experience has shown that the Newton technique will converge to a 3 decimal precision within 5 or 6 iterations.

Flow Diagram for BUBLPT Subroutine



TT.......is the temperature calculated by the subroutine

TOL 1....is the tolerance or minimum difference between successive estimates of temperature

EQULK....is a function variable and represents the equilibrium ratio regression

DEQULK.....is the derivative of the equilibrium ratio regression

SUMKX......is the summation represented by (63)

SUMDKX.....is the summation represented by (65)

Appendix IV.2. Dew Point Temperature Calculation

When the composition of the vapour and the pressure are known it is necessary to again apply Henry's Law and stipulate that the sum of the liquid mole fractions must equal unity or

$$\sum_{i=1}^{NC} x_{i,j} = \sum_{i=1}^{NC} \frac{y_{i,j}}{K_{i,j}} = 1 \tag{66}$$

In functional form (53) becomes

$$f_6(T_j) = \sum_{i=1}^{NC} \frac{y_{i,j}}{Ki,j} - 1 \tag{67}$$

and $$f_6(T_j) = -\sum_{i=1}^{NC} \frac{y_{i,j}}{K_{i,j}}$$

The positive root of $f_6(T_j) = 0$ is obtained using the Newton slope method as described for the bubble point temperature calculation. The flow diagram for the DEWPT subroutine is identical to that for the BUBLPT subroutine. The XX vector however contains vapour mole fractions in the former case rather than liquid mole fractions as in the latter case.

SUMKX.....is the summation represented by (67)

SUMDKX....is the summation represented by (68)

```
      SUBROUTINE  BUBLPT(   XX)
C
C  NEWTON ITERATIVE TECHNIQUE UTILIZED TO SEEK OUT ROOT OF FUNCTION
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),PC(10),
     1           TC(10),ZC(10),TEMPX(10),XX(10)
      COMMON  A,B,C,D,AE,BE,CE,PC,TC,ZC,TT,PSI,TOL1,ZZ,HTCON,PRESS,
     1        TCMIX,PCMIX,ZCMIX ,NC
      EQULK(A,B,C,D,T) = A+B*T+C*T*T+D*T*T*T
      DEQULK(B,C,D,T) = B+2.0*C*T+3.0*T*T*D
  800 SUMKX= -1.0
      SUMDKX= 0.0
      DO   801          I=1,NC
      SUMKX= SUMKX + (EQULK(A(I),B(I),C(I),D(I),TT)*XX(I))
  801 SUMDKX= SUMDKX + (DEQULK(B(I),C(I),D(I),TT)*XX(I))
      TNEW= TT - (SUMKX/SUMDKX)
      IF(ABS(TNEW-TT) - TOL1)  803,803, 802
  802 TT= TNEW
      GO TO   800
  803 TT= TNEW
      RETURN
      END
```

……

```
      SUBROUTINE  DEWPT(   XX)
C
C  NEWTON ITERATIVE TECHNIQUE UTILIZED TO SEEK OUT ROOT OF FUNCTION
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),PC(10),
     1           TC(10),ZC(10),TEMPX(10),XX(10)
      COMMON  A,B,C,D,AE,BE,CE,PC,TC,ZC,TT,PSI,TOL1,ZZ,HTCON,PRESS,
     1        TCMIX,PCMIX,ZCMIX ,NC
      EQULK(A,B,C,D,T) = A+B*T+C*T*T+D*T*T*T
      DEQULK(B,C,D,T) = B+2.0*C*T+3.0*T*T*D
  800 SUMKX= -1.0
      SUMDKX= 0.0
      DO   801          I=1,NC
      SUMKX= SUMKX + (XX(I)/ EQULK(A(I),B(I),C(I),D(I),TT))
  801 SUMDKX= SUMDKX - (XX(I)*DEQULK(B(I),C(I),D(I),TT)/(EQULK(A(I),B(I)
     1,C(I),D(I),TT)**2))
      TNEW= TT - (SUMKX/SUMDKX)
      IF(ABS(TNEW-TT) - TOL1)  803,803, 802
  802 TT= TNEW
      GO TO   800
  803 TT= TNEW
      RETURN
      END
```

Appendix IV.3. Flash Vaporization

The flash problem occurring in the demethanizer-absorber is the formation of 2 phases of feed F_2 at the tray temperature T_{N4}. If the temperature T_{N2} is high, flashing of F_1 can also occur at tray N2. The feed composition and the feed tray temperature are known. It is required to determine the liquid-vapour split of the feed stream.

Consider F_2: a steady state material balance for component i is

$$F_2 . X_{i,2} = \bar{V}_2 . y_{i,2} + \bar{L}_2 . x_{i,2} \tag{69}$$

and
$$F_2 = \bar{V}_2 + \bar{L}_2 \tag{70}$$

applying the equilibrium equation (1) and (70) into (69) and rearranging results in

$$y_{i,2} = \frac{X_{i,2}}{1 - \frac{\bar{L}_2}{F_2} . (1 - \frac{1}{K_{i,N4}})} \tag{71}$$

but
$$\sum_{i=1}^{NC} y_{i,2} = 1 = \sum_{i=1}^{NC} \left[\frac{X_{i,2}}{1 - \frac{\bar{L}_2}{F_2} . \left(1 - \frac{1}{K_{i,N4}}\right)} \right] \tag{72}$$

To apply Newton's root finding technique (72) is rearranged in functional form

$$f_7\left(\frac{\bar{L}_2}{F_2}\right) = \sum_{i=1}^{NC} \left[\frac{X_{i,2}}{1 - \left(\frac{\bar{L}_2}{F_2}\right)\left(1 - \frac{1}{K_{i,N4}}\right)} \right] - 1 \tag{73}$$

and
$$f_7'\left(\frac{\bar{L}_2}{F_2}\right) = \sum_{i=1}^{NC} \frac{X_{i,2}\left(1 - \frac{1}{K_{i,N4}}\right)}{\left[1 - \left(\frac{\bar{L}_2}{F_2}\right)\left(1 - \frac{1}{K_{i,N4}}\right)\right]^2} \tag{74}$$

The solution to (73) is that positive value of $\frac{\bar{L}_2}{F_2}$ for which $f_7\left(\frac{\bar{L}_2}{F_2}\right) = 0$. Since $\frac{\bar{L}_2}{F_2} = 0$ is a root of f_7, it is necessary to use $\frac{\bar{L}_2}{F_2} = 1.0$ as the initial value of the required ratio.

It should be noted that T_{N4} must lie between the bubble point and dew point temperatures of F_2 for this analysis to be valid. The flow diagram for FLASH is basically identical to that used for BUBLPT.

PSI.....the $\bar{L}/F$ ratio, initial estimate is 1.0.

Appendix IV.4. The TEST Subroutine

The TEST subroutine is used in the steady state solution. It compares a value ZZZ to see if it lies within the maximum-minimum specification TESTMX and TESTMN respectively.

```
      SUBROUTINE  FLASH(   XX)
C
C  NEWTON ITERATIVE TECHNIQUE UTILIZED TO SEEK OUT ROOT OF FUNCTION
C  PSI........LIQUID/(TOTAL FEED) RATIO
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),PC(10),
     1           TC(10),ZC(10),TEMPX(10),XX(10)
      COMMON  A,B,C,D,AE,BE,CE,PC,TC,ZC,TT,PSI,TOL1,ZZ,HTCON,PRESS,
     1        TCMIX,PCMIX,ZCMIX ,NC
      EQULK(A,B,C,D,T) = A+B*T+C*T*T+D*T*T*T
      DEQULK(B,C,D,T) = B+2.0*C*T+3.0*T*T*D
      PSI= 1.0
  800 SUMKX= -1.0
      SUMDKX= 0.0
      DO   801          I=1,NC
      SPARE4=1.0 - (1.0/EQULK(A(I),B(I),C(I),D(I),TT))
      SUMKX= SUMKX + (XX(I)/(1.0 - PSI*SPARE4))
  801 SUMDKX= SUMDKX + (XX(I)*SPARE4/((1.0 - PSI*SPARE4)**2))
      PSINEW= PSI - (SUMKX/SUMDKX)
      IF(ABS(PSINEW-PSI) - TOL1)  803,  803,  802
  802 PSI= PSINEW
      GO TO   800
  803 PSI= PSINEW
      RETURN
      END
```

```
      SUBROUTINE  TEST(ZZZ,TESTMX,TESTMN)
C
C  ZZZ.........IS TESTED TO LIE BETWEEN TESTMX AND TESTMN,IF NOT THEN IS
C              EQUATED TO NEAREST LIMIT
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),PC(10),
     1           TC(10),ZC(10),TEMPX(10),XX(10)
      COMMON   A,B,C,D,NC,TT,PSI,TOL1,SUMKX,SUMDKX,ZZ
      COMMON  AE,BE,CE,TEMPX,HTCON,PRESS
      COMMON  PC,TC,ZC,TCMIX,PCMIX,ZCMIX
      IF(TESTMX -ZZZ)   800,   803,   801
  800 ZZ  = TESTMX
      GO TO 804
  801 IF(ZZZ- TESTMN)   802,   803,   803
  802 ZZ  = TESTMN
      GO TO 804
  803 ZZ= ZZZ
  804 RETURN
      END
```

Appendix V.1. Steady State Solution Program

The calculation of the steady state situation in the demethanizer-absorber model is outlined in detail in section 5. The steps in the procedure are specified in section 5.3. The corresponding flow diagram is presented in this appendix along with the Fortran listing of the main program (DABBLE). In addition the data input for the 10 component-20 tray model is included as a sample. The terms used in the Fortran program are defined in the comment statement preceding the formal calculation listing.

The program is written in a general form with the following options readily available.

(1) EQULK and DEQULK are the equilibrium ratio and corresponding derivative expressions. They are presented in functional form and can easily be converted to any other function containing up to four distinct coefficients.

(2) The tray temperatures can be calculated using the DEWPT subroutine by replacing statements 69, 70, and 75 with

```
69  SUMLIJ = SUMLIJ + RV(I,J)*CTOP(I)
70  X(I,J) = RV(I,J)*CTOP(I)/SPARE 1
75  CALL DEWPT(XX)
```

Canik (9) and Holland (30) claim that the dew-point calculation of tray temperatures is slower to converge than the bubble-point method.. This particular aspect has not been tested on the demethanizer-absorber.

(3) By setting KPRNT equal to unity a complete flow and temperature mapping of the model is obtained at each iteration.

(4) To limit the maximum number of iterations and thereby reduce computation time, ITERF specifies the total possible iterations for the specific case being considered. Experience has shown that if a 10 component-10 tray case has not converged in 60 passes then no convergence will indeed occur. For the 10 component-30 tray model ITERF is normally set at 130.

(5) The feeds to the column can be expressed as mole fractions, moles or Lbs. and this feature is controlled by the variable MFEED. See the program listing for the necessary specifications.

(6) Any number of cases can be run sequentially (specify NPROB). The successive cases will use the answer to the previous column calculation thereby bypassing the first two iterations assuming constant molal overflow. The largest model (in trays) should appear first in this sequence otherwise the column map for a successive case could contain zero flows or mole fractions which would lead to divergence of the iterative calculation. The listed version of the program requires initial estimates of temperatures and flows.

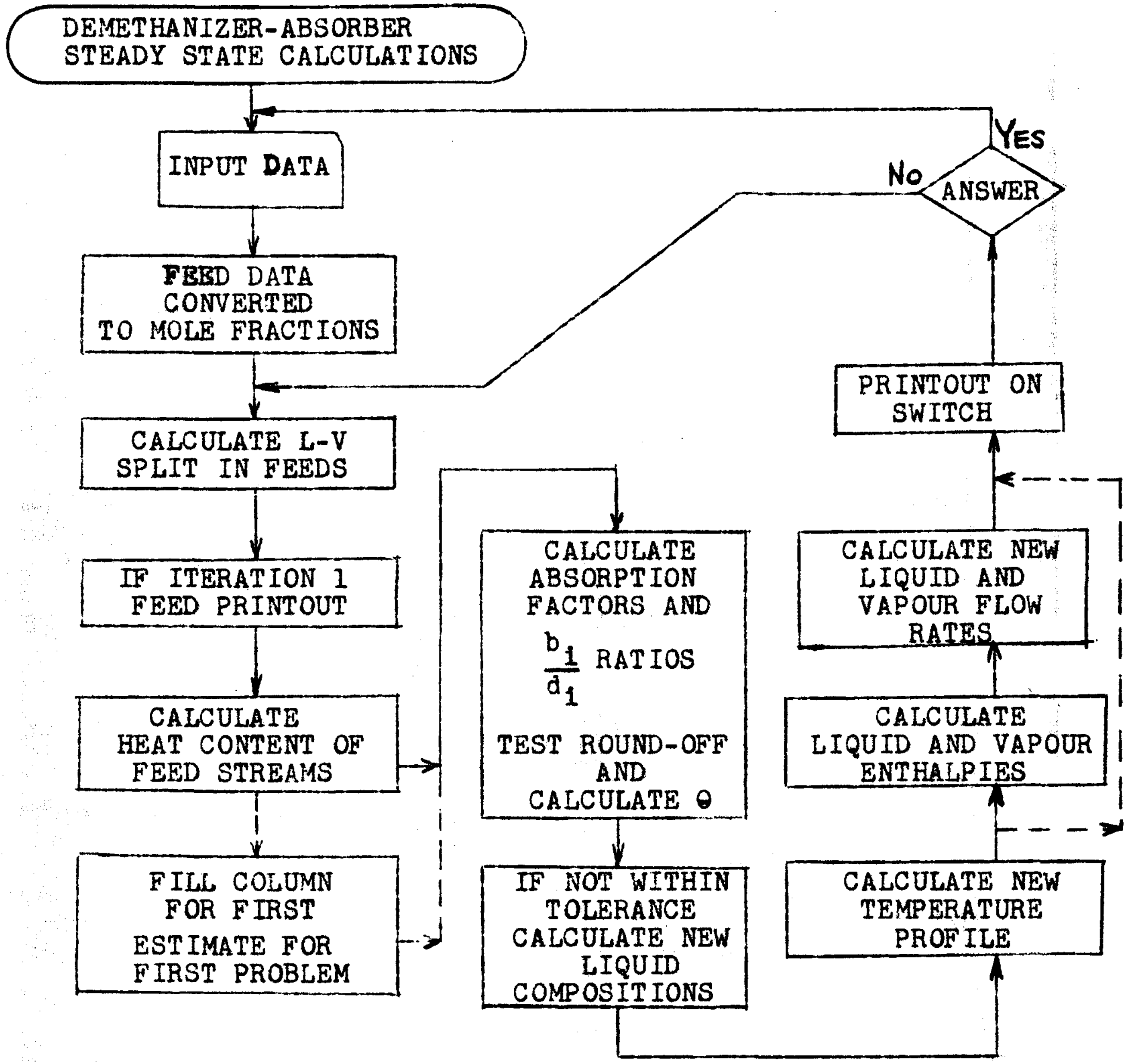
(7) KSTOP specifies the maximum number of iterations for the Newton root finding technique applied to the Θ-function. This value is normally set at 20. The Newton technique never exceeded 8 iterations to obtain the temperature to ±0.001°F. for the cases in which it was traced.

(8) The Θ-function printout can be obtained for every iteration by setting KTHETA equal to zero.

Another technique which has not as yet been mentioned is a "perturbation method" which is used to dislodge the Θ-root when it is consistently equal to either the maximum allowable Θ or the minimum allowable Θ. When the Θ appears on a boundary for say 5 successive iterations it is desirable to artificially vary Θ to obtain a new concentration profile and therefore a temperature profile which may lead to successful convergences. This method was discovered to be only marginally successful; only two cases in twenty converged after having the Θ-root repeated up to 5 successive times at a boundary value. Further evaluation of this method is recommended for any future work.

LMAX is the Fortran term which specifies how many successive repititions of a Θ-value are allowed. AMULT is the factor by which the Θ-value is multiplied to artificially "perturb" the concentration profile.

FLOW DIAGRAM: STEADY STATE SOLUTION



----Represents either the route taken during the first or second iteration.

```
C
C       LIGHT ENDS RECOVERY UNIT-------------POLYMER CORPORATION LTD.
C     DEMETHANIZER-ABSORBER (E-100)           STEADY STATE CALCULATION
C     CONTAINING BOTH HEAT AND MATERIAL BALANCES............WFP  JULY/64
C
C
C  I..........COMPONENT                                    J.........IDEAL STAGE
C  SUMTOP.....SPECIFICATION OF TOTAL MOLAR FLOW OVERHEAD
C  NC.........NUMBER OF COMPONENTS TO A MAXIMUM OF 15
C  NR.........TOTAL TRAYS TO A MAXIMUM OF 30
C  NT1........TRAYS IN TOP SECTION INCLUDING LIQUID FEED TRAY
C  NT2........TRAYS IN MIDDLE SECTION INCLUDING GAS FEED TRAY
C  NT3........TRAYS IN BOTTOM SECTION EXCLUDING THE REBOILER
C
C  MFEED......FEED IS EXPRESSED IN               MOLE FRACTION IF  LT  1
C                                                        MOLES IF E TO 1
C                                                          LBS IF  GT  1
C
C  NPROB......THE NUMBER OF PROBLEMS TO BE ATTEMPTED PER 7040 PASS
C  ITER.......ITERATION NUMBER                ITERF......FINAL ITERATION
C  KPRNT......EVERY (KPRNT)TH ITERATION WILL FORCE INTERMEDIATE PRINTOUT
C  ITEMP......SPECIFIES THE ITERATION AT WHICH THE TEMPERATURE DAMPING
C             FACTOR (PART) WILL BE APPLIED
C  THETAI.....INITIAL VALUE OF THETA FOR EACH ROOT SEARCH
C  ITHETA.....SPECIFIES THE ITERATION AT WHICH THETA CONVERGENCE BEGINS
C  KTHETA.....IF 0--THETA PLUS FUNCTION PRINTOUT,  GT 0--NO PRINTOUT
C  KHEAT......SPECIFIES THE ITERATION  FROM  WHICH THE FLOWS ARE TO BE
C                           BASED ON THE HEAT BALANCES
C  KSTOP......MAXIMUM NUMBER OF ITERATIONS FOR THE NEWTON ROOT-FINDING
C                            TECHNIQUE(THETA-FUNCTION)
C
C            MAXIMUM AND MINIMUM RESTRICTIONS ON PARAMETERS
C          RATMAX....RATIO(B/D)            RVMAX.....RATIO(V/D)
C          RATMIN                          RVMIN
C          AFMAX.....RATIO(L/K.V)          RLMAX.....RATIO(L/B)
C          AFMIN                           RLMIN
C          TMAX......TEMPERATURE           TLMAX.....TOTAL LIQUID
C          TMIN                            TLMIN
C          XMAX......MOLE FRACTION         TVMAX.....TOTAL VAPOUR
C          XMIN                            TVMIN
C          THMAX.....THETA(CONVERGENCE)
C          THMIN
C
C  REBOIL.....IS THE RATIO   V(NR)/TLIQ(NR)
C  PART.......FRACTION OF TEMPERATURE DIFFERENCE BETWEEN 2 SUCCESSIVE
C             ITERATIONS TO BE USED FOR NEXT ITERATION
C  WALL.......FRACTION BY WHICH THETA MAX-MIN RESRICTIONS ARE REDUCED
C  P..........LIMITING FACTOR FOR ITERATIVE FLOW ESTIMATES
C  CONST......FACTOR USED IN THE P RELATION-- P=1.0+ 1.0/EXP(ITER/CONST)
C  FLOW.......FACTOR BY WHICH FLOW RATES(CONSTANT MOLAR OVERFLOW) ARE
```

```
C                       MULTIPLIED FOR PRIMARY ESTIMATE
C  LMAX.......MAXIMUM NO. OF REPEATED THETAS BEFORE IMPULSE INJECTED
C  AMULT......FACTOR BY WHICH THETA IS MULTIPLIED WHEN NO CHANGE
C  PART2......FACTOR TO SLACKEN TEMPERATURE RESTRICTION,APPROACH SOL,N
C  PRESS......COLUMN PRESSURE IN ATMOS. (ABSOLUTE)
C  SUMTOT.....SUM OF ALL COMPONENTS ENTERING (IN MOLES)
C
C  ABSLIQ(I)..                                    ABSORBING STREAM
C  ABSVAP(I)..
C  FDLIQL(I).. MOLES COMPONENT(I) IN              LIQUID STREAM
C  FDLIQV(I)..
C  FDGASL(I)..                                    GAS STREAM
C  FDGASV(I)..
C  SUMFD(K)...TOTAL MOLES IN FEEDS           TF(K).....TEMPERATURES OF FEEDS
C  FEED(I,K)..ENTERING FEED STREAMS             (K=1,2,3)   (I=1 TO NC)
C
C  HABS,HFO...MOLAR AND TOTAL HEAT CONTENTS OF ABSORBING STREAM  FO
C  HFDLIQ,HF1.MOLAR AND TOTAL HEAT CONTENTS OF LIQUID FEED       F1
C  HFDGL,HF2L.MOLAR AND TOTAL HEAT CONTENTS OF LIQUID PORTION    F2
C  HFDGV,HF2V.MOLAR AND TOTAL HEAT CONTENTS OF VAPOUR PORTION    F2
C  HF2........TOTAL HEAT CONTENT OF GAS FEED     F2
C  HEATIN.....TOTAL HEAT CONTENT OF ENTERING STREAMS   FO,F1,F2
C  HDIST,HD...MOLAR AND TOTAL HEAT CONTENTS OF OVERHEAD VAPOUR
C  HBOT,HB....MOLAR AND TOTAL HEAT CONTENTS OF BOTTOMS PRODUCT
C  HJ.........MOLAR HEAT CONTENT OF LIQUID LEAVING TRAY J
C  HHJP1......MOLAR HEAT CONTENT OF VAPOUR ENTERING TRAY J
C  Q(J).......INTERCOOLER HEAT DUTY ON TRAY J
C
C  RATIO(I)...RATIO OF B(I)/D(I)
C  TOP(I).....D(I)                                        BOT(I)......B(I)
C  CTOP(I)....CORRECTED D(I)                    CBOT(I).....CORRECTED B(I)
C  TEMPY(I)  TEMPX(I)............TEMPORARY STORAGE VECTORS
C  TLIQ(J)  TVAP(J)............TOTAL MOLES TO AND FROM A TRAY
C  A(I) B(I) C(I) D(I).........COEFFICIENTS FOR EQUILIBRIUM K REGRESSION
C                              EQUATION
C  AE(I),BE(I),CE(I).........COEFFICIENTS FOR HEAT CAPACITY RELATIONSHIP
C                            CP=F(T) OF GASES AT THE IDEAL GAS STATE
C  TC,PC,ZC...CRITICAL CONSTANTS FOR THE HYDROCARBON COMPONENTS
C  WM(I)......COMPONENT MOLECULAR WEIGHT VECTOR
C  AF(I)......ABSORPTION FACTOR(L/K.V) FOR COMPONENTS ON A GIVEN TRAY
C  T(J).......TEMPERATURES AT EACH STAGE
C  XX(I)......TEMPORARY VECTOR OF COMPONENT CONCENTRATIONS FOR ENTERING
C             SUBROUTINES
C  TOT(I).....SUM OF FEEDS BY COMPONENT
C  RV(I,J)....(V/D) RATIO FOR COMPONENT I ON TRAY J
C  RL(I,J)....(L/B) RATIO FOR COMPONENT I ON TRAY J
C  X(I,J).....MOLE FRACTION   COMPONENT I ON TRAY J
C  PSIR(K)....(L/F) RATIO FOR THE FEED STREAMS
C
C  TOL1.......BUBBLE POINT AND DEW POINT TOLERANCE
```

```
C   TOL2.......THETA FUNCTION TOLERANCE
C   TOL3.......THETA CRITERIA OF SOLUTION(TERMINATION IF WITHIN TOL3)
C
C                              SUBROUTINES USED
C   ENTHAL-----MOLAR HEAT CONTENT BASED ON PHILLIPS PETROLEUM CORRELAT,N
C   CRITIC-----CALCULATES PSEUDOCRITICAL CONSTANTS
C   FLASH------FLASH VAPOURIZATION,CALCULATES L/F RATIO
C   BUBLPT-----BUBBLE POINT CALCULATION
C   DEWPT------DEW POINT CALCULATION
C   TEST-------TESTS FOR NUMBER BEING WITHIN MIN-MAX RESTRICTION
C
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),WM(10),
     1           PC(10),TC(10),ZC(10),ABSLIQ(10),FDLIQL(10),FDGASV(10),
     2           FDGASL(10),FEED(10,3),TOP(10),CTOP(10),BOT(10),Q(30),
     3           CBOT(10),RATIO(10),TEMPY(10),TEMPX(10),XX(10),TOT(10),
     4           TLIQ(30),TVAP(30),AF(30),T(30),RV(10,30),RL(10,30),
     5           X(10,30),SUMFD(3),TF(3),PSIR(3),ABSVAP(10),FDLIQV(10)
      COMMON   A,B,C,D,NC,TT,PSI,TOL1,SUMKX,SUMDKX,ZZ
      COMMON  AE,BE,CE,TEMPX,HTCON,PRESS
      COMMON  PC,TC,ZC,TCMIX,PCMIX,ZCMIX
      EQULK(A,B,C,D,T) = A+B*T+C*T*T+D*T*T*T
      DEQULK(B,C,D,T) = B+2.0*C*T+3.0*T*T*D
C
C                              HEADING PAGE OF OUTPUT
C
      READ (5,992)  NPROB
      NCALC = 1
C
C                            BEGINNING OF DATA INPUT
C
 1000 WRITE(6,999)
      DO    1           M=1,3
    1 WRITE(6,998)
      WRITE(6,997)
      WRITE(6,966)
      DO    2           M=1,6
    2 WRITE(6,998)
      WRITE(6,996)
      WRITE(6,995)
      WRITE(6,994)
      WRITE(6,993)
      WRITE(6,999)
      WRITE(6,991)  NCALC
      WRITE(6,998)
      READ (5,992)  NC,NT1,NT2,NT3,ITERF,KPRNT
      READ (5,990)  SUMTOP,TEMP1,TEMP2,TEMP3 ,THETAI
      READ (5,992)  MFEED,ITEMP,ITHETA,KTHETA,KHEAT,KSTOP,LMAX
      READ (5,990)  TOL1,TOL2,TOL3,PRESS,PART2
      READ (5,990)  PART,WALL,CONST,FLOW,REBOIL,AMULT
```

```
      N1=NT1-1
      N2=NT1
      N3=NT2+N1
      N4=NT2+N2
      N5=NT3+N4
      NR=N5+1
      TCALC=0.0
      THETA = 0.0
C
C                         READ MAX-MIN RESTRICTIONS
C
      READ (5,990)  RATMAX,RATMIN,RVMAX,RVMIN,RLMAX,RLMIN
      READ (5,990)   AFMAX, AFMIN,TVMAX,TVMIN,TLMAX,TLMIN
      READ (5,990)    TMAX,  TMIN, XMAX, XMIN,THMAX,THMIN
      WRITE(6,989)
      WRITE(6,988)
      WRITE(6,987)  NC,N2,N4,NR,ITERF,KPRNT,MFEED,ITEMP,ITHETA
      WRITE(6,965)  KTHETA,KHEAT,      TEMP1,TEMP2,TEMP3
      WRITE(6,998)
      WRITE(6,986)
      WRITE(6,985)  RATMAX,AFMAX,RVMAX,RLMAX,TLMAX,TVMAX,TMAX,XMAX,THMAX
      WRITE(6,985)  RATMIN,AFMIN,RVMIN,RLMIN,TLMIN,TVMIN,TMIN,XMIN,THMIN
      READ (5,984)  (WM(I),PC(I),TC(I),ZC(I),  I=1,NC)
      DO   199          J=1,NR
  199 Q(J) = 0.0
      READ (5,984)  (A(I),B(I),C(I),D(I),  I=1,NC)
      DO   200          I=1,NC
  200 READ (5,984)  AE(I),BE(I),CE(I)
      READ (5,981)  (T(J),                   J=1,NR)
      WRITE(6,998)
      WRITE(6,983)
      DO   3            I=1,NC
    3 WRITE(6,964)  I,A(I),B(I),C(I),D(I),AE(I),BE(I),CE(I)
      WRITE(6,998)
      KLM = 0
      WRITE(6,963)
      WRITE(6,979)  (I,WM(I),PC(I),TC(I),ZC(I),  I=1,NC)
      WRITE(6,998)
      WRITE(6,978)  TOL1,TOL2,TOL3
      LLL = 1
      FRACT = 1.0
C
C                  READ IN 2 FEEDS PLUS ABSORPTION STREAM DATA
C
      DO   5            K=1,3
      SUMFD(K) = 0.0
      DO   4            I=1,NC
      READ (5,981)  FEED(I,K)
    4 SUMFD(K) = SUMFD(K) + FEED(I,K)
    5 CONTINUE
```

```
      DO   6             I=1,NC
    6 TOT(I) = 0.0
      TOTAL = 0.0
      DO   7             I=1,NC
      TOT(I) = FEED(I,1) + FEED(I,2) + FEED(I,3)
    7 TOTAL = TOTAL + TOT(I)
      WRITE(6,998)
      WRITE(6,998)
      WRITE(6,980)
      DO   8             I=1,NC
    8 WRITE(6,979)  I,FEED(I,1),FEED(I,2),FEED(I,3),TOT(I)
      WRITE(6,979)  KLM,SUMFD(1),SUMFD(2),SUMFD(3),TOTAL
      WRITE(6,998)
C
C                            CONVERT FEEDS TO FRACTIONS
C
      DO   13            K=1,3
      IF(MFEED-1)   14,   11,   9
    9 DO   10            I=1,NC
   10 FEED(I,K)= FEED(I,K)/WM(I)
   11 SUMFD(K)= 0.0
      DO   12            I=1,NC
   12 SUMFD(K)= SUMFD(K)+FEED(I,K)
      DO   13            I=1,NC
   13 FEED(I,K)= FEED(I,K)/SUMFD(K)
   14 ITER = 1
C
C               CALCULATION OF LIQUID-VAPOUR SPLITS IN FEED STREAMS
C
      DO   4000          LL=1,ITERF
      DO   36            K=1,3
      PSIR(K)=0.0
      IF (LLL)   9999,   400,   401
  400 TEMP1 = T(1)
      TEMP2 = T(N2)
      TEMP3 = T(N4)
  401 IF (K-2)   15,   16,   17
   15 TF(K) = TEMP1
      GO TO   18
   16 TF(K) = TEMP2
      GO TO   18
   17 TF(K) = TEMP3
   18 DO   19            I=1,NC
   19 XX(I)= FEED(I,K)
      TT= TF(K)
C
C                        BUBBLE POINT TEMPERATURE CALCULATION
C
      CALL  BUBLPT(   XX)
      TBP= TT
```

```
      IF(TBP-TF(K))    20,    26,    26
   20 TT = TF(K)
C
C                    DEW POINT TEMPERATURE CALCULATION
C
      CALL  DEWPT(   XX)
      TDP= TT
      IF(TF(K)-TDP)    21,    31,    31
   21 TT = TF(K)
C
C                    FLASH................PSI= (L/F)  RATIO
C
      CALL  FLASH(   XX)
      PSIR(K)= PSI
      DO   25            I=1,NC
      SPARE1= 1.0-(1.0/EQULK(A(I),B(I),C(I),D(I),TF(K)))
      TEMPY(I)= FEED(I,K)/(1.0-PSIR(K)*SPARE1)
      TEMPY(I)= TEMPY(I)*SUMFD(K)*(1.0-PSIR(K))
      TEMPX(I)= (FEED(I,K)*SUMFD(K))-TEMPY(I)
      GO TO  ( 22,  23,  24),  K
   22 ABSVAP(I)= TEMPY(I)
      ABSLIQ(I)= TEMPX(I)
      GO TO   25
   23 FDLIQV(I)= TEMPY(I)
      FDLIQL(I)= TEMPX(I)
      GO TO   25
   24 FDGASV(I)= TEMPY(I)
      FDGASL(I)= TEMPX(I)
   25 CONTINUE
      GO TO   36
C
C                              ALL LIQUID FEED STREAM
C
   26 PSIR(K)= 1.0
      DO   30            I=1,NC
      GO TO  (   27,   28,   29),   K
   27 ABSLIQ(I)= FEED(I,K)*SUMFD(K)
      GO TO   30
   28 FDLIQL(I)= FEED(I,K)*SUMFD(K)
      GO TO   30
   29 FDGASL(I)= FEED(I,K)*SUMFD(K)
   30 CONTINUE
      GO TO   36
C
C                              ALL VAPOUR FEED STREAM
C
   31 PSIR(K)= 0.0
      DO   35            I=1,NC
      GO TO  (   32,   33,   34),   K
   32 ABSVAP(I)= FEED(I,K)*SUMFD(K)
```

```
      GO TO   35
   33 FDLIQV(I)= FEED(I,K)*SUMFD(K)
      GO TO   35
   34 FDGASV(I)= FEED(I,K)*SUMFD(K)
   35 CONTINUE
      WRITE(6,985)  TBP, TDP,PSIR(K),TF(K)
   36 CONTINUE
C
C          TOTAL THE MOLES IN ENTERING STREAMS  (BY COMPONENT)
C
      IF (LLL)   9999, 6000,   37
   37 WRITE(6,977)
      SUMTOT = 0.0
      SUM1 = 0.0
      SUM2 = 0.0
      SUM3 = 0.0
      SUM4 = 0.0
      SUM5 = 0.0
      SUM6 = 0.0
      DO   38             I=1,NC
      SUM1 = SUM1 + ABSLIQ(I)
      SUM2 = SUM2 + ABSVAP(I)
      SUM3 = SUM3 + FDLIQL(I)
      SUM4 = SUM4 + FDLIQV(I)
      SUM5 = SUM5 + FDGASL(I)
      SUM6 = SUM6 + FDGASV(I)
      TOT(I)= ABSLIQ(I)+ABSVAP(I)+FDLIQL(I)+FDLIQV(I)+FDGASV(I)+FDGASL(I
     1)
      SUMTOT = SUMTOT + TOT(I)
   38 WRITE(6,976)  I,ABSLIQ(I),ABSVAP(I),FDLIQL(I),FDLIQV(I),FDGASL(I),
     1             FDGASV(I),TOT(I)
      LLL= 0
      WRITE(6,976)  LLL,SUM1,SUM2,SUM3,SUM4,SUM5,SUM6,SUMTOT
C
C                         CALCULATE HEAT IN FEED STREAMS
C
      DO   201            I=1,NC
  201 XX(I) = ABSLIQ(I)/SUM1
      CALL  CRITIC(  XX)
      CALL  ENTHAL(4,TEMP1,XX)
      HABS = HTCON
      HFO = HTCON*SUM1
      DO   202            I=1,NC
  202 XX(I) = FDLIQL(I)/SUM3
      CALL  CRITIC(  XX)
      CALL  ENTHAL(4,TEMP2,XX)
      HFDLIQ = HTCON
      HF1 = HTCON*SUM3
      DO   203            I=1,NC
  203 XX(I) = FDGASL(I)/SUM5
```

```
      CALL  CRITIC(  XX)
      CALL  ENTHAL(3,TEMP3,XX)
      HFDGL = HTCON
      HF2L = HTCON*SUM5
      DO   204           I=1,NC
  204 XX(I) = FDGASV(I)/SUM6
      CALL  CRITIC(  XX)
      CALL  ENTHAL(2,TEMP3,XX)
      HFDGV = HTCON
      HF2V = HTCON*SUM6
      HF2 = HF2L + HF2V
      HEATIN = HFO + HF1 + HF2
C
C                    FILL UP COLUMN FOR FIRST ITERATION
C
      WRITE(6,998)
 6000 IF(ITER - KHEAT)  6001,  6001,  6002
 6001 DO   39            J=1,N1
   39 TLIQ(J)= SUM1*FLOW
      DO   40            J=N2,N3
   40 TLIQ(J)=(SUM1 + SUM3)*FLOW
      DO   41            J=N4,N5
   41 TLIQ(J)=(SUM1 + SUM3 + SUM5)*FLOW
C
      TLIQ(NR) = TLIQ(N5)/(1.0 + REBOIL)
      DO   42            J=N4,NR
      K= NR+N4-J
   42 TVAP(K)= TLIQ(NR) *REBOIL
      DO   43            J=N2,N3
      K= N2+N3-J
   43 TVAP(K) = TLIQ(NR)*REBOIL + SUM6
      DO   44            J=1,N1
      K= N1+1-J
   44 TVAP(K) = TLIQ(NR)*REBOIL + SUM6 + SUM4
      TVAP(1) = TVAP(1) + SUM2
      IF (KTHETA)  9999,   45,  6002
   45 WRITE(6,974)  (J,TLIQ(J),TVAP(J),T(J),  J=1,NR)
C
C         CALCULATE ABSORPTION FACTORS + COMPONENT MATERIAL BALANCES
C
 6002 DO   2000          I=1,NC
      DO   46            J=1,NR
      AF(J)= TLIQ(J)/(EQULK(A(I),B(I),C(I),D(I),T(J))*TVAP(J))
      CALL  TEST(AF(J),AFMAX,AFMIN)
   46 AF(J)= ZZ
C
      RL(I,NR) = 1.0
      RL(I,N5) = 1.0 + (1.0/AF(NR))
      LAST = N5-1
      DO   47            J=N4,LAST
```

```
      K = LAST+N4-J
      RL(I,K) = (RL(I,K+1)/AF(K+1)) + 1.0
      CALL  TEST(RL(I,K),RLMAX,RLMIN)
   47 RL(I,K) = ZZ
      RVAPN4 = RL(I,N4)/AF(N4)
C
C                                  CALCULATE BI/DI
C
      ALPHA = 1.0
      BETA = 1.0
      GAMMA = 0.0
      DELTA = 0.0
      DO   48           J=1,N1
      ALPHA = ALPHA/AF(J)
   48 DELTA = DELTA+ALPHA
      DO   49           J=N2,N3
      BETA = BETA/AF(J)
   49 GAMMA = GAMMA+BETA
      CALL  TEST(ALPHA,RLMAX,RLMIN)
      ALPHA = ZZ
      CALL  TEST(BETA ,RLMAX,RLMIN)
      BETA  = ZZ
      CALL  TEST(GAMMA,RLMAX,RLMIN)
      GAMMA = ZZ
      CALL  TEST(DELTA,RLMAX,RLMIN)
      DELTA = ZZ
      SPARE1 = ALPHA*GAMMA*(FDGASV(I)+FDGASL(I))
      SPARE2 = (1.0+DELTA)*(FDGASV(I)+FDGASL(I)+FDLIQV(I)+FDLIQL(I))
      SPARE3 = ABSLIQ(I)+ABSVAP(I)
      Z1 = SPARE1+SPARE2+SPARE3-(ALPHA*BETA*FDGASV(I))-(ALPHA*FDLIQV(I))
      SPARE1 = 1.0+DELTA+(ALPHA*GAMMA)
      SPARE2 = ALPHA*BETA*RVAPN4
      RATIO(I) = Z1/(TOT(I)*(SPARE1+SPARE2) - Z1)
      TOP(I) = TOT(I)/(1.0+RATIO(I))
      BOT(I) = RATIO(I)*TOP(I)
C
      SPARE1 = 1.-((FDGASV(I)+FDGASL(I))/BOT(I))
      RL(I,N3) = (RL(I,N4)/AF(N4)) - (FDGASL(I)/BOT(I)) + 1.0
      CALL  TEST(RL(I,N3),RLMAX,RLMIN)
      RL(I,N3) = ZZ
      LAST = N3 - 1
      DO   50           J=N2,LAST
      K = LAST+N2-J
      RL(I,K) = (RL(I,K+1)/AF(K+1)) + SPARE1
      CALL  TEST(RL(I,K),RLMAX,RLMIN)
   50 RL(I,K) = ZZ
C
      SPARE2 = SPARE1 - ((FDLIQV(I)+FDLIQL(I))/BOT(I))
      RL(I,N1) = (RL(I,N2)/AF(N2)) + (FDLIQV(I)/BOT(I)) + SPARE2
      CALL  TEST(RL(I,N1),RLMAX,RLMIN)
```

```
      RL(I,N1) = ZZ
      LAST = N1-1
      DO   51           J=1,LAST
      K = LAST+1-J
      RL(I,K) = (RL(I,K+1)/AF(K+1)) + SPARE2
      CALL  TEST(RL(I,K),RLMAX,RLMIN)
   51 RL(I,K) = ZZ
      RATUP = AF(1)/RL(I,1)
C
      RV(I,1) = 1.0
      SPARE1 = 1.0 - ((ABSLIQ(I)+ABSVAP(I))/TOP(I))
      DO   52           J=2,N1
      RV(I,J) = (RV(I,J-1)*AF(J-1)) + SPARE1
      CALL  TEST(RV(I,J),RVMAX,RVMIN)
   52 RV(I,J) = ZZ
      SPARE2 = SPARE1 - ((FDLIQV(I)+FDLIQL(I))/TOP(I))
      RV(I,N2) = (RV(I,N1)*AF(N1)) + (FDLIQL(I)/TOP(I)) + SPARE2
      CALL  TEST(RV(I,N2),RVMAX,RVMIN)
      RV(I,N2) = ZZ
      LAST = N2+1
      DO   53           J=LAST,N3
      RV(I,J) = (RV(I,J-1)*AF(J-1)) + SPARE2
      CALL  TEST(RV(I,J),RVMAX,RVMIN)
   53 RV(I,J) = ZZ
      RV(I,N4) = (RV(I,N3)*AF(N3)) + (FDGASL(I)/TOP(I)) + SPARE2 -
     1          ((FDGASL(I)+FDGASV(I))/TOP(I))
      CALL  TEST(RV(I,N4),RVMAX,RVMIN)
      RV(I,N4) = ZZ
      RATDN = RV(I,N4)*AF(N4)/RL(I,N4)
C
C                TEST DOWN AND UP CALCULATIONS FOR ROUND-OFF ERROR
C
      TESTDN = (RATDN/RATIO(I)) - 1.0
      TESTUP = (RATUP/RATIO(I)) - 1.0
      IF(ABS(TESTDN)-ABS(TESTUP))   54,   56,   56
   54 DO   55           J=1,N4
      RL(I,J) = RV(I,J)*AF(J)/RATIO(I)
      CALL  TEST(RL(I,J),RLMAX,RLMIN)
   55 RL(I,J) = ZZ
      GO TO   58
   56 DO   57           J=1,N4
      RV(I,J) = RL(I,J)*RATIO(I)/AF(J)
      CALL  TEST(RV(I,J),RVMAX,RVMIN)
   57 RV(I,J) = ZZ
   58 K = N4+1
      DO   59           J=K,NR
      RV(I,J) = RL(I,J)*RATIO(I)/AF(J)
      CALL  TEST(RV(I,J),RVMAX,RVMIN)
   59 RV(I,J) = ZZ
      IF (KTHETA)  9999, 1999, 2000
```

```
 1999 WRITE(6,982)  I,TESTDN,TESTUP
 2000 CONTINUE
C
C             THETA MUST BE WITHIN THMAX AND THMIN LIMITS
C                   THETA--FORCING FUNCTION CALCULATION
C
      THEOLD = THETA
      THETA = 1.0
      IF (ITER-ITHETA) 683 ,   60,   60
   60 THETA = THETAI
      KKK= 0
   61 FUNCT=-SUMTOP
      DFUNCT= 0.0
      DO   62           I=1,NC
      FUNCT= FUNCT + (TOT(I)/(1.0 + THETA*RATIO(I)))
   62 DFUNCT= DFUNCT - ((RATIO(I)*TOT(I))/((1.0 + THETA*RATIO(I))**2))
      THETAN= THETA - (FUNCT/DFUNCT)
      IF (ABS (THETAN-THETA) - TOL2)   67,   67,   63
   63 THETA = THETAN
      IF (KTHETA)   9999,   64,   65
   64 WRITE(6,982)  KKK,   THETA,FUNCT,DFUNCT
   65 IF (KKK - KSTOP)   66,   67,   67
   66 KKK= KKK + 1
      GO TO   61
   67 THETA= THETAN
      IF (THETA-THMIN)   671,  680,  672
  671 THETA = THMIN
      GO TO  680
  672 IF (THETA-THMAX)   674,  680,  673
  673 THETA = THMAX
      GO TO  680
  674 IF (THETA-1.000)   675,  680,  676
  675 THMIN = THMIN + ((1.0-THMIN)*WALL)
      GO TO  680
  676 THMAX = THMAX - ((THMAX-1.0)*WALL)
  680 CONTINUE
      IF(ABS(THEOLD-THETA) - TOL2)  681,  681,  683
  681 LTHETA = LTHETA + 1
      IF(LTHETA - LMAX)  683,  683,  682
  682 THMAX = 8.0
      THMIN = 0.20
      THETA = THETA*AMULT
      FRACT = PART2
      LTHETA = 0
  683 SIGMAD = 0.0
      SIGMAB = 0.0
      DO   68           I=1,NC
      CTOP(I) = TOT(I)/(1.0 + (THETA*RATIO(I)))
      SIGMAD = SIGMAD + CTOP(I)
      CBOT(I) = RATIO(I)*CTOP(I)*THETA
```

```
   68 SIGMAB = SIGMAB + CBOT(I)
      TVAP(1) = SIGMAD
C
C                          CALCULATE LIQUID MOLE FRACTIONS
C
      DO   70              J=1,NR
      SUMLIJ= 0.0
      DO   69              I=1,NC
   69 SUMLIJ= SUMLIJ + RL(I,J)*CBOT(I)
      CALL  TEST(SUMLIJ,TLMAX,TLMIN)
      SPARE1 = ZZ
      DO   70              I=1,NC
   70 X(I,J) = RL(I,J)*CBOT(I)/SPARE1
C
C                CALCULATE NEW TEMPERATURE DISTRIBUTION IN COLUMN
C
      IF (ITER - ITEMP)   72,   72,   71
   71 FRACT = PART
   72 DO   79              J=1,NR
      TT= T(J)
      DO   73              I=1,NC
   73 XX(I)= X(I,J)
   75 CALL  BUBLPT(   XX)
   76 CALL  TEST(TT,TMAX,TMIN)
      TCALC = ZZ
      IF(T(J)-TCALC)   78,   77,   77
   77 T(J) = T(J) - FRACT*ABS(T(J)-TCALC)
      GO TO   79
   78 T(J) = T(J) + FRACT*ABS(T(J)-TCALC)
   79 CONTINUE
C
C                         CALCULATE HEAT BALANCES AND FLOW RATES
C
      IF(ITER-KHEAT)   82,   300,   300
  300 DO   301             I=1,NC
  301 XX(I) = CTOP(I)
      CALL  CRITIC(  XX)
      CALL  ENTHAL(2, T(1) ,XX)
      HDIST = HTCON
      HD = HTCON*SIGMAD
      DO   302             I=1,NC
  302 XX(I) = CBOT(I)
      CALL  CRITIC(  XX)
      CALL  ENTHAL(3, T(NR) ,XX)
      HBOT = HTCON
      HB = HTCON*SIGMAB
      SUMQ = 0.0
      DO   314             J=1,N5
      IF (J .GT. 1)        SUMQ = SUMQ + Q(J-1)
      DO   303             I=1,NC
```

```
 303 XX(I) = X(I,J)
     CALL  CRITIC(  XX)
     CALL  ENTHAL(3, T(J) ,XX)
     HJ = HTCON
     SUMVIJ = 0.0
     DO   304         I=1,NC
 304 SUMVIJ = SUMVIJ + RV(I,J+1)*CTOP(I)
     CALL  TEST(SUMVIJ,TVMAX,TVMIN)
     SUMVIJ = ZZ
     DO   305         I=1,NC
 305 XX(I) = RV(I,J+1)*CTOP(I)/SUMVIJ
     CALL  CRITIC(  XX)
     CALL  ENTHAL(2, T(J+1) ,XX)
     HHJP1 = HTCON
     IF (J-N1)   306,   306,   308
 306 F1 = 0.0
     FL2 = 0.0
     FV2 = 0.0
     GO TO   313
 307 F1 = SUM3
     FL2 = 0.0
     FV2 = 0.0
     GO TO   313
 308 IF (J - N3)   307,   309,   310
 309 F1 = SUM3
     FL2 = 0.0
     FV2 = SUM6
     GO TO   313
 310 F1 = SUM3
     FL2 = SUM5
     FV2 = SUM6
 313 PREVS = TLIQ(J)
     TLIQ(J) = (SUM1*(HABS-HHJP1) + F1*(HFDLIQ-HHJP1) + FL2*HFDGL +
    1           FV2*HFDGV - (FL2+FV2)*HHJP1 + SIGMAD*(HHJP1-HDIST)+
    2           SUMQ)/(HJ-HHJP1)
     XI = ITER
     P = 1.0 + (1.0/EXP(XI/CONST))
     SMALL = PREVS/P
     BIG = PREVS*P
     CALL  TEST( TLIQ(J), TLMAX, TLMIN)
     TLIQ(J) = ZZ
     IF (TLIQ(J) .LT. SMALL)     GO TO 1002
     IF (TLIQ(J) .GT. BIG)       GO TO 1003
     GUESS = TLIQ(J)
     IF (TLIQ(J) .GE. TLMAX)     GO TO 1004
     IF (TLIQ(J) .LE. TLMIN)     GO TO 1004
     Q(J) = 0.0
1001 TVAP(J+1) = GUESS + SIGMAD - SUM1 - F1 - FL2 - FV2
     GO TO 314
1002 TLIQ(J) = SMALL
```

```
      GUESS = SMALL
      GO TO 1004
 1003 TLIQ(J) = BIG
      GUESS = BIG
 1004 Q(J) = GUESS*(HJ-HHJP1) - SUM1*(HABS-HHJP1) - F1*(HFDLIQ-HHJP1) -
     1       FL2*HFDGL - FV2*HFDGV + (FL2+FV2)*HHJP1 - SIGMAD*(HHJP1-
     2       HDIST) - SUMQ
      GO TO 1001
  314 CONTINUE
  312 TLIQ(NR) = SIGMAB
      SUMQ = SUMQ + Q(N5)
      Q(NR) = HD + HB - HEATIN - SUMQ
      REBOIL = TVAP(NR)/SIGMAB
      IF (KTHETA) 9999,  316,  315
  316 WRITE(6,979)  ITER,HEATIN,HDIST,HBOT,Q(NR)
C
C              PRINTOUT THIS ITERATION OR NOT................
C                         INTERMEDIATE AND FINAL OUTPUT
C
  315 IF (ABS(THETA-1.00) - TOL3)   81,   81,   82
   81 JACC = 1
      GO TO 83
   82 IF (KLM)   83,   83,   88
   83 WRITE(6,999)
      KLM = KPRNT
      WRITE(6,975)
      DO   84            J=1,NR
   84 WRITE(6,979)  J,TLIQ(J),TVAP(J),T(J),Q(J)
      WRITE(6,967)  SUMTOP,REBOIL,PART,TOL3
      WRITE(6,962)  HFO,HF1,HF2,HEATIN,HD,HB,Q(NR),SUMQ
      WRITE(6,998)
      WRITE(6,973)
      DO   85            I=1,NC
   85 WRITE(6,972)  I,TOP(I),CTOP(I),RATIO(I),BOT(I),CBOT(I)
      WRITE(6,999)
C
      IF (ITER .LT. ITHETA)   JACC = 0
      IF (JACC)   88,   88,   86
   86 WRITE(6,971)
      WRITE(6,959)  (I,  I = 1,NC)
      DO   87            J = 1,NR
   87 WRITE(6,970)  J,(X(I,J),  I = 1,NC)
      WRITE(6,999)
      WRITE(6,961)  (I,  I = 1,NC)
      DO   90            J = 1,NR
      DO   91            I = 1,NC
   91 X(I,J) = X(I,J)*EQULK(A(I),B(I),C(I),D(I),T(J))
   90 WRITE(6,970)  J,(X(I,J),  I = 1,NC)
      WRITE(6,969)
      GO TO   5000
```

```
   88 KLM = KLM - 1
      WRITE(6,960)  ITER,THMAX,THETA,THMIN,REBOIL ,PSIR(3),P,T(N5),
     1              SIGMAB,T(N4),T(N2),T(1),SIGMAD
      ITER = ITER + 1
 4000 CONTINUE
 5000 NCALC = NCALC + 1
C
C              LAST PROBLEM THIS RUN OR NOT..................
C
      IF (NPROB-NCALC)   9999,   1000,   1000
 9999 STOP
C
C
  999 FORMAT(1H1)
  998 FORMAT(///)
  997 FORMAT(44X,45HSTEADY-STATE MODEL OF A DEMETHANIZER-ABSORBER//26X,
     1       80HINCLUDES HEAT BALANCES AT EACH TRAY AND UTILIZES THE THE
     2TA METHOD OF CONVERGENCE)
  996 FORMAT(112X,14HW.F.PETRYSCHUK)
  995 FORMAT(1X,56HTWO INDEPENDENT FEEDS PLUS AN ABSORPTION STREAM ENTER
     1ING,55X,19HDEPT. OF CHEM. ENG.)
  994 FORMAT(2X,54HBOTTOMS PRODUCT TAPPED BEFORE RECYCLE THROUGH REBOILE
     1R,56X,19HMCMASTER UNIVERSITY)
  993 FORMAT(13X,32HNO OVERHEAD CONDENSER OR RECYCLE,74X,4H1964)
  992 FORMAT(9(3X,I5))
  991 FORMAT(10X,14HPROBLEM NUMBER,I4,84X,10HINPUT DATA)
  990 FORMAT(2X,6E13.4)
  989 FORMAT(1X,9HNUMBER OF,6X,11HLIQUID FEED,6X,8HGAS FEED,6X,11HTOTAL
     1IDEAL,6X,7HMAXIMUM,6X,18HITERATIONS BETWEEN,6X,8H MFEED   ,6X,5HITE
     2MP,6X,6HITHETA)
  988 FORMAT(1X,10HCOMPONENTS,7X,7HON TRAY,9X,7HON TRAY,9X,6HSTAGES,7X,1
     10HITERATIONS,9X,9HPRINTOUTS/)
  987 FORMAT(3X,I5,4(10X,I5),2(14X,I5),2(7X,I5))
  986 FORMAT(50X,32HMAXIMUM AND MINIMUM RESTRICTIONS)
  985 FORMAT(3X,9E13.4)
  984 FORMAT(4E13.6)
  983 FORMAT(1X,12HCOEFFICIENTS,23X,6HK=F(T),65X,7HCP=F(T)/16X,1HA,14X,
     1       1HB,14X,1HC,14X,1HD,33X,2HAE,13X,2HBE,13X,2HCE)
  982 FORMAT(24X,I5,4E20.6)
  981 FORMAT(1X,E19.8)
  980 FORMAT(23X,9HCOMPONENT,5X,17HABSORPTION STREAM,6X,11HLIQUID FEED,
     111X,8HGAS FEED,14X,5HTOTAL)
  979 FORMAT(24X,I5,4F20.1)
  978 FORMAT(34X,5HTOL1=,E10.3,10X,5HTOL2=,E10.3,10X,5HTOL3=,E10.3)
  977 FORMAT(52X,29HMOLES OF COMPONENT I IN FEEDS//35X,2HL1,8X,2HV1,8X,
     12HL2,8X,2HV2,8X,2HL3,8X,2HV3,7X,5HTOTAL/)
  976 FORMAT(24X,I5,7F10.3)
  975 FORMAT(24X,4HTRAY,9X,14HLIQUID LEAVING,6X,14HVAPOUR LEAVING,9X,
     111HTEMPERATURE,9X,11HINTERCOOLER/102X,4HDUTY)
  974 FORMAT(31X,I5,3F20.3)
```

```
  973 FORMAT(30X,1HI,8X,3HTOP,11X,4HCTOP,10X,5HRATIO,12X,3HBOT,11X4HCBOT
     1/)
  972 FORMAT(26X,I5,5E15.5)
  971 FORMAT(  /60X,12HTOWER  TRACE//  29X,18HROW REFERS TO TRAY,
     1           30X,26HCOLUMN REFERS TO COMPONENT/)
  970 FORMAT(3X,I5,10F12.5)
  969 FORMAT(54X,27HAN ANSWER HAS BEEN ATTAINED/49X,37HTHETA CONVERGENCE
     1 HAS BEEN SUCCESSFUL//)
  967 FORMAT(/16X,2HD=,F9.3,16X,7HREBOIL=,F6.3,16X,5HPART=,F6.3,16X,
     1        5HTOL3=,F11.8/)
  966 FORMAT(/27X,78HLIQUID FLOWS CALCULATED BY ENTHALPY BALANCES VAPOUR
     1 FLOWS BY MATERIAL BALANCES)
  965 FORMAT(/12X,7HKTHETA=,I3,12X,6HKHEAT=,I3,12X,8HFO TEMP=,F6.1,12X,
     1        8HF1 TEMP=,F6.1,12X,8HF2 TEMP=,F6.1)
  964 FORMAT(2X,I5,4E15.5,20X,3E15.5)
  963 FORMAT(42X,6HMOL WT,13X,8HP CRITIC,12X,8HT CRITIC,12X,8HZ CRITIC)
  962 FORMAT(15X,3HHFO,13X,3HHF1,13X,3HHF2,10X,6HHEATIN,14X,2HHD,14X,
     1        2HHB,5X,11HREBOIL DUTY/2X,7F16.1/32X,34HSUM OF ALL J=1 TO N
     25 INTERCOOLERS=,F16.1)
  961 FORMAT(  5X,21HVAPOUR MOLE FRACTIONS/11X,I3,9(9X,I3))
  960 FORMAT(3X,I5,6F10.5,6F10.3)
  959 FORMAT(  5X,21HLIQUID MOLE FRACTIONS/11X,I3,9(9X,I3))
C
      END
```

```
...................DATA INPUT TO THE STEADY STATE PROGRAMME....................

+++++++++++++++++++++++++++++ VARIABLE PARAMETERS +++++++++++++++++++++++++++++
    1
   10         7         6         6      125       124
 48.00          -5.0            0.0               0.0
    2         2         2         1        3        20         10
  0.0010          0.000001      0.00150           32.3              1.0
  0.20            0.200         15.0              1.60              1.500     2.00
  0.1     E10     0.1  E-10     0.1      E10      0.1     E-10      0.1     E10     0.1      E-10
   0.1    E10    0.1   E-10       700.0           10.0              700.00          10.0
  240.0           -40.0          0.1      E10     0.1     E-10       7.00            0.20

................................................................................

+++++++++++++++++++++++++++++++ CRITICAL DATA +++++++++++++++++++++++++++++++++
 16.00          45.80          343.7           0.290              METHANE              1
 28.00          51.0           510.0           0.270              ETHYLENE             2
 30.1           48.2           550.1           0.285              ETHANE               3
 42.1           45.4           656.5           0.279              PROPYLENE            4
 44.1           42.0           666.3           0.277              PROPANE              5
 56.1           39.5           752.5           0.277              BUTENE-1, IC4-       7
 58.10          37.40          766.0           0.274              BUTANE               8
 56.1           37.0           773.0           0.275              BUTENE-2      ***    9
 72.1           32.6           846.5           0.269              PENTANE              11
 100.2          26.8           972.5           0.260              HEPTANE              13

................................................................................

++++++++++++++++ COEFFICIENTS OF EQUILIBRIUM RATIO REGRESSION +++++++++++++++++
  .40112E 1      .22325E-1     -.48979E-4      .70899E-7         METHANE              1
  .88377E00      .72166E-2      .28217E-4      .14034E-7         ETHYLENE             2
  .56412E00      .68113E-2      .45843E-5      .31325E-7         ETHANE               3
  .18231E00      .26766E-2      .14937E-4     -.14939E-7         PROPYLENE            4
  .15712E00      .20996E-2      .15374E-4     -.10029E-7         PROPANE              5
  .51048E-1      .10488E-2      .55619E-5      .11980E-7         BUTENE-1, IC4-       7
  .41062E-1      .82358E-3      .64406E-5      .72920E-8         BUTANE               8
  .36037E-1      .50236E-3      .11830E-4     -.12915E-7         BUTENE-2             9
  .11103E-1      .27875E-3      .27425E-5      .10569E-7         PENTANE              11
  .10751E-2      .38833E-4      .58433E-7      .66929E-8         HEPTANE              13

................................................................................

++++++++++++++++++ COEFFICIENTS OF SPECIFIC HEAT REGRESSION ++++++++++++++++++
  8.22803        0.32005E-02  0.10119E-04                        METHANE              1
  9.38125        0.12295E-01  0.61924E-05                        ETHYLENE             2
 11.45850        0.13965E-01  0.91570E-05                        ETHANE               3
 13.77065        0.18575E-01  0.91157E-05                        PROPYLENE            4
 15.64702        0.24190E-01  0.10007E-04                        PROPANE              5
 18.92936        0.30839E-01  -.58362E-05                        BUTENE-1,IC4-        7
 21.16456        0.28756E-01  0.14171E-04                        BUTANE               8
 18.03599        0.30787E-01  0.77777E-06                        BUTENE-2  ***        9
 25.22668        0.45541E-01  -.75878E-05                        PENTANE              11
 35.11518        0.59477E-01  -.19890E-05                        HEPTANE              13
```

```
++++++++++++++++++++++++++++++++++ TEMPERATURE ++++++++++++++++++++++++++
    5.0
    10.0
    15.0
    20.0
    25.0
    30.0
    40.0
    50.0
    60.0
    70.0
    80.0
    90.0
    100.0
    120.0
    140.0
    160.0
    180.0
    200.0
    220.0
    240.0
+++++++++++++++++++++++++++++ ABSORPTION STREAM L0 ++++++++++++++++++++++
    0.0
    0.0
    0.0
    0.0
    27.9
    276.2
    1132.7
    625.0
    600.0
    117.0
++++++++++++++++++++++++++++++++ LIQUID FEED F1 +++++++++++++++++++++++++
    25.4
    32.3
    57.2
    447.3
    484.0
    289.3
    2086.4
    780.1
    500.0
    241.0
++++++++++++++++++++++++++++++++++ GAS FEED F2 ++++++++++++++++++++++++++
    580.0
    560.0
    600.0
    1000.0
    280.0
    600.0
    300.0
    500.0
    500.0
    200.0
```

Appendix V.2. Transient Behaviour Program

The general functional relationship for liquid mole fractions varying with time is

$$x'_{i,j} = f_8(x_{i,j},T_j,V_j,L_j,y_{i,j})\Big|_p \tag{74}$$

which describes the dynamic behaviour of the component concentrations on tray j. Because of the equilibrium relationship (1) this differential equation is non-linear in nature. The problem is to solve

$$x_{i,j}\Big|_{t+\Delta t} - x_{i,j}\Big|_t = \int_t^{t+\Delta t} f_8(x_{i,j},T_j,V_j,L_j,y_{i,j})_p.dt \tag{75}$$

where i = 1, 2....NC and j = 1, 2.....NR.

The differential equation describing the change in heat content on tray j is given in functional form by

$$h'_j = (f_9(x_{i,j},T_j,V_j,L_j,y_{i,j})\Big|_p \tag{76}$$

$$\text{or} \quad h_j\Big|_{t+\Delta t} - h_j\Big|_t = \int_t^{t+\Delta t} f_9(x_{i,j},T_j,V_j,L_j,y_{i,j})dt \tag{77}$$

Integral equations (75) are solved over the time increment Δt and since h_j can be calculated via an analytic function (9), (76) was rearranged to yield the new value of L_j (see equations (54)).

The differential equations are solved in a sequential tray-to-tray manner for fixed time intervals. The program is written in such a manner that short computer runs are possible. The output of the column profiles is in printed and punched card form. These cards form the input for the next go at the computer. It is only at these interruptions that the step length can be altered.

The 3rd order Runge-Kutta (R-K) technique was utilized to solve the 110 differential equations comprising the 10 component-10 tray model. For a derivation of the R-K equations, the reader is directed to the following references (16), (35), (40). The author is concerned here with the application of this method to the integration of the family or set of non-linear differential equations comprising the aforementioned model.

For a given tray j

$$k_{i,1} = \Delta t.f_8(x_{i,j}, T_j)_p \tag{78}$$

$$k_{i,2} = \Delta t.f_8\left(x_{i,j} + \frac{k_{i,1}}{2}, \bar{T}_j\right)_p \tag{79}$$

$$k_{i,3} = \Delta t.f_8(x_{i,j} + 2.k_{i,2} - k_{i,1}, \bar{\bar{T}}_j)_p \tag{80}$$

and

$$x_{i,j}\Big|_{t+\Delta t} = x_{i,j}\Big|_{t} + \frac{1}{6}.(k_{i,1} + 4.k_{i,2} + k_{i,3}) \tag{81}$$

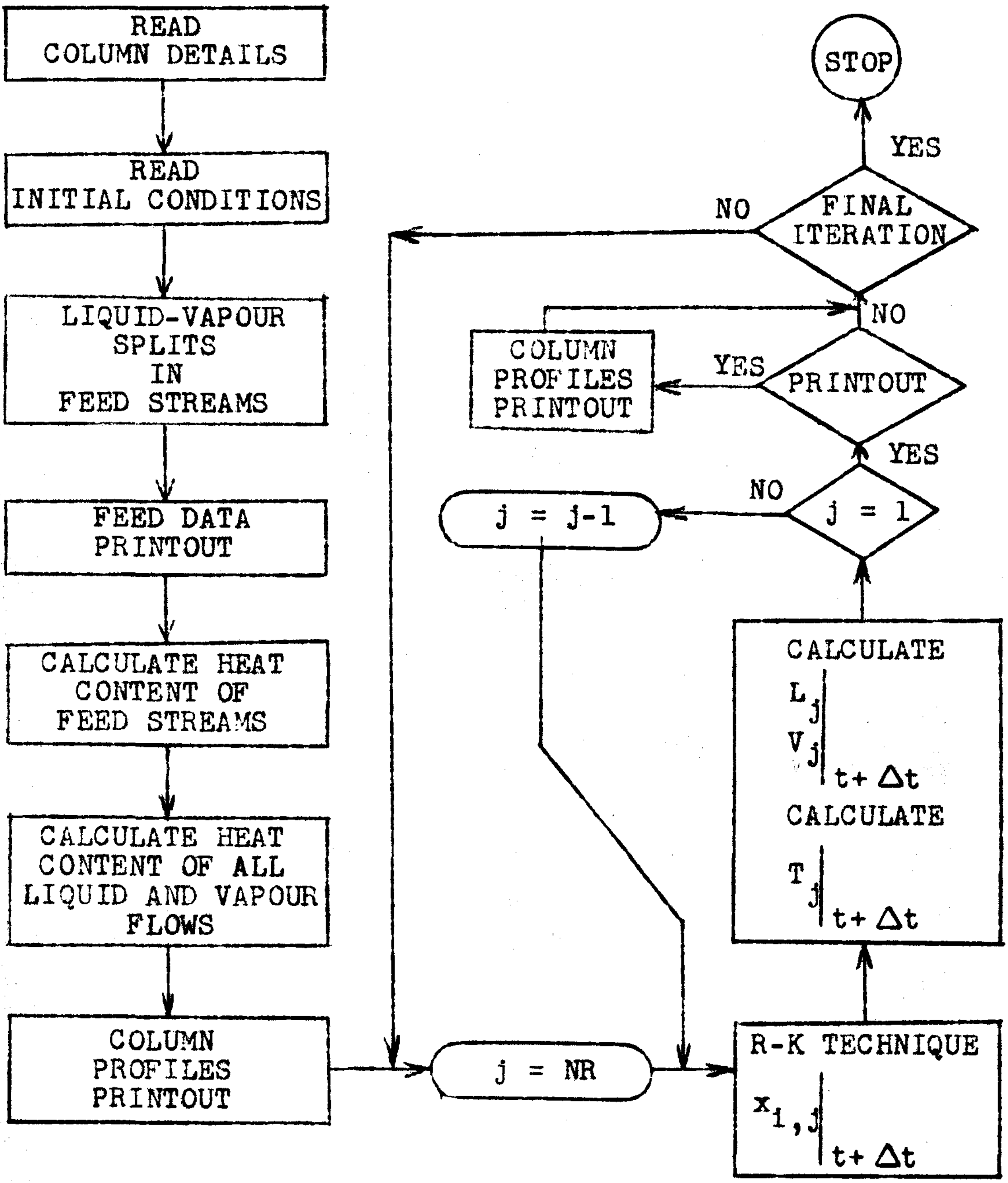
$i = 1,2,.....NC$

where $\overline{T}_j$ is the new temperature at r calculated using the (r-1)th estimate of $x_{i,j}$ i.e. the temperature is corrected for the variation in $x_{i,j}$ from $k_{i,1}$ to $k_{i,2}$ to $k_{i,3}$. If the temperature is assumed constant over the time interval, excessive errors are introduced to the mole fraction estimates and instability occurs. These equations, (78) to (81) inclusive, are solved for each tray beginning at the reboiler and proceeding to tray 1 before the time is incremented to $t + 2.\Delta t$.

Before proceeding to calculate the new component compositions on tray $j - 1$, the new molar enthalpy of the liquid on tray j is calculated from equation (9). The new liquid flow rate, $L_j\Big|_{t+\Delta t}$ and vapour flow rate, $V_j\Big|_{t+\Delta t}$ are then calculated from equations (54) and (55) respectively.

This appendix contains the flow diagram of the calculation sequence outlined in section 6.4. The Fortran listing and sample data input are also included. The terms used in the listing are explained in the comment statements preceding the formal program.

FLOW DIAGRAM: TRANSIENT BEHAVIOUR PROGRAM



```
C   MODEL OF THE DYNAMIC BEHAVIOUR OF THE DEMETHANIZER-ABSORBER (E-100)
C                                MODDAB
C
C   PARTIAL REBOILER                             10 COMPONENTS-30 TRAYS MAXIMUM
C   CONSTANT LIQUID HOLDUP                          NEGLIGIBLE VAPOUR HOLDUP
C
C   RUNGE-KUTTA 3RD ORDER INTEGRATION TECHNIQUE UTILIZED
C
C   WHERE POSSIBLE ,THE TERMS USED IN THE STEADY STATE PROGRAMME HAVE
C   BEEN RETAINED IN MODDAB
C
C   TEMP1,TEMP2,TEMP3......TEMPERATURES OF THE 3 FEEDS LO, F1, F2
C   NHEAT(1),NHEAT(2),NHEAT(3)......THERMAL CONDITION OF THE 3 FEEDS
C                                   IF  2  SUBCOOLED LIQUID
C                                       1  SATURATED LIQUID
C                                       1  SATURATED VAPOUR
C                                       0  SUPERHEATED VAPOUR
C   TOL1.......DAMPING FACTOR USED IN SUCCESSIVE ESTIMATES OF FLOW RATES
C   TOL2.......TOLERANCE IN BUBBLE AND DEW POINT SUBROUTINES
C   TOL3.......FINAL DELSUM,THE DURATION OF CALCULATION (U.T.)
C   DELSUM.....REAL TIME (U.T.)
C   DELTA......STEP LENGTH, TIME INCREMENT
C   QNR........REBOILER HEAT LOAD, (B.T.U./U.T.)
C   U(J).......TRAY HOLDUP, (MOLES)
C   HF0........TOTAL HEAT CONTENT OF FEED  L0
C   HF1........TOTAL HEAT CONTENT OF FEED  F1
C   HF2........TOTAL HEAT CONTENT OF FEED  F2
C   FDHEAT(F)......MOLAR HEAT CONTENTS OF FEEDS
C   FDSTRM(I,F).....FEED COMPOSITIONS
C   F(I,NK)....RUNGE-KUTTA PARAMETERS
C   EXTRA(I)...VECTOR CONTAINING FEED COMPOSITIONS IF AT FEED TRAY,
C              OTHERWISE CONTAINS ZEROES
C   QHEAT......CONTAINS EXTERNAL SOURCE HEAT
C   EQULK......EQUILIBRIUM RATIO FUNCTION
C
      DIMENSION  A(10),B(10),C(10),D(10),AE(10),BE(10),CE(10),WM(10),
     1           PC(10),TC(10),ZC(10),U(32),XL(32),YV(32),T(32),X(10,32)
     2           ,FEED(10,3),SUMFD(3),TF(3),TOT(10),TOP(10),BOT(10),
     3           SUM(6),FDSTRM(10,6),XX(10),FDHEAT(6),HL(32),HV(32),
     4           EXTRA(10),AA(10),BB(10),F(10,3),HJ(3),NHEAT(3),PSIR(3)
      COMMON  A,B,C,D,AE,BE,CE,PC,TC,ZC,TT,PSI,TOL1,ZZ,HTCON,PRESS,
     1        TCMIX,PCMIX,ZCMIX ,NC
      EQULK(A,B,C,D,T) = A + (B*T) + (C*T**2) + (D*T**3)
C
C                           HEADING PAGE OF REPORT
C
      WRITE(6,973)
      WRITE(6,998)
      WRITE(6,999)
C
C                                DATA INPUT
C
      READ (5,992)  NC,NT1,NT2,NT3,JPRNT
      N1 = NT1 - 1
      N2 = NT1
```

```
      READ (5,990)  DELTA, QNR, XLMIN ,VMIN, TMIN
      N3 = NT2 + N1
      N4 = NT2 + N2
      READ (5,990)  RELAX,TOL1,TOL2,TOL3,PRESS
      N5 = NT3 + N4
      READ (5,990)  TEMP1,TEMP2,TEMP3
      NR = N5 + 1
      WRITE(6,997)  NC,N2,N4,NR
      READ (5,992)  NHEAT(1),NHEAT(2),NHEAT(3)
C
C                           INITIAL CONDITIONS
C
      READ (5,991)  (WM(I),PC(I),TC(I),ZC(I) ,    I = 1,NC)
      READ (5,991)  (A(I),B(I),C(I),D(I),     I = 1,NC)
      DO   100     I = 1,NC
  100 READ (5,991)  AE(I),BE(I),CE(I)
      WRITE(6,996)
      DO   101     I = 1,NC
  101 WRITE(6,995)  I,A(I),B(I),C(I),D(I),AE(I),BE(I),CE(I)
      WRITE(6,994)
      DO   102     I = 1,NC
  102 WRITE(6,993)  I,WM(I),PC(I),TC(I),ZC(I)
      READ (5,975)  ((X(I,J+1) , I=1,NC) , J=1,NR)
      READ (5,974)  (U(J+1),XL(J+1),YV(J+1),T(J+1) , J=1,NR)
      JJPRNT = JPRNT
      TOTAL = 0.0
      DELSUM = 0.0
      SUMFD(1) = 0.0
      SUMFD(2) = 0.0
      SUMFD(3) = 0.0
      DO   104     I = 1,NC
      TOT(I) = 0.0
      READ (5,990)  FEED(I,1),FEED(I,2),FEED(I,3)
      SUMFD(1) = SUMFD(1) + FEED(I,1)
      SUMFD(2) = SUMFD(2) + FEED(I,2)
      SUMFD(3) = SUMFD(3) + FEED(I,3)
      TOT(I) = FEED(I,1) + FEED(I,2) + FEED(I,3)
  104 TOTAL = TOTAL + TOT(I)
C
C                         L - V  SPLIT IN FEEDS
C
      N1 = N1 + 1
      N2 = N2 + 1
      N3 = N3 + 1
      N4 = N4 + 1
      N5 = N5 + 1
      NFINAL = NR + 1
      TF(1) = TEMP1
      TF(2) = TEMP2
      TF(3) = TEMP3
      DO   199     K = 1,6
      SUM(K) = 0.0
```

```
      DO   199     I = 1,NC
  199 FDSTRM(I,K) = 0.0
      DO   211     K = 1,3
      L2 = 2*K
      L1 = L2 - 1
      DO   200     I = 1,NC
  200 XX(I) = FEED(I,K)/SUMFD(K)
      TT = TF(K)
      CALL  BUBLPT(XX)
      TBP = TT
      IF (TBP - TF(K))  201,  207,  207
  201 TT = TF(K)
      CALL  DEWPT(XX)
      TDP = TT
      IF (TF(K) - TDP)  202,  209,  209
  202 TT = TF(K)
      CALL  FLASH(XX)
      PSIR(K) = PSI
      DO   203     I = 1,NC
      PSIV = 1.0 - PSIR(K)
      FDSTRM(I,L2) = FEED(I,K)*PSIV/(PSIV + (PSIR(K)/EQULK(A(I),B(I),
     1               C(I),D(I),TF(K))))
      FDSTRM(I,L1) = FEED(I,K) - FDSTRM(I,L2)
      SUM(L1) = SUM(L1) + FDSTRM(I,L1)
  203 SUM(L2) = SUM(L2) + FDSTRM(I,L2)
      GO TO  211
C
C                           ALL LIQUID
C
  207 PSIR(K) = 1.0
      DO   208     I = 1,NC
  208 FDSTRM(I,L1) = FEED(I,K)
      SUM(L1) = SUMFD(K)
      GO TO 211
C
C                              ALL VAPOUR
C
  209 PSIR(K) = 0.0
      DO   210     I = 1,NC
  210 FDSTRM(I,L2) = FEED(I,K)
      SUM(L2) = SUMFD(K)
  211 CONTINUE
C
C                         FEED DATA OUTPUT REPORT
C
  106 WRITE(6,989)
      DO   105     I = 1,NC
  105 WRITE(6,988)  I,FDSTRM(I,1),FDSTRM(I,2),FDSTRM(I,3),FDSTRM(I,4),
     1                FDSTRM(I,5),FDSTRM(I,6),TOT(I)
      I = 0
      WRITE(6,988)  I,SUM(1),SUM(2),SUM(3),SUM(4),SUM(5),SUM(6),TOTAL
      WRITE(6,999)
C
C                        HEAT CONTENT OF FEED STREAMS
C
```

```
  107 DO   312      K = 1,3
      L2 = 2*K
      L1 = L2 - 1
      IF (SUM(L1) - 0.0000001)  305,  305,  300
  300 DO   301      I = 1,NC
  301 XX(I) = FDSTRM(I,L1)/SUM(L1)
      M = 0
      IF (NHEAT(K) - 1)  9999,  302,  303
  302 KEQUAT = 3
      GO TO  304
  303 KEQUAT = 4
  304 CALL  CRITIC(XX)
      CALL  ENTHAL(KEQUAT,TF(K),XX)
      FDHEAT(L1) = HTCON
      IF (M)  313,  313,  312
  305 FDHEAT(L1) = 0.0
  313 IF (SUM(L2) - 0.0000001)  311,  311,  306
  306 DO   307      I = 1,NC
  307 XX(I) = FDSTRM(I,L2)/SUM(L2)
      M = 1
      IF (NHEAT(K) - 1)  308,  309,  9999
  308 KEQUAT = 1
      GO TO   310
  309 KEQUAT = 2
  310 L1 = L2
      GO TO  304
  311 FDHEAT(L2) = 0.0
  312 CONTINUE
      HEATIN = FDHEAT(1) + FDHEAT(2) + FDHEAT(3) + FDHEAT(4) + FDHEAT(5)
     1                   + FDHEAT(6)
      XL(1) = SUM(1)
      HL(1) = FDHEAT(1)
C
C                         TOTAL FEED HEAT CONTENTS
C
      HF0 = FDHEAT(1)*SUM(1) + FDHEAT(2)*SUM(2)
      HF1 = FDHEAT(3)*SUM(3) + FDHEAT(4)*SUM(4)
      HF2 = FDHEAT(5)*SUM(5) + FDHEAT(6)*SUM(6)
C
C
C                         CALCULATE HEAT CONTENT OF ALL STREAMS
C
  319 DO   322      J = 2,NFINAL
      DO   320      I = 1,NC
  320 XX(I) = X(I,J)
      CALL  CRITIC(XX)
      CALL  ENTHAL(3,T(J),XX)
      HL(J) = HTCON
      SIGMA = 0.0
      DO   321      I = 1,NC
      XX(I) = X(I,J)* EQULK(A(I),B(I),C(I),D(I),T(J))
  321 SIGMA = SIGMA + XX(I)
      DO   213      I=1,NC
  213 XX(I) = XX(I)/SIGMA
      CALL  CRITIC(XX)
```

```
      CALL  ENTHAL(2,T(J),XX)
      HV(J) = HTCON
  322 CONTINUE
C
C
      WRITE(6,979)
      DO   212     J = 2,NFINAL
      JS = J - 1
      WRITE(6,978)  X(1,J),X(2,J),X(3,J),X(4,J),X(5,J),X(6,J),X(7,J),
     1              X(8,J),X(9,J),X(10,J)
  212 WRITE(6,981)  JS,XL(J),YV(J),T(J),HL(J),HV(J)
      WRITE(6,976)  (FDHEAT(LR),  LR = 1,6)
      WRITE(6,999)
C
      DO   4999    I = 1,NC
 4999 X(I,1) = FEED(I,1)/SUMFD(1)
C
C                           START OF 3RD ORDER  R-K TECHNIQUE
C
      YV(NFINAL+1) = 0.0
 5000 DO   1000    JJ=2,NFINAL
      J = NFINAL - JJ + 2
      R = DELTA/U(J)
      DO   1       I=1,NC
      AA(I) = XL(J-1)*X(I,J-1)
      EXTRA(I) = 0.0
    1 BB(I) = YV(J+1)*X(I,J+1)*EQULK(A(I),B(I),C(I),D(I),T(J+1))
      EE = XL(J-1)*(HL(J-1)-HV(J))
      FF = YV(J+1)*(HV(J+1)-HV(J))
      FINPUT = 0.0
      GG = HL(J)-HV(J)
      IF(J-NFINAL)  3,  2,  2
C
C                                J = REBOILER
C
    2 QHEAT = QNR
      GO  TO  13
    3 IF  (J-N4)  7,  5,  4
C
C                             N4+1. LT .J. LE .N5
    4 QHEAT = 0.0
      GO  TO  13
C
C                                   J = N4
    5 DO   6       I=1,NC
    6 EXTRA(I) = FDSTRM(I,5) + FDSTRM(I,6)
      FINPUT = SUM(5) + SUM(6)
      QHEAT = HF2
      GO  TO  13
    7 IF  (J-N2)  12,  10,  8
C
C                            N2+1. LT .J. LE .N3
    8 DO   9       I=1,NC
    9 EXTRA(I) = 0.0
      FINPUT = 0.0
```

```
      GO  TO  4
   10 DO   11       I=1,NC
   11 EXTRA(I) = FDSTRM(I,3) + FDSTRM(I,4)
      FINPUT = SUM(3) + SUM(4)
      QHEAT = HF1
      GO  TO  13
C
C                          1. LE .J. LE .N1
C
   12 IF(J-2)  1000,  8,  8
C
   13 NK = 1
   20 GO TO  (21, 22, 23,  24), NK
   21 DO   25       I = 1,NC
   25 XX(I) = X(I,J)
      GO TO  28
   22 DO   26       I = 1,NC
   26 XX(I) = X(I,J) + (0.5*F(I,1))
      GO TO  28
   23 DO   27       I = 1,NC
   27 XX(I) = X(I,J) + (2.0*F(I,2)) - F(I,1)
   28 CALL  BUBLPT(XX)
      TEMP = TT
      DO   29       I = 1,NC
   29 F(I,NK) = R*(AA(I) + BB(I) - XL(J)*XX(I) - YV(J)*XX(I)*EQULK(A(I),
     1              B(I),C(I),D(I),TEMP) + EXTRA(I))
      T(J) = TEMP
      NK = NK + 1
      GO TO  20
   24 DO  425       I = 1,NC
      X(I,J) = X(I,J) + ((F(I,1) + 4.0*F(I,2) + F(I,3))/6.0)
  425 XX(I) = X(I,J)
      CALL  BUBLPT(XX)
      T(J) = TT
      IF (T(J) - TMIN)  3019, 3020, 3020
 3019 T(J) = TMIN
 3020 CALL  CRITIC(XX)
      CALL  ENTHAL (3,T(J),XX)
      DELH = HTCON - HL(J)
      SLOPE = DELH/DELTA
      CHANGE = U(J)*SLOPE
C
C                       FLOW RATE CALCULATION
C
      XLNEW = (EE + FF + QHEAT - FINPUT*HV(J) - CHANGE)/GG
      DIFFER = XL(J) - XLNEW
      IF (ABS(DIFFER) - TOL3)  3012,3012,3013
 3012 XL(J) = XLNEW
      GO  TO  3014
 3013 XL(J) = XL(J) - (RELAX*DIFFER)
 3014 IF (XL(J) - XLMIN)  3015,3016,3016
 3015 XL(J) = XLMIN
```

```
 3016 YV(J) = YV(J+1) + XL(J-1) - XL(J) + FINPUT
      IF (YV(J) - VMIN)  3017, 3018, 3018
 3017 YV(J) = VMIN
 3018 HL(J) = HTCON
      SUMXIJ = 0.0
      DO   450      I = 1,NC
      XX(I) = X(I,J)*EQULK(A(I),B(I),C(I),D(I),T(J))
  450 SUMXIJ = SUMXIJ + XX(I)
      DO   451      I = 1,NC
  451 XX(I) = XX(I)/SUMXIJ
      CALL  CRITIC(XX)
      CALL  ENTHAL(2,T(J),XX)
      HV(J) = HTCON
      SUMXIJ = 0.0
      DO   1002     I = 1,NC
 1002 SUMXIJ = SUMXIJ + X(I,J)
      DO   1003     I = 1,NC
 1003 X(I,J) = X(I,J)/SUMXIJ
      JS = J - 1
 1000 CONTINUE
 3000 DELSUM = DELSUM + DELTA
C
C                             PRINTOUT...........
C
      IF (JJPRNT - JPRNT)  9998,  400,  400
  400 WRITE(6,999)
      WRITE(6,983)  DELSUM
      JJPRNT = 0
      WRITE(6,987)
      DO  428       M = 1,NFINAL
      J = M - 1
  428 WRITE(6,986)  J,X(1,M),X(2,M),X(3,M),X(4,M),X(5,M),X(6,M),X(7,M),
     1                X(8,M),X(9,M),X(10,M),T(M),XL(M),YV(M),HL(M),HV(M)
      WRITE(6,985)
      TOTOP = 0.0
      TOBOT = 0.0
      DO  429       I = 1,NC
      BOT(I) = X(I,NFINAL)*XL(NFINAL)
      TOBOT = TOBOT + BOT(I)
      TOP(I) = X(I,2)*EQULK(A(I),B(I),C(I),D(I),T(2))*YV(2)
      TOTOP = TOTOP + TOP(I)
      TOT(I) = TOP(I) + BOT(I)
  429 WRITE(6,984)  I,TOP(I),BOT(I),TOT(I)
      I = 0
      TOTAL = TOTOP + TOBOT
      WRITE(6,984)  I,TOTOP,TOBOT,TOTAL
 9998 JJPRNT = JJPRNT + 1
      IF (DELSUM - TOL2)  5000,  5000,  9999
 9999 WRITE(7,975)  ((X(I,J), I=1,NC) , J=2,NFINAL)
      WRITE(7,974)  (U(J),XL(J),YV(J),T(J) , J=2,NFINAL )
      WRITE(6,999)
      WRITE(6,972)
      DO   9997    J=2,NFINAL
```

```
      SUMXIJ = 0.0
      DO   9995    I=1,NC
      M = J-1
      X(I,J) = X(I,J)*EQULK(A(I),B(I),C(I),D(I),T(J))
 9995 SUMXIJ = SUMXIJ + X(I,J)
      DO   9996    I=1,NC
 9996 X(I,J) = X(I,J)/SUMXIJ
 9997 WRITE(6,986)  M,X(1,J),X(2,J),X(3,J),X(4,J),X(5,J),X(6,J),X(7,J),
     1                 X(8,J),X(9,J),X(10,J)
      STOP
C
  999 FORMAT(1H1)
  998 FORMAT(//////////45X,41HDEMETHANIZER-ABSORBER,E-100,POLYMER CORP./
     1/36X,60HTRANSIENT BEHAVIOUR INCLUDING HEAT BALANCES AND PART REBOI
     2L  /////////////////
     3  20X, 14HW.F.PETRYSCHUK,20X,19HDEPT. OF CHEM. ENG.,20X,19HMCMASTE
     4R UNIV. 1964)
  997 FORMAT(  10X,19HNO. OF COMPONENTS =,I3,9X,19HLIQUID FEED ON TRAY,
     1              I3,9X,18HMIXED FEED ON TRAY,I3,9X,17HTOTAL IDEAL TRAY
     2S,I3  )
  996 FORMAT(//1X,12HCOEFFICIENTS,23X,6HK=F(T),65X,7HCP=F(T)/16X,1HA,
     1             14X,1HB,14X,1HC,14X,1HD,33X,2HAE,13X,2HBE,13X,2HCE / )
  995 FORMAT(  2X,I5,4E15.5,20X,3E15.5)
  994 FORMAT(  //42X,6HMOL WT,13X,8HP CRITIC,12X,8HT CRITIC,12X,8HZ CRIT
     1IC  / )
  993 FORMAT(24X,I5,4F20.3 )
  992 FORMAT(9(3X,I5))
  991 FORMAT(4E13.6)
  990 FORMAT(2X,6E13.4)
  989 FORMAT(  ///21X,5HCOMP.,6X,17HABSORPTION STREAM,12X,11HLIQUID FEED
     1             ,14X,10HMIXED FEED/35X,1HL,11X,1HV,11X,1HL,11X,1HV,11X
     2             ,1HL,11X,1HV,9X,6HTOTALS  )
  988 FORMAT(  22X,I4,7F12.3  )
  987 FORMAT(  //3X,1HJ,39X,6HX(I,J),38X,5HTEMP.,8X,5HFLOWS,8X,18HMOLAR
     1HEAT CONTENT/ 8X,1H1,7X,1H2,7X,1H3,7X,1H4,7X,1H5,7X,1H6,7X,1H7,7X,
     21H8,7X,1H9,6X,2H10,17X,1HL,7X,1HV,11X,1HL,10X,1HV/)
  986 FORMAT(  1X,I3,10F8.4,3F8.1,3X,F10.0,1X,F10.0  )
  985 FORMAT(  ///45X,1HI,9X,6HTOP(I),9X,6HBOT(I),9X,6HTOT(I) /)
  984 FORMAT(  41X,I5,3F15.3  )
  983 FORMAT(  //,60X,5HTIME=,F10.5  )
  982 FORMAT(10F8.5)
  981 FORMAT( 8X,I5,5E20.6)
  980 FORMAT( 23X,I5,4E20.8)
  979 FORMAT(/43X,45HX(I,J) ACROSS PLUS FLOWS,T(J),AND HT. CONTENT  /)
  978 FORMAT(  /1X,10F13.5)
  977 FORMAT(40X,20HTOTAL MOLE FRACTION=,F20.8,2X,7HON TRAY,I3/)
  976 FORMAT(2X,6E20.8//)
  975 FORMAT(5E15.8)
  974 FORMAT(4E15.8)
  973 FORMAT(////////////)
  972 FORMAT(  //3X,1HJ,39X,6HY(I,J)
     1             / 8X,1H1,7X,1H2,7X,1H3,7X,1H4,7X,1H5,7X,1H6,7X,1H7,7X,
     21H8,7X,1H9,6X,2H10/)
C
      END
```

```
......................DATA INPUT TO THE TRANSIENT PROGRAMME.................

++++++++++++++++++++++++++++++++ VARIABLE PARAMETERS ++++++++++++++++++++++++++
    10        3        3        3       20
    .0002          .1700  E07       0.0            0.0          -40.0
  .02          .001         0.036          1.0           32.3
   -5.0          0.0             0.0
    2         2        1

.............................................................................

+++++++++++++++++++++++++++++++++++ CRITICAL DATA +++++++++++++++++++++++++++++
   16.00         45.80         343.7         0.290            METHANE
   28.00         51.0          510.0         0.270            ETHYLENE
   30.1          48.2          550.1         0.285            ETHANE
   42.1          45.4          656.5         0.279            PROPYLENE
   44.1          42.0          666.3         0.277            PROPANE
   56.1          39.5          752.5         0.277            BUTENE-1, IC4-
   58.10         37.40         766.0         0.274            BUTANE
   56.1          37.0          773.0         0.275            BUTENE-2    ***
   72.1          32.6          846.5         0.269            PENTANE
   100.2         26.8          972.5         0.260            HEPTANE

.............................................................................

+++++++++++++++++ COEFFICIENTS OF EQUILIBRIUM RATIO REGRESSION ++++++++++++++
    .40112E 1     .22325E-1    -.48979E-4     .70899E-7          METHANE
    .88377E00     .72166E-2     .28217E-4     .14034E-7          ETHYLENE
    .56412E00     .68113E-2     .45843E-5     .31325E-7          ETHANE
    .18231E00     .26766E-2     .14937E-4    -.14939E-7          PROPYLENE
    .15712E00     .20996E-2     .15374E-4    -.10029E-7          PROPANE
    .51048E-1     .10488E-2     .55619E-5     .11980E-7          BUTENE-1, IC4-
    .41062E-1     .82358E-3     .64406E-5     .72920E-8          BUTANE
    .36037E-1     .50236E-3     .11830E-4    -.12915E-7          BUTENE-2
    .11103E-1     .27875E-3     .27425E-5     .10569E-7          PENTANE
    .10751E-2     .38833E-4     .58433E-7     .66929E-8          HEPTANE

.............................................................................

+++++++++++++++++++ COEFFICIENTS OF SPECIFIC HEAT REGRESSION ++++++++++++++++
   8.22803      0.32005E-02  0.10119E-04                         METHANE
   9.38125      0.12295E-01  0.61924E-05                         ETHYLENE
  11.45850      0.13965E-01  0.91570E-05                         ETHANE
  13.77065      0.18575E-01  0.91157E-05                         PROPYLENE
  15.64702      0.24190E-01  0.10007E-04                         PROPANE
  18.92936      0.30839E-01  -.58362E-05                         BUTENE-1,IC4-
  21.16456      0.28756E-01  0.14171E-04                         BUTANE
  18.03599      0.30787E-01  0.77777E-06                         BUTENE-2   ***
  25.22668      0.45541E-01  -.75878E-05                         PENTANE
  35.11518      0.59477E-01  -.19890E-05                         HEPTANE

.............................................................................
```

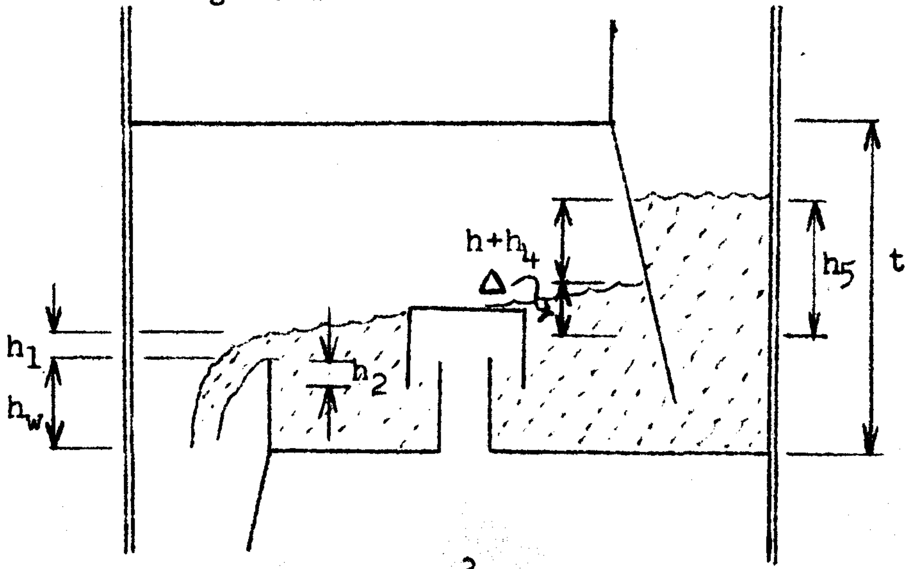
```
+++++++++++++++++++++++++ X(I,J) LIQUID MOLE FRACTIONS ++++++++++++++++++++
 0.18543138E-00 0.27795815E-00 0.63679083E-01 0.44064779E-02 0.10094416E-01
 0.51098392E-01 0.20031986E-00 0.11326635E-00 0.82357738E-01 0.11388179E-01
 0.11154138E-00 0.33139139E-00 0.97696114E-01 0.16338460E-01 0.18858112E-01
 0.46624702E-01 0.18749942E-00 0.10429556E-00 0.75302179E-01 0.10452709E-01
 0.86253625E-01 0.33647445E-00 0.12379268E-00 0.48966377E-01 0.48038290E-01
 0.33658306E-01 0.18256359E-00 0.81893931E-01 0.47506136E-01 0.10852651E-01
 0.49631102E-01 0.33924296E-00 0.16084181E-00 0.55354414E-01 0.50190817E-01
 0.32753030E-01 0.17665295E-00 0.79467770E-01 0.45528615E-01 0.10336564E-01
 0.36958575E-01 0.30851404E-00 0.18964558E-00 0.71404820E-01 0.56687099E-01
 0.32688260E-01 0.17070979E-00 0.78424886E-01 0.44833905E-01 0.10133076E-01
 0.32568845E-01 0.26803208E-00 0.21232197E-00 0.11107941E-00 0.74903389E-01
 0.34103774E-01 0.13460858E-00 0.75352168E-01 0.45905574E-01 0.11124241E-01
 0.99823812E-02 0.23489194E-00 0.23178657E-00 0.13024548E-00 0.86766149E-01
 0.35248482E-01 0.13778824E-00 0.77206292E-01 0.45298493E-01 0.10785985E-01
 0.28178941E-02 0.17143017E-00 0.22011297E-00 0.15823067E-00 0.10685995E-00
 0.40336879E-01 0.15530282E-00 0.86683329E-01 0.47432479E-01 0.10792862E-01
 0.72628349E-03 0.97508520E-01 0.16878052E-00 0.17678479E-00 0.12404497E-00
 0.52141909E-01 0.20022595E-00 0.11042436E-00 0.57876977E-01 0.11485742E-01
 0.15829337E-03 0.37388477E-01 0.90667197E-01 0.15321301E-00 0.11208703E-00
 0.66405554E-01 0.26720997E-00 0.14991499E-00 0.98254251E-01 0.24701257E-01

++++++++++++ HOLDUP,LIQUID FLOW,VAPOUR FLOW, AND TEMPERATURE BY TRAY ++++++
 0.25000000E 01 0.10277135E 03 0.56314266E 02-0.63693818E 01
 0.25000000E 01 0.11169607E 03 0.11340262E 03 0.29843763E 02
 0.36000000E 01 0.33162944E 03 0.12206966E 03 0.42161021E 02
 0.36000000E 01 0.34966253E 03 0.25118063E 03 0.63863441E 02
 0.36000000E 01 0.35618946E 03 0.26897128E 03 0.74864853E 02
 0.47000000E 01 0.50389090E 03 0.27529509E 03 0.81139297E 02
 0.47000000E 01 0.52207256E 03 0.28133591E 03 0.10211918E 03
 0.47000000E 01 0.52625100E 03 0.29936633E 03 0.12399880E 03
 0.47000000E 01 0.53214674E 03 0.30340103E 03 0.15769403E 03
 0.50000000E 01 0.22302004E 03 0.30922428E 03 0.21023219E 03

.............................................................................

+++++++++++++++++++++++++++++++++ FEEDS L0,F1,F2 ++++++++++++++++++++++++++++
   0.0          1.587        45.4
      .0        1.154        25.00
   0.0          1.90         24.9
   0.0          10.625       29.70
   .633         10.975        17.00
   4.923        5.157        6.25
   19.496       35.910       6.46
   11.141       13.906       11.15
   8.322        6.935        8.66
   1.168        2.405         2.50

.............................................................................
```

Appendix VI: Preliminary Calculation of Tray Hydraulics

Appendix II contains the individual plate details for the demethanizer-absorber. To determine whether constant holdup during the transient situation is a valid assumption, the following calculation was made.

Reference is made to "Mass Transfer Operations", Treybal, McGraw-Hill, 120, (1955).

Figure 16: CROSS FLOW TRAY



q........liquid flow rate (Ft.^{3}/sec.)

Weff.....effective weir length (Ft.)

h_1.......liquid head (in.)

k_w.......correction to allow for velocity with which liquid approaches weir

t........tray spacing

A_d.......minimum cross-section area for flow of liquid (Ft.^{2})

d........column diameter (Ft.)

V........tray holdup (Lb. moles)

For case considered

$W = 1.85$ ft.

$h_w = 2.25$ in.

no. of caps is 26

$A_d = 0.657$ Ft.^{2}

Consider flow in the top section of the column,

$q = 0.45$ Lb.mole/sec. at 40°F.

The average molecular weight is 34.

From reference (42) the specific gravity of the liquid is 0.445.

$$q/W = 0.55/1.85 = 0.3 \text{ Ft.}^2/\text{sec.}$$

Applying the Francis' weir formula

$$h_1 = 5.38.kw.\left(\frac{W}{Weff}\right)^{2/3}.\left(\frac{q}{W}\right)^{2/3} \tag{82}$$

and (1) assuming for an initial estimate that W = Weff

(2) from the graph on page 122 from Treybal $k_w = 0.957$

therefore $h_1 = 5.38.(0.957).(0.3)^{2/3} = 2.32$ in.

and $\frac{h_1}{d} = \frac{2.32}{3.5 \times 12} = 0.055$

This leads to a new estimate of Weff or $\left(\frac{W}{Weff}\right)^{2/3}$ from p.122 is 1.02.

Therefore $h_1 = 2.32 \times 1.02$ or 2.4 in.

Now $h_5 = h + h_4 + \Delta$ (83)

where $h_4 = 0.558 \left(\frac{q}{A_d}\right)^2$ (84)

Assume h is negligible in comparison to h_4 and Δ. Δ is estimated to be 1.5 in.

Therefore $h = 0.558\left(\frac{0.55}{0.657}\right)^2 + 1.5 = 1.9$ in.

The average liquid depth over tray is given by

$$h_a = \frac{(h_5 + h_1 + h_w) + (h_1 + h_w)}{2} \tag{85}$$

$$\text{or } h_a = \frac{(1.9 + 2.4 + 2.25) + (2.4 + 2.25)}{2}$$

$$= 5.65 \text{ in.}$$

Also the liquid area is given by

$$L_a = (\text{Tower area}) - (\text{Top down flow area}) - (\text{Bubble Cap area})$$

$$= 9.62 - 1.63 - 26.\left(\frac{3.14}{4}\right)\left(\frac{4}{12}\right)^2$$

$$= 5.6 \text{ Ft.}^2$$

or $U = (5.6 \text{ Ft.}^2)\left(\frac{5.65}{12} \text{ Ft.}\right) \times .82\left(\frac{\text{Lb.mole}}{\text{Ft.}^3}\right)$

therefore U = 2.2 Lb. mole

Similarly for q = 0.225 Lb./mole/sec.

U = 1.85 Lb. mole

For a 50% change in flow rate, the relative change in holdup is

$$\Delta U = \frac{(2.20 - 1.85)}{220} . 100 = 16\%$$

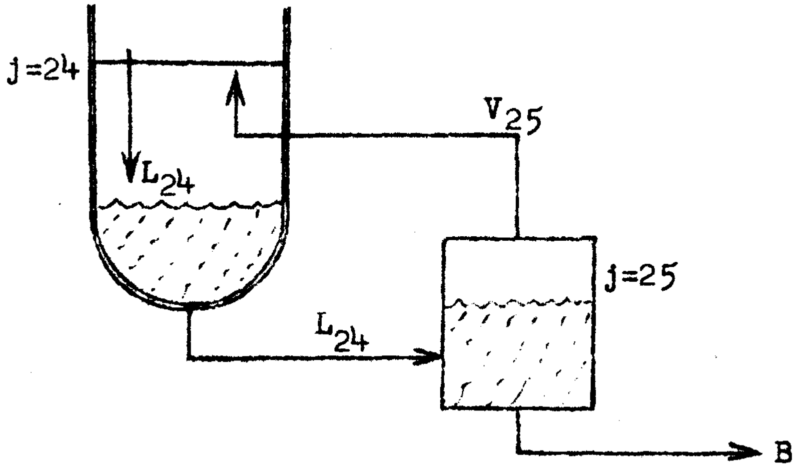
For more detailed tray calculation methods, the reader is directed to the classic paper on the subject by Cicalese et al (11) and the more recent work by Bolles (4), (5), (6), (7).

Appendix VII. Steady State Solution Assuming Constant Molal Flows

A 10 component-25 tray model was solved assuming constant molal overflow and constant molal vaporization. The feed trays are 6 for F1 and 18 for F2.

This simplified model treated tray 25 as a "total reboiler". Schematically the reboiler situation, as treated here, is depicted in the following figure.

Figure 17: REBOILER MODEL



It is evident from the temperature profile that this model bears no relationship to the real demethanizer absorber. The overhead specification of D = 150 moles/U.T. is too high to approach the real situation. It can be seen from Table 15 that the bulk of the vapour flow in the upper reaches of the column comes from feed F_2. The feed tray temperature is high thereby vaporizing in excess of 89% of F_2. This situation leads to a very low vapour rate in the bottom of the column.

Any reduction in the overhead specification succeeds in reducing the vapour flow rate in the bottom section even further. The feed tray temperature is not sufficiently reduced by a lower D to eliminate the unusual temperature profile. In the limit, as D decreases, the vapour flow rate tends towards zero in the bottom section. This certainly is a prepostrous result.

It should be noted that without the heat balances, the above solution was obtained in only 28 column iterations.

Table 15: STEADY STATE SOLUTION, CONSTANT L AND V

D = 150 Moles/U.T.

Tray j	Liquid Leaving Moles/U.T.	Vapour Leaving Moles/U.T.	Temperature °F.
1	45.67	150.	209.907
2	45.67	150.	195.779
3	45.67	150.	191.602
4	45.67	150.	189.566
5	45.67	150.	188.055
6	136.21	150.	186.661
7	136.21	150.	177.817
8	136.21	150.	174.005
9	136.21	150.	171.897
10	136.21	150.	170.480
11	136.21	150.	169.331
12	136.21	150.	168.222
13	136.21	150.	166.991
14	136.21	150.	165.483
15	136.21	150.	163.513
16	136.21	150.	160.912
17	136.21	150.	158.141
18	155.039	27.387	163.676
19	155.039	27.387	194.831
20	155.039	27.387	196.014
21	155.039	27.387	197.604
22	155.039	27.387	200.361
23	155.039	27.387	206.474
24	155.039	27.387	224.507
25	127.652	27.387	

$-9999 \le \theta \le 1.0001$

Table 16: LIQUID COMPOSITION PROFILE, CONSTANT L AND V

	Liquid Mole Fractions		
Tray	Methane	Ethylene	Ethane
1	.0349	.0306	.0374
2	.0372	.0358	.0453
3	.0376	.0372	.0473
4	.0377	.0377	.0481
5	.0378	.0381	.0486
6	.0379	.0384	.0490
7	.0403	.0455	.0596
8	.0408	.0486	.0655
9	.0410	.0501	.0688
10	.0411	.0509	.0708
11	.0412	.0515	.0721
12	.0412	.0520	.0731
13	.0413	.0525	.0741
14	.0414	.0531	.0751
15	.0416	.0539	.0764
16	.0418	.0551	.0782
17	.0420	.0564	.0803
18	.0347	.0607	.0834
19	.0032	.0622	.0863
20	.0024	.0612	.0866
21	.0017	.0590	.0867
22	.0011	.0546	.0856
23	.0007	.0460	.0802
24	.0003	.0297	.0619

Appendix VIII: Boiling Range of Column Feeds

The bubble point and dew point of each of the three feeds was calculated. The feeds were considered on a nitrogen-free basis (only applicable to F_2) and 12 components were included to represent the streams. Flash calculations were carried out over the boiling range of these three streams and are presented here in graphical form in Figures 18, 19, and 20.

Table 17 presents the concentration breakdown used in this 12 component study.

Table 17: CONCENTRATIONS OF FEED STREAMS

Component	Mole %		
	L_o	F_1	F_2
Methane	0	1.2	25.9
Ethylene	0	.9	9.1
Ethane	0	3.3	9.7
Propylene	0	20.6	20.4
Propane	1.4	10.9	10.3
Isobutane	21.8	17.6	7.1
Butene-1	11.0	12.0	5.0
n-Butane	21.8	16.6	8.4
Pentane	11.1	2.9	2.4
Hexane	3.1	.8	.7
Heptane	2.7	.7	.6
Octane	2.3	.6	.5

Figure 18: BOILING RANGE OF ABSORPTION OIL - F_o, L_o

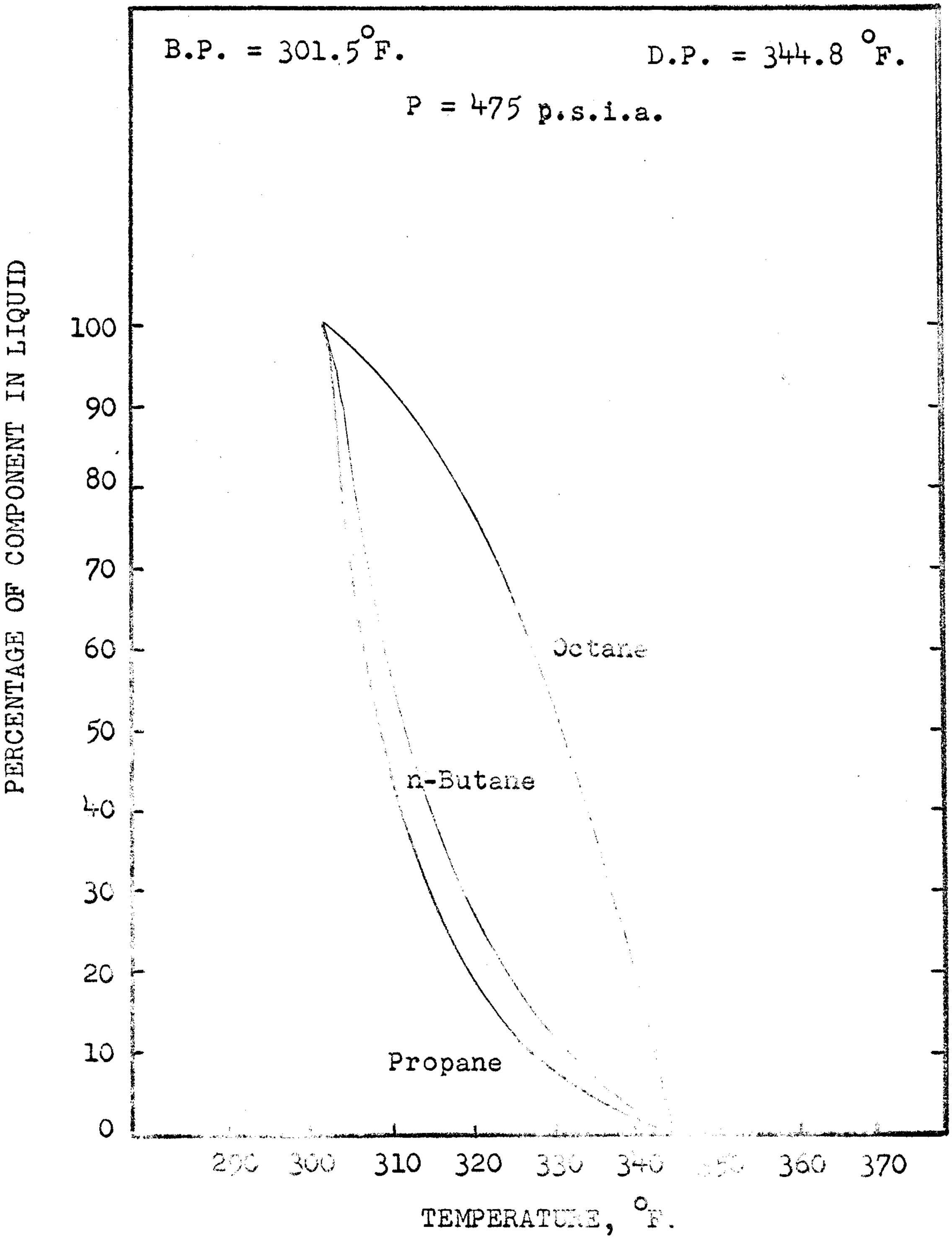


Figure 19: BOILING RANGE OF LIQUID FEED-F_1

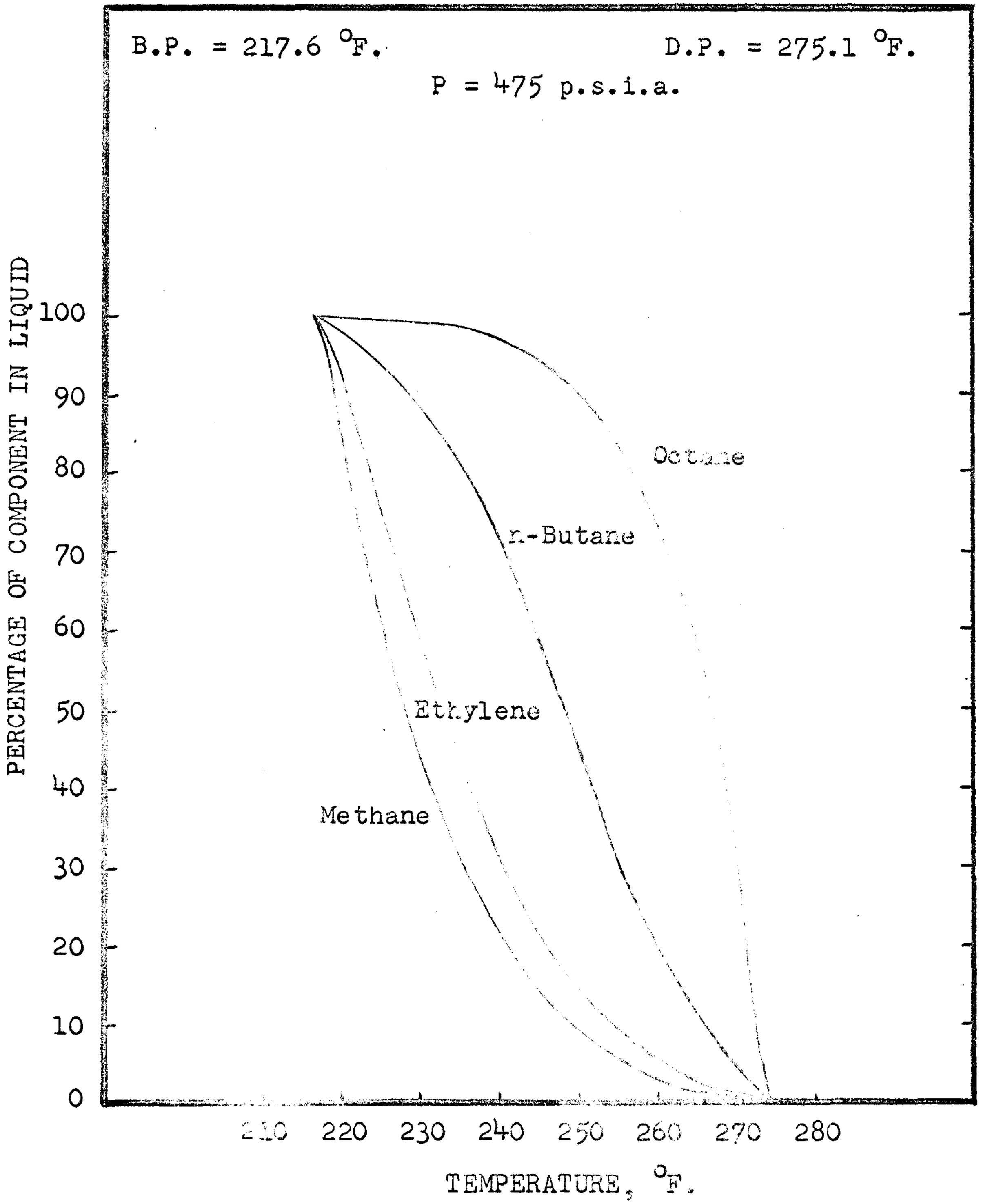
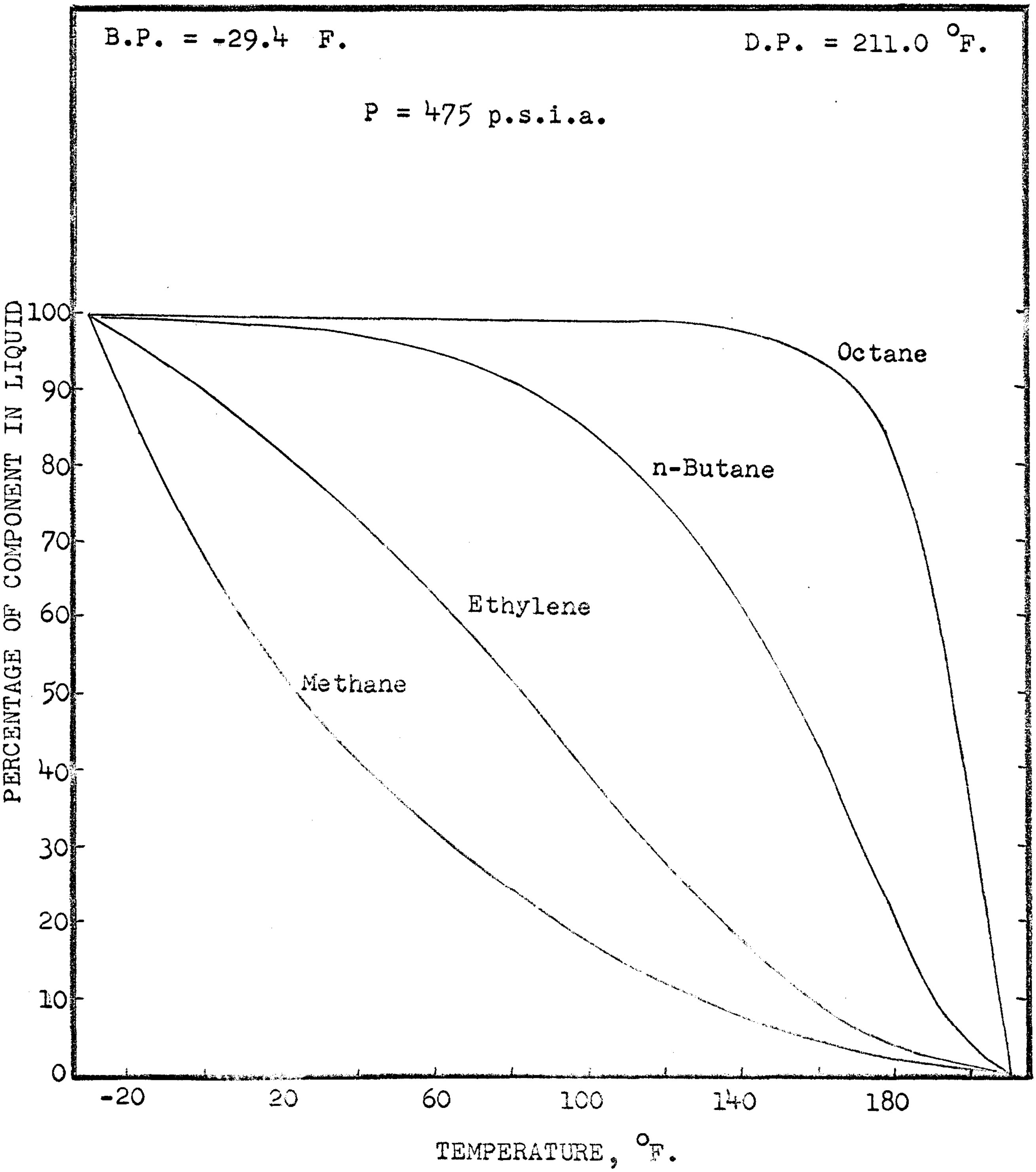


Figure 20: BOILING RANGE OF GAS FEED-F_2



Appendix IX: Actual Demethanizer-Absorber Operation

This appendix contains some of the data forwarded to the author by Polymer Corporation Ltd. The flow data cover a period of 8 days and represent 1/2 day averages. The temperature profile covers a one day operation (not corresponding to the period for which the flow data applies).

It should be noted from Figure 22 that the tray 28 temperature profile crosses the tray 23 temperature profile.

Figure 21: DEMETHANIZER-ABSORBER EXTERNAL FLOWS

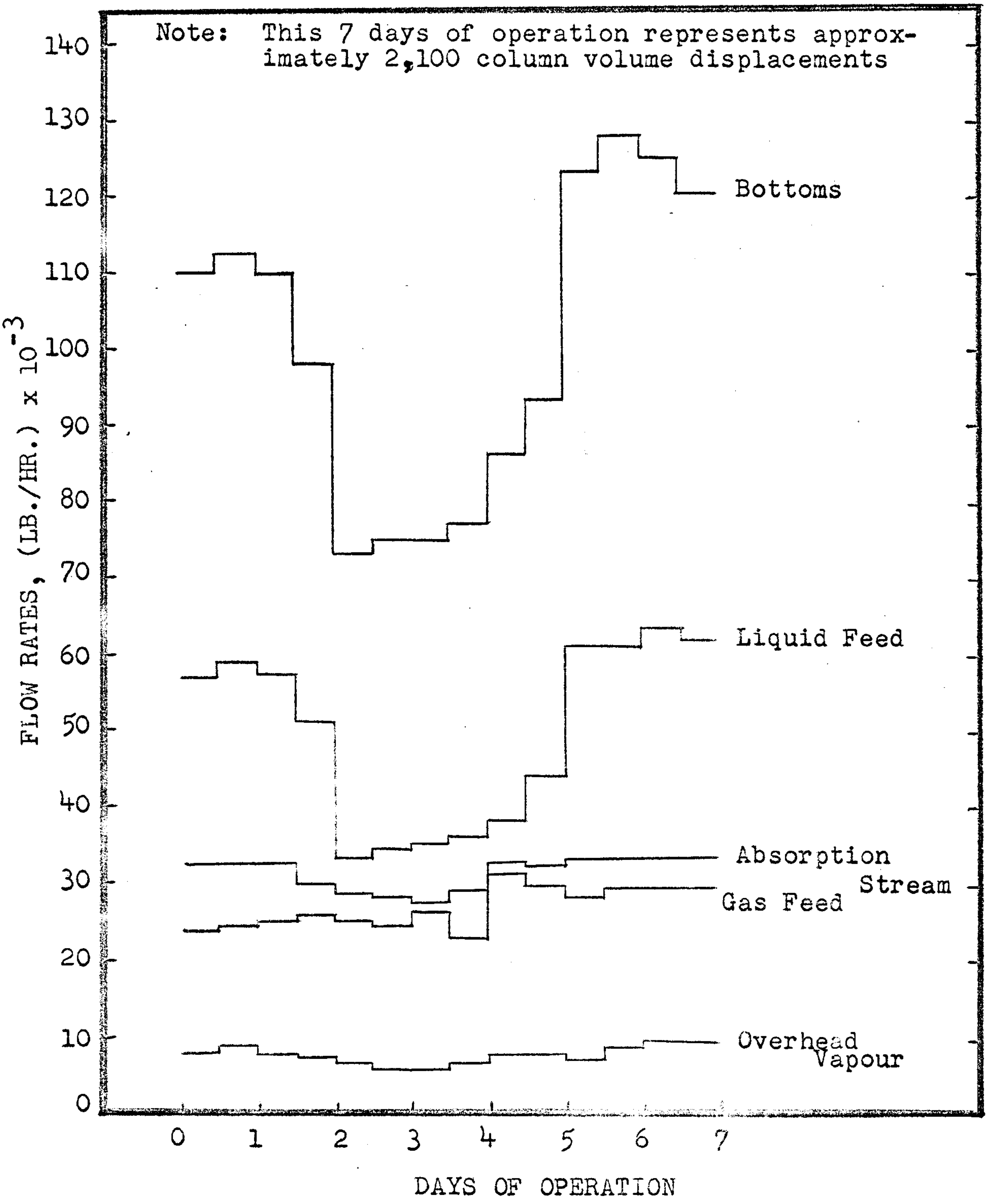
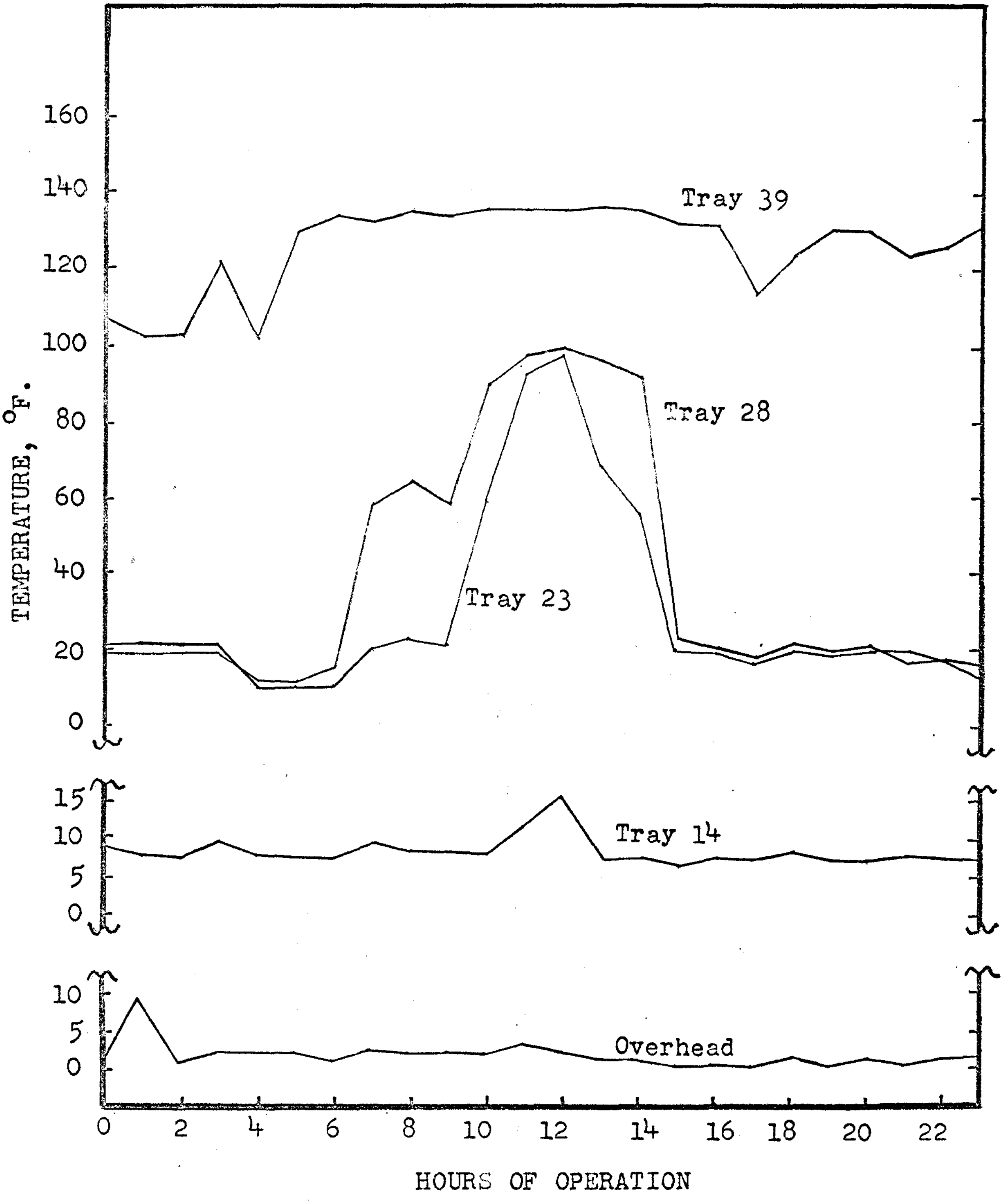


Figure 22: ACTUAL TEMPERATURE CHANGES IN THE DEMETHANIZER-ABSORBER



Appendix X: Steady State Solution Reproducibility

Four cases are compared in the succeeding tables of figures to indicate the reproducibility of the steady state solution of the demethanizer-absorber model to a fixed set of conditions. The initial temperature profiles are varied in the first three cases while the initial flow profile is varied in case 4. These initial profiles are tabulated in Table 18. The comparison of the reproducibility of the steady state solution is given in Table 19.

Table 19 indicates that the final solution is reproducible to a minimum of 3 figure significance for a θ criterion of 0.0015. Although not tabulated, the concentration profiles showed the same reproducibility as the flow and temperature profiles.

Datum: 10 component-20 tray model

$\theta = 0.0015$

$m = 0.20$

$D = 48.0$ moles/U.T.

fixed feed flows and concentrations

Table 18: INITIAL CONDITIONS FOR THE STEADY STATE SITUATION

Tray	Flow Rates for Case 1,2,3 Moles/U.T.		Case 1	Case 2	Case 3,4	Flow Rates Case 4 Moles/U.T.	
j	L_j	V_j	T_j	T_j	T_j	L_j	V_j
1	68.5	76.3	-5.0	0.0	5.0	73.1	85.3
2	68.5	250.5	0.0	5.0	10.0	73.1	265.9
3	68.5	250.5	5.0	10.0	15.0	73.1	265.9
4	68.5	250.5	10.0	15.0	20.0	73.1	265.9
5	68.5	250.5	15.0	20.0	25.0	73.1	265.9
6	68.5	250.5	20.0	25.0	30.0	73.1	265.9
7	204.4	250.5	25.0	30.0	40.0	218.0	265.9
8	204.4	250.5	30.0	40.0	50.0	218.0	265.9
9	204.4	250.5	40.0	50.0	60.0	218.0	265.9
10	204.4	250.5	50.0	60.0	70.0	218.0	265.9
11	204.4	250.5	60.0	70.0	80.0	218.0	265.9
12	204.4	250.5	70.0	80.0	90.0	218.0	265.9
13	385.4	231.2	80.0	90.0	100.0	411.0	246.6
14	385.4	231.2	90.0	100.0	120.0	411.0	246.6
15	385.4	231.2	100.0	120.0	140.0	411.0	246.6
16	385.4	231.2	120.0	140.0	160.0	411.0	246.6
17	385.4	231.2	140.0	160.0	180.0	411.0	246.5
18	385.4	231.2	160.0	180.0	200.0	411.0	246.6
19	385.4	231.2	180.0	200.0	220.0	411.0	246.6
20	154.1	231.2	200.0	220.0	240.0	164.4	246.6

The vapour flow rate is a calculated value based on the temperature and individual component flows at tray 1. For Case 2, V_1 = 81.2 and for Case 3, V_1 = 85.4

Table 19: COMPARISON OF STEADY STATE SOLUTIONS -FINAL SOLUTIONS

Tray	Temperatures - T_j				Vapour Flow Rates - V_j			
	Cases				Cases			
j	1	2	3	4	1	2	3	4
1	-3.1	-3.2	-3.1	-3.1	48.0	48.0	48.0	48.0
2	23.3	23.3	23.4	23.3	84.6	84.6	84.6	84.6
3	35.4	35.4	35.4	35.4	89.9	89.9	89.9	89.9
4	40.3	40.4	40.4	40.4	92.7	92.6	92.7	92.7
5	42.1	42.1	42.1	42.1	94.0	93.9	94.0	94.0
6	41.0	41.0	41.0	41.0	94.9	94.9	94.9	94.9
7	30.5	30.4	30.5	30.5	97.2	97.2	97.3	97.2
8	50.7	50.7	50.7	50.7	214.2	214.2	214.2	214.2
9	58.5	58.5	58.5	58.5	231.0	231.0	231.0	231.0
10	61.9	61.9	61.9	61.9	237.8	237.8	237.8	237.8
11	64.9	64.9	64.9	64.9	240.1	240.1	240.2	240.1
12	70.1	70.1	70.1	70.1	240.4	240.4	240.4	240.4
13	82.2	82.2	82.2	82.2	221.8	221.8	221.8	221.8
14	88.4	88.4	88.4	88.4	264.1	264.0	264.1	264.1
15	92.2	92.2	92.2	92.2	272.2	272.1	272.2	272.2
16	96.5	96.5	96.5	96.5	275.5	275.5	275.5	275.5
17	104.0	104.0	104.0	104.0	277.0	276.9	277.0	277.0
18	119.3	119.3	119.3	119.3	277.0	277.0	277.1	277.1
19	150.1	150.1	150.1	150.1	275.7	275.7	275.7	275.7
20	204.4	204.4	204.4	204.4	276.4	276.4	276.4	276.4

The liquid flow rates show the identical vairation indicated by the vapour flow rates since these two variables are directly related through the material balance equations (46).