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DYNAMICS OF A CONTINUOUS DISTILLATION COLUMN USING A NON-IDEAL MULTICOMPONENT MIXTURE

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APPENDICES

CHAPTER 1

SUMMARY

1. A Steady State model has been developed which characterises the Steady State profile of a continuous distillation column with a total condenser. It takes into account the non-ideality of the system under investigation. The system being Acetone, Methanol, and Isopropyl Alcohol. Experimental results have been obtained and compared with the numerical experimentation.

2. A Dynamic model has been developed.

3. Analytical expressions and solutions to characterise the dynamics have been obtained making use of matrix techniques. The Analytical solution works equally well for both distinct and complex conjugate eigenvalues.

4. Numerical method determining the transients of a continuous distillation column is based on Markov's Probabalistic technique. Numerical and Analytical results compare very well.

5. Two techniques, namely, Sargent's and Wood's formulation of dynamic equations has been investigated. It was found that Wood's formulation due to more interactions in its equations, represents a multi-component distillation system better, as compared to Sargent's.

6. A method of analysis to investigate the effect of non-linearity on a change in feed composition is suggested as further work.

CHAPTER 2

INTRODUCTION

1. INTRODUCTION

The control of industrial processes has become a very interesting and exiting subject for the members of the Chemical Engineering profession. The control of distillation columns has been in the forefront of this increased interest because distilling operations are found in almost every phase of the chemical industry, and through effective control of distillation columns, the industry can reap considerable dividends.

The research in distillation column control has been primarily concerned with determination and prediction of the dynamic behaviour of distillation columns. In general, two different paths have been followed in studying distillation column dynamics. One path has been to use a "rigorous" approach. According to this "rigorous" approach, a distillation column is considered to consist of a known number of plates. Each of the plates is assumed to play an equal role in the dynamic behaviour of the column and a separate differential equation is written for each component on each plate. A simultaneous solution of all of these differential equations results in the dynamic behaviour of the column. Obviously, the simultaneous solution of a large number of differential equations is a time consuming task, even with most modern computer. To add to the computational difficulties, the "rigorous" model should consider the vapour-liquid contacting efficiency, so that the theoretical model will have practical applications. When all of the factors have been considered the resulting model is usually too complex to be useful in an operating control scheme.

To avoid the computational difficulties encountered with the "rigorous" model, some researchers have used an alternate approach in determining the dynamic behaviour of a distillation column. This approach is to consider the column according to a section concept. According to that concept, the portion of the column that lies between points where either material or energy enters or leaves the column is a section. In the present investigation the "rigorous" approach was felt to be more satisfactory for these reasons:

1) it gives more accurate predictions about experimental results in areas of operation well away from the region of recorded data;

2) it computes plate compositions and flow rates as well as product data;

3) it gives a greater insight into the behaviour of the actual system.

Distillation columns are very good examples of units exhibiting time lags. Such lags occur in internal and external flows of vapour and liquid. A change in reflux flow will be transmitted from plate to plate inside the column. The rate at which the change is transferred will consequently depend on the volume of liquid (or 'hold-up') present on each tray. Neither will the effect of a change in feed composition can be instantaneously transmitted through the column, but will be subject to an accumulative time-lag on each plate, which again is a function of plate hold-up. The controlability of the plant is dependent upon the time- lag it produces, particularly if input disturbances are rapid.

The usual control criterion for a fractionator is to produce products of particular specifications and to keep within those specifications. Occasionally one product composition is required to be controlled, e.g., overhead product composition. Sometimes bottom product composition is also specified. Often in the case of multi-component mixture there are more than two products to keep within specification.

Disturbances in column operation are generally produced by variations in feed composition, feed flow and feed quality. These may be termed uncontrolled variables although, if intermediate storage is used, it is possible to control feed-flow to the unit by a simple feed-back flow control system. Furthermore, feed quality may be controlled using a preheater of some kind.

Other principal variables are column pressure, reflux quality, reflux and reboil-vapour flow rates. The former two are held constant using feed back control for a particular distillation operation. The latter two have a very considerable effect on column performance and are easily controlled. They are thus generally used as controlling variables to correct variations in products due to uncontrolled disturbances.

Because of the time lags present the distillation unit lends itself well to the applications of predictive control. For binary distillation with two product streams it may be necessary to control either or both by feed-forward systems. It is necessary to employ at least one controlling variable for each output variable controlled in this manner. For example, to control both overhead and bottom product compositions in the face of fluctuations in feed compositions it is necessary to use both reflux and reboil-vapour flow rates as controlling variables. For steady state on dynamic control the relations (transfer functions) between feed composition, reflux and reboil vapour flow rates as inputs, and product compositions as outputs, must be determined. The control model will then be based on the criteria that variations in the latter be zero. This model can itself be specified in terms of transfer functions. In order to be useful in practice the action of the controller must at least approximate the transfer function of the model. This may raise some difficult problems for the more complex control schemes.

In order to obtain starting or boundary conditions for an unsteady state calculations, a solution must be obtained for the steady state preceding transient operation. Equation for steady state can be obtained by reducing the normal equations by imposing the condition of time independence of all variables; that is, the steady state equations are a special case of the unsteady state equations.

If a column has reached a steady state in given operating conditions, then a small change in the operating conditions will initiate a transient response. After sufficient time the column will have reached a new steady state. Calculation of transient response is difficult whereas the initial and final steady states, however, can be calculated relatively easy. Transient section for the problem under discussion has been developed both Analytically and numerically in Chapter 5 & 6.

For purpose of control, there are two main types of information which can be drawn from such calculations. First, the calculations show the extent of change which is to be measured. Secondly, although the composition will be estimated and controlled at a point within the column, the real concern of control is to achieve satisfactory products at the top and bottom of a column.

A problem confronting the operation of a distillation column is in the controllability of the top and bottom product to a specified purity and accuracy. What happens is that some sort of disturbance in the form of limit cycle occurs internally, which effects the purity of the product. In other words, the product goes off specification at one half of the cycle and returns to the desired specification later on. This clearly indicates that the purity of the said product is undergoing an oscillatory phenomeon. This limit cycle is due to the fact that distillation is a non-linear operation. It would be worthwhile to study the effect of non linearity on changes in feed composition and reflux ratio and see their effect on product compositions. Suggestions of these lines have been included in the scope for further work. For the present, it needs to be proved that the above mentioned phenomenon is theoretically explainable and justified.

The dynamic equations have been formulated in two ways, namely Sargent's method and Wood's method. Both these techniques are discussed in Chapter(6).

Method proposed by Sargent uses an approximating system which reproduces correctly the complete qualitative behaviour of the real system and further does not depend on estimates of x_i to determine dxi/dt. On the other hand in Wood's method the slopes g (n, i) in eq(1) for multi component mixtures

$$g(n, i) = d\bar{Y}^{*}{}_{n,i}/d\bar{x}_{n,i} = \sum_{r=1}^{k} \left(\partial f_i/\partial\bar{x}_{n,r} \cdot x_{n,r}/x_{n,i} \right) \qquad \text{\_\_\_\_\_}(\ 1\ )$$

depend on all the perturbations in composition on a plate n. This is because the slope of the equilibrium data is no longer a line of fixed gradient, but is a line in a vector space. In order to determine the direction of such a line in such a space it is necessary for the liquid compositions to be specified i.e., $x_{n,i}$ must be known. It is evident that as $g_{n,i}$ are functions of $x_{n,i}$ with $j = 1, \ldots .k$, that it will be necessary to solve the equations for all k components simultaneously. In other words it will be impossible to obtain a solution for the transient behaviour of one component in isolation.

Wood has reported that there are essential differences between the transient behaviour of multicomponent and binary distillation columns. The differences arise because, in binary distillation if one component increases in composition, the other must decrease by an equal amount and the linearised response to individual disturbances are simple monotonic exponential decay function. However, in multicomponent distillation, the time response for a given component on a given plate may go through a maximum and change sign. For flow disturbances, because the steady state profiles for the least and most volatile components are monotonic, the responses for these components would be expected to have a similar form to those for binary distillation responses. However, for the components of intermediate volatility, the steady state profiles can go through a maximum value and this is part of the reason why the responses for these components can be substantially different even on adjacent plates in a distillation column.

The eigenvalues obtained by Wood's method are negative and have a complex pair indicating an oscillatory system as compared to Sargent's method, which gives distinct and negative eigenvalues.

It would be appropriate to define few of the terms used in this investigation for specifying control system performance.

They are as follows:

> The STEADY STATE RESPONSE is that part of the total response which does not approach zero as time approaches infinity.
>
> The TRANSIENT RESPONSE is that part of the total response which approaches zero as time approaches infinity.
>
> The TOTAL RESPONSE is a sum of steady state response and transient response.
>
> The UNIT IMPULSE RESPONSE of a linear system is the output $y(t)$ of the system when the input $x(t) = \partial(t)$ and all initial conditions are zero.
>
> The UNIT STEP RESPONSE is the output $y(t)$ when the input $x(t) = u(t)$ and all initial conditions are zero.

CHAPTER 3

REVIEW OF THE PAST WORK

3 REVIEW OF PAST WORK

Considerable interest has been given to the study of the transient behaviour of a fractionation column in recent years. Some investigators have considered the problem of the start up and the rate of approach to equilibrium of a column. Since the present investigation is concerned mainly with the behaviour of the column subjected to feed composition disturbances, reflux ratio disturbance and boil up rate disturbances, and its control, the works of those investigators will not be mentioned here.

Prior to 1932 almost no work had been done in developing dynamic models of industrial processes. In 1932 Ivanhoff (12) presented a paper in which he made the first attempt at developing a mathematical model, from a strictly emperical point of view. From the discussion accompanying the article, the results of his experiments appear to have been widely accepted. Several other early authors (1, 39) also approached the development of dynamic models from an emperical point of view. These men correlated statistically the behaviour of a process with changes in independent variables and developed and approximate model of the process. Several other researchers (8, 10, 18, 14) approached the problem of developing a dynamic model by constructing small scale plants and then developing a dynamic model from the results obtained. Although these early workers were not interested in the control of distillation columns, but in transient systems in general, their works formed the foundation of modern process dynamics.

Of the earliest theoretical treatments on the transient behaviour of a distillation column was given by Amundson and Acrivos (2), who employed matrix algebra to the linearized model and proved that for an uncontrolled column all the roots of the characteristic equation are real and negative. This was later on supported by other workers notably Sargent (51, 50).

In 1947, Marshall and Pigford (16) proposed the first mathematical model of a distillation column. Their model was based on the equilibrium stage as shown in Figure 1. According to the equilibrium tray concept, each tray must be considered individually, and the differential equation that predicts the transient behaviour must be written for each component in the form

$$\frac{d\delta_n L x_n}{dt} + \frac{d\delta_n V y_n}{dt} = (L_{n-1}\,x_{n-1} + V_{n+1}\,y_{n+1}) - (L_n\,x_n - V_n\,y_n) \text{ ——— (1)}$$

where

$d\delta_n L x_{n}/dt$ = change in liquid holdup of a component on tray n with time

$d\delta_n V y_{n}/dt$ = change in vapour hold up of a component above tray n with time.

$L_{n-1}x_{n-1}+V_{n+1}y_{n+1}$ = rate at which a component flows to tray n.

$L_n x_n + V_n y_n$ = rate at which a component flows away from tray n.

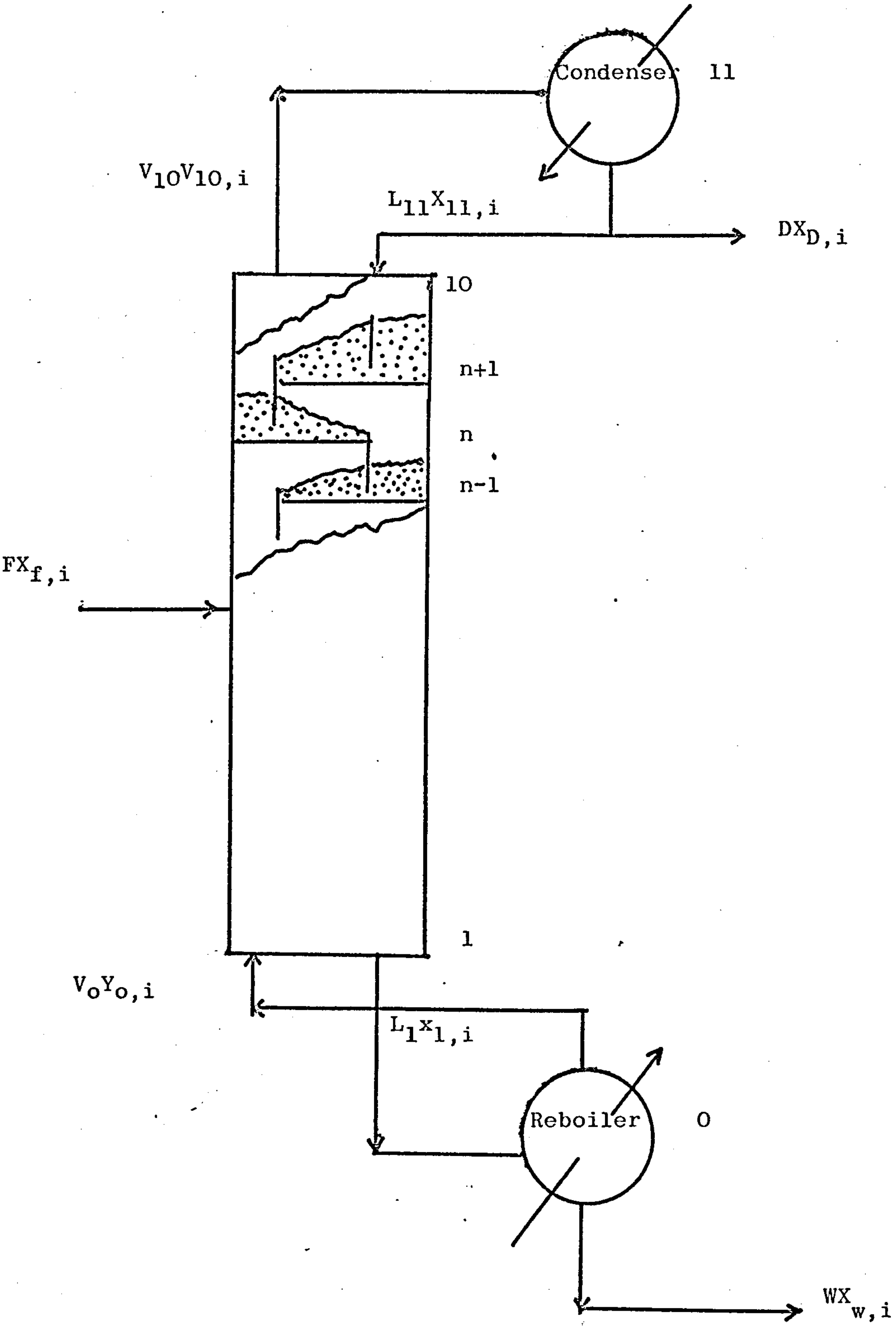


Fig 1. A SCHEMATIC DIAGRAM OF A DISTILLATION COLUMN HAVING TRAYS

While this concept is theoretically sound, there are several drawbacks in the vast number of equations that must be solved. This problem is perhaps best illustrated by an example. If the column under investigation has n trays and i components, the number of differential equations that must be solved is of the order of n times i. Thus, the model is severely limited in its complexity. Since neither Digital nor Analog computers were well developed at the time that Marshall and Pigford developed the plate-to-plate model, a rigorous solution of the equations was almost impossible. The difficulty in using the Marshall and Pigford model was compounded further by the fact that the trays are not normally equilibrium ones. Thus, some method of estimating the efficiency, or the approach to equilibrium, of each tray was required. In order to make their model more useful, Marshall and Pigford made the following assumptions :

1. Constant molal overflow,
2. Negligible vapour holdup above a tray,
3. Approach to equilibrium between the liquid on the tray and the vapour above the tray could be represented by a straight pseudo equilibrium line.

While these assumptions enabled Marshall and Pigford to obtain an analytical solution to the differential equations, the accuracy of the model was reduced considerably. The assumption of negligible vapour holdup is normally a good one, but since the assumption of constant molal overflow required that the molar heats of vaporization of the components be equal and the assumption of a straight line requires that the concentration of the component be small, the integrated equations are normally too restricted to be useful on actual systems.

Sometime after Marshall and Pigford developed their model, Rose and his co-workers (26, 23, 24, 25) applied the basic equation, equation (1), to a batch distillation column. In this application, Rose etal. avoided the assumption that limited the usefulness of the Marshall and Pigford equations by programming the differential equations on a digital computer. They were, however, confronted by the problem of excessive computer time.

About the same time that Rose et al. were publishing their work, Robinson and Gilliland (21) developed an approximate graphical method for predicting the approach to steady state of a distillation column. Their method was restricted to cases where the column was upset by a change in the feed composition, and, like previous models, was based on the equilibrium tray concept.

Voetter (34) was perhaps the first to combine experimental data with a theoretical analysis. He compared the equations of Marshall and Pigford with experimental data that he obtained on a sixty tray oldershaw distillation column. He studied the response of an uncontrolled column to step and sinusoidal disturbances in the concentration of the feed stream. The experimental and the calculated values compared excellently during the early portion of the transient period, but as the column approached steady-state the experimental and calculated values differed considerably. By means of finite difference method two sets of response equations were obtained, one connecting the top composition response with feed composition disturbances and one connecting the bottom composition response with the feed composition disturbances. The two equations were coupled mathematically to obtain the response for a complete column under the influence of a frequency response function. An equation for calculating the retention time was also given. The effect of various simplifying assumptions were discussed in terms of additional retention time over and above that obtained for the simplified model. An error of up to 40% was said to be possible with the simplified model.

In 1957, Wilkinson and Armstrong (5, 37, 36) presented experimental data that were obtained as a response of 21 tray four-inch diameter column operating with a mixture of benzene and carbon tetzachloride to step disturbances in feed concentration and in reflux ratio. For the systems investigated fair agreement was obtained between the experimentally determined time response curves of various plates and the digital computer solutions of Rosenbrock (29).

Wilkinson and Armstrong (37) also derived an approximate mathematical solution for the response of a distillation column to step disturbances in feed composition. The assumptions made in deriving the equation were the same as those made by Voetter, except that the equilibrium line was replaced by two-straight lines, one for the enriching section and one for the stripping section. Theoretical response curves were compared with those obtained by experiment. Fair agreement was obtained for the initial part of the curves, but the agreement was poor when the system approached the new equilibrium state.

By using the same theoretical model as that of Wilkinson and Armstrong (37), Wood and Armstrong (39) were able to obtain an improved expression which gives better prediction of the response curve when the column approaches the new state of equilibrium after a step disturbance. The agreement between theory and experiment was within 20%.

By using a linearised model and then taking laplace transformation of the linearised equations, Armstrong and Wood (4) were able to obtain an analytical expression for the response of a distillation column to step changes in reflux flow rates from total to practical reflux conditions with the change being made so as to keep the feed plate constant composition. This expression was then extended to cover the more practical case of varying feed-plate composition. At the top of the column the experimental and the calculated values were in good agreement, but at the bottom of the column the experimental and calculated values did not agree well.

Rose and Williams (28) studied the control problem of a five plate distillation column subjected to step and sinusoidal variations in feed composition with the aid of an analogue computer. The composition sampling arrangements included two point sampling using top plate and bottom plate samplers, two point sampling using distillate and bottom plate samplers, single point sampling from distillate only, single point sampling from top plate only, single point sampling from bottom plate only. All three types of controllers (proportional, integral and derivative) were used in the study; they were used either singly or in combination with each other. Top plate sampling with proportional controller used either singly or in combination with integral controller was found to be the most effective. The use of derivative controller either singly or in combination with others was not recommended.

Williams, Harnett, and Rose (38) extended the study of Rose and Williams (27) to cover the effect of cold reflux and imperfect sampler on the overall controlability of the column. It was found that if the minimum composition variation detectable by a particular sampler was 1.5% or less, top plate sampling should be used. The deviation of the temperature was found to be significant only if the resulting change in vapour rate amounts to 50% or more of the original liquid rate for intermediate plate sampling. In the case of the top plate sampling, the difference between the relux temperature and the top plate boiling temperature was significant only if the resulting change in vapour rate amounts to 80% or more of the original liquid rate.

In 1961 Baber (7, 6) presented the most extensive experimental and calculational study that has been published. He programmed a series of differential equations that were developed by Lamb and Pigford (14), but were based on the earlier Marshall and Pigford equations, on an analog computer. Baber compared the results obtained on the computer with the experimental data he obtained. The data were obtained on a five tray, single section distillation column. The method of operating the column was to allow the column to come to steady-state at total reflux and then change one of the operating variables; either the reflux rate, the reflux composition, or the vapour rate.

The flow rates and compositions of the various streams were determined before the step change was made and the compositions were measured at intervals throughout the transient period. When the column reached steady-state, the flow rates and the compositions were again measured. For some of the experimental runs, Baber was able to get good agreement between the experimental and the computer calculated values, but for most of the runs he was unable to obtain good agreement.

At the Baltimore meeting of the American Institute of Chemical Engineers, Marr (15) suggested a new concept for predicting the transient behaviour of a distillation column. He suggested that in order to get away from the conventional and complicated plate-to-plate model, some parameter which could be used to describe the degree of separation that was occuring in a distillation column should be developed. However, after suggesting the simplified model, Marr complicated it by considering all aspects of the mechanics of construction of the column. Due to these additions, the final model was almost as complex as the plate-to-plate model. Little simplification was actually accomplished. After Marr's work, no further efforts were made to develop a simplified model until Reynolds (21) began his work.

Reynolds envisioned a distillation column as being composed of several sections in which there could be any number of trays. According to the section concept as shown in figure 2, a section of a distillation column is that part of the column which lies between the points at which either feed streams enter or product streams leave the column according to Reynolds, the rate at which mass is transferred from the vapour phase to the liquid phase can be expressed by the equation

$$N^{v}_{n,i} = - J_{n,i} \, (y^{*} - y)_{n,i} \qquad (2)$$

where $J_{n,i}$ is the parameter which describes the degree of separation occuring in a section and $(y^{*} - y)_{n,i}$ is the driving force for mass transfer in the section.

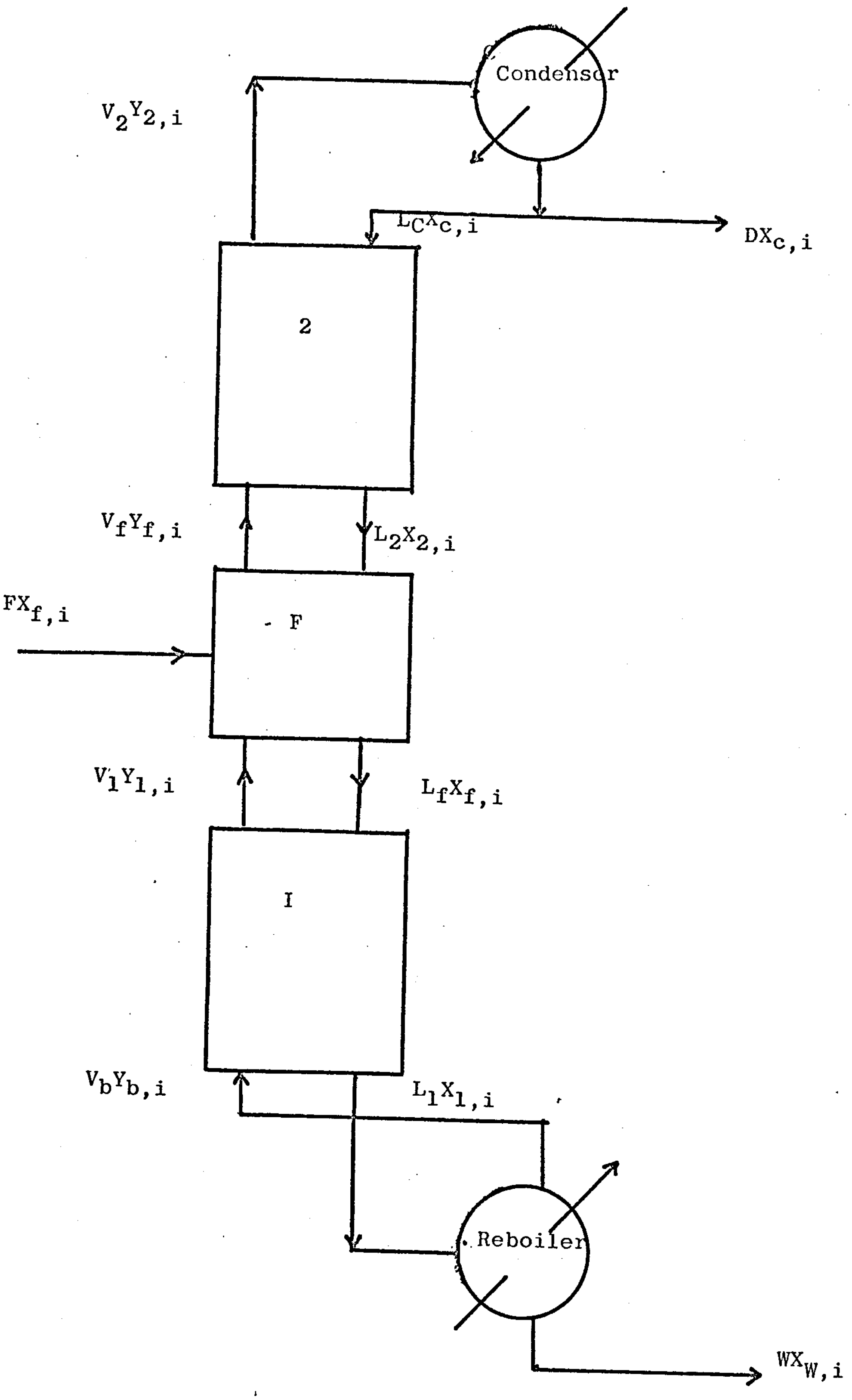


Fig 2. A DISTILLATION COLUMN ACCORDING TO THE SECTION CONCEPT.

The reader will notice that equation (2) is identical in form with the equation that is normally used for mass transfer

$$N = K (y^* - y)$$

There are, however, fundamental differences between equation (2) and the conventional mass transfer equation. In deriving the conventional equation, the coefficient K is related to the diffusivity of the components being transferred. The coefficient in equation (2), however, is not related directly to the physical properties of the component being transferred. The coefficient, $J_{n,i}$, is a parameter that describes the degree of separation occuring in a section and is an emperically determined factor.

Using this idea for the rate of mass transfer in the section, Reynolds developed a set of differential equations for the transient behaviour of the liquid and vapour streams leaving the section. In developing the equations, Reynolds made two major assumptions. The first of these assumptions was that $J_{n,i}$ remained constant for small changes of column conditions and the second was that of constant molal overflow throughout the section. After developing the model, Reynolds attempted to prove the model by comparing the values predicted with the model with experimental data, but was unable to obtain good agreement.

In the time since Reynolds completed his work using the lumped parameter model, the research in distillation column dynamics has followed two distinctly different paths. One path has been toward the investigation of the use of lumped parameter models. The other path has been toward the use of increasingly more complex models.

In the direction of the lumped parameter models, Osborne (20) has shown that the model proposed by Reynolds could be used to reproduce the transient behaviour of a column. Murrill (19) has shown experimentally that the transient behaviour of the composition of the liquid leaving a tray can be accurately represented by an equation of the form

$$x(t) = x_\infty \left[1 - e^{-(t/T)} \right] + x_o \, e^{-(t/T)} \qquad (3)$$

Finally, Moczek, et al. (17) have shown theoretically that the transient behaviour of the composition of the products from a distillation column can be represented by a simple method using a dead time and two time constants.

In the opposite direction, i.e. toward the use of increasingly more complex models, Huckaba et al. (11) have shown that by using plate efficiencies and continuous heat balancing the unsteady state behaviour of the composition of the distillation column products can be accurately represented. The model that they used is based on the plate concept and is restricted to binary systems.

Waggoner and Holland (35) developed a theoretical model for the transient behaviour of the multicomponent distillation column. They assumed plate efficiencies were known, and used an external material balance to force the column into material balance at the final steady state.

Following the trend towards increasingly more complex models, Tetlow, Groves and Holland (32) proposed a method for estimating transient plate efficiencies in a distillation column. Using this method for estimating efficiencies, the same authors (33) presented a transient model in which they considered the hydrodynamics on each tray in the column. They proposed that the liquid on each tray could be represented by a combination of plug flow, ideal mixing and bypassing. Independently Duffin and Gamer (9) developed a mathematical model in which they used the FrancisWeir formula to determine the holdup of each tray. Neither Holland, et al, nor Duffin and Gamer presented any experimental data to prove their proposed model.

A great deal of attention is being devoted to improvement of generalised stage models for rigorous, plate-to-plate, multi-component, continuous distillation of ideal and non-ideal systems, assuming implementation by a computer.

Tierney and Bruno (41) reported on use of the Newton-Raphson iteration method. Billingsley (42) demonstrated the mathematical basis for the Holland θ method of convergence, as well as introducing techniques based on Jacobian matrices. Petryschuk and Johnson (45) compared the θ and block relaxation methods for convergence. Tri-diagnol matrices were introduced by Wang and Henke (46). Wilhelm (47) developed an analytical solution to the differential equations describing open distillation of ideal mixtures. Takamatsu and Tosaka (48) proved that plate-column models can be rigorously employed in packed column applications, provided the proper physical model transformations are made. A number of dynamic analyses of distillation columns were repeated.

Wood (49) studied the theoretical frequency response of multi-component distillation columns followed imposed disturbances.

He found out that under some conditions the transient responses for a multi-component can be quite unlike those obtained under similar conditions from binary mixtures.

CHAPTER 4

STEADY STATE MODEL

4.1 INTRODUCTION

The program is designed for a distillation system using a total condenser. The nomenclature used in Fortran listing has been given in Appendix (A1).

The system under investigation being non-ideal, it was necessary to recognise the effect of composition on the equilibrum relation, which can be expressed by means of activity coefficient as follows:

$$(k)\ \text{modified} = \gamma\ (k)\ \text{ideal}$$

where the values of gamma (activity coefficient) are determined by a three suffix Margles equation for multi-component systems. The γ values are determined in subroutine - ACTO - and are stored in a two dimensional array for use by the main program. The γ values are also made use of in bubble point calculation. It should be noted that only mass balance and no energy balance has been programmed

4.2 PROPOSED MATHEMATICAL MODEL FOR NON-IDEAL, STEADY STATE DISTILLATION IN A PLATE COLUMN

The extensive use of fractionating columns, which often determine the quality of the final products, in the chemical industry justifies the interest of investigators in search for new calculation methods and improvement of the existing ones. Mathematical analog methods are of special significance in this respect, as they allow comprehensive studies of a given process for determination of the most effective means of economic production, even at the planning stage.

The following ASSUMPTIONS are made in the present case for description of the steady state in operation of a frationating column:

1) the column operates adiabatically;

2) the molar flows of liquid and vapor are constant along the column;

3) there is no entrainment of liquid from the plates with the vapour;

4) complete mixing of the liquid occurs on the plates.

Figure 1 is a schematic representation flows in a frationating column, with the plates numbered from bottom to top.

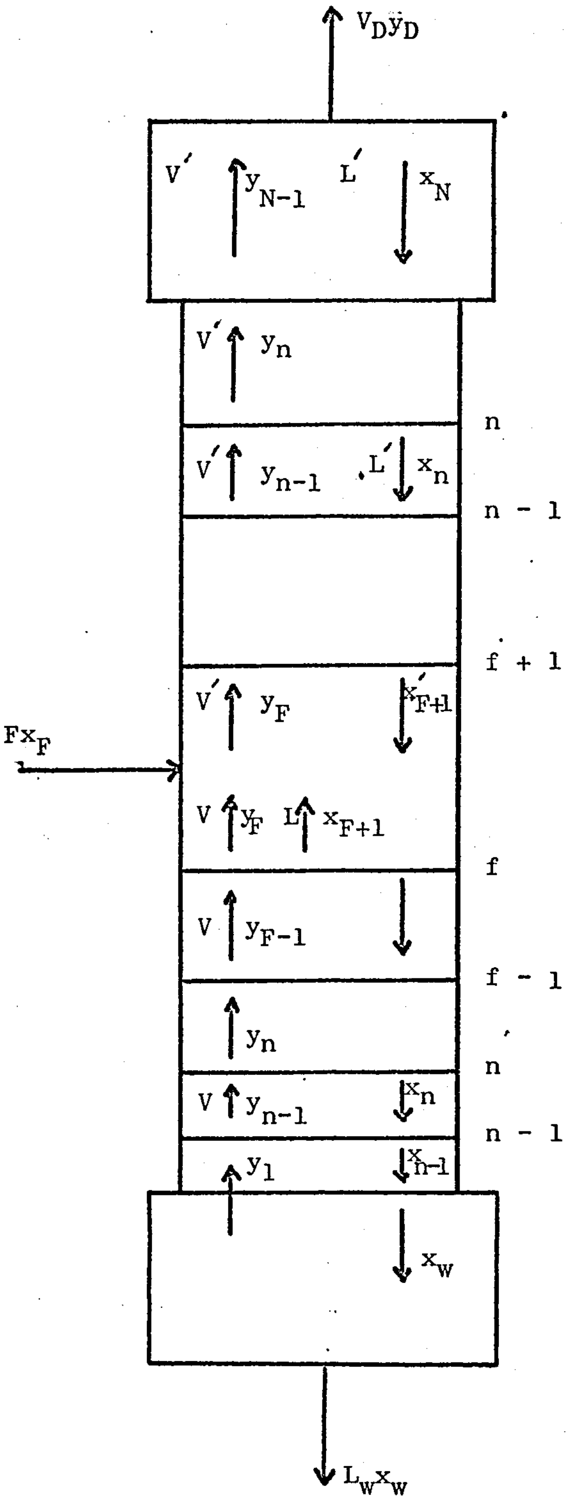


Fig (1) Schematic Diagram of Flows in
a Fractionating Column

The overall material balance equation for the column is

$$L_F = L_W + V_D \tag{1}$$

The equation for the enriching section is

$$L^i = V + L_W - L_F \tag{2}$$

and for the stripping section

$$L = V + L_W \tag{3}$$

where

L = liquid rate.

V = vapour rate.

F, D and W = Feed, Distillate and bottoms respectively.

The material balance of the column for component i is

$$L_F \; x_{Fi} = L_W \, x_{Wi} + V_D \, y_{Di} \, , \quad i = 1, 2, \ldots\ldots k \tag{4}$$

For any plate in the enriching section

$$L^1 x_{ni} = V y_{n-1,i} + L_W x_{ni} - L_F x_{Fi}, \; f + 1 \leqslant n \leqslant N, \; i = 1, 2 \ldots\ldots k \tag{5}$$

For the stripping section

$$L x_{ni} = V_{yn-1,i} + L_W x_{Wi}, \; 2 \leqslant n \leqslant f, \; i = 1, 2, \ldots\ldots\ldots k \tag{6}$$

and for the feed plate

$$y'_{f,i} = \frac{1}{V'}\left(Vy_{fi} + V_F\, y_{Fi}\right), \quad n = f, \; i = 1,2.....k \tag{7}$$

where,

X_{ni} = conc. of comp. i in the liquid flowing down from plate n,

Y_{ni} = conc. of comp. i in the vapor leaving plate n;

X_{Fi} = conc. of comp. i in the feed;

n = plate index;

N = indicates that the given quantity relates to the condenser;

f = number of feed plate;

V_F = content of vapor phase in the feed.

If it is assumed that the still operates as a partial boiler and a total condenser is used, we obtain,

$$(V + L_W)\, X_{2i} - (L_W - VK_i)\, x_{1i} = 0, \quad i = 1,2.........k \tag{8}$$

$$y_{Ni} = x_{Ni}\,, \quad i = 1,2........k \tag{9}$$

where Ki is the index referring to the particular component.

The various equations used in our model for predicting the vapor comp. leaving any plate are as follows:

$$\sum_{n=1}^{N} x_{ni} = 1,\ i = 1, 2 \ldots\ldots\ldots k \tag{10}$$

$$\sum_{n=1}^{N} y_{ni} = 1,\ i = 1, 2 \ldots\ldots\ldots k \tag{11}$$

$$\pi \left(\sum_{n=1}^{N} y_{ni} \right) = 760 \tag{12}$$

where π = vapor pressure

Also $$y_{ni} = \frac{p^{o}_{ni} x_{ni}}{P_i \frac{\Sigma P_n x_n}{Pi}} \tag{13}$$

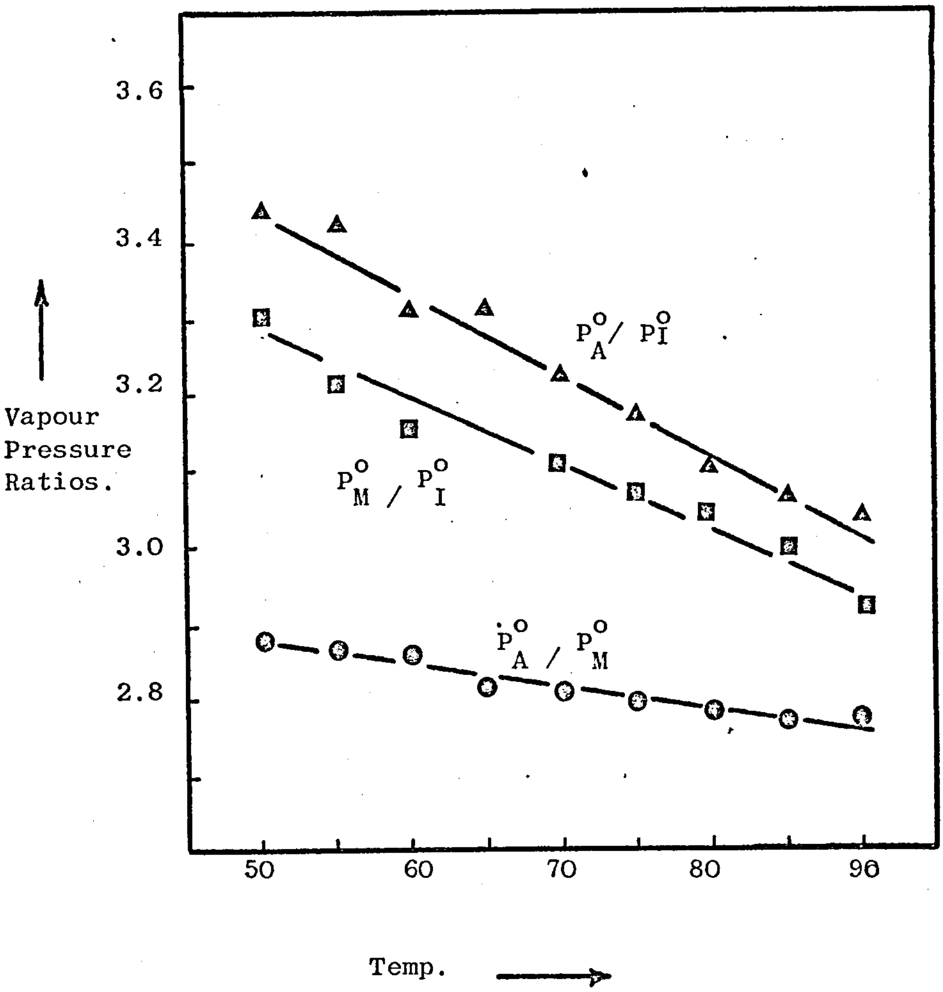
$$= \frac{P^{o}_{n} x_{ni}}{\pi} \tag{14}$$

$$= \frac{\gamma_{ni} P^{o}_{ni} x_{ni}}{\pi} \text{ (for non ideal mixtures)} \tag{15}$$

where γ_{ni} = activity coeff

P^{o}_{ni} = Partial pressure

$$P^{o} = M t + C \tag{16}$$


3.6
3.4
3.2
3.0
2.8
Vapour Pressure Ratios.
P^o_A / P^o_I
P^o_M / P^o_I
P^o_A / P^o_M
50
60
70
80
90
Temp.

combining 14, 11 and 16, we get

$$\{ (\Sigma (\gamma_{ni} M_{ni} x_{ni}^{k}) t + \Sigma (\gamma_{ni} C_{ni} x_{ni}^{k}) \} = \pi \qquad (17)$$

or

$$t = 760 - \frac{\Sigma (\gamma_{ni} C_{ni} x_{ni}^{k})}{\Sigma (\gamma_{ni} M_{ni} x_{ni}^{k})} \qquad (18)$$

Rewriting eq. 15, using 16, the vapor composition can be calculated if the liquid composition, the activity coefficients and the values of constants M and C over the workable temperature range for the particular mixture are known.

Hence the final equation

$$y_{ni}^{k} = \frac{\gamma_{ni} x_{ni}^{k} (M_1 t + C_1)}{\pi} \qquad (19)$$

Putting the value of t from equation 18, we get

$$y_{ni}^{k} = \gamma_{ni} x_{ni}^{k} \left(M_1 \frac{(760 - \Sigma (\gamma_{ni} x_{ni}^{k} C_{ni})}{\Sigma(\gamma_{ni} x_{ni}^{k} M_{ni})} + C_1\right) \qquad (20)$$

TEMP.	M_1	C_1	M_2	C_2	M_3	C_3
50	23.5	609.1	19.64	417.1	9.96	177.4
55	26.96	726.6	23.4	515.3	12.2	227.2
60	30.72	861.4	27.58	632.3	14.96	288.3
65	35.2	1015	32.4	770.2	18.1	363.1
70	39.4	1191	37.76	932.2	21.8	453.6
75	44.6	1388	44	1121	26.1	562.6
80	50	1611	50.4	1341	30.98	693.1
85	55.6	1961	58.2	1593	36.6	848.0

Values of M and C constants.

The activity coefficient can be calculated by making use of the morgules equation for Ternery mixture.

$$\ln \gamma_1 = x_2^2 \left[A_{12} + 2_{x1}(A_{21} - A_{12})\right] + x_3^2\left[A_{13} + 2_{x1}(A_{31} - A_{13})\right] +$$

$$+ x_2\, x_3 \Big[\tfrac{1}{2}(A_{21} + A_{12} + A_{31} + A_{13} - A_{23} - A_{32}) + \qquad (21)$$

$$+ x_1 \quad (A_{21} - A_{12} + A_{31} - A_{13}) + (x_2 - x_3)(A_{23} A_{32}) \Big]$$

The rotation of the coefficient in the above equation to find out the other two activity coeff. would be as follows:

$$\begin{array}{ccc} 1 & 2 & 3 \\ 2 & 3 & 1 \\ 3 & 1 & 2 \end{array} \qquad (22)$$

After having calculated the composition of the vapor leaving any plate, we come to finding the composition of the equilibrium ratio on the pate, which is given by the solution of the system of equations.

$$y_{ni}^{*} = K_i x_{ni}$$

$$\sum_{i=1}^{k} y_{n\,i}^{*} = 1 \qquad (23)$$

where K are phase equilibrium constants and can be represented by

$$K_{ni} = \mathrm{EXP}\left(A_{ni} - \frac{B_{ni}}{0.555T+212.3} + C_{ni}(0.555T+212.3)-5.487\right) \qquad (24)$$

The calculation comprises two independent problems. The first involves calculation of the concentration distribution between the plates in the column, and the second requires determination of the compositions of the bottoms and distillate satisfying the overall material balance equations for each component of the original mixture. Each of these problems present its own specific calculation difficulties. The "plate to plate" method is suitable for calculation of the composition distribution. The general form of the system of equations 5, 6, 10 to 22 leads to the conclusion that the preferable direction of the calculation is from the boiler to the condenser, as in calculations from condenser to the boiler, it becomes necessary to solve the systems of equations 5, 6 and 10 to 22 for the variables in the R.H.S. This could result in complication of the calculation scheme, an increase in the required computer memory capacity, and could lengthen the computer time. The advantage of "plate to plate" method is that these calculations can be performed for a virtually unlimited number of plates with a minimum computer memory capacity. This scheme could exhibit instability because of the fact that for a given precision in determination of the composition of the bottoms in calculations in an upward direction, the precision in the determinations of the compositions of the more volatile component on the plates decreases with increasing plate number. The instability of the computation scheme in the plate to plate method has been seen to become especially pronounced in calculations for conditions such that the column contains zones of nominally constant concentrations (regions of very low separation power); the instability is not eliminated in such cases even by increase of the precision in the calculations.

4.3 BREAKDOWN OF THE STEPS

The following functions are performed in the first section of the program.

1. Reads input data and writes data on line printer before starting calculation.

2. Sets various counters to zero.

3. Calculates stage dependent indexes for later use in DOloops and other places.

4. Calculates total feed of each component for subsequent use in program.

5. Fills the GENX, GENY, and GAML arrays with starting values needed for the equations involving mass balances.

The statements from that just prior to 13 to and including statement 24 decide whether the feed to the system is all liquid, all vapour or both liquid and vapour. Depending on the feed state, a liquid and/or vapour composition is calculated and stored in the composition arrays. Activity coefficients are all set to 1.0 to start the calculation.

6. Calculation of Plate compositions:

   Normally the equilibruim constant, K, for a component is a function of composition. In many cases, including the present investigation, due to non ideality, the equilibrium constants must also be corrected for composition. The competing effects on the composition map of first temperature and second composition dependent activity coefficients often result in severe oscillation of the composition profile from iteration to iteration, with little or no tendency to converge. Hence an iterative scheme based on a method of balance, which approaches convergence in an asymptotic fashion but with less tendency to oscillate, becomes necessary.

The method proposed by Hanson, et. al, is one derived from the basic differential equation of the system, and can be called the method of successive flashes. The unsteady state equation for any component i on any plate n would be:

$$H_{Vn} \frac{dyn}{dt} + H_{L\,n} \frac{dxn}{dt} = V_{n-1}\, y_{n-1} + L_{n+1}\, x_{n+1} - (V_n y_n + L_n x_n)$$

where

H_{Vn} = vapour holdup on plate n, assumed constant,

H_{Ln} = liquid holdup on plate n, assumed constant,

t = time

If $Y_n = K x_n$ and assumption made that H_{Vn} is much smaller than H_{Ln}, then for any component one has

$$H_{L_n} \left(\frac{dxn}{dt}\right) = V_{n-1}\, K_{n-1}\, x_{n-1} + L_{n+1}\, x_{n+1} - x_n\, (V_n K_n + L_n)$$

Substituting the definition

$$\tau = t/H_{Ln}$$

$$d\tau = dt/H_{Ln}$$

results in

$$\frac{dxn}{d\tau} = V_{n-1} K_{n-1} x_{n-1} + L_{n+1} x_{n+1} - x_n (V_n K_n + L_n)$$

If $\alpha = V_{n-1} K_{n-1} x_{n-1} + L_{n+1} x_{n+1}$

and $\beta = (V_n K_n + L_n)$

Putting these terms in the above equation and separating variables leads to

$$d\tau = \frac{dx_n}{\alpha - x_n \beta}$$

An iterative type of solution can be obtained by intergerating from the point x_n at iteration r to the point x_n at iteration r + 1, with the corresponding finite difference in τ being $\Delta\tau$. The assumption needed to carry out this integeration is that α and B are constant across the iteration. The resulting equation is:

$$\frac{\alpha - (x.n)_{r+1}\beta}{\alpha - (xn)_r} \approx \exp(-\beta\Delta\tau)$$

which can be rearranged as follows:

$$(x n)_{r+1} \approx (x.n)_r \exp(G\psi) + \frac{\alpha}{\beta}(1 - \exp(-\psi))$$

where $\psi = \beta\Delta\tau$

Since steady-state values of the composition were the object of the calculation, it was desirable to use large values of Ψ to obtain rapid convergence on the steady state composition.

If it is arbitrarily assumed that the values of Ψ are chosen so that exp $(-\Psi) = 0$ for each iteration, then the very simple basic expression for the r + 1st value of (χn) becomes.

$$(\chi n)_{r+1} \approx \frac{\alpha}{B} = \frac{V_{n-1} K_{n-1} x_{n-1} + L_{n+1} x_{n+1}}{V_n K_n + L_n}$$

This equation has the exact form of the well-known flash equations, so that repeated application of this equation across iterations leads to the naming of this method as the method of successive flashes.

In the use of method, it is necessary to assume all stage temperatures and set all vapour and liquid flows. Also the starting composition on every stage must be assumed. It is not necessary to have accurate compositions, since the steady-state solution is independent of any starting compositions. A single way of starting is to fill every stage with feed liquid at its bubble point while the vapour is in equilibrium.

4.4 CORRECTION OF PRODUCT COMPOSITIONS

The over-all material balance for any component in a process yielding two products can be written as:

$$X^d = \frac{F X_F}{b\,({}^{xb}/xd\,) + d}$$

If the distribution ratios, xb/xd, have been calculated for all components through calculation of the composition map, this equation can be used to determine a more accurate estimate of the product compositions. From the nature of the calculation, it can be seen that all of the distribution ratios for the components will be in error in the same direction. As a first assumption it can be said that the distribution ratios are all in error by the same factor. This factor can be found by altering all of the distribution ratios by a factor, ϕ, such that when the altered component distribution ratios are used in the above equation, the calculated values of xd sumto unity. Thus:

$$(xd)_{corr} = \frac{F.X}{b\,(\frac{xb}{xd})\,\phi + d}$$

and

$$(xb)_{corr} = (\frac{xb}{xd})\,\phi\,(xd)\,\text{corr.}$$

Thus, even though the temperature map is quite different from the correct temperature map for the given flow map, and hence the calculated product compositions do not sum to unity, the corrected compositions obtained from the above equation are usually quite close to the correct composition for the product amounts set.

In the same way these equations can be used to predict the product compositions which would result from a change in the bulk split, i.e., a change in d and b. If the set of distribution ratios is known for a given bulk split the product compositions can be obtained for any other bulk split by using the new values of b and d and determining the value of ϕ such that $\sum (xd)\ \text{corr} = 1$.

If it is desired to find the total amounts of the products which will yield a certain ratio bx_b/dx_d for a particular component, the similar equation.

$$(dx_d)\ \text{corr} = \frac{Fx_F}{\dfrac{bx_b}{dx_d}\ \phi + 1}$$

can be used, where now

$$\phi = \frac{\left(\dfrac{bxb}{dxd}\right) \text{ desired for a certain component}}{\left(\dfrac{bxb}{dxd}\right) \text{ calculated for the same component}}$$

The corrected value of d will then be

$$(d)_{\text{corr}} = \sum (dx_d)_{\text{corr.}}$$

4.5 CORRECTION OF STAGE COMPOSITIONS

In the iterative scheme of column calculation used for this investigation, the total amount of top and bottom products is held throughout the calculation. Thus, it is desirable to calculate a corrected set of compositions for the set amounts of top and bottom product. The corrected product compositions can then be used to correct the compositions on the stages before determining a new temperature map, and convergence on the correct temperatures considerably speeded.

Each component is considered separately. The mole fraction of all components in either product will, of course, be corrected in the same direction. If, for example, the correction is such that $(x_d)_{corr}$ is greater than $(x_d)_{calc}$ $(\phi < 1)$, the temperature map was predominantly low. At the same time, $(x_b)_{corr}$ will be lower than $(x_b)_{calc}$.

It is logical then to reduce the mole fraction of the component in the stages below the feed stage and raise the mole fraction of the component in the stages above the feed stage, so as to follow the corrected product mole fraction. It has been found that a simple ratio correction such as:

$$(x_n)_{corr} = (x_n)_{calc.} \frac{(x_b)_{corr}}{(x_b)_{calc}}$$

where n is any plate below the feed, is in general over correcting by a considerable amount. Perhaps the most logical correction would be to hold the shape of the gradient of mole fraction anchored at the feed stage, with no change in the fraction, but yielding a larger and larger degree of correction as the end stage from which the product is drawn is approached.

7. This small section of program is essentially self-explanatory as written in the FORTRAN language. It deals with Product amounts, Recovery Fractions and Summations.

8. The results are output when the convergences takes place. The final exit from this section is always to statement 1000 where the program is directed to read another set of data and proceed with the next problem.

9. All vapour and liquid compositions are normalized. Following this, control is transferred to subroutine ACTCO where a whole new array of γ values is calculated based on the current values of composition at every stage. The new γ values are calculated a stage at a time and are then stored in the GAML array.

SUB ROUTINE - ACTO

This a subroutine for supplying the main program with activity coefficients calculated using the following three-suffix Margules equation for component I in a mixture of L components

$$\gamma(I) = \exp\left[2x_I \sum_{J=1}^{L} x_J A_{JI}\right] + \left[\sum_{I=1}^{L} (X_I)^2 A_{IJ}\right] + \left[\sum_{\substack{J=1 \\ I\neq J \\ I\neq K \\ J<K}}^{L} \sum_{K=1}^{L} X_J X_K A^*_{IJK}\right]$$

$$- \left[2 \sum_{I=1}^{L} (X_I)^2 \sum_{J=1}^{L} X_J A_{IJ}\right] - 2\left[\sum_{\substack{I=1 \\ I\neq J \\ I\neq K \\ J<K}}^{L} \sum_{J=2}^{L} \sum_{K=3}^{L} X_I X_J X_K A^*_{IJK}\right]$$

The constants used are the one's reported by Pike ([illegible]) and are as follows:

	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}
Acetone/Methanol	0.2740	0.2468				
Acetone/IPA			0.2572	0.2343		
Methanol/IPA					-0.0305	-0.0469

The ACTO subroutine evaluates the γ values and stores them in an erasable vector, GAMMA (I), for use by the main program when control is returned to it. The information that ACTCO gets from the main program consists of stage compositions which are stored in the erasable vector QUIDX (I) at the time of transfer to the subroutine and the number of actual components, L, used.

10. Correction of temperatures. At this point the new γ values just obtained are used in the BUBPTG subroutine to correct the temperature map of the system.

11. Following this, control is returned to the "Calculation of Plate compositions" section.

SUBROUTINES - BUBT AND DEWPT

Both of these subroutines operate in essentially the same way. The data needed by the subroutines are the existing stage temperature (an approximate first temperature guess), the number of components, and the composition of the liquid or vapour to be used in the calculation.

Using the composition and existing temperature, one of the following sums is formed.

$$\sum y = \sum Kx \qquad \text{for bubble point}$$

$$\sum x = \sum y/K \qquad \text{for dew point}$$

and compared to 1. If it is not arbitrarily close (BPERR) to 1, an extrapolation process is started and finds that temperature which makes the above sums fall in the range of 1 plus or minus the allowable error. To start the process, a second point is needed and is arbitarily calculated at the existing temperature plus 10 deg.

CHAPTER 5

DYNAMIC MODEL

THE PREDICTION OF THE DYNAMIC PERFORMANCE OF A MULTI-COMPONENT DISTILLATION COLUMN

5.1 Introduction

A mathematical model of a 10 plate distillation column separating a multi-component mixture is described. This model takes the form of a set of non-linear ordinary differential equations in which the component liquid concentrations are the dependent variables and time is the independent variable.

5.2 A general discussion of the variables which describe the dynamic behaviour of a plate distillation column

It can be assumed that a plate distillation column is completely described quantitatively by the values of the following variables in the reboiler, and in the condenser, and on each plate.

1) the average molar fraction of each component in the liquid hold-up;

2) the average molar fraction of each component in the vapour hold-up;

3) the liquid molar hold-up;

4) the vapour molar hold-up;

5) the average molar enthalpy of the liquid hold-up;

6) the average molar enthalpy of the vapour hold-up;

7) the heat content of the dry plate;

8) the molar fraction of each component in the feed;

9) the molar flow rate of the feed;

10) the enthalpy of the feed;

11) the molar flow rates of the products;

12) the rate of heat transfer to the reboiler and from the condenser.

The externally applied control variables 8 to 12 are assumed to be given fixed functions of the independent variable time for the duration of the distillation operation. The state variables 1 to 7 are functions of time over the operating period and are such that they must be solutions of non-linear ordinary differential equations with time as the independent variable. These equations result from heat and material balances on the plates. The derivatives of the state variables 1 to 7 with respect to time are functions of the variables 1 to 12 and the compositions, flow rates, and enthalpies of the liquid and vapour streams leaving each plate and the heat transfer from each plate to the surroundings. It is assumed that these are given as algebraic functions of the variables 1 to 12 at each instant of time. The values of the variables 1 to 12 which describe the Column are all given at the start of the operating period. The time trajectories of the state variables 1 to 7 can be determined by integrating the differential equations with respect to time with the given initial conditions. In practice a large number of plates are often required to achieve a given separation. This, together with the vapour liquid equilibrium relationships, gives rise to a very large set of non-linear differential equations.

Some assumptions were made in order to simplify the model. These assumptions are as follows :

1) The vapour hold-up is zero. This is a reasonable assumption since the vapour hold-up is usually small.

2) There is no heat transfer from the column to its surroundings.

3) The temperature dynamics on a plate are neglected by assuming that the vapour and liquid hold-up on the dry plate have no heat capacity. The temperature of the plate and its contents are given at each instant of time by a boiling point calculation of the liquid on the plate. That is to say that this temperature is a function of composition alone. This is a reasonable assumption except for periods immediately following large changes in the boil up rate.

4) The liquid hydrodynamics are neglected by assuming that the liquid hold-ups on each plate, in the reboiler, and in the condenser are constant.

5) The liquid hold-up is perfectly mixed so that the composition of the liquid leaving a plate is the same as the average composition of the liquid hold-up on that plate.

6) The total vapour pressure on a plate is constant and is therefore independent of the liquid and vapour flow rates to and from the plates.

7) The vapour and liquid phases on each plate are assumed to be in equilibrium. This means that the Murphee plate efficiency is 100%.

Assumptions 1, 2 and 3 are relatively unimportant. Assumptions 4, 5, 6 and 7 result in large differences between the complete model and the simplified model. It is reasonable to neglect plate hydrodynamics except for periods immediately following large changes in the controls since the time constant for the flow response is much lower than that for the concentration response. The temperature on each plate and the composition of the vapour leaving a plate are functions of the composition of the liquid leaving that plate only by a boiling point calculation. This results from assumptions 5, 6 and 7. Since the boiling point varies strongly with the total pressure the assumption that this is independent of the liquid and vapour flow rates is very unrealistic. The Murphee plate efficiency is usually significantly less than 100% in practice. Since it varies strongly with the liquid and vapour flow rates, assumption 7 will effect any kind of control scheme which may be determined by the simplified model.

The simplified model is described in detail in the next section.

5.3 Description of the Mathematical Model of the Distillation Column

The dynamic performance of a plate distillation column can be solved by integrating a set of non-linear ordinary differential equations over the required operating time period. The solution is completely determined by:

i) the conditions in the column at the start of the operating period,

ii) the external inputs to the column given as a function of time over the operating period, and the

iii) differential equations describing the column.

The distillation column is made of C plates, a general plate n of which is shown in Fig. 1. The reboiler is taken to be plate O and the condenser is taken to be plate C (11th). The mixture to be separated is made up of k components. Namely, Acetone, Methanol and Isopropanol. It has already been mentioned that this is a non-ideal mixture and all the steady state concentrations have been corrected taking the activity coefficient into consideration.

It follows from the definition of mole fractions, that:

$$\left.\begin{aligned} \sum_{i=1}^{k} x_{i,n} &= 1 \\ \sum_{i=1}^{k} y_{i,n} &= 1 \end{aligned}\right\} \quad \begin{aligned} i &= 1, \ldots\ldots, k \\ n &= 1, \ldots\ldots, c \ , \end{aligned}$$

THEORY

5.4 Derivation of Differential Equations

Figure 1 shows the conditions inside a plate-type distillation column separating a ternary mixture. A material balance of the more volatile component around the nth plate yields:

$$\frac{d}{dt}\left(H_n X''_n + H_n Y''_n\right) = L_{n+1} X_{i,n+1} - L_{i,n} X_{i,n} - V_n X_{i,n} \qquad (1)$$

$$+ V_{n-1} Y_{i,n-1} \qquad ; \; i = 1, \ldots\ldots, k \quad n = 1, \ldots\ldots, c$$

where L_n, L_{n+1} = Liquid flow rate from the nth plate and the n+1th plate respectively in mols/hr.

V_n, V_{n-1} = Vapour flow rate from the nth plate and the n-1th plate respectively in mols/hr.

H_n = Liquid hold-up on the nth plate in mols.

h_n = Vapour hold-up on the nth plate in mols.

X_n, X_{n+1} = Composition of the more volatile component in L_n and L_{n+1} respectively in mol fraction.

Y_n, Y_{n-1} = Composition of the more volatile component in V_n and V_{n-1} respectively in mol fraction.

X''_n, Y''_n = Composition of the more volatile component in the liquid hold-up and in the vapour hold-up respectively in mol fraction; these are equal to X_n and Y_n respectively if perfect mixing is assumed.

t = is the independent variable and denotes the time from the start of the operating period.

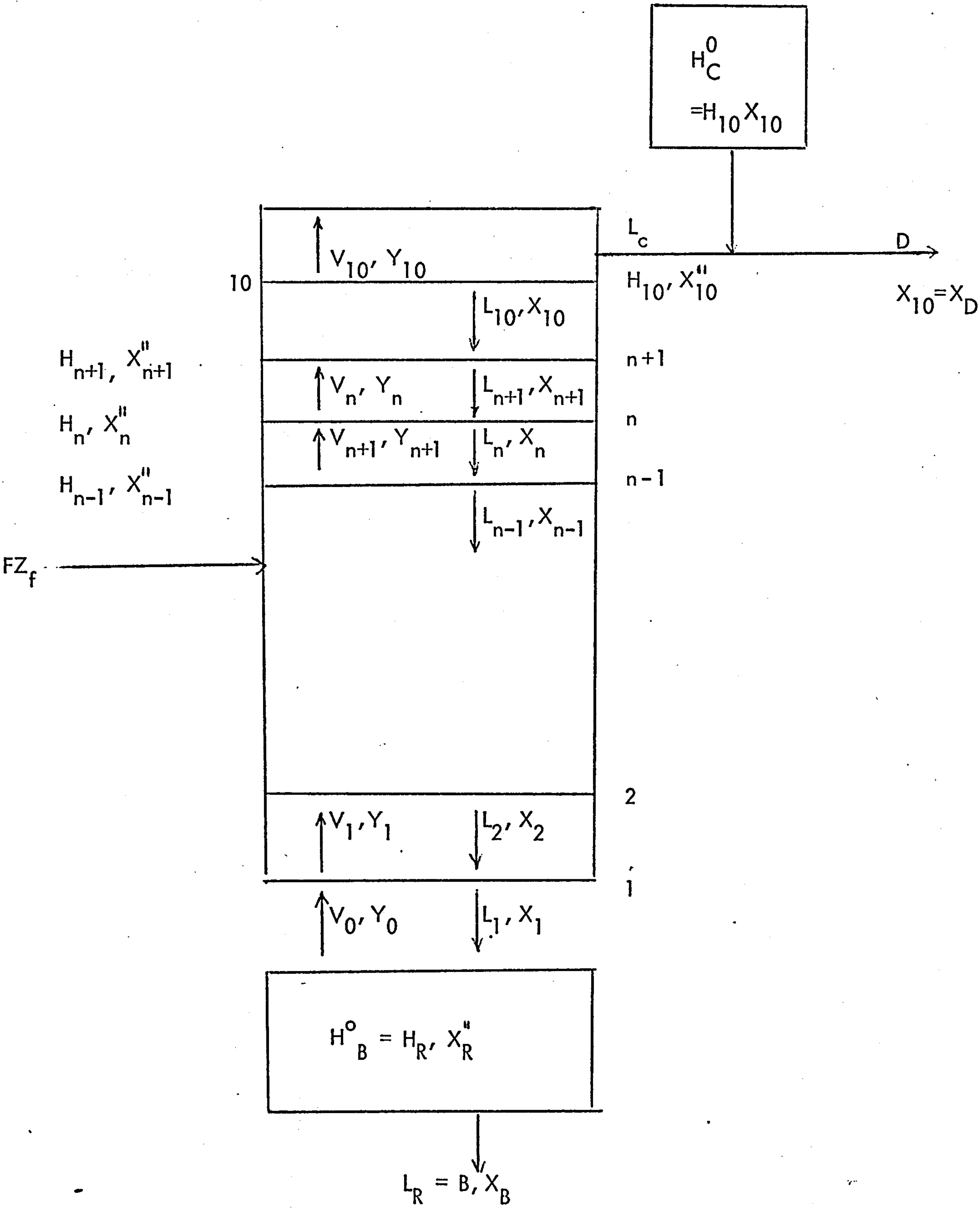

H_C^0
$=H_{10}X_{10}$
L_c
D
V_{10}, Y_{10}
10
H_{10}, X''_{10}
$X_{10}=X_D$
L_{10}, X_{10}
H_{n+1}, X''_{n+1}
n+1
V_n, Y_n
L_{n+1}, X_{n+1}
H_n, X''_n
n
V_{n+1}, Y_{n+1}
L_n, X_n
H_{n-1}, X''_{n-1}
n-1
L_{n-1}, X_{n-1}
FZ_f
2
V_1, Y_1
L_2, X_2
1
V_0, Y_0
L_1, X_1
$H^o_B = H_R, X''_R$
$L_R = B, X_B$

Figure 1

A total material balance gives:

$$\frac{d}{dt}(H_n + h_n) = L_{n+1} - L_n - V_n + V_{n-1}; \quad n=1,\ldots,c \tag{2}$$

Similarly, for the condenser:

$$\frac{d}{dt}(H_c X_c + h_c y_c) = V_{10} Y_{10} - L_c X_c - DX_c \tag{3}$$

$$\frac{d}{dt}(H_c + h_c) = V_{10} - L_c - D \tag{4}$$

for the feed plate:

$$\frac{d}{dt}(H_f X_f'' + h_f y_f'') = L_{f+1} X_{f+1} - L_f X_f - V_f Y_f + V_{f-1} Y_{f-1} + FZ_f \tag{5}$$

$$\frac{d}{dt}(H_f + h_f) = L_{f+1} - L_f - V_f + V_{f-1} \tag{6}$$

where F is the feed rate in mols/hr, and Zf is the feed composition of the more volatile component in mol fraction.

for the reboiler:

$$\frac{d}{dt}(H_R X_R'' + h_R y_R'') = L_{R+1} X_1 - L_R X_R - V_0 Y_0 \tag{7}$$

$$\frac{d}{dt}(H_R + h_R) = L_{R+1} - L_R - V_0 \tag{8}$$

To make the equations amenable to numerical solution and also for the sake of simplicity in programming, the following assumptions are adopted for the problem under consideration.

1) Negligible vapour hold-ups; i.e. $h_{n=0}$ for all n.

2) Complete liquid mixing on each plate; $X_n'' = X_n$.

3) Ideal plates; i.e. the vapour leaving a plate is in equilibrium with the liquid leaving that plate.

4) Constant relative volatility; i.e.

$$Y_n^* = \frac{\alpha X_n}{1+(\alpha-1)X_n} \qquad (9)$$

5) Constant condenser hold-up and constant reboiler hold-ups; i.e. $H_{10} = H_C^o$ = constant, and $H_R = H_B^o$ = constant, where H_C^o and H_B^o are the steady state liquid hold-up of the condenser and that of the reboiler respectively.

6) The variation of the liquid hold-up from the steady state liquid hold-up is proportional to the variation of the liquid flow rate from the steady state liquid flow rate for each plate except the condenser and the reboiler, i.e.

$$a\,(H_n - H_n^o) = L_n - L_n^o \quad \text{for } n \neq C \text{ or } R \qquad (10)$$

where a is a constant, and H_n^o and L_n^o are the steady state liquid hold-up and liquid flow rate respectively for the nth plate.

7) The plate heat and mass transfer efficiencies are 100%, so that the composition and temperature of the vapour leaving a plate are given directly by a steady state boiling point calculation on the liquid leaving the plate. It follows that:

$$Y_{i,n} = K_{i,n}\, x_{i,n} \quad ; \quad \begin{array}{l} i = 1,\ldots\ldots, k \\ n = 1,\ldots\ldots, c \end{array}$$

where the equilibrium constants $(K_{i,n})$ are functions of the liquid mole fractions on plate n only.

8) $V_{n-1} = V_n$ except at the feed plate; i.e.

$V_n = V_e$ = constant for $n \leq f$

$V_n = V_s$ = constant for $n > f$

Making use of the above assumptions and combining equation 3 with equation 4, equation 1 with equation 2, equation 5 with equation 6, and equation 7 with equation 8 field:

$$\frac{dX_c}{dt} = \frac{V_{10}}{H_{10}} Y_{i,10} - \left(\frac{L_{10+D}}{H_{10}}\right) X_{i,10}; \quad i = 1, \ldots\ldots, k \tag{11}$$

$$\frac{dX_n}{dt} = \frac{L_{n+1}}{H_n} X_{i,n+1} - \frac{L_{n+1}}{H_n} X_{i,n} - \frac{V_n}{H_n} Y_{i,n} + \frac{V_{n-1}}{H_n} Y_{i,n-1};$$

$$i = 1, \ldots\ldots, k$$
$$n = 10, \ldots\ldots, 1$$
$$n \neq f. \tag{12}$$

$$\frac{dX_f}{dt} = \frac{L_{f+1}}{H_f} X_{i,f+1} - \frac{L_{f+1} + F + V_{fr} - V_f}{H_f} X_{i,f}$$

$$+ \frac{V_{f-1}}{H_f} Y_{i,f-1} - \frac{V_f}{H_f} Y_{i,f} + \frac{F}{H_f} Z_f; \quad i = 1, \ldots\ldots, k \tag{13}$$

$$\frac{dX_R}{dt} = \frac{L_{R+1}}{L_R} X_{i,R+1} - \frac{V_R}{H_R} Y_{i,R} - \frac{L_R}{H_R} - X_{i,R}; \quad i = 1, \ldots\ldots, k \tag{14}$$

This set of equations can be written in the vector form:

$$\frac{d\vec{X}}{dt} = \vec{F} \tag{15}$$

where $\vec{X}$ and $\vec{F}$ are vectors.

5.5 Linearization

The system of non-linear differential equations derived above can be readily linearised by means of perturbation methods. Suppose that the distillation column is initially operating at a certain steady state. When the disturbances are small, all quantities can be assumed to be displaced from their steady state values by small amounts. Under these conditions, the instantaneous values of Z, X, H, L, Y, etc. can be expressed as:

$$
\begin{aligned}
Z_f &= Z_f^o + \Delta Z_f \\
X_n &= X_n^o + \Delta X_n \\
H_n &= H_n^o + \Delta H_n \qquad n = 1, 2 \ldots\ldots c \\
L_n &= L_n^o + \Delta L_n \\
Y_n &= L_n^o + \Delta Y_n
\end{aligned}
\tag{16}
$$

where ΔZ_f, ΔH_n, ΔX_n, ΔL_n, ΔY_n are small quantities. Substituting these expressions into equation 15 and ignoring all second order terms yields a set of linear first order ordinary differential equations with constant coefficients. These set of differential equations can be written in the form:

$$\frac{d\vec{X}}{dt} = \left[A\right] \vec{X} + \vec{B} \tag{17}$$

where $\left[A\right]$ is a Jacobian matrix whose elements a_{ij} can be obtained by the operation.

$$a_{ij} = \left(\frac{\partial F_i}{\partial X_j} \quad x_j = X_j^o \qquad \begin{aligned} i &= 1, \ldots\ldots, c \\ j &= i+1,\ i,\ i-1 \end{aligned} \tag{18}$$

The vector B is defined as:

$$\vec{B} = \vec{F} - \left[A\right] \vec{X} \tag{19}$$

In summary, the elements a_{ij} of the matrix $\left[A\right]$ are:

$$a_{11} = -(L_1^o + D^o)/H_1^o$$

$$a_{ii} = -(L^o_{i+1} + V_i^o P_i^o)/H_i^o \qquad i \neq f$$

$$a_{ff} = -\left[(L^o_{f+1} + F^o + V^o_{f-1} - V^o_f) + V_f^o P_f^o\right]/H_f^o$$

$$a_{ij} = -L^o_{i+1}/H_i^o \qquad i = 2,3,\ldots,c; \; j = i+1 \tag{20}$$

$$= V^o_{i-1} P^o_{i-1}/H_i^o \qquad i = 1,2,3,\ldots c-1; \; j = i-1$$

$$= 0 \qquad i = 1,2,3,\ldots c; \; j \leq i+2, \; j \geq i-2$$

where p_i^o is defined as

$$p_i^o = \left(\frac{\partial Y}{\partial X}\right) X_i^o = \frac{\alpha}{\left[1 + (\alpha - 1) X_i^o\right]^2} \tag{21}$$

The elements B_i of the column vector $\overrightarrow{B}$ are:

$$B_1 = \frac{V_2^o q_2^o}{H_1^o}$$

$$B_i = -\frac{V_i^o q_i^o + V^o_{i-1} q^o_{i-1}}{H_i^o} + \frac{(X^o_{i+1} - X_i^o)(L_{i+1} - L^o_{i+1})}{H_i^o}$$

$$i = 2, \ldots, c-1$$
$$i \neq f \tag{22}$$

$$B_f = - \frac{V_f^o q_f^o + V_{f-1}^o q_{f-1}^o + FZ + (X_{f+1}^o - X_f^o)(L_{f+1} - L_{f+1}^o)}{H_f^o}$$

$$B_R = - \frac{V_R^o q_R^o + (X_{R+1}^o - X_R^o)(L_{R+1} - L_{R+1}^o)}{H_R^o}$$

where

$$q_i^o = Y_i^o - \left(\frac{\partial Y}{\partial X}\right)_{X_i^o} X_i^o = \frac{\alpha(\alpha-1)(X_i^o)^2}{\left[1 + (\alpha-1)X_i^o\right]^2} \tag{23}$$

The set of non-linear differential equations, equation 15, can also be written in the form of equation 17. In this case the elements a_{ij} of the matrix $[A]$ and the elements B_i of the vector $\vec{B}$ can also be obtained from equation 18 and 19, respectively, provided instantaneous values of X_i, L_i, H_i, etc. instead of the steady state values are used. In other words, the elements a_{ij} of the matrix $[A]$ for the non-linear case are defined as:

$$a_{ij} = \left(\frac{\partial F_i}{\partial X_j}\right) X_i \tag{24}$$

5.6 Derivation of Forcing Vectors

5.6.1 Feed Change

If a step change is made in the feed, then the forcing vector are added only to the equations describing the feed plate, which is:

The $Lx_{n+1} + Vy_{n+1} - Lx_{n+2} - Vy_n + Fx_{f=0}$ (25)

as $y = Kx$ (26)

Hence the dynamic equation will become:

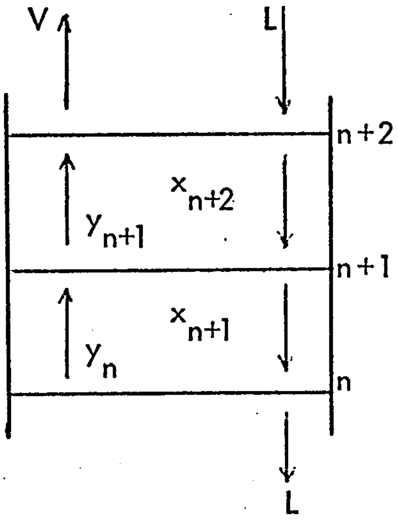
$$VKx_n - (L+VK)\,x_{n+1} + Lx_{n+2} + Fx_f = H\dot{x} \tag{28}$$

for a step change equation (28) will take the form:

$$VKx_n - (L+VK)\,x_{n+1} + Lx_{n+2} + F\Delta F(x_f + \Delta x_f) = H\dot{x} \tag{47}$$

5.6.2 Boil Up Change

a) For a plate



The steady state material balance for one component on plate n+1 is:

$$Lx_{n+1} + Vy_{n+1} - Lx_{n+2} - Vy_n = 0 \qquad (25)$$

Now $y = Kx$ (26)

∴ Equation (25) becomes:

$$VKx_n - (L+VK)\,x_{n+1} + Lx_{n+2} = 0 \qquad (27)$$

The dynamic equation is:

$$VKx_n - (L+VK)\,x_{n+1} + Lx_{n+2} = H\dot{x} \qquad (28)$$

For a step change in V and L at t = 0, equation (28) becomes:

$$(V+\Delta V)\,K\,(x_n+\Delta x_n) - \Big[(L+\Delta L)+(V+\Delta V)\,K\Big]$$

$$(x_{n+1}+\Delta x_{n+1}) + (L+\Delta L)(x_{n+2}+\Delta x_{n+2}) = H\dot{x} \qquad (29)$$

Expand equation (29) to get:

$$K\Big[Vx_n + V\Delta x_n + \Delta V x_n + \Delta V \Delta x_n\Big] - \Big[(L+VK)$$

$$(x_{n+1}+\Delta x_{n+1}) + (\Delta L + \Delta V.K)\,(x_{n+1}+\Delta x_{n+1})\Big]$$

$$+ (L+\Delta L)\,(x_{n+2}+\Delta x_{n+2}) = H\dot{x} \qquad (30)$$

Subtract (27) from equation (30):

$$VK\Delta x_n + K\Delta V x_n + K\Delta V\Delta x_n - (L+VK)\,\Delta x_{n+1}$$

$$+ (\Delta L + \Delta V.K)\,(x_{n+1}+\Delta x_{n+1}) + \Delta L x_{n+2}$$

$$+ (L+\Delta L)\,\Delta x_{n+2} = H\dot{x} \qquad (31)$$

Re-arrange equation (31):

$$(V + \Delta V)\, K\Delta x_n - \left[(L + \Delta L) + (V + \Delta V)\, K\right]$$

$$\Delta x_{n+1} + (L+\Delta L)\, \Delta x_{n+2} + \Delta VKx_n - (\Delta L+\Delta V.K)\, x_{n+1}$$

$$+ \Delta L.x_{n+2} \quad = \quad H\dot{x} \qquad (32)$$

For reboiler and the condenser the above equation (32) will not be valid, hence separate expressions for the forcing vectors have to be found for the two.

b) Reboiler

Steady state material balance around the reboiler section gives:

$$H\dot{x}_o = - Bx'_o - Vy'_o + (V + B)\, x'_1 \qquad (33)$$

For a step change in V and L, equation (33) becomes:

$$H\Delta\dot{x}_o = - B(x_o + \Delta x_o) - (V + \Delta V)\, (y_o + \Delta y_o)$$

$$+ \, (V + \Delta V + B)\, (x_1 + \Delta x_1) \qquad (34)$$

Subtracting (34) from (33):

$$H\dot{x}_o = - B\Delta x_o - (V + \Delta V)\, \Delta y_o + (V + \Delta V + B)\, \Delta x_1 \qquad (35)$$

Comparing it with $(- B_o\, x_o - Vy_o + (V+B)\, x_1)$ (36)

the forcing function is:

$$H\dot{x}_o = - \, \Delta Vy_o + \Delta Vx_1 \qquad (37)$$

c) Condenser

Steady state material balance around the condenser section gives:

$$H\dot{x}'_{10} = Lx'_{11} - Lx'_{10} - Vy'_{10} + Vy'_{9} \qquad (38)$$

As the vapour from plate 10 is being returned as liquid reflux, hence:

$$x'_{11} = y'_{10} \qquad (39)$$

Substituting (39) in (38)

$$H\dot{x}'_{10} = (L-V)\, y'_{10} - Lx'_{10} + Vy'_{9} \qquad (40)$$

For a step change in V and L, equation (40) changes to:

$$H\Delta\dot{x}_{10} = (L-V)\,\Delta y_{10} - (L+\Delta L)\,\Delta x_{10} + (V+\Delta V)\,\Delta y_{9} \quad (41)$$

resulting in the forcing function, which is:

$$\left[-\Delta L\, x_{10} + \Delta V y_{9} \right] \qquad (42)$$

5.6.3 Reflux Change

For a reflux change the vapour flow up the column remain unchanged, but the liquid flows down the column core altered corresponding to the change in the reflux rate or ratio.

Hence equation (25) becomes for a step change only in the liquid flow rate:

$$(L+\Delta L)(x_{n+1} + \Delta x_{n+1}) + Vy_{n+1} - (L+\Delta L)(x_{n+2} + \Delta x_{n+2})$$

$$- Vy_n = H\dot{x} \qquad (43)$$

or

$$Lx_{n+1} + L\Delta x_{n+1} + \Delta Lx_{n+1} + \Delta L\Delta x_{n+1} + Vy_{n+1} - \Big[Lx_{n+2}$$

$$+ \Delta Lx_{n+2} + L\Delta x_{n+2} + \Delta L\Delta x_{n+2} \Big] - Vy_n = H\dot{x} \qquad (44)$$

Take away (43) from equation (44):

$$L\Delta x_{n+1} + \Delta Lx_{n+1} + \Delta L\Delta x_{n+1} - L\Delta x_{n+2} - \Delta Lx_{n+2} - \Delta L\Delta x_{n+2}$$

$$= H\dot{x} \qquad (45)$$

Re-arranging equation (45), the forcing function is obtained, which is:

$$(L+\Delta L)\,\Delta x_{n+1} - (L+\Delta L)\,\Delta x_{n+2} - \underbrace{\Delta L(x_{n+1} - x_{n+2})}_{\text{FORCING FUNCTION}} \qquad (46)$$

Summary of Equations for Forcing Vectors

1) Feed Change

2) Reflux Change

$$- \Delta L\,(x_{i,n+1} - x_{i,n+2})\,; \quad i = 1, \ldots\ldots, k$$

3) <u>Boil-up-rate change</u>

a) <u>For a Plate</u>

$$\Delta R \left\{ \Delta V y_{i,n} - \Delta L x_{i,n+1} - \Delta V y_{i,n+1} + \Delta L x_{i,n+2} \right\}$$

$$i = 1, \ldots\ldots, k$$

where $\Delta R = \Delta V = \Delta L$

b) <u>For the Reboiler</u>

$$(-\Delta V y_{i,0} + \Delta V x_{i,1}) \; ; \quad i = 1, \ldots\ldots, k$$

c) <u>For the Condenser</u>

$$(-\Delta L x_{i,10} + \Delta V y_{i,9}) \; ; \quad i = 1, \ldots\ldots, k$$

5.7.1 Sargents Method

A material balance for a typical stage yields :

$$H_n \frac{dx_{1,n}}{dt} = Vy_{1,n-1} - Lx_{1,n} - Vy_{1,n} + Lx_{1,n+1} \qquad (1)$$

Similar equations can be written for the other components. These equations have been solved for two steady states at which the left hand sides of all these equations are zero.

To define the problem completely it is necessary to prescribe further relations between x and y, and between the average compositions at the inlet and outlet of any stage. These correspond to the equilibrium relations and mixing characteristics of the flow system.

If equilibrium ratios are introduced :

$$y_{i,n} = K_{i,n} x_{i,n} \qquad (2)$$

then

$$H_n \frac{dx_{1,n}}{dt} = VK_{1,n-1} x_{1,n-1} - (L+VK) x_{1,n} + Lx_{1,n+1} \qquad (3)$$

The equation (3) can be written for each component in the following time varying form :

$$\frac{d}{dt} \underline{x_i} (t) = \underline{A_i} (t) \underline{x_i} (t) + \underline{\varphi_i} (t) ; \quad i = 1, \ldots\ldots, k \qquad (4)$$

where $\underline{x_i}$ (t) is the column vector concentrations in the liquid phase on the successive stages and $\underline{A_i}$ (t) is the nxn tridiagonal matrix whose non-zero elements are :

$$a_{i,n,n-1} = \frac{V_{n-1} K_{i,n-1}}{H_n}$$

$$a_{i,n,n} = \frac{V_n K_{i,n} + L_n}{H_n}$$

$$a_{i,n,n+1} = \frac{L_{n+1}}{H_n} \; ; \qquad n = 1, \ldots\ldots, c$$

and $\underline{\varphi_i}$ (t) is the column vector whose elements are:

$$\frac{F_n \, x_{Fi,n}}{H_n} \; ; \quad n = 1, \ldots\ldots, c \, ,$$

where

$K_{i,n}$, V_n, L_n, F_n, $x_{Fi,n}$ and H_n are evaluated using $\underline{x_i}$ (t); $i = 1, \ldots\ldots, k$.

The matrix representation has been given in Figure (1).

Sargent's Matrix   Figure (1) + 5.7.1

$$\begin{array}{ccccccc}
x_{0,1} & x_{1,1} & x_{2,1} & x_{3,1} & x_{4,1} & x_{5,1} & x_{6,1} \\
-(L+KV) & L & & & & & \\
KV & -(L+KV) & L & & & & \\
 & KV & -(L+KV) & L & & & \\
 & & KV & -(L+KV) & L & & \\
 & & & KV & -(L+KV) & L & \\
 & & & & KV & -(L+KV) & L \\
 & & & & & KV & -(L+KV)
\end{array}$$

5.7.2 Wood's Method

Material balances for three components on a stage yield:

$$H \frac{dx_{1,n}}{dt} = Vy_{1,n-1} - Lx_{1,n} - Vy_{1,n} + Lx_{1,n+1} \tag{1}$$

$$H \frac{dx_{2,n}}{dt} = Vy_{2,n-1} - Lx_{2,n} - Vy_{2,n} + Lx_{2,n+1} \tag{2}$$

$$H \frac{dx_{3,n}}{dt} = Vy_{3,n-1} - Lx_{3,n} - Vy_{3,n} + Lx_{3,n+1} \tag{3}$$

These equations have been solved for two steady states at which the L.H.S's of all these equations are zero.

Whereas Sargent considers a change in composition to be directed towards each component separately, Wood has suggested that a change effects all the components simultaneously, hence

$$y_{i,n} = K_{1,n}\, x_{1,n} + K_{2,n}\, x_{2,n} + K_{3,n}\, x_{3,n} \tag{4}$$

Substitutions (4) in equation (1), (2), (3).

$$H \frac{dx_{1,n}}{dt} = (VK_{1,1,n-1}, x_{n-1}) (VK_{1,2,n-1}, x_{n-1}) (VK_{1,3,n-1}, x_{n-1}) - \left[(L+VK_{1,1,n})x_{1,n} + VK_{1,2,n} x_{2,n} + VK_{1,3,n} x_{3,n}\right] + Lx_{1,n+1} \tag{5}$$

$$H \frac{dx_{2,n}}{dt} = (VK_{2,1,n-1} x_{n-1}) (VK_{2,2,n-1} x_{n-1}) (VK_{2,3,n-1} x_{n-1}) - \left[VK_{2,1,n} x_{1,n} + (L+VK_{2,2,n})x_{2,n} + VK_{2,3} x_{3,n}\right] + Lx_{2,n+1} \tag{6}$$

$$H \frac{dx_{3,n}}{dt} = (VK_{3,1,n-1} x_{n-1}) (VK_{3,2,n-1} x_{n-1}) (VK_{3,3,n-1} x_{n-1}) - \left[VK_{3,1,n} x_{1,n} + VK_{3,2,n} x_{2,n} + (L+VK_{3,3,n})x_{3,n}\right] + Lx_{3,n+1} \tag{7}$$

For the matrix, all K coefficients are different and can be calculated as explained in the next paragraph. The diagonal terms are negative and the elements around the diagonal are positive as they are negative in the first place being the values of K calculated by equation (5 6 & 7)

As an example, consider the case of a step change in composition feed to demonstrate the calculation of the elements for the matrix depicted in Figure (3) formed by Wood's method.

Let $$Y_1 = f(x_1, x_2, x_3). \qquad (8)$$

For a step change

$$Y_1 + \Delta Y_1 = f(x_1 + \Delta x_1, x_2 + \Delta x_2, x_3 + \Delta x_3) \qquad (9)$$

$$\therefore \Delta Y_1 = \frac{\partial f_1}{\partial x_1} \Delta x_1 + \frac{\partial f_1}{\partial x_2} \Delta x_2 + \frac{\partial f_1}{\partial x_3} \Delta x_3 \qquad (10)$$

Similarly

$$\Delta Y_2 = \frac{\partial f_2}{\partial x_1} \Delta x_1 + \frac{\partial f_2}{\partial x_2} \Delta x_2 + \frac{\partial f_2}{\partial x_3} \Delta x_3 \qquad (11)$$

and

$$\Delta Y_3 = \frac{\partial f_3}{\partial x_1} \Delta x_1 + \frac{\partial f_3}{\partial x_2} \Delta x_2 + \frac{\partial f_3}{\partial x_3} \Delta x_3 \qquad (12)$$

Thus, in contrast to binary distillation, where the slopes are constants, the slopes g (n,i) for multi-components mixtures depend on all the pertubations in composition on platen.

$$g_{n,i} = \frac{d\bar{y}^{*}_{n,i}}{d\bar{x}_{n,i}} = \sum_{r=1}^{k} \left(\frac{\partial f_i}{\partial x_{n,r}} \quad \frac{x_{n,r}}{x_{n,i}} \right) \qquad (13)$$

This is because if more than two components are present in a mixture the slope of the equilibrium data is no longer a line of fixed gradient but is a line in a vector space. In order to determine the direction of a line in such a space it is necessary for the liquid compositions to be specified, i.e. $x_{n,i}$ must be known.

It is evident from this discussion that as $g_{n,i}$ are functions of $x_{n,j}$ with $J = 1, \ldots\ldots, K$, that it will be necessary to solve the equations for all k components simultaneously. In other words, it will be impossible to obtain a solution for the transient behaviour of one component in isolation.

Equation (13) can be expanded as:

$$g_{n,i} = \frac{\partial f_i}{\partial \bar{x}_{n,r}} \frac{x_{n,i}}{x_{n,i}} + \frac{\partial f_i}{\partial \bar{x}_{n,r}} \frac{x_{n,2}}{x_{n,i}} + \frac{\partial f_i}{\partial \bar{x}_{n,2}} \frac{x_{n,2}}{x_{n,i}} \qquad (14)$$

Equations (10), (11) and (12) are linear with respect to the compositions perturbations because although $g_{n,i}$ is non-linear with respect to $x_{n,i}$, the terms which appear in these equations are of the form $g_{n,i}\, x_{n,i}$, which from equation (14) may be seen to be a linear function of the composition perturbations.

The partial derivatives of equation (14) are evaluated from the appropriate steady state plate compositions. For example, if the equilibrium data may be represented by constant relative volatilities:

i.e. $$Y_i^* = \frac{\alpha_i x_i}{\sum_{r=1}^{k} \alpha_r x_r} \qquad (15)$$

then $$\frac{\partial f_i}{\partial \bar{x}_i} = \frac{\alpha_1 (\alpha_2 x_2 + \alpha_3 x_3)}{(\sum_{i=1}^{k} \alpha_i x_i)^2} \qquad (16)$$

and $$\frac{\partial f_i}{\partial \bar{x}_j} = - \frac{\alpha_1 \alpha_2 x_2}{(\sum_{i=1}^{k} \alpha_i x_i)^2} \tag{17}$$

and $$\frac{\partial f_i}{\partial \bar{x}_k} = - \frac{\alpha_1 \alpha_3 x_3}{(\sum_{i=1}^{k} \alpha_i x_i)^2} \tag{18}$$

Substitution of these partial derivatives in expression (14), yields the slope of the equilibrium data for all the three components as follows:

$$g_{1,1} = \frac{\alpha_1 (\alpha_2 x_2 + \alpha_3 x_3)}{(\sum_{i=1}^{3} \alpha_i x_i)^2} \frac{x_{1,1}}{x_{1,1}} - \frac{\alpha_1 \alpha_2 x_1}{(\sum_{i=1}^{3} \alpha_i x_i)^2} \frac{x_{1,2}}{x_{1,1}}$$

$$- \frac{\alpha_1 \alpha_3 x_1}{(\sum_{i=1}^{3} \alpha_i x_i)^2} \frac{x_{1,3}}{x_{1,1}} \tag{19}$$

$$g_{1,2} = - \frac{\alpha_1 \alpha_2 x_2}{(\sum_{i=1}^{3} \alpha_i x_i)^2} \frac{x_{1,1}}{x_{1,2}} + \frac{\alpha_2 (\alpha_1 x_1 + \alpha_3 x_3)}{(\sum_{i=1}^{3} \alpha_i x_i)^2} \frac{x_{1,2}}{x_{1,2}}$$

$$- \frac{\alpha_1 \alpha_3 x_3}{(\sum_{i=1}^{3} \alpha_i x_i)^2} \frac{x_{1,3}}{x_{1,2}} \tag{20}$$

$$g_{1,3} = - \underbrace{\frac{\alpha_1 \alpha_3 x_3}{(\sum_{i=1}^{3} \alpha_i x_i)^2}}_{K_1} \frac{x_{1,1}}{x_{1,3}} - \underbrace{\frac{\alpha_2 \alpha_3 x_3}{(\sum_{i=1}^{3} \alpha_i x_i)^2}}_{K_2} \frac{x_{1,2}}{x_{1,3}} + \underbrace{\frac{\alpha_3 (\alpha_1 x_1 + \alpha_2 x_2)}{(\sum_{i=1}^{3} \alpha_i x_i)}}_{K_3} \frac{x_{1,3}}{x_{1,3}}$$

(21)

Equations 5, 6, 7 apply for all components and plates apart from the feed stage, but similar equations may be set up for the feed stage, the condenser and the reboiler.

The equations so obtained for all components and stages may be combined into the single matrix equation:

$$AX = C$$

where A = a banded matrix with real coefficients,

X = the column vector of composition perturbance for all components and plates,

and C = the forcing vector for the particular disturbance.

The elements in x are written in the order:

$$x_{0,1}, \; x_{0,2} \cdots\cdots \; x_{o_k} \; x_{1,1} \cdots\cdots \; x_{1,k} \cdots\cdots \; x_{N+1,k}$$

The width of the non-zero bands is 3k, because three plate numbers, each having k components appear in equation 5, 6 and 7. The matrix representation for wood is given in Figure (3). A matrix comparison with sargents matrix is given in Figure (4).

WOOD'S MATRIX FIG (3) + 5.7.2

$$
\begin{array}{ccccccccc}
x_{0,1} & x_{0,2} & x_{0,3} & x_{1,1} & x_{1,2} & x_{1,3} & x_{2,1} & x_{2,2} & x_{2,3} \\
-(L+g_{0,1,1}V) & (g_{0,1,2}V) & (g_{0,1,3}V) & L & & & & & \\
(g_{0,2,1}V) & -(L+g_{0,2,2}V) & (g_{0,2,3}V) & & L & & & & \\
(g_{0,3,1}V) & (g_{0,3,2}V) & -(L+g_{0,3,3}V) & & & L & & & \\
(g_{0,1,1}V) & -(g_{0,1,2}V) & -(g_{0,1,3}V) & -(L+g_{1,1,1}V) & (g_{1,1,2}V) & (g_{1,1,3}V) & L & & \\
-(g_{0,2,1}V) & (g_{0,2,2}V) & -(g_{0,2,3}V) & (g_{1,2,1}V) & -(L+g_{1,2,2}V) & (g_{1,2,3}V) & & L & \\
-(g_{0,3,1}V) & -(g_{0,3,2}V) & (g_{0.3.3}V) & (g_{1,3,1}V) & (g_{1,3,2}V) & -(L+g_{1,3,3}V) & & & L \\
 & & & (g_{1,1,1}V) & -(g_{1,1,2}V) & -(g_{1,1,3}V) & -(L+g_{2,1,1}V) & & \\
 & & & -(g_{1,2,1}V) & (g_{1,2,2}V) & -(g_{1,2,3}V) & & -(L+g_{2,2,2}V) & \\
 & & & -(g_{1,3,1}V) & -(g_{1,3,2}V) & (g_{1,3,3}V) & & & -(L+g_{2,3,3}V)
\end{array}
$$

REBOILER			1ST PLATE			2ND PLATE			3RD PLATE			CONDENSER			
x_{01}	x_{02}	x_{03}	$x_{1,1}$	$x_{1,2}$	$x_{1,3}$	$x_{2,1}$	$x_{2,2}$	$x_{2,3}$	$x_{3,1}$	$x_{3,2}$	$x_{3,3}$	$x_{4,1}$	$x_{4,2}$	$x_{4,3}$	
(S) W	W	W	(S) W												$x_{0,1}$
W	(S) W	W		(S) W											$x_{0,2}$
W	W	(S) W			(S) W										$x_{0,3}$
(S) W	W	W	(S) W	W	W	(S) W									$x_{1,1}$
W	(S) W	W	W	(S) W	W		(S) W								$x_{1,2}$
W	W	(S) W	W	W	(S) W			(S) W							$x_{1,3}$
			(S) W	W	W	(S) W	W	W	(S) W						$x_{2,1}$
			W	(S) W	W	W	(S) W	W		(S) W					$x_{2,2}$
			W	W	(S) W	W	W	(S) W			(S) W				$x_{2,3}$
						(S) W	W	W	(S) W	W	W	(S) W			$x_{3,1}$
						W	(S) W	W	W	(S) W	W		(S) W		$x_{3,2}$
						W	W	(S) W	W	W	(S) W			(S) W	$x_{3,3}$
									(S) W	W	W	(S) W			$x_{4,1}$
									W	(S) W	W		(S) W		$x_{4,2}$
									W	W	(S) W			(S) W	$x_{4,3}$

SARGENT'S MATRIX = KN^2

WOOD'S MATRIX = $(KN)^2$

FIG(4) + 5.7.3

5.7.2.1 Steps involved in calculation of constants for Wood's case

1. Calculation of relative volatility for each plate form:

$$\alpha_{12} = {}^{y_1}/_{y_2} \times {}^{x_2}/_{x_1}$$

where values of x's and y's are steady state values.

2. Calculate the partial derivatives of w.r.t. all three components form the equilibrium relationship:

$$y_i^* = \alpha_i x_i \Big/ \sum_{r=1}^{k} \alpha_r x_r$$

α being calculated as in step (1).

3. Calculation of the slope of the equilibrium data for all the three components by expression:

$$g_{n,i} = \frac{\partial f_i}{\partial \bar{x}_{n,r}} \frac{x_{n,i}}{x_{n,i}} + \frac{\partial f_i}{\partial \bar{x}_{n,r}} \frac{x_{n,2}}{x_{n,i}} + \frac{\partial f_i}{\partial \bar{x}_{n,r}} \frac{x_{n,r}}{x_{n,i}}$$

so for three components on three plates the above expression takes the form:

$$g_{1,1} = \frac{\alpha_1(\alpha_2 x_2 + \alpha_3 x_3)}{(\sum_{i=1}^{k} \alpha_i x_i)^2} - \frac{\alpha_1 \alpha_2 x_1}{(\sum_{i=1}^{3} \alpha_i x_i)^2} - \frac{\alpha_1 \alpha_3 x_1}{(\sum_{i=1}^{3} \alpha_i x_i)^2}$$

$$g_{1,2} = -\frac{\alpha_1 \alpha_2 x_2}{(\sum_{i=1}^{3} \alpha_i x_i)^2} + \frac{\alpha_2(\alpha_1 x_1 + \alpha_3 x_3)}{(\sum_{i=1}^{3} \alpha_i x_i)^2} - \frac{\alpha_1 \alpha_3 x_2}{(\sum_{i=1}^{3} \alpha_i x_i)^2}$$

$$g_{1,3} = -\frac{\alpha_1\alpha_3 x_3}{(\sum_{i=1}^{3}\alpha_i x_i)^2} - \frac{\alpha_2\alpha_3 x_3}{(\sum_{i=1}^{3}\alpha_i x_i)^2} + \frac{\alpha_3(\alpha_1 x_1 + \alpha_2 x_2)}{(\sum_{i=1}^{3}\alpha_i x_i)^2}$$

4. Calculation of constant K ($\partial f_i/\partial x_i$ etc). Multiply it with the vapour rate and addition of liquid rate to the diagonal elements of the matrix only.

CHAPTER 6

CALCULATION OF THE TRANSIENTS

6.1 Summary

The sets of ordinary differential equations can be written in matrix form:

$$\dot{x} = A\,x, \quad t = o, \quad x = x(o) \quad - \qquad (1)$$

which has the solution (56):

$$x = e^{At}\,x\,(o) \quad - \qquad (2)$$

To convert the matrix from e^{At} into a usable equation a number of procedures can be adopted.

Analytical Solution

Find the eigenvalues and eigenvectors of the matrix A and then

$$x = Q\,e^{\lambda t}\,Q^{-1}\,x\,(o) \quad - \qquad (3)$$

λ is the matrix of eigenvalues and Q and Q^{-1} are the matrices of the eigenvectors and their inverse. The numerical calculations involved are often large and there may be stability problems in evaluating Q and Q^{-1} numerically.

Numerical Methods

As the series expansion:

$$\exp (At) = 1 + At + A^2 \frac{t^2}{21} \; \ldots \qquad - \qquad (4)$$

always converges a numerical procedure can be developed using a truncated expansion:

$$\exp (At) = \exp (A \Delta \; tn) \qquad - \qquad (5)$$

$$\doteqdot (I + A \Delta t)^n \qquad - \qquad (6)$$

Equation (6) is a matrix representation of the Euler method. By a similar procedure it is possible to obtain a matrix representation of other numerical methods such as that of Crank-Nicolson.

Equation (7) can be obtained by substituting equation (5) in (2):

$$x = \left[\exp (A \Delta \; t) \right]^n x \, (o) \qquad - \qquad (7)$$

Any numerical method can be obtained by inserting a suitable approximation for the matrix form exp (A Δt) and this can be represented in general by equation (8)

$$x \doteqdot A^n x \, (o) \qquad - \qquad (8)$$

By using a probabilative method (57) it has been possible to choose a form of A which is absolutely stable whatever the choice of Δt and, in addition, the largest suitable value of Δt is of the same order of magnitutde as that for the Crank-Nicolson method. In this case the relationship between the matrix A and the transition method is given by the equation:

$$P^T = A \qquad - \qquad (9)$$

Both the techniques described above have been used to calculate the transients of a continuous Distillation column. A detailed description of the two techniques has been discussed in later sections.

6.2. Analytical Solution of the Dynamic Equations for a non-ideal multicomponent mixture in a continuous distillation column

6.2.1 Description and Discussion

The material balance equations of a Distillation Column can be represented as a set of linear differential equations and can be written in the form given below for matrix representation.

$$\dot{\underline{x}} = A\,\underline{x} + B; \quad x(o) = o \qquad (1)$$

where A is the system matrix and B represents the forcing vector.

Equation (1) can be separated into two equations whose solution can be considered independently, i.e.,

$$A\,\underline{x} + B = o \qquad (2)$$

$$\dot{\underline{x}} = A\,\underline{x}\,; \quad \underline{x} = x\,(o), \ t = o \qquad (3)$$

A new set of dependent variables, y, can be defined as follows

$$\underline{y} = \underline{x} - \underline{x}\ (o) \qquad (4)$$

But from equation (3)

$$\underline{x}\ (o) = - A^{-1} B$$

Therefore $\underline{y} = \underline{x} + A^{-1} B$

or $$A\,\underline{y} = A\,\underline{x} + B \qquad (5)$$

and $$\dot{\underline{y}} = \dot{\underline{x}}\,;\ y\,(o) = \underline{x}\ (o) \qquad (6)$$

so that the equation may now be written as

$$\dot{\underline{y}} = A\,\underline{y} \qquad (7)$$

Subject to $\underline{y} = y\ (o)$ at $t = o\,;\ \underline{y}\ (o) = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$

The formal solution of equation (7) may be written down as for a scalar equation (in terms of the conventional method of solution via Eigenvalues and eigenvectors), i.e.,

$$\underline{y} = e^{At}\,\underline{y}\ (o) \qquad (8)$$

To convert the exponential term in equation (8) into a useful form, first define a matrix E such that the following result is obtained:

$$E\,A\,G = \Lambda \qquad (9)$$

where Λ is a diagonal matrix. These coefficients are known as EIGENVALUES and the matrix E is known as the matrix EIGENVECTORS corresponding to the above mentioned eigenvalues. G is the inverse of E.

$$e^{At} = I + At + A^2 \frac{t^2}{2!} + A^3 \frac{t^3}{3!}$$

$$E\,e^{At}\,G = E\left[I + At + A^2 \frac{t^2}{2!} + \frac{A^3 t^3}{3!}\right] G$$

$$= E\,G + E\,A\,G\;t + E\,A\,G\;E\,A\,G\;\frac{t^2}{2!}$$

$$= I + \Lambda t + \Lambda^2 \frac{t^2}{2!} +$$

$$= e^{\Lambda t} \qquad (10)$$

According to matrix rules, equation (10) is a diagonal matrix or, we can write:

$$G\;E\,e^{At}\,G\;E = G\;e^{\Lambda t}E$$

$$e^{At} = G\;e^{\Lambda t}\,E \qquad (11)$$

The desired solution may be obtained by substituting equation (11) in equation (8).

$$\underline{y} = G \quad e^{\Lambda t} \; E \; \underline{y}\,(o) \qquad (12)$$

The eigenvalues and eigenvectors involved in equation (12) may be calculated by Q - R method.

This method is available as a computer library sub-routine developed by Wilkinson (58). This technique is really only useful for numerical evaluations carried out on a Digital computer. Theprocedure can be used for real unsymmetric matrixes and the routines available furnish excellent results. The program making use of these routines shall be discussed later.

If, for example, in equation (12), complex conjugate eigenvalues are encountered, they can also be handled in exactly the same way as real eigenvalues by putting complex conjugate columns in the transformation matrix. This, however, wastes computer storage space and calculation time because each of the array must be doubled in size to hold the imaginary components. Rather than doing this it may be advantageous to modify the Jordan canonical form as suggested by Ogata (59). The modification is based on the fact that one of a pair of complex conjugate vector contains all of the essential information of the pair.

Consider, for example, the case where the Jordan Canonical form is diagonal. Notice that the diagonal matrix

$$J = \begin{bmatrix} \lambda_1 & & & & \\ & \ddots & & & \\ & & \sigma + jw & & \\ & & & \sigma - jw & \\ & & & & \ddots & \\ & & & & & \lambda_n \end{bmatrix}$$

can be transformed into the form

$$\hat{J} = \begin{bmatrix} \lambda_1 & & & \\ & \ddots & & \\ & & \begin{array}{|cc|} \hline \sigma & w \\ -w & \sigma \\ \hline \end{array} & \\ & & & \ddots \\ & & & & \lambda_n \end{bmatrix}$$

by means of the transformation matrix

$$K = \begin{bmatrix} 1 & & & \\ & \ddots & & \\ & & \begin{array}{|cc|} \hline \frac{1}{2} & -\frac{j}{2} \\ \frac{1}{2} & \frac{j}{2} \\ \hline \end{array} & \\ & & & \ddots \\ & & & & 1 \end{bmatrix}$$

whose inverse is given by

$$K^{-1} = \begin{bmatrix} 1 & & & & \\ & \ddots & & & \\ & & \boxed{\begin{matrix} 1 & 1 \\ i & -i \end{matrix}} & & \\ & & & \ddots & \\ & & & & 1 \end{bmatrix}$$

Namely the modified Jordan Canonical form $\hat{J}$ is given as

$$\hat{J} = K^{-1} J K = K^{-1} P^{-1} A P K \qquad (13)$$

Not only does $\hat{J}$ have only real elements but, more significantly, $K^{-1} P^{-1}$ and PK have only real elements. It may be seen that the effect of post multiplying P by K is to set one column equal to the real part, and the next to the imaginary part of the complex eigenvectors. Both vectors are entirely real. All other columns of P are merely copied. K^{-1} has similar effect upon the rows of P^{-1}

Setting $\quad E = PK$

and $\quad E^{-1} = \left[PK\right]^{-1}$

the transformation is given the standard form of

$$\hat{J} = E^{-1} A E \qquad 14(a)$$

or

$$A = E \hat{J} E^{-1} \qquad 14(b)$$

In use, simply the real and imaginary parts of the appropriate eigenvectors as two adjacent columns of P are entered, and it should be used as though it were a true transformation matrix.

Coming back to the case of complex conjugate eigenvectors, equation (12) can be modified and written as

$$\underline{x} = E \, e^{\hat{J}t} \, G \quad \underline{x}\,(o) \qquad (15)$$

where $\underline{x}\,(o)$ is the initial state vector.

Let $G \quad \underline{x}\,(o) = \underline{y}$ (16)

Taking the case of a 3 x 3 matrix

$$e^{\hat{J}t} = \begin{bmatrix} e^{\lambda_1 t} & 0 & 0 \\ 0 & e^{\lambda_2 t} \cos w_2 t & - e^{\lambda_2 t} \sin wt \\ 0 & e^{\lambda_2 t} \sin w_2 t & e^{\lambda_2 t} \cos wt \end{bmatrix}$$

$$= \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \alpha_2 & - \beta_2 \end{bmatrix} \qquad (17)$$

According to equation (15)

$$\begin{bmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{bmatrix} \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \alpha_2 & - \beta_2 \\ 0 & \beta_2 & \alpha_2 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix} \qquad (18)$$

$$= \begin{bmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{bmatrix} \begin{bmatrix} \lambda_1 y_1 & & \\ \alpha_2 y_2 & - & \beta_2 y_3 \\ \beta_2 y_2 & + & \alpha_2 y_3 \end{bmatrix} \tag{19}$$

$$= \begin{bmatrix} e_{11} \lambda_1 y_1 + e_{12} (\alpha_2 y_2 - \beta_2 y_3) + e_{13} (\beta_2 y_2 + \alpha_2 y_3) \\ e_{21} \lambda_1 y_1 + e_{22} (\alpha_2 y_2 - \beta_2 y_3) + e_{23} (\beta_2 y_2 + \alpha_2 y_3) \\ e_{31} \lambda_1 y_1 + e_{23} (\alpha_2 y_2 - \beta_2 y_3) + e_{33} (\beta_2 y_2 + \alpha_2 y_3) \end{bmatrix} \tag{20}$$

Rearranging (20)

$$= \begin{bmatrix} e_{11} y_1 & (e_{12} y_2 + e_{13} y_3) & (e_{13} y_2 - e_{12} y_3) \\ e_{21} y_1 & (e_{22} y_2 + e_{23} y_3) & (e_{23} y_2 - e_{22} y_3) \\ e_{31} y_1 & (e_{32} y_2 + e_{33} y_3) & (e_{33} y_2 - e_{32} y_3) \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \alpha_2 \\ \beta2 \end{bmatrix} \tag{21}$$

$$= \begin{bmatrix} B \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \sigma_2 \\ \beta_2 \end{bmatrix} \tag{22}$$

The constants in matrix B can be evaluated by the rules given in TABLE 1.

Alternatively expression (18) can also be expressed as

$$\begin{bmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{bmatrix} \begin{bmatrix} y_1 & 0 & 0 \\ 0 & y_2 & -y_3 \\ 0 & y_2 & +y_3 \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \alpha_2 \\ \beta_2 \end{bmatrix} \tag{23}$$

In this case the above mentioned coefficient matrix B can be calculated by a straight matrix multiplication.

TABLE 1

COLUMNS OF MATRIX B

1) FOR REAL EIGENVALUES

$$b_{ij} = e_{ij} \, y_j \quad ; \quad i = 1, 2 \ldots\ldots\ldots N$$

2) FOR COMPLEX EIGENVALUES

(a) first column

$$b_{ij} = e_{ij} \, y_j + e_{i,\, j+1} \, y_{j+1} \quad ; \quad i = 1, 2 \ldots\ldots N$$

(b) second column

$$b_{ij} = e_{i,\, j+1} \, y_j - e_{i,\, j} \, y_{j+1} \quad ; \quad i = 1, 2 \ldots\ldots\ldots N$$

The constants in matrix B provide a good indication of the transient behaviour of the distillation column under investigation. Further to that if the final time solution to the problem has to be calculated, then the complex eigenvalue vector has to be multiplied to the constants of matrix B in equation (22) in the following way.

$$\underline{\dot{x}} = B_{11} \, e^{-\lambda_1 t} \pm B_{12} \, e^{-\alpha_2 t} \cos(\beta_2 t) \pm B_{13} \, e^{-\alpha_2 t} \sin \beta_2 t \qquad (23)$$

This can either be incorporated in the main computer program or a separate routine may be written to calculate the transients to any kind of input disturbance.

6.2.2 Example of the Analytical Solution Technique

A 3 x 3 matrix illustrating the above technique to find out the time solutions of a separation problem is given below. The computer program confirms the hand calculation. For the present investigation, the technique has been successfully applied to a 40 x 40 matrix and may be used for larger matrices.

$$A = \begin{bmatrix} -1 & 0 & -3.375 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \end{bmatrix}$$

Having calculated the eigenvalues, the eigenvectors and the inverse of eigenvectors, the values are substituted in equation (15)

$$\underbrace{\begin{bmatrix} 1.0 & 1.0 & 0 \\ -0.6667 & 0.3333 & 0.5774 \\ 0.4444 & -0.2222 & 0.3849 \end{bmatrix}}_{E} \underbrace{\begin{bmatrix} -2.5 & 0 & 0 \\ 0 & -0.25 & -1.299 \\ 0 & 1.299 & -0.25 \end{bmatrix}}_{e^{\Lambda t}} \underbrace{\begin{bmatrix} 0.3333 & -0.5 & 0.75 \\ 0.6667 & 0.5 & -0.75 \\ 0 & 0.8660 & 1.299 \end{bmatrix}}_{G} \underbrace{\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}}_{\underline{x}\ (o)}$$

$$= \begin{bmatrix} 0.3333 & 0.6667 & 0.6667 \\ -0.2222 & 0.2222 & 0.3849 \\ 0.1481 & -0.1481 & 0.2566 \end{bmatrix} \begin{bmatrix} -2.5 \\ -0.25 \\ \pm 1.299 \end{bmatrix}$$

Finally the time solution can then be calculated using equation (23)

$$\dot{x} = \begin{bmatrix} 0.3333\ e^{-2.5t} + 0.6667\ e^{-0.25t}\cos(1.299t) + 0.6667\ e^{-0.25t}\sin(1.299t) \\ -0.2222\ e^{-2.5t} + 0.2222\ e^{-0.25t}\cos(1.299t) + 0.3849\ e^{-0.25t}\sin(1.299t) \\ 0.1481\ e^{-2.5t} - 0.1481\ e^{-0.25t}\cos(1.299t) + 0.2566\ e^{-0.25t}\sin(1.299t) \end{bmatrix}$$

6.3 Numerical Approach

6.3.1 Introduction

Differential equations describing the dynamic response of a distillation column have been solved by both analytical and numerical techniques; the formulations of the problems as well as the methods of solution being fully deterministic in character. But the problems themselves can often be probabilistic in nature, or at least capable of a probabilistic interpretation. Gibilaro and Kropholler[57] have developed a powerful method for solving flow models consisting of networks of completely mixed vessels. This method is similar in many ways to more conventional numerical techniques, but has the considerable advantage, from the engineering point of view, that the physical significance of the treatment is not obscured by the mathematics. The program to be described computes the response of continuous flow models that comprise a finite number of ideal mixing stages is based on simple probability method and can be treated as a simple Markov process. The input data comprises of the volumes of the stages and the magnitudes of the flows between the stages. The response of the model to impulse, step, or arbitrary inputs can be obtained.

6.3.2 Theory

Let the concentration of tracer in the Nth stage at time t be $X_n(t)$. The general equation describing the behaviour of a number of mixing stages is, by mass balance:

$$V_n \frac{dx_n}{dt} = \sum_{i=1}^{N} q_{in}\, x_i + \left[- \sum_{i=1}^{N} q_{ni} \right] x_n \ldots\ldots \qquad (1)$$

A numerical method for solving equation (1) has been derived using a simple probability approach (57).

The principle of the method of solution can be illustrated by considering a single ideal mixing stage of volume V with a continuous flow q as shown in Fig (1).

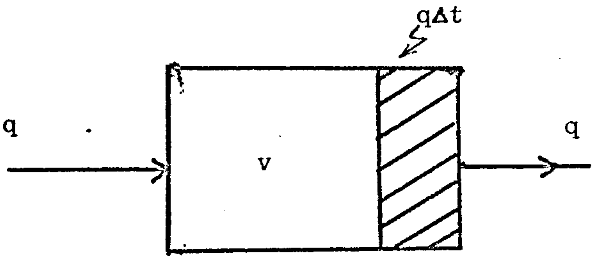


FIG (1)

If the concentration of tracer x in the vessel at time t and $t + \Delta t$ is $x(t)$ and $x\ (t + \Delta t)$ then the probability of a tagged element remaining in the vessel, p_y, at time $t + \Delta t$ is equivalent to the fraction of material remaining in the vessel. Similarly the probability of a tagged element leaving the vessel, pq, is equivalent to the fraction of the material which has left the vessel at time $t + \Delta t$. Hence:

$$\frac{Vx\ (t + \Delta t)}{Vx(t)} = Py = e^{-q\,\Delta t/_v} \qquad - \qquad (2)$$

$$\frac{Vx\ \ (t) - Vx\ (t + \Delta t)}{Vx(t)} = pq = 1 - e^{-q\Delta\, t/_v} \qquad - \qquad (3)$$

If this vessel is now considered as the ith vessel in a network of N vessels then the probabilities of an element remaining in vessel i will be :

$$P_{ii} = e^{\left(-\sum\limits_{k=1}^{N} q_{ik}\ \Delta\, t/v_i\right)} \qquad - \qquad (4)$$

and the probability of transferring to any other vessel j will be given by

$$p_{ij} = \frac{q_{ij}}{\sum\limits_{k=1}^{N} q_{ik}} \qquad (1 - p_{ii}) \qquad - \qquad (5)$$

These probabilities of remaining in a stage and of transferring to another stage are independent of the past history of the tagged element, and therefore enable the process to be treated as a simple Markov process.

6.3.3 Summary of Definations

1) p_{ij} = the probability of a transition from state i to state j.

2) P = the transition matrix containing the elements p_{ij}. The rows P consist of all possible transitions from a given state and so sum to 1.

This matrix completely describes the Markov Process, so that:

$$P = \begin{bmatrix} P_{11} & P_{12} & P_{13} \cdots\cdots\cdots P_{1N} \\ P_{21} & P_{22} & P_{23} \cdots\cdots\cdots P_{2N} \\ \cdots & \cdots & \cdots \quad \cdots \quad \cdots\cdots \\ \cdots & \cdots & \cdots \quad \cdots \quad \cdots\cdots \\ P_{N1} & P_{N2} & P_{N3} \quad \cdots \quad P_{NN} \end{bmatrix}$$

A pictorial representation of P is given in fig (1)

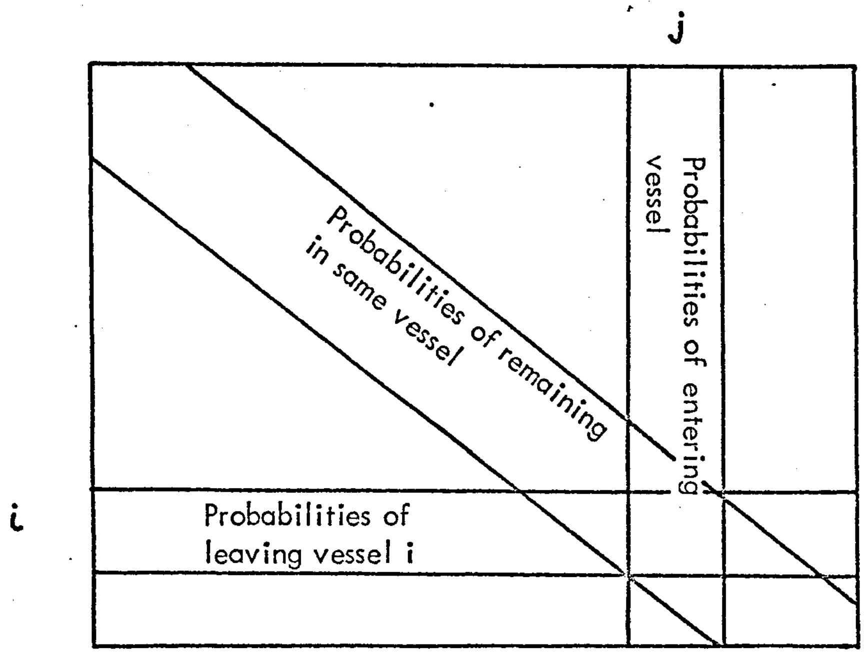


fig (1)

3) $S_i(N)$ = the state probability. Defined as the probability that the system will be in state i after n transitions from a given starting point.

4) $S\ (N)$ = the state probability vector: a line vector composed of elements Di (n)

$= (S_1\ (n),\ S_2\ (n),\ S_3\ (n), \ldots., S_n\ (n))$

6.3.4 The Markov Process

As an example of a Markov Process, Howard (Ref. 60) has chosen the frog in a lily pond. The frog can jump from one lily leaf to another, so that if there are N leaves, numbered in any fashion from 1 to N, the state of the system at any time may be unambiguously defined as the number of the leaf occupied by the frog at the time considered. Thus the state of the system can be 1, 2, ..., N.

A 'state transition' occurs when the frog jumps from one leaf to another: a jump from leaf i to leaf j being referred to as a transition from state i to state j.

By considering discrete time increments Δt small enough to exclude, for all practical purposes, the possibility of the frog making two jumps in one time increment, then the analogy between this system and the network of stirred vessels becomes apparent; the tagged fluid element in the latter case replacing the frog as the means of determining the state of the system, and the well mixed vessels replacing the numbered lily leaves.

If we are able to assign probabilities to all possible state transitions, the Markov Process is completely described. These probabilities must depend solely on the state of the system. The probability P_{ij}, of the frog jumping from leaf i to leaf j must be quite independent of how it got to leaf i in the first place, or of any changing internal or external conditions: if the frog tires with time or the leaves drift further apart we no longer have a Markov process; analogies may still be drawn between such systems and some non-linear chemical process systems but the following analysis cannot be used.

The probability that the frog will be on a particular leaf, i, after a given number of transitions n from a particular starting point is referred to as the state probabilities at any subsequent time as shown below. It will be seen that this computation for the case of the fluid network provides us with the model solution.

The system transition matrix, P, has elements p_{ij} and equations (4) and (5) can be used to construct P from the data.

Given that the frog makes a transition from a certain starting point, there exist probabilities that it will end up on each leaf. The sum of these probabilities must be 1

$$\sum_{i=1}^{N} S_i(n) = 1$$

S(o) is the initial state vector. The elements of S (o), S(o), S_2(o), ..., S_N (o) , are the probabilities that a tracer module at time o is in vessels 1, 2,.........., N.

Multiplying P by S(o) yields the vector S(1) - the state probabilities after time Δ t or

$$S\ (n+1) = S\ (n).\ P \qquad - \qquad (6)$$

Thus a knowledge of the state probabilities at any time enables the new state probabilities after one transition to be computed.

6.3.4 a Derivation of First Order MARKOV Formulation

The problem to be solved can be stated as

$$V\dot{\underline{x}} = A\,\underline{x} \qquad \underline{x} = \underline{x}(o) \text{ at } t = o$$

hence $\dot{\underline{x}} = V^{-1}A\,\underline{x}$

$\therefore \quad \underline{x} = e^{V^{-1}At}$

i.e., $\dot{\underline{x}} = \frac{d}{dt}\left(e^{V^{-1}At}\right) = V^{-1}A\,e^{V^{-1}At} = V^{-1}A\,\underline{x}$

Let D be a matrix containing the diagonal elements of A (negative).

$V\dot{\underline{x}} - D\underline{x} = (A - D)\,\underline{x} = Q\,\underline{x}$; where $Q = A - D$

multiplying both sides by the integration factor $e^{-V^{-1}Dt}$

$$V\,e^{-V^{-1}Dt}\,\dot{\underline{x}} - D\,e^{-V^{-1}Dt}\,\underline{x} = e^{-V^{-1}Dt}\,(A - D)\,\underline{x}$$

Now

$$V\frac{d}{dt}\left(e^{-V^{-1}Dt}\,\underline{x}\right) = V\,e^{-V^{-1}Dt}\,\dot{\underline{x}} - VDV^{-1}e^{-v^{-1}Dt}\,\underline{x} = \text{L.H.S.}$$

Hence

$$V\,\frac{d}{dt}\left(e^{-V^{-1}Dt}\,\underline{x}\right) = e^{-V^{-1}Dt}\,(A - D)\,\underline{x} = e^{-V^{-1}Dt}\,Q\,\underline{x}$$

assuming V, D, and A to be constant and defining $E = e^{V^{-1}D}$.

The integrating w.r.t. time between the limits t, t + Δt

$$\left[E^{-(t+\Delta t)} \underline{x}\,(t+\Delta t) - E^{-t}\,\underline{x}\,(t) \right] =$$

$$= \int_{t}^{t+\Delta t} V^{-1} e^{-V^{-1}Dt} . Q \;.\; \underline{x}\,(t+\Delta t/_{2})\, dt \qquad (1)$$

$$= -\left[V^{-1} V\, D^{-1} e^{-V^{-1}Dt} \right]_{t}^{t+\Delta t} Q\, \underline{x}\,(t+\Delta t/_{2})$$

$$= -\left[E^{-(t+\Delta t)} - E^{-t} \right] D^{-1}\, Q\, \underline{x}\,(t+\Delta t/_{2})$$

Multiplying through by $E^{t+\Delta t}$

$$\therefore \quad \underline{x}\,(t+\Delta t) - E^{\Delta t}\,\underline{x}(t) = \left[E^{\Delta t} - I \right] D^{-1} Q\, \underline{x}\,(t+\Delta t/_{2}) \qquad (2)$$

The first order approximation uses $\underline{x}\,(t)$ as an approximation for $\underline{x}\,(t+\Delta t/2)$, thus equation (2) becomes

$$\underline{x}\,(t+\Delta t) - E^{\Delta t}\,\underline{x}\,(t) = (E^{\Delta t} - I)\; D^{-1}\, Q\, \underline{x}\,(t)$$

Rearranging

$$\underline{x}\,(t+\Delta t) = \left[E^{\Delta t} + (E^{\Delta t} - I)\, D^{-1} Q \right] \underline{x}\,(t)$$

or

$$\underline{x}\;(t+\Delta t) = \left[c + (c - I)\, D^{-1} Q \right] \underline{x}\,(t)\; ; \text{ if } C = E^{\Delta t}$$

Following the above procedure, the second order formulation can be derived by substituting $\Delta t/2$ for Δt in equation (2)

$$\underline{x}(t+\Delta t/2) - E^{\Delta T/2}\,\underline{x}(t) = \left[E^{\Delta T/2} - I\right]D^{-1}Q\underline{x}(t+\Delta t/4) \qquad (3)$$

$x(t+\Delta t/2)$ can now be eliminated between equations (2) and (3)

$$\underline{x}(t+\Delta t) = E^{\Delta t}\underline{x}(t) + \left[E^{\Delta T} - I\right]D^{-1}Q\left[E^{\Delta T/2} - I\right]D^{-1}Q\underline{x}(t+\tfrac{\Delta t}{4}) + E^{\frac{\Delta T}{2}}\,\underline{x}(t) \qquad (4)$$

The second order approximation $\underline{x}(t) = \underline{x}(t+\Delta t/4)$ is now made, hence

$$\underline{x}(t+\Delta t) = \left[E^{\Delta t} + \left[E^{\Delta T/2} - I\right]D^{-1}Q\left[E^{\Delta t/2} + \left[E^{\Delta t/2} - I\right]D^{-1}Q\right]\right]\underline{x}(t)$$

or substituting $C = E^{\Delta t}$

$$\underline{x}(t+\Delta t) = (C + (C-I)D^{-1}Q\,(C^{\frac{1}{2}} + (C^{\frac{1}{2}} - I)\,D^{-1}Q))\,\underline{x}(t)$$

6.3.4 b Formulation

It has been showin the derivation that the first order Markov procedure may be formulated as:-

$$x\,(t + \Delta t) = \left[C + (C - I)\, D^{-1} Q \right] x\,(t) = P_1\, x\,(t)$$

where D contains the diagonals of the flow matrix A (negative) and $Q = A - D$; $C = e^{V^{-1} D\, \Delta t}$; C and D are both diagonal matrices.

A single element of P_1 may thus be expressed as:

$$(P_1\; i,\; j)_{\,i \neq j} = \left(e^{V_i^{-1} D_i\, \Delta t} - 1 \right) D_i^{-1}\, Q_{ij}$$

$$= (\mathrm{EXP}\,(D(I) * \Delta T/V(I)) - 1.) * Q(I,J)/D(I)$$

and

$$(P_1\; i, j) = e^{V_i^{-1} D_i \Delta T} + \left(e^{V_i^{-1} D_i\, \Delta T} - 1 \right) D_i^{-1}\; Q\, i\, j$$

$$= \mathrm{EXP}(D(I) * \Delta T/V(I)) + (\mathrm{EXP}(D(I) * \Delta T/V(I)) - 1.) * Q(I,J)/D(I)$$

Similarly from the formulation for the second order Markov procedure

$$x\,(t + \Delta t) = \left[C + (C - I)\, D^{-1} Q \left(C^{\frac{1}{2}} + (C^{\frac{1}{2}} - I)\, D^{-1} Q \right) \right] x(t) = P_2\, x(t)$$

If $D_1 = (C - I)\, D^{-1}$

and $D_2 = (C^{\frac{1}{2}} - I)\, D^{-1}$

then the above expression becomes

$$= \left[C + D_1 \left(Q\, C^{\frac{1}{2}} + Q D_2 Q \right) \right] x\,(t)$$

A single element of P_2 may be expressed:

$$(P_2\, ij)_{i \neq j} = D_1\, i\, (Qij\, e^{V_jD_j \frac{\Delta T}{2}} + \sum_{k=1}^{N} Q\, ik\, D_2 k\, Q_{kj})$$

$$\text{and } (P_{2ij}) = (P_{2ij})_{\,i=j} + e^{V_i^{-1} D_i\, \Delta T}$$

$$\text{where } D_{1i} = (e^{V_i^{-1} D_i \Delta T} - 1.) / D_i$$

$$\text{and } D_{2i} = (e^{V_i^{-1} D_i\, \Delta T/2} - 1.) / D_i$$

In the FORTRAN terminology, the above expressions can be written as

$$P_2(I,J)_{I \neq J} = \text{DI(I)*((Q(I,J)* EXP (D(J)/V(J) * DT/2.)} + \sum_{k=1}^{N} \text{Q (I, K)} * D_2\text{(K) * Q (K, J))}$$

$$P_2(I,J) = P_2(I,J)_{\,I=J} + \text{EXP (D(I) /V(I) * DT)}$$

$$\text{D1 (I)} = \text{((EXP (D(I) /V(I) * DT) - 1. /D(I))}$$

$$\text{D2 (I)} = \text{((EXP (D(I) /V(I) * DT/}_2\text{.) - 1. /D(I))}$$

When D_i is zero the expression $e^{V_i^{-1} D_i \Delta T}$ becomes 1 and the expression $(e^{V_i^{-1} D_i \Delta T} - 1.) / D_i$, on differentiation of numerator and denomenator using L'Hopitals' rule, becomes

$V_i^{-1} \Delta T$.

Similarly for $V_i = 0$, the above two expressions become zero and $-1./D_i$ respectively.

Provided all elements of D are non positive, all the exponential terms will have values between zero and unity irrespective of the size of ΔT.

6.3.5 Breakdown and Discussion of Linear Problem Using Margot

Dimensioning

Allocate the necessary storage space to the dimensioned variables using Equivalence Statement to minimise core storage.

```
DIMENSION Q (40,40), D(40), IV(40), V(40), F(40,40,2), R(40,40)
EQUIVALENCE (Q(1), F(160)), (R(1), F(1))
```

Count Number

Commence an example count number

```
N Z = 0
```

Read in First Part of Data

This data is read in using free integer format.

N ... The size of the flow matrix without integration states.

NR.. Total number of stages from which responses are required.

The VECTOR (IV) containing the above stage numbers.

NTR.. The total number of trapping states.

```
98      READ (1,101) N,NR, (IV(I), I = N-NR+1, N), NTR
101     FORMAT (900 I 0).
```

To provide the user with a print out of the time taken for each example, the time at the beginning is stored in I1.

```
CALL ITIME (I 1)
```

The total number of stages, including integration states, should be stored in the variable NT.

```
NT = N + NTR
```

Test for Control Data

Test the data for a control data card to stop the program

```
IF (NTR + 1) 30, 99, 0
```

Read in Second Part of the Data:

The flow matrix (square (N x N)), column by column

((Q(I,J), I = 1,N), J = 1, N))

volume matrix V, which is a diagonal matrix, is handled as a vector

(VCI), I = 1, N)

Time increment of output...... H

The length of time over which output is required ..... TMAX

Volumetric throughput rate ..... QTHRO

Total volume of the system ......VTOT

Minimum probability of an element remaining in a stage during the time interval Δ T.......STAYP

```
READ (1, 104) ((Q(I,J), I = 1,N), J = 1,N), (V(I), I = 1,N), H,
1 TMAX, QTHRO, VTOT, STAYP
104 FORMAT (1600 F0.0)
```

Test if there are not any Integration States:

```
IF (NTR.EQ.0) GO TO 203
```

Integration States

If there are any integration states, then each one of these require a set of N numbers.

If these numbers were A1, A2, A3, ... An, for the kth integration stage, then the output from this integration stage would correspond to

$$C_k + \sum_{i=1}^{N} A_i \int \text{stage } i$$

where C_k is a constant read in as data later in the program (see Initial State Vector)

```
READ (1, 104) ((Q(1,J), J = 1,N), I = N + 1, NT)
```

Also increase the size of the vector IV from N to NT so that responses from the integration states are outputted.

```
DO 201 J = N + 1, NT
201 IV (J) = J
```

The intrinsic routine AMIN 1 is used in this program to find the minimum of a set of numbers. This routine, in the first instance, requires a dummy argument (CC) which initially must be set to a very large number.

```
203 CC = 1.0E + 76
```

Form the "D" Matrix

This matrix is a diagonal matrix formed from the elements of the matrix Q; however, it may be treated as a column vector whose elements are the corresponding elements of the diagonals of Q

```
Do 1 I = 1,N
D(I) = -Q(I,I)
```

In order to preserve the formulation used in this program to derive the terms in the transition matrix, the matrix Q must have zero elements on its leading diagonal. Thus having formed D, the diagonal elements of Q must be made zero.

Calculation of the time Increment

The program alows for zero volume stages and these must not be considered in this calculation, so a test must be made for testing this condition.

The maximum allowable time increment ΔT that an element may remain in any stage is related to the stated minimum acceptable probability of any element staying in any stage during this time and also the minimum stage time constant of the system, by the equation:

$$\Delta T = -\frac{\text{LOG (Minimum acceptable staying probability)}}{\text{minimum stage time constant}} \qquad (i)$$

A stage time constant can be expressed as V/D and the minimum stage time constant of a system is found using the routine AMIN 1, the final result being stored in CC.

```
    IF (ABS (V(I)). GE.1.OE-10)  CC = AMIN 1 (CC, V(I)/D(I))
1   Q(I,I) = O.O
```

The value of Δ T, as calculated above, must be constrained, so that its corresponding value on the normalised time scale ΔT_n

$$(\Delta T_n = \frac{\Delta T \times \text{volumetric throughput rate}}{\text{total system volume}})$$

is an exact multiple (2^{IX} — where IX is an integer) of the printout interval H.

```
IX = (1. + DIM (ALOG(H * VTOT/C-ALOG (STAYP)*CC*QTHRO))/
                    ALOG (2), 0))
```

The time increment ΔT is calculated from the equation :-

$$\Delta Tn \times 2^{IX} = H$$

```
Δ T = H | (2. **IX) * VTOT | QTHRO
```

This is the largest value of Δ which :-

a) fits the constraint that it is a 2^{IX} multiple of H. and

b) is less than the maximum allowable time increment determined from the minimum acceptable probability of an element staying in any stage.

However, this final value of ΔT will correspond to a higher value of the staying probability than that originally read in, therefore the probability is recalculated from (i)

```
STAYP = EXP (-DT/CC)
```

Calculation of $e^{\frac{-DV^{-1}DT}{2}}$ and $1-\bar{e}\,\frac{DV^{-1}DT}{2} \Big/ D$:

When calculating the terms in the transition matrix, two matrices are predominant. These matrices are

$$\bar{e}\,\frac{DV^{-1}DT}{2}$$

and $$1-\bar{e}\,\frac{DV^{-1}DT}{2} \Big/ D$$

Both of these matrices are diagonal matrices and may be stored in vectors, in this program

$$\bar{e}\,\frac{DV^{-1}DT}{2}$$ is stored in V, and

$$1-\bar{e}\,\frac{DV^{-1}DT}{2} \Big/ D$$ is stored in D

However, the program allows for zero volumes, and the values of the expressions for zero volumes must be pre-determined.

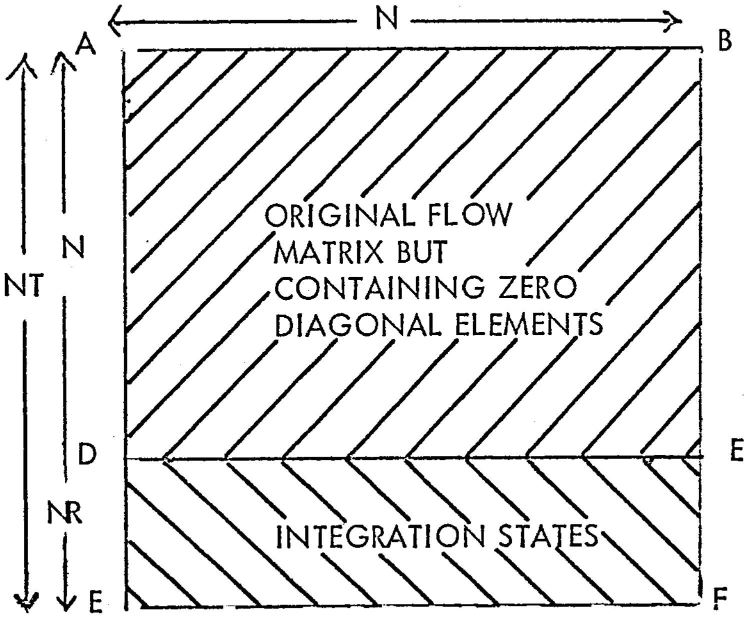
i.e. $$\bar{e}\,\frac{DV^{-1}DT}{2} = \bar{e}^{\,\infty} = 0$$

so $$1-\bar{e}\,\frac{DV^{-1}DT}{2} \Big/ D \underset{V\to 0}{=} 1/D = D^{-1}$$

```
   DO 3 I = 1,N
   IF (ABS(V (I)).GE. 1. OE-10) V(I)=EXP(-D(I)*DT/(2.*V(I)))
3  D(I) = (1. - V(I))/D(I)
```

Formation of the Transition Matrix:

At present the Q matrix is a N x NT matrix, which comprises thus:-



The general term R(I, J), $I \neq J$ in the transition matrix can be expressed as

$$R(I,J) = \frac{1-e^{-D(I)V(I)^{-1}DT}}{D(I)} \left[\sum_{K=1}^{N} \frac{1-e^{-\frac{D(K)V(K)^{-1}DT}{2}}}{D(K)} * Q(I,K)*Q(K,J) + e^{-\frac{D(J)V(J)^{-1}DT}{2}} * Q(I,J) \right]$$

The term expressing the diagonal element R(I, I) is given by

$$R(I,I) \doteq R(I,J)_{I=J} + e^{-D(I)V(I)^{-1}} T$$

When formulating the terms in the transition matrix, two cases must be considered.

1. when the terms result directly from the Q matrix and lie within the area ABCD (M x M)

2. Terms resulting from the integration states.

These are cases when the value of Δ is zero and the expression $\frac{1-e^{-DV^{-1}\Delta T}}{D}$ is found by L'hopital's rule to be equal to ΔT,

The transition matrix Q is of size NTXNT, however, all the terms in the last NTR columns are zero, except the diagonal elements of the integration states. These terms can be omitted and are not considered The matrix is formed row by row

D04 I = 1,NT

A test must be made to ascertain exactly which row of the transition matrix is being formed.

If the terms are resulting from the original Q matrix, i.e. being within the area ABCD then the term $\frac{1-e^{-DV^{-1}\Delta T}}{D}$ must be set equal to ΔT. This and any subsequent rows must initially contain unit diagonal elements.

```
   IF (I-N-1) 0,8,10
   CC = (1.0 + V(I))*D(I)
   GO TO 9
8  CC = DT
10 R (I,I), V(I) = 1.0
```

Also the value of $\bar{e}^{DV^{-1}\frac{\Delta T}{2}}$ for D = 0 (i.e., integration states) must be set equal to unity for use later in the program

Individual terms are calculated in cash row.

```
9  DO5  J = 1,N
```

When calculating the general term R (I,J) it is necessary to compute the sum

$$\sum \left\{ \frac{1-e^{-D(K)\,\bar{V}^{1}(K)\,\frac{\Delta T}{2}}}{D(K)} \quad * \; Q(I,K) * Q(K,J) \right\}$$

```
   CD = 0
   DO 6  K = 1,N
6  CD = CD + D(K) * Q(I,K) * Q (K, J)
```

Having computed this value the term $e^{-D(J)V(J)^{-1}\,\Delta T} * Q(I,J)$ must be added and the total multiplied by the appropriate value of

$$\frac{1 - \bar{e}^{DV^{-1}\Delta T}}{D}$$

```
5         R(I,J) = CC * (CD + V(J) * Q (I,J))
```

The diagonal term R (I,I) is computed from the general term $R\,(I,J)_{I=J}$ by adding on the term $e^{-D(I)\,V(I)^{-1}\Delta T}$

```
4         R(I,I) = R(I,I) + V(I) * V (I)
```

Matrix Powering

It is necessary to power the transition matrix by squaring it IX times. Since it is impossible to square a matrix and at the same time overwrite the answers in the original matrix, it is necessary to have available storage space equal to twice of the matrix being squared (i.e. F(40,40,2)

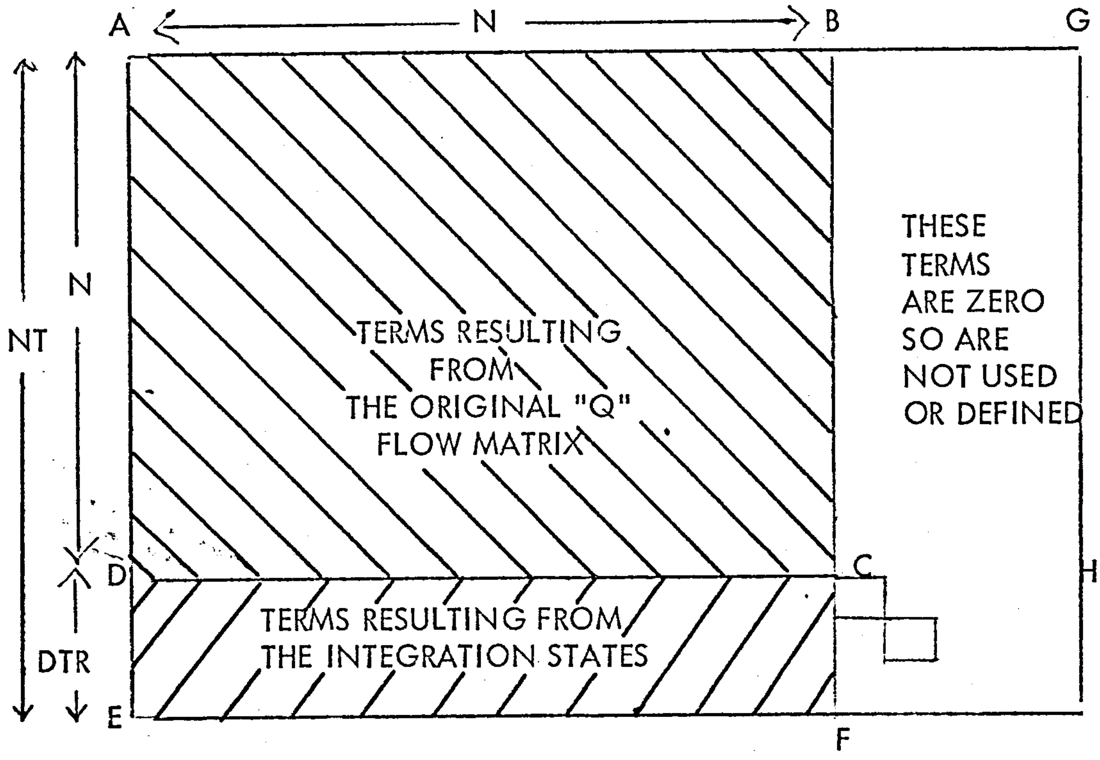
The original transition matrix is stored in R so that the first half of F and R can be made equivalent. Also, the elements of the matrix Q can be made equivalent to the second half of F. Hence the equivalence statement.

```
EQUIVALENCE (Q(I), F(1601)), (R(1), F(1))
```

As it is necessary during consecutive squaring to store the resulting matrices in F (*, *, t) and F (*, *, 2) alternatively, two variables L, and LI must be defined so that when L = 1, LI = 2 and when LI = 1 L=1, etc.

```
L = 1
DO 37 M = 1, IX
L = 3 -L
LI = 3-L
```

consider the terms that are presently stored in the transition matrix,; which is of size N X NT



when squaring the matrix, the calculation is simplified since all the terms in the area BGHC are zero, whence terms of the resulting squared matrix may be calculated in two pasts.

1. If the resultant term lies within the area ABCD, then no multiplication of terms outside the limits N x N need be considered as they are multiplied by zero.

2. If the resultant term lies within the area DCFE, then because the diagonal element in the row corresponding to this is unity, then all that is necessary is to calculate the result as though it were within the N x N matrix and add itself to the sum.

These two parts need not be considered separtely as a variable may be defined such that when computing terms within the area ABCD the variable has the value zero, and when computing terms within the area DCFE it has value of unity. Such a variable is ATR.

```
    DO  37  I = 1, NT
    ATR  = FLOAT ((I + NL) / N)
```

The matrix is then squared

```
    DO  37  J = 1,N
    CA  =  0.0
    DO  38 K = 1,N
38  CA  =  CA  +  F (I, K, LI ) * F (K, J, LI)
37  F (I,J,L)  =  CA + ATR * F (I, J, LI)
```

Response Stages

As previously mentioned when reading in the first part of the data that if the values of the response stage numbers were stored in consecutive elements at the end of the vector IV, that when using these values, whether for the column heading or as subscripts, programming is easier.

To commence the output of these values at the correct element of the vector IV an integer variable NS is defined as: NS = N-NR+1

The Initial State Vector:

The initial state vector contains NT elements. The first N elements of which correspond to the initial concentration in the respective real stages, whilst the remaining NTR elements correspond to the constant of integration for the respective stages. The vector is read in using free format.

```
READ (1,104)  (V(I), I = 1,NT)
```

Page and column Headings

For each case a new page is started giving details of:-

1. The Case number
2. The volumetric throughput of the system)
) read in as data
3. The total volume of the system)
4. The corrected value of the probability of an element remaining in any stage over the time increment used.
5. The number of times which the transition matrix has been squared.
6. The column headings.

```
      WRITE (2,103) NZ, QTHRO, VTOT, STAYP, IX, (IV(I)), I=NS, NT)
103   FORMAT (1H1, 8HCASE No, I3// 17H THROUGHPUT RATE =, G12.4/
     1  14 TOTAL VOLUME =, G12.4/7H STAYP = , G12.4///
     2  3H  M=, I3// 5H TIME, 25X, 21H STAGE CONCENTRATIONS /
     3  10x, 10 (5X, I2, 5X)/)
```

Set the variable time equal to zero

```
TIME = 0.0
```

The value of the normalised time and the stage concentrations are outputted.

```
 97   WRITE (2, 102) TIME, (V(IV (I)), I=NS, NT)
102   FORMAT (F6.2, 4X, 10G12.4)
```

Test the value of the variable TIME against the value of TMAX to find sufficient output has been given.

```
IF (TIME.GE.TMAX) GO TO 151
```

Calculation of Stage Responses

The concentrations of the stages after each print out time internal are obtained by successive premultiplication of the stage vector by the powered transition matrix. When calculating the elements in the state vector corresponding to integration states. The same arguments apply as when powering the transition matrix.

```
     DO 42   I = 1,NT
     CB = 0.
     DO 43   J = 1,N
43   CB = CB + V(J) * F (I,J,L)
42   D(I) = CB + FLOAT ((I+NL)/NT) * V(I)
```

The vector D is stored in the vector V so that after the time count has been increased an amount equal to the print and interval, the write statement labelled 97 may be used to output the stage concentrations.

```
     DO 45   I = 1,NT
45   N(I)  =  D(I)
     TIME = TIME + H
     GO TO 97
```

The time at the end of each run is recorded in I2. By the Subtraction of the time at the beginning, the total time taken for each run can be outputted.

```
151        CALL   I   TIME (I2)
           I2  =  I2 - I1
           WRITE (2, 150)   NZ, I2
150        FORMAT (1Ho, 23H  TIME TAKEN FOR CASE
                          NO, I2, 2H  =  ,  I4, 5H SECS)
```

The value of the state vector can be outputted for the last time.

```
107        WRITE (2, 102) TIME, (V(I), I = 1, NT )
```

control is transferred to start another case, and the segment is finished.

```
      GO TO 98
99    CONTINUE
      STOP
      END
```

6.3.6 Operational Details

Data required as the input for this program can be devided into four sections. Each section starts on a new card. All the data is in free format.

Section 1

All variables of type ' Integer '

Variable List	Significance in the Program
N	Number of system stages excluding integration states;
NR	Numbers of the N stages for which a time response is required, followed by NR numbers corresponding to these stages;
NTR	Number of integration states required.

Section 2

Type of variables used 'Real'

Variable List	Significance in the Program
Q	An array of N x N numbers giving the system intestage flows. The numbers are input in matrix; form as follows:- Q (1,1) the flow through stage 1 (a + tive number) Q (2,1) flow from stage 1 to stage 2. Q (3,1) flow from stage 1 to stage 3 . Q (N,1) flow from stage 1 to stage N. Q (1,2) flow from stage 2 to stage 1. Q (2,2) the flow through stage 2. Q (2,3) etc to Q (NxN)

V	N numbers corresponding to the volumes of the N stages.
H	The print out interval in normalised time
TMAX	The maximum normalised time value for which responses are required.
QTHRO	The volumetric throughput
VTOT	Total volume of the N stages
STAYP	The minimum acceptable probability of an element remaining in any stage during time DT.

Note:

Normalised time $T = t x \frac{VTOT}{QTHRO}$, where 't' is real time, i.e., it is time expressed as multiples of the mean system time constant. Artificial values of VTOT and QTHRO may be used to alter the normalisation i.e., VTOT = QTHRO will give the real time response.

Section 3 (Omit if NTR = 0)

Variables used are of type 'Real'.

This section consists of Nx NTR numbers. Each block of N numbers gives information concerning one trapping state or integral. For the first block let these numbers be A_1, A_2 ... , A_n then the output integral will be

$$C + \sum_{i=1}^{N} \left[A_i \quad X \quad \int_0^T (\text{Stage } i)\, dT \right. \qquad (1)$$

where T is at 0, H, 2H etc to TMAX and C is a constant. Hence if the integral response of stage 1 were required, the data would comprise of a 1 followed by N-1 Zeros giving

$$1 \times \int_0^T (\text{Stage 1})\, dT, \text{ since } A_2 \ldots A_n \text{ are zero}$$

Section 4

All variables used are of type 'Real'

This section comprises of N + NTR numbers which are the initial states of all the stages. The first N numbers should be the required concentrations of the tracer component in each stage at time 0. The next NTR numbers correspond to the values of C in equation (1) for each trapping state.

Note:

Stages within the system may be numbered arbitrarily provided there are assigned numbers from 1 to N. These numbers represent the order in which information concerning the N stages is put. All the integration stages will have their time responses outputted and will be numbered N + 1 to N + NTR by the machine in the order in which the data is presented.

6.3.7. Advantages of Using Markov Procedure

In the deriation it has been shown that the first order Markov procedure uses the approximation

$$e^{V^{-1}A\Delta T} = I + V^{-1}A\Delta T \qquad (1)$$

and the second order Markov procedure uses the approximation

$$e^{V^{-1}A\cdot\Delta T} = I + V^{-1}A\ \Delta T + (V^{-1}A)^2\ \frac{\Delta T^2}{2!} \qquad (2)$$

The advantages of the Markov procedures as compared to the evaluation of the right hand sides of the two equations given above are as follows:

First let us consider the term ΔT, for the required accuracy in equation (1), terms containing ΔT^2 must be negligible. Hence ΔT itself must be small so that unless the elements of $V^{-1}A$ approximate to the reciprocal of ΔT, the product, when added to the unit matrix, will loose significant digits of accuracy, but the elements of $V^{-1}A$ may not be adjusted in this way since $(V^{-1}A)2 \quad \Delta T^2/2!$ would then certainly not be negligible, and in fact the accuracy of the approximation is increased if the elements of $V^{-1}A$ are made small. This problem increases as higher order approximations are taken since $\Delta T^n \rightarrow \Delta T^{n+1}$ as in increases.

The Markov procedures depend on the evaluation of diagonal matrices of the form e^K, where K is $V^{-1}D\Delta TG$, and G is a constant between zero and one. If $\Delta T=$ lin (STAYP)/(-max (D/V)), then e^K will have values between STAYP and one, hence the loss of significant digits is held to a minimum.

Secondly, $V^{-1}A$ cannot be evaluated if an element of V is zero. No such restriction applies to the Markov procedure, since the exponent K (which is always negative) becomes $-\infty$ and e^K becomes zero,

The Markov procedure can also be used if elements of D are zero since e^K becomes unity and $e^{V^{-1}D\,\Delta T\,G} - 1/D$ can be evaluated by L'Hopitals rule

$$= \frac{\frac{\Delta T\,G}{V}\; e^{V^{-1}D\,\Delta T\,G}}{1} \quad \text{at} \quad D = 0 = \frac{\Delta TG}{V}$$

The significance of allowing V to become zero is that differential equations can be mixed with algebraic equations, whilst if D is zero, integration of the inputs to this stage is implicit.

Integration routine written in the computer program is in fact explicit, since the computer is unable to evaluate $\frac{e^{V-1\,D\,\Delta T}-1}{D}$, when D is zero. Since this possibility must therefore be allowed for separately, advantage has been taken, of the knowledge that the columns of the flow matrix corresponding to integration states are all zero in order to reduce the amount of computation. For example, for a system comprising of ten stages and ten integration states the program uses a ten by twenty matrix and not a twenty by twenty matrix.

CHAPTER 7

EXPERIMENTAL WORK

7.1 . PURITY OF MATERIALS

After the preliminary investigation by using a gas liquid chromatograph to measure and check the purity of the starting materials, a further comparison was made of some of the physical properties.

The refractive indices and specific gravities of the three compounds were measured and compared with values taken from International Critical Tables (61) and the Handbook of Chemistry and Physics (62). In all cases the agreement was excellent which confirmed that a very high degree of purity had been obtained. The values taken experimentally together with the values obtained from the references given above, as presented as Table 7.1.

	Refractive Index at 20°c		Specific Gravity at 20°c	
Component	Ref.(61)	Purified Material	Ref.(62)	Purified Material
Acetone	1.3588	1.3590	0.7900	0.7902
Methanol	1.3288	1.3287	0.7914	0.7915
Isopropanol	1.3776	1.3775	0.7851	0.7850

Table 7.1 Physical Properties of the Pure Materials

The normal boiling points of the three materials were also measured for several samples of the purified materials. The results were averaged and compared with values from International Critical Tables (61) as shown in Table 7.2.

Component	Boiling Point at 760 mm Hg Pressure Ref (61)	Purified materials
Acetone	56.10°C	56.25°C±0.05
Methanol	64.60°C	64.45°C±0.05
Isopropanol	82.26°C	82.30°C±0.05

Table 7.2 Boiling Points of the Pure Materials

The redetermined values were very close to the temperatures given in column three apart from slight variations in the last decimal place which were within the accuracy of the temperature measurements. Other physical property sources (63, 64, 65) were then considered and the spread of the quoted boiling points at 760 mm Hg pressure are now given; 56.10°C to 56.50°C; Methanol, 64.96°C to 64.1°C; Isopropanol, 82.5 to 82.26°C.

With these figures in mind and also the close agreement between the values of specific gravity and refractive index, it was decided that the purity of the materials was sufficient for this investigation. To avoid deterioration of the compounds by sunlight or other light sources, they were stored in a dark place. Oxidation was overcome by keeping the containers tightly stoppered.

7.2 DESCRIPTION OF THE EQUIPMENT

General arrangement. The overall height of the unit above ground is 19 ft. All valves etc. which require manual adjustment during a run will be accessible from ground level.

Process flow scheme. The unit operates as follows:-

(a) Feed section. The feed material is first charged to a 200 gallon feed tank. From here it is metered by a gear pump to the pre-heater and then to the column. During vacuum operation a needle valve in the feed line is partially closed to ensure that the pump is working against a positive head. The feed rate is indicated locally and also recorded on the instrument panel.

The feed pre-heater consists of a coil immersed in a heated lead bath. A temperature controller regulates a portion of the electrical load on the pre-heater to maintain a constant feed temperature to the column. The feed lines between the pre-heater and column are electrically heated. The load on the windings is adjusted by a variac at the start of a run and then the feed temperature controller compensates for any change in heat loss during a run.

(b) Column and Reboiler. The feed enters the column at any one of eight points, depending on the relative amounts of rectification and stripping required. The column is made up of two 4 ft. lengths of 3 in. I.D. pipe packed with a protruded stainless steel packing to a depth of 7 ft. 10 in.. Conical packing supports made of metal gauze are fitted in the base of each section. A gauze packing retainer is fitted at the top of the column.

Electrical heating cables compensate for any heat losses from the column. The cables are wound round a mild steel sheath surrounding the column. Lagging is placed on top of the cables. An adjustable portion of the power input to the cables is switched off or on by an automatic temperature difference controller. The controller operates in order to keep the temperature of the sheath equal to the temperature inside the column.

A tube flanged directly to the bottom of the packed column acts as the reboiler.

The boil-up heat is provided by electrical resistance heaters clamped to the outside of the tube.

The composition of either product from the column is maintained at the specified value by controlling either the temperature in the reboiler or the temperature at some point in the column. This is done by an automatic temperature controller which adjusts the electrical load on the reboiler heaters. A multipoint temperature indicator is used to show the temperature pattern in the column.

(c) Bottoms section. The liquid level in the reboiler is kept constant by pumping off excess liquid as bottoms product. The gear pump runs continuously (P.753). When the level in the reboiler exceeds the desired value, then a control valve (CV.753) opens and liquid passes through the cooler (E.755) to the product receiver. If this valve is closed then the bottoms liquid is continually recirculated by the pump through another valve (CV.755). The receivers are used alternatively so that the product can be run off into drums while the column is running. Automatic level detectors (L.1752) are fitted to the receivers so that a warning light shows on the control panel when the receivers are nearly full. The receivers are steam jacketed and the lines steam traced so that the bottoms product with high melting points can be handled.

(d) Overheads section. The vapours from the top of the column pass through an electrically heated line to the condenser (E.753). The pressure in the condenser is kept constant during a run. It is controlled during vacuum operation by a manostat (PC.751) and during high pressure operation by the pressure controller (PRC.751). The latter controller acts in one of two ways: if sufficient inerts are present then it regulates the rate at which these are vented to atmosphere; if only a small quantity of inerts are present then it regulates the flow of cooling water to the condenser.

The reflux divider (RD.751) works on a time cycle basis and maintains a constant reflux ratio throughout a run. Liquid reflux returns to the column under gravity through an electrically heated line. The distillate product passes to a cooler (E.754) and then to the receiver (V.753). When the column is operating either above or below atmospheric pressure then a liquid seal is maintained in the product line by a level controller (LC.752).

7.2.1 DESIGN CONSIDERATIONS

1. Selection of duty

The column was intended for general use as a pilot plant. It had therefore to be flexible enough to operate over a wide range of conditions. However this flexibility had to be balanced against the cost of construction and ease of operation of the unit.

(a) Feed capacity. A column which would handle feed rates up to approximately 5 gallons/hour seemed to be the most suitable size of column for the pilot plant (the quantity of feed material to be treated being of the order of 40-500 gallons). With a larger column excessive amounts of material would be lost before the column settled down. The capacity is reduced considerably when the distillation pressure is reduced and therefore a smaller column would probably have too low a capacity when operating under a vacuum.

(b) Pressure. Operation at pressures both above and below atmospheric was desirable and a column which could operate from 20 mm Hg to 150 psig would be capable of handling most distillation problems. (By limiting the maximum pressure to 150 psig, the use of class 150 flanges for most of the joints was possible and so simplified the construction of the process equipment).

(c) Temperature. Reboiler temperatures up to 300°C were possible without introducing undue complications in the construction. A water-cooled condenser would cope with most overheads and thus the installation of a refrigerated condenser did not appear to be justified.

(d) Separation power. A column having the equivalent of 20-30 theoretical stages would cope with most of the separations encountered in the pilot plant.

(e) Reflux ratio. This had to be adjustable. A standard timer with a range of ratios from 1:1 up to 50:1 was considered adequate.

(f) General construction. The column had to be constructed of F.M.B. stainless steel so that it could handle corrosive fluids. All equipment had to be flame-proof. The unit should be adequately instrumented so that only one operator is required to run it.

2. Design of more important items

(i) Column

(a) Type. The required flexibility of operation could only be achieved by using a packed column. To reduce the height of the column a protruded metal pack with low H.E.T.P. values was used. (This type of packing has a very low pressure drop per plate and is therefore particularly suitable for vacuum distillation). A column filled with this packing is more compact than one filled with a conventional packing and it should therefore take less time to reach steady conditions after start up.

(b) Calculation of the column diameter. The diameter was calculated by considering the vapour liquid loading at the flood point. The vapour velocity at the flood point for this type of packing is given by the equation:-

$$G = 270\,(\rho_L)^{.58}\,(\rho_g)^{.42}\ \text{lb./hr.ft.}^2 \qquad (1)$$

ρ_L = liquid density lb./ft.^{3}

ρ_g = vapour density lb./ft.^{3}

Consider below the simple hypothetical separation used in order to obtain some idea of the columns diameter.

Hypothetical separation:-

Feed composition = 0.3 mole fraction m.v.c.

Distillate product composition = 0.99 mole fraction m.v.c.

Bottom product composition = 1.10 mole fraction m.v.c.

Feed as boiling liquid

M.W. of m.v.c. = 100

M.W. of l.v.c. = 200

Pressure = 150 psig

Reboiler temperature = 260°C

Density of liquid in reboiler = 50 lb./ft.^{3}

For most separations, flooding will begin at the lower end of the column. Therefore in equation (1) the physical properties of the materials entering and leaving the reboiler have been used.

Average M.W. of vapour = 190

Then vapour density = 3.0 lb./ft.^{3}

Then in equation (1)

Vapour velocity at flooding = $270 \times 50^{.58} \times 3^{.42}$

= 4,100 lb./hr.ft.^{2}

If maximum vapour velocity is taken as 70% of that at flooding, then maximum vapour velocity = 2,870 lb./hr.ft.^{2}

A mass balance over the column shows that:

Flow of vapour up column (lb.) = 2.21 x feed rate (lb.)

Now feed rate = 5 gallons/hr.

= 45 lbs./hr.

∴ Flow of vapour up the column = 99.5 lb./hr.

Then X-sectional area required = $\frac{99.5}{2,870} = 0.0348$ ft.^{2}

∴ I.D. of column = 2.2 ins.

This calculation is based on a single hypothetical separation and therefore only gives an approximate idea of the column diameter.

A more reliable estimate of the required column diameter can be obtained by referring to a description of an existing pilot plant column. This column is filled with the same type of packing and can cope with a feed rate of up to 10 galls./hour of a wide variety of hydrocarbon liquids. The I.D. of the column is 3 inches. The maximum pressure is 600 psig.

From equation (1) we see that the capacity of the column is proportional to ${}_{.42}\ \rho_g^{.42}$ and therefore approximately proportional to (absolute pressure). The proposed column operates at a maximum pressure of 150 psig. Then it should have an inside diameter of 3 inc. to deal with feed rates up to 5 galls./hour. The column is made of 3 in. N.B. tube.

(c) Height of packing. Experimental data is available which gives the values of H.E.T.P. for protruded packings at different vapour rates. The H.E.T.P. is of the order of 2-3 inches at normal vapour velocities (0.5 - 1.5 ft./sec.). However, these values of H.E.T.P. were measured at total reflux. At finite reflux ratios the H.E.T.P. would be somewhat higher.

A packed height of 7 ft. 10 ins. is then used to provide the 20-30 plates required. The overall length of the column is 8 ft. and for ease of handling and construction it is divided into two sections of length 4 ft. Liquid redistributors are not used because they are of little value in a 3 in. diameter column.

(d) Pressure drop. Experimental data shows that the pressure drop per foot of protruded packing varies from 0.4 mm Hg at a vapour velocity of 0.5 ft./sec. up to 4.5 mm Hg at a vapour velocity of 1.8 ft./sec.

Then the pressure drop across the packed column will vary approximately from 3 mm Hg up to 33 mm Hg depending on the vapour velocity.

The vacuum pump should provide a condenser pressure of 10 mm Hg. Therefore the pressure in the reboiler could reach as low as say 15 mm Hg under low liquid and vapour loadings.

(ii) Reboiler

(a) Heat load. For most separations the boil-up rate will not exceed 60 lb./hour.

Average latent heat of organic liquids = 80 C.H.U./lb.

Then maximum heat load = 4,800 C.H.U./lb.

= 2.52 k.W.

To allow for heat losses and for the possibility of dealing with liquids of high latent heat, electrical resistance heaters with a total load of 4 kW are provided.

(b) Design. The total heat load is made up by 8 electrical resistance heaters clamped to the outside of the reboiler tube. It was attempted to reduce the heat capacity of the reboiler plus contents to a minimum. The liquid hold is only of the order of 1 gallon. Thus any change in the heat input quickly produces a change in the boil-up rate.

Fins are welded to the inside of the reboiler tube to increase the heat transfer area and so reduce the chance of local overheating of liquid. The maximum heat flux will then be 2600 CHU/hr.ft.^{2}

The heat input is varied by varying the number of heaters connected to the electrical supply. Fine control is achieved by connecting one of the heaters to a variac and an on/off controller. The on/off controller will tend to make the boil-up rate oscillate. The load on the heater is reduced by adjusting the variac until this oscillation has been diminished.

(iii) Condenser

(a) Heat load and area required. A heat balance over the whole column shows that the maximum heat load on the condenser will be approximately equal to maximum heat load on the reboiler. Then take maximum heat load as 4 kW = 7,600 CHU/hr.

The area required for heat transfer will be greatest when the overhead vapours are at a low temperature.

Theoretically, it should be possible to condense vapours at 20°C using water at 15°C. However, if the column were also operating at full capacity then a very large condenser would be required.

The condenser is therefore sized on a vapour temperature of 55°C when the column is running at full capacity.

Using water as coolant, average temperature = 35°C. Take overall heat transfer coefficient as 70 CHU/hr.ft.^{2} °C.

$$\text{Then area of heat transfer} = \frac{7,600}{35 \times 70}$$

$$= 3.5 \text{ ft.}^2$$

(b) Design. An area of 3.1 ft.^{2} is provided by 30 ft. of $^1/_8$" NB tube wound into two concentric coils. These coils are fitted inside a length of 6" NB tube. Hold up of water in the tubes is low and high water velocities are achieved. Therefore the condensation rate will respond rapidly to changes in the flow of the water. An additional heat transfer area of 1.5 ft.^{2} is provided by jacketing the 6" tube. This jacket will only be used when the heat load is abnormally high. Under normal circumstances it would tend to produce excessive subcooling of condensate.

(iv) Feed preheater

(a) Heat load

Maximum feed rate = 45 lb./hr.

Then take maximum feed temperature as 275°C when operating at this rate.

Assume average specific heat of 0.6 CHU/lb.

Then maximum heat load = 45 x 0.6 x 255

= 6,900 CHU/hr.

= 3.63 kW.

To allow for heat losses a 4.0 kW. maximum heat impact is provided.

(b) Design. In order to obtain feed temperatures up to 300°C, lead is used as the heat transfer medium in the preheater. The feed passes through a coiled tube which is immersed in lead. The lead is contained in a 6" NB tube and 8 heaters, each of 0.5 kW., are clamped to the outside of this tube. The feed temperature is controlled by regulating the electrical load on these heaters. Several of the heaters are switched on to provide a base load. The fine control of temperature is achieved by manually adjusting a variac connected to a single heater and then allowing a temperature controller to switch this small load on and off as required.

(v) Vacuum pump

The size of this pump can only be determined by past experience on vacuum systems. Condenser pressures as low as 5 mm Hg were achieved on a similar pilot plant column by using a pump with a capacity of 13 $ft.^3/min$.

The proposed column has a vacuum pump with a capacity of 16 $ft.^3/min$. The pump is of the rotary type so that a non-pulsating pressure is obtained.

(vi) Control system

The aim of nearly all distillation operations is to make a product of specified composition. The proposed control method is based on the principle that the temperature of a vapour is a direct measure of its composition at constant pressure. This method of control is used because it should work equally well during pressure and vacuum operation.

7.2.2 CONTROL OF DIFFERENT VARIABLES

After the initial start up period the control of the different variables is as follows:-

(i) Composition

The composition of either product is maintained at the required specification by controlling the temperature at some point in the column or in the reboiler. The temperature to be controlled will be that temperature on which the product composition is most dependent.

When the bottom product is the specified product, then the controlled temperature will be that of the reboiler of some point in the lower section of the column.

When the top product is specified, then the controlled temperature will probably be in the upper section of the column. There are eight alternative temperature control points in the column itself and one in the reboiler.

The temperature at these points is in turn controlled by the boil-up rate. The temperature is measured by a thermocouple connected to a Honeywell Brown Electronic Controller (TIC 751). This controller then varies the heat input to the reboiler. The set temperature on the controller can be adjusted by $\frac{1}{2}^{\circ}$C divisions.

The overall action of the system is as follows:

Suppose the top product contains too much of the least volatile component. Then the value of the controlled temperature must be reduced; the set point on the controller is lowered so that heat input to the reboiler is reduced; the boil up rate is reduced so that temperatures throughout the column are reduced; then the proportion of the less volatile components in the top product also decreases. There should be little time lag before these changes occur because the hold up of liquid in the packing and reboiler is low.

(ii) Feed Rate

This should remain constant throughout a run. The speed of the gear pump is set at the beginning of the run.

(iii) Feed Temperature

Automatic adjustment of the heat input to the preheater ensures that this temperature is constant during a run.

(iv) Reflux Ratio

A constant reflux ratio is used during a run. It is unaffected by changes in the condensate rate.

(v) Pressure

The pressure should remain constant throughout a run. When the column is operating under vacuum, then the presssure is controlled by a manostat (P.751). When the column is operating above atmospheric pressure, then the pressure in the condenser is controlled by PRC 751 in one of two ways:

If the overheads contain sufficient inert gases, then a constant pressure is maintained by controlling the rate at which these are vented to the atmosphere.

If the quantity of inerts is low, then the constant pressure is maintained by controlling the flow of cooling water to the condenser.

(vi) Product Rates

Both products are allowed to come off freely; no attempt is made to maintain a constant rate. The rate at which distillate product is delivered varies with the condensation rate. The rate at which bottoms product is delivered depends on the liquid level in the reboiler.

(vii) Liquid level in reboiler

The level of the liquid in the reboiler should remain constant. The discharge pump (P.753) operates continuously. The control valve (CV.753) only opens when the liquid level in the reboiler exceeds the desired level.

When this control valve closes, then the pump discharge pressure increases. The controller (PIC 751) is set to open the control valve (CV.755) when the pressure is about 10 p.s.i. higher than the reboiler pressure. The liquid then recirculates through the pump and cooler and so reduces the operating temperature of the pump and the possibility of vaporization in the pump.

7.3 MECHANICAL TESTING

Before the rig could be operated as a distillation unit, it had to be checked for mechanical defects, omissions and other inconsistencies according to the flow diagram (R.555). Each of the individual plant items had to be checked and certified.

The following work scheme was adopted:-

(i) By following the flow scheme all omissions and inconsistencies are to be found and rectified.

(ii) All valves to be labelled as indicated on the flow scheme to facilitate operation.

(iii) All thermocouples to be checked and defects replaced.

(iv) All relief valves to be checked in place and certified.

(v) All process lines to be purged with compressed air to eliminate scale and accumulated water blown from the instrument air lines.

(vi) All leaks to be reduced to a minimum.

(vii) Air purge system to be tested and flow rates to instruments and heaters adjusted.

(viii) All gear pumps to be run in with lubricating oil, after being checked.

(ix) Feed metering system to be checked and made operational.

(x) Level control system on the reboiler has to be completed and adjusted.

(xi) Reflux divider has to be checked and calibrated.

(xii) All electrical wiring to the heaters should be tested and anomalies corrected.

(xiii) Control equipment to be repaired and connected up.

7.4 STARTING UP PROGRAMME FOR THE PLANT

(Based on Dwg. R.555 (Mod.2))

Steps

1. Valves to coolers opened, where required, and cooling water to condenser turned on.

   The required valves are located

   (i) on ground floor opposite main entrance (Mains Valves).

   (ii) on 1st floor behind coolers (Distillate and Bottoms Coolers).

   (iii) on upper platform at top of column (Condenser).

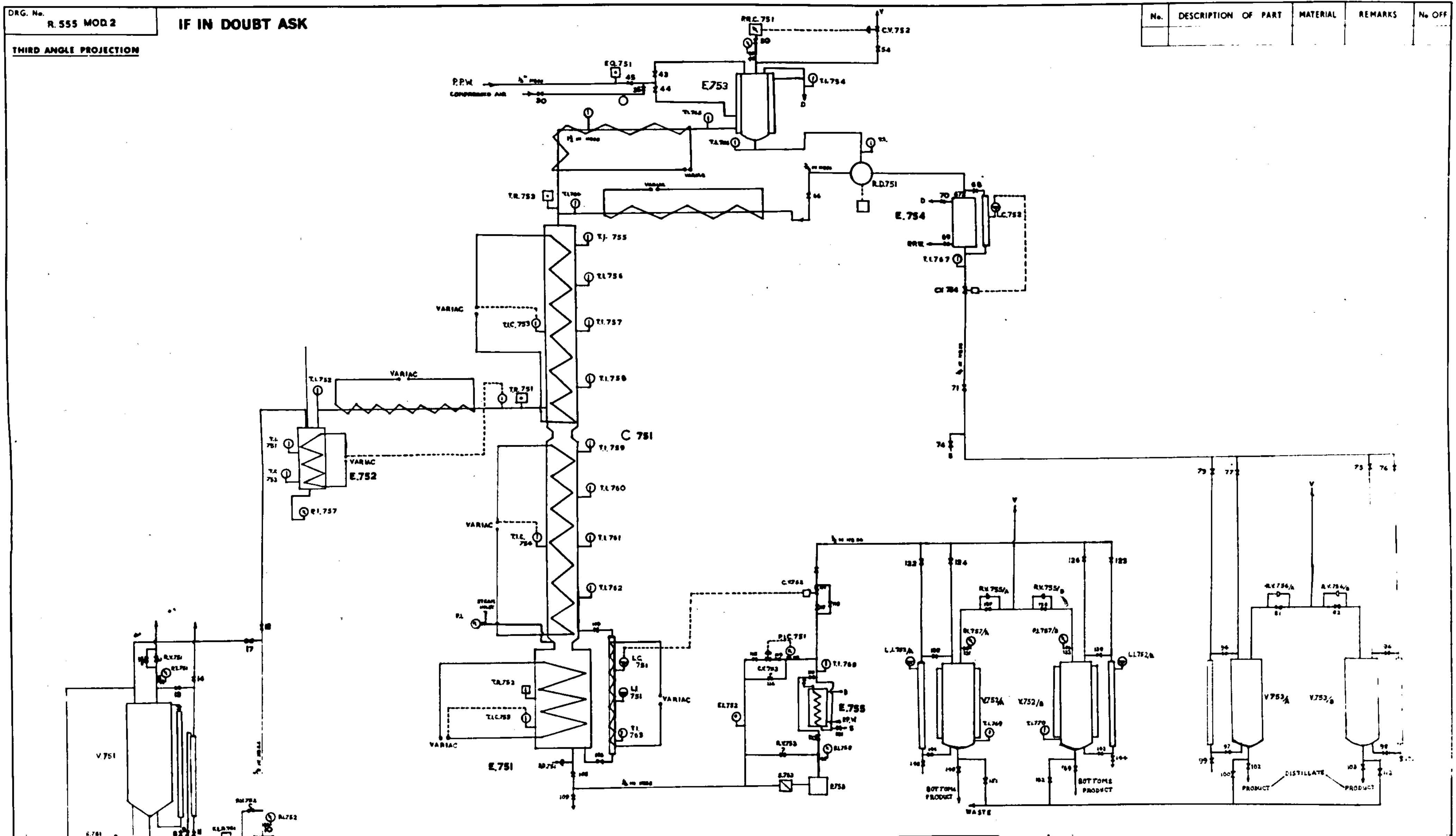
2. Feed line connected to appropriate feed point on column. There are eight such feed points on the column, the most suitable one for any particular case being determined by trial and error initially and by calculations from desired product and feed compositions once some experiment data is obtained from the plant. (Connect TR.751 to appropriate feed point thermocouple).

DRG. No. R.555 MOD.2

IF IN DOUBT ASK

THIRD ANGLE PROJECTION

No.	DESCRIPTION OF PART	MATERIAL	REMARKS	No OFF



NOTES
V—VENT
D—DRAIN
P.P.W.—PUMPED PONDS WATER
S—SAMPLE POINT

A GENERAL TOLERANCE OF PLUS OR MINUS ·010" IS ALLOWED ON ALL MACHINING DIMENSIONS UNLESS OTHERWISE STATED. REMOVE ALL BURRS AND SHARP EDGES UNLESS OTHERWISE STATED. LIMITS CONFORM TO B.S. 1916 P.T.1 1953 UNILATERAL SYSTEM. MACHINING SYMBOL ✓ SURFACE ROUGHNESS TO B.S. INDEX NUMBERS

LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY

MATERIAL —
PRODUCT
SCALE N.T.S.
TITLE UNIT 750 PILOT PLANT 1 CONTINUOUS DISTILLATION UNIT
PROCESS ENGINEERING FLOWSCHEME
DRAWN
TRACED
APP'd
DATE MAY '69
SCHEDULE No
PART No
DRG No R 555 MOD.2

GROUP CHEM. ENG.

A	DATE MOD	SIGN	B	DATE MOD.	SIGN.	C	DATE MOD.	SIGN.	D	DATE MOD.	SIGN.
E	DATE MOD.	SIGN.	F	DATE MOD.	SIGN.						

3. All valves to manometers should be shut along with all outlet valves (i.e. from various tanks - not including different sections of plant) and vents to product receivers opened. The column is vented by opening valve (54) on diagram, located near top of column but not labelled.

4. Feed now pumped to storage tank by means of air pump, ensuring valves (1) and (3) are open and valves (4) and (18) are closed. Tank should be filled in 1-1½ hours; no quicker since considerable pressure drop before pump.

5. Feed Stock may now be blended by opening valve (2) and closing valve (1) i.e. recirculated to feed tank using Pump (P.752) and using vessel (V.755) as guide to condition of feed.

6. Level in tank may be observed by opening valve (15) and shutting valve (8).

7. Calibration of FI.751/P. Open valves (9), (11) and fill (V.755) with feed liquid. Shut valves (9), (6) and (18) and open valve (17). Then pump back into storage tank. Flow rate being measured by time interval for the liquid level to fall between adjacent Jubilee clips (the volume between top and second clips is (440 m/s), between second and third clips (400 m/s) and between third and fourth clips (340 m/s).

This measure of flow rate must be carried out for each change of feedstock.

8. Valves (9), (11) and (17) now closed and valves (18) and (6) opened and enough liquid pumped into column through preheater to fill reboiler. Feed metering pump set to give required flow rate and then feed preheater turned on. These should be trimmed down to maintain a constant feed temperature when TI.751 nears boiling point of liquid (provided feed is liquid at boiling point).

9. All heaters, i.e. reboiler, column and trace heaters are turned on (many trace heaters are missing or not connected).

10. Bottoms take-off pump is switched on, having set the pressure indicator/controller to about 20 p.s.i. Liquid must pass across pressure control system and valve (114) may need to be adjusted.

11. Valves (120), (110), (111) and (124) must be open (valves to bottom tank). The controller which maintains the reboiler level at about 3" below the top may also have to be adjusted.

12. Switch on all instruments.

13. No trace heaters are connected, therefore adjustements to bring in line the temperature indicators and controllers are not possible.

14. The temperature recorder and controller installed for control of the boil up rate is unsuitable because of ambient pressure changes. The only manual way of altering the B.U.R. is by way of the reflux ratio. Once the heating to the reboiler is reset, the boil up rate in the column remains reasonably constant. The reflux time is set to an arbitrary value and top take-off rate is measured (D). The boil up rate is thus equal to D(R+1). By trial and error the boil up rate can be set to the required value and to give the required flow conditions in the column the reflux ratio is set.

15. Continuous watch on temperatures to check that they remain constant.

16. The top and bottoms tank may be changed by opening and closing valves (126) and (124) respectively for bottoms and (75) and (77) for tops. (For numbers refer to Dwg. R.555 Mod (ii)).

Shutting Down

(i) Switch off all heaters.

(ii) Switch off pumps.

(iii) Switch off instruments.

Imp. Note

If the Alarm Bell sounds either the reboiler or the feed heaters will have exceeded their maximum temperature (400°C), or the liquid level in the reboiler will be below its minimum. This will be indicated by the appropriate instruments. In any event the heaters and pumps should be switched off immediately and the defect rectified.

CHAPTER 8

ANALYSIS OF LIQUID SAMPLES

8. ANALYSIS OF LIQUID SAMPLES

In the present experimental work a new method of analysis is suggested, (Ref.66), using a gas liquid chromatograph connected directly to a data logging system. It will be interesting to note that, though the method has been developed and tested on a ternary mixture, it is easily extended to handle multi-component mixtures.

The method is discussed under the following headings.

The Gas Liquid Chromatograph
Data Processing
The Digital Computer Programme
Analysis Procedure
Observations on the Analysis Procedures.

8.1 THE GAS LIQUID CHROMATOGRAPH

8.1.1 Summary

The chromatograph used was a Perkin Elmer Model 800 with a flame ionisation detector. The chromatograph column was 2 metres, $^1/_8$" O.D. tube packed with 80% chromosorbp, and Disodecylpthalate was used as the stationery liquid phase. This column was maintained at 85°C as the separation of the three components was best at this temperature. The carrier gas was pure N_2 and the flow rate was regulated using a soap film flowmeter. After passage through the chromatograph column the carrier gas was burnt at a small jet in the combustion chambers, air being supplied to the combustion chambers at an inlet pressure of 35 Psig. The output voltage of the thermoscope was an indication of the flame temperature and the flame size, and was recorded on the Sunvic chart recorder.

Before a sample was injected into the chromatograph column, the temperature and size of the flame would be steady and the recorder would have a straight line recorded as the base line. When a sample was injected the components of the sample were separated into distinct bands of each component which finally reached the flame burning at the jet in the combustion chamber. The band of each component was burnt in the flame with the effect that the size and temperature of the flame increased according to the amount and the nature of the respective components. As the three components were separated into distinct bands by the chromatograph column there were three separated peaks shown on the chart recorded.

The area of these peaks were measured by recording a large number of peak height values, read at regular intervals, and performing an integration to obtain the area.

8.1.2 Description of the Perkin Elmer Chromatograph

The Model 800 gas chromatograph,
is a sensitive laboratory instrument designed to separate complex mixtures of organic compounds with wide boiling ranges. This instrument is a dual column temperature program chromatograph. It can be operated with either one or two columns under isothermal conditions. Close column temperature control is ensured by use of a proportional temperature controller and a high velocity circulating air bath.

One of the unique features of this instrument is the incorporation of a differential flame ionization detector which provides the high sensitivity inherent in flame ionization detectors over the entire temperature program range. The Model 800 provides programmed analysis with minimum signal instability due to column substrate elution. In the differential detector, a reference flame compensates for base line shift due to the substrate elution of the column. Other features are two separate pneumatic flow controllers for the independent control of column flow and a dual liquid injector which allows sample introduction into both chromatograph columns.

This instrument consists of two major sections:

1. the upper oven cabinet containing the circulating heated air bath, the injection columns, the columns and the detector and

2. the lower cabinet which contains the carrier gas flow controller, fuel gas controls, and the electronic and mechanical assembles associated with the detector, programmer and oven thermostat.

The analytical or pneumatic system is equipped with two independent proportional flow controllers which assure constant flow during the temperature programme cycle.
The flow to either column can be controlled independently by means of a needle valve adjustment. Sample is injected into the carrier stream by inserting a hypodermic syringe through a self-sealing rubber septum into an injector capable of operation to 500°C. The injector is designed so that the carrier gas is preheated to a temperature approximating the injector block temperature before reaching the point of sample injection. As the sample is vapourised it immediately passes to the column as a discrete 'slug' of vapour.

The sample is separated into its various components within the column and as each component elutes it is carried into the column effluent splitter. The column effluents entering the detector are mixed with hydrogen and burned at the flame jets in an atmosphere of purified air. As organic sample molecules are burned, ions are formed and collected on their associated electrodes. Under steady state conditions i.e. both columns eluting equally, the ions currents in each flame oppose each other and no signal is generated at the output. The presence of sample ions in one flame unbalances the detector and yields an output current. This current is simplified and converted to a signal suitable for driving an auxilliary recording device. The recorder pen follows the increase and decrease of the signal and therefore traces peaks on the chart. The area under each peak is proportional to the concentration of the ionized sample component.

The Model 800 is designed primarily for use with either one or two packed columns with outside diameters of $^1/_8$ inch. The standard coil diameter of both $^1/_8$ inch and $\frac{1}{4}$ inch O.D. columns is 2.5 inches. The column outlets are connected directly to a receiving block where either the entire flow or a portion of the flow can be passed to the flame detector.

Excess flow can be split off and vented to suitable sample collection devices or auxilliary detecting units.

The basic features of the flame ionisation detector are many including wide dynamic, low effective volume resistance to contamination, and capability of operating over the entire temperature range of the instrument. The detector consists of two flame ionisation units housed within a single chamber. The column effluent from each stream mixes with hydrogen and flows to the associated flame jet. The platinum electrodes for each flame are arranged in such a way as to form a differential circuit. The flames are oppositely polarised and have a common output electrode. While the ionization caused by the substrate elution in one flame gives a positive going output, the ionization in the other, oppositely polarised flame gives a negative going output. When operated together, the flames tend to give a zero output signal when temperature programming chromatograph columns at elevated temperatures. As sample components are eluted into the sensing flame, the ionization current produced by this flame increases over that of the reference flame and gives an output signal proportional only to the amount of sample present.

The output from the detector is connected directly to the input of an electrometer amplifier capable of driving either galvanometer or potentiometric recorders. The negative feedback amplifier has a full scale sensitivity of 2.4×10^{-12} amperes and has an eighteen stop attenuator which attenuates the sensitivity from X1 to X500,000. The special amplifier design yields a time constant of no greater than 100 milliseconds which allows the instrument to be used for high speed analysis with both small diameter packed columns and capillary columns. The sensitivity of the Model 800 is such that a two ppm sample of propane (or C_3 equivalent at 50cc/min) eluting into the detector gives approximately full scale deflection on maximum sensitivity.

A centrifugal blower circulates air within the oven chamber. The air flow is approximately 125 cubic feet per minute, and air within any section of the chamber changes approximately seven times per second. The interior of the oven is constructed entirely of stainless steel. The low mass construction ensures efficient heating and cooling of the entire structure with minimum gradients and close temperature control. The oven temperature controller is a proportional controller which uses a silicon rectifier and platinum sensor. The rectifier continuously delivers the exact power to the heater required to maintain the desired column temperature. A thermocouple is installed in the oven chamber to monitor the temperature. Oven temperatures can be controlled anywhere between 50°C and 400°C and can be set to within 2.5°C. The column assembly can be cooled from 400°C to 50°C in less than 8 minutes.

Automatic column temperature programming is provided by selection of any of twelve different linear program rates ranging from 0.5°C/min to 48°C/min.

8.2 DATA PROCESSING

Although it is possible to obtain quantitative analyses by measuring only the maximum heights of peaks from a chart record, the accuracy obtainable is not sufficient for a rigorous investigation of any ternary organic mixture sample. Quantitative analysis by using the areas of peaks is however a method which can provide analyses of sufficient accuracy, ±0.1%. The area of a peak can be measured by a folded peak chart recorder, a shaft encoded counter, a planimeter or by cutting out and weighing of the actual peaks on the chart. All of these methods, to varying degrees, involves the manipulation of equipment by an operator to obtain peak areas. The operator also has the role of deciding on the acceptability of the peak areas obtained for further manipulation to obtain analysis of samples. The method of analysis used for this project avoids the use of an operator to interpret recorded peak data and produces as an answer, the analyses result expressed in percentages of molefractions.

A data logging system, available for the recording of experimental information was used to record information on peak heights at short time intervals. It may be mentioned that the data logger was directly linked to the Model 800 chromatograph. The system consisted of a data source scanner, a digital voltmeter and a paper tape punch. Ancilliary equipment in the system drove these units and supplied a trigger pulse for the scanner to read data at precise time intervals. The time interval used to scan the signal voltage supplied by the chromatograph as it went along the peaks was one second, but there could be one, two or four readings taken per second depending on the operator. The magnitude of the signal voltage was measured by the digital voltmeter and recorded on punched paper tape. Then a computer program was written in Fortran code and using the above obtained data tape calculated the areas.

8.3 COMPUTER PROGRAMME

The computer program has been included as Appendix (A2). The programme operates on a count routine from a marker voltage on the data tape at the commencement of each chromatograph analysis cycle. The three components were well resolved with a sufficient time interval between each peak to allow a base line voltage to be calculated, hence only the area of the peak above the baseline was determined. The small baseline drift which occasionally occurs in a prolonged investigation with a gas liquid chromatograph could thus be discounted. Before each peak emerged a number of signal voltage readings were averaged to give a value of the baseline voltage. This value was then subtracted from the values of the signal voltage recorded while the peak was emerging. The values of peak heights above the baseline were then integrated using Simpson's rule in the form

$$f(x)dx = \frac{h}{3}(y_o + 4y_1 + y_2) + \frac{h}{3}(y_2 + 4y_3 + y_4) + \frac{h}{3}(y_4 + 4y_5 + y_6) + \ldots\ldots\ldots + \text{Error function} \qquad (1)$$

where h = increment, one second

y = peak height above baseline

which gives

$$f(x)dx = \frac{h}{3}(y_o + 4y_1 + 2y_2 + 4y_3 + 2y_4 + \ldots\ldots) + \text{Error function} \qquad (2)$$

For the type of peaks obtained, with the signal voltage equalling the baseline voltage immediately before and after a peak, the first and last terms tended to zero and were negligible for the size of the increment being considered.

8.4 ANALYSIS PROCEDURE

Samples from the Reboiler and top of the column were taken and analysed by the chromatograph. Each sample from the bottom of the column took four minutes and from the top three minutes. On the average about thirty samples were taken from each run of the column and analysis of these thirty took at least three and a half hours.

The tape of peak height data was processed by the Argus (Ferranti) computer using the programme written for this analyses to give percentage of each component with respect to others. The average processing time for these data tape was five minutes.

8.5 OBSERVATIONS ON THE ANALYSIS PROCEDURE

The sole function of the operator in this analysis procedure is to insert either samples or data tapes into machines. The operator takes liquid samples for injection into the gas liquid chromatograph and the next stage is the processing of a data tape by a digital computer.

The remoteness of the operator, from the manipulation of interim results to obtain actual analysis, is a distinct advantage over the more traditional methods of analysis used. The chromatographic analysis method can be easily extended to the analysis of more complex mixtures which makes the method of particular interest now that vapour liquid equilibrium relationships of multicomponent systems are being increasingly considered.

The accuracy of analysis results which are produced by this method compare favourably with the accuracy obtained by other analytical methods of ±0.2%. A drawback to the method is the time taken between the sampling time and the production of the analysis results for the samples. Having an operator to inject each sample into the chromatograph is also a limitation though not a serious one. The principal source of sampling error is that air and vapour bubbles can be included in the volume of liquid sample to be injected into the chromatograph. Other sampling errors can arise from failure to change serum caps before leakage occurs and from pre-vapourization of part of the liquid sample by accidental contact between the tip of the syringe needle and the hot metal mounting at the injection point.

CHAPTER 9

RESULTS

9.1 Steady State Runs (R.S.S. No)

9.1.1 Numerical Experimentation

To develop a dynamic model, the initial requirement is to study the steady state behaviour of the multicomponent system under investigation. If a knowledge of two steady states is available, then a change (step or impulse) in one of them can provide the transients conditions till the new steady state is reached. This change may also be reversed to obtain the initial steady state.

Hence, various runs were made at different physical conditions (TABLE 1). The parameters altered were feed composition, reflux ratio, changing feed composition and reflux ratio simultaneously and varying the amount of top and bottom take offs. An appreciation of the steady state runs is given here by

RUNS 1→9 A few runs were made with 0.3 Top product and 0.7 Bottom product take offs. It can be seen FIG(1), that not a very good separation was obtained in the column of the three components for all the reflux ratios (1:1 to 30:1) tried. But the trend was towards better separation between the three components as the reflux ratio increased, but still did not meet the requirements set.

/

TABLE (1)

STEADY STATE NUMERICAL RUNS

Run No.	Feed Composition			Distillate	Bottom	Reflux	Feed
	Acetone	Methanol	IPA	Rate	Rate	Ratio	Plate
R.S.S.1	0.475	0.05	0.475	0.3	0.7	1 1	5th
R.S.S.2	"	"	"	"	"	2:1	"
R.S.S.3	"	"	"	"	"	3:1	"
R.S.S.4	"	"	"	"	"	4:1	"
R.S.S.5	"	"	"	"	"	5:1	"
R.S.S.6	"	"	"	"	"	10:1	"
R.S.S.7	"	"	"	"	"	20:1	"
R.S.S.8	"	"	"	"	"	30:1	"
R.S.S.9	"	"	"	"	"	60:1	"
R.S.S.10	0.475	0.05	0.475	0.5	0.5	1:1	5th
R.S.S11	"	"	"	"	"	2:1	"
R.S.S12	"	"	"	"	"	3:1	"
R.S.S13	"	"	"	"	"	4:1	"
R.S.S14	"	"	"	"	"	5:1	"
R.S.S15	"	"	"	"	"	10:1	"
R.S.S16	0.465	0.05	0.485	0.5	0.5	5:1	"
R.S.S17	0.485	0.05	0.465	0.5	0.5	5:1	"
R.S.S18	0.465	0.05	0.485	"	"	4:1	"
R.S.S.19	0.485	0.05	0.465	"	"	4:1	"
R.S.S.20	0.475	0.05	0.475	0.6	0.4	4:1	"
R.S.S.21	0.465	0.05	0.485	"	"	4:1	"
R.S.S.22	0.485	0.05	0.465	"	"	4:1	"

TABLE (1) contd.../

Run No.	Feed Composition			Distillate Rate	Bottom Rate	Reflux Ratio	Feed Plate
	Acetone	Methanol	IPA				
R.S.S.23	0.475	0.05	0.475	0.5	0.5	5:1	4th
R.S.S.24	"	"	"	"	"	"	3rd
R.S.S.25	"	"	"	"	"	"	6th
R.S.S.26	0.475	0.05	0.475	0.5	0.5	5:1	7th

RUNS 10 → 19

The feed composition and the feed rate were allowed to remain the same as in the previous runs, but the top and bottom take offs were altered to 0.5. top and 0.5 bottom, and runs were made at 6 different reflux ratios . The resultant separation was highly encouraging as can be seen from the composition profile in FIG (2-8). Separation was good right from lower reflux ratios and improved considerably with increasing reflux ratios.

By changing the top and bottom take off rate, a marked difference in the composition profiles of the ternary system was observed. The separation throughout the column became better and more even. Acetone increased in the distillate, Methanol increased and Isopropanol had no effect. On the other hand, Acetone and Methanol decreased considerably in the bottom product and thereby increasing the quantity of Isopropanol in the bottom product.

RUNS 20 → 22

In Runs 10 →19, both vapour and liquid flow rates changed as the reflux ratio was changed, in other words the profiles could well be interpreted as boil up rate change profiles. In order to keep the vapour flow constant in the column or to have conditions of constant boil up rate, top and bottom product take offs were changed to 0.6 and 0.4 respectively. Hence these runs may also be accounted for as the changes in reflux ratio only.

The separation was not very good, but the profiles provided, fig (11, 12, 13) were used for studying the dynamics of the system to a reflux change.

RUNS 23 → 26

Composition profiles for feed on different plates were computed and are given in Fig (14, 15, 16, 17). Plate 6 and 7 were above the original feed plate and 3 and 4 were below.

It canbe seen that the separation is'nt effected very much by feeding in plate 3 and 4, but changes considerably when the feed is on 6th and 7th plate. The whole concentration profile is shifted towards the top half of the column. It could be due to the presence of methanol which is more volatile than I.P.A. that its tendency to separation takes it towards the distillate, end, but then it drops down as there is so little of it in the feed. It can be seen that when the feed plate is moved upto 7, the concentration profile also shifts slightly further up.

The effect of reflux ratio on composition profils of all the three components is shown in figure (18). Briefly, the graph can be interpreted as follows:
Acetone increases in purity with increase in reflux ratio.
Methanol, which gives a double peak effect intially (at lower R.R.), gets well distributed over the column later on. Finally, the quantity of isopropanol on top of the column decrease with increase in reflux ratio.

Next, from one steady states, two step changes in the feed composition were made and the profiles have been compared with the initial steady state in fig (19). It was very interesting to find that whole profile (including methanol although no disturbance was made in that particular component) moves in the direction of increment in the feed composition of Acetone or isopropanol.

Fig (21) shows that the values of K (equilibruim constants) increase slightly in the lower reflux ratios, but become appreciably constant as the reflux ratio was increased.

The values of K decrease from bottom to top of the column as shown in fig (22) for all the three components.
The effect of volatility can also be deduced from this fig.

which is that the equilibruim constents K's decrease with decreasing volatility.

The liquid compositions vary considerably from in the initial changes in the reflux ratio, but became constant with increasing reflux ratio as can be see from fig (23). It should be remembered that these are all steady state compositions & Methanol is very evenly distributed throughout, just like suggested by general composition profiles of runs 10 to 19.

A similtaneous change in feed composition and reflux ratio can be seen in fig (20)

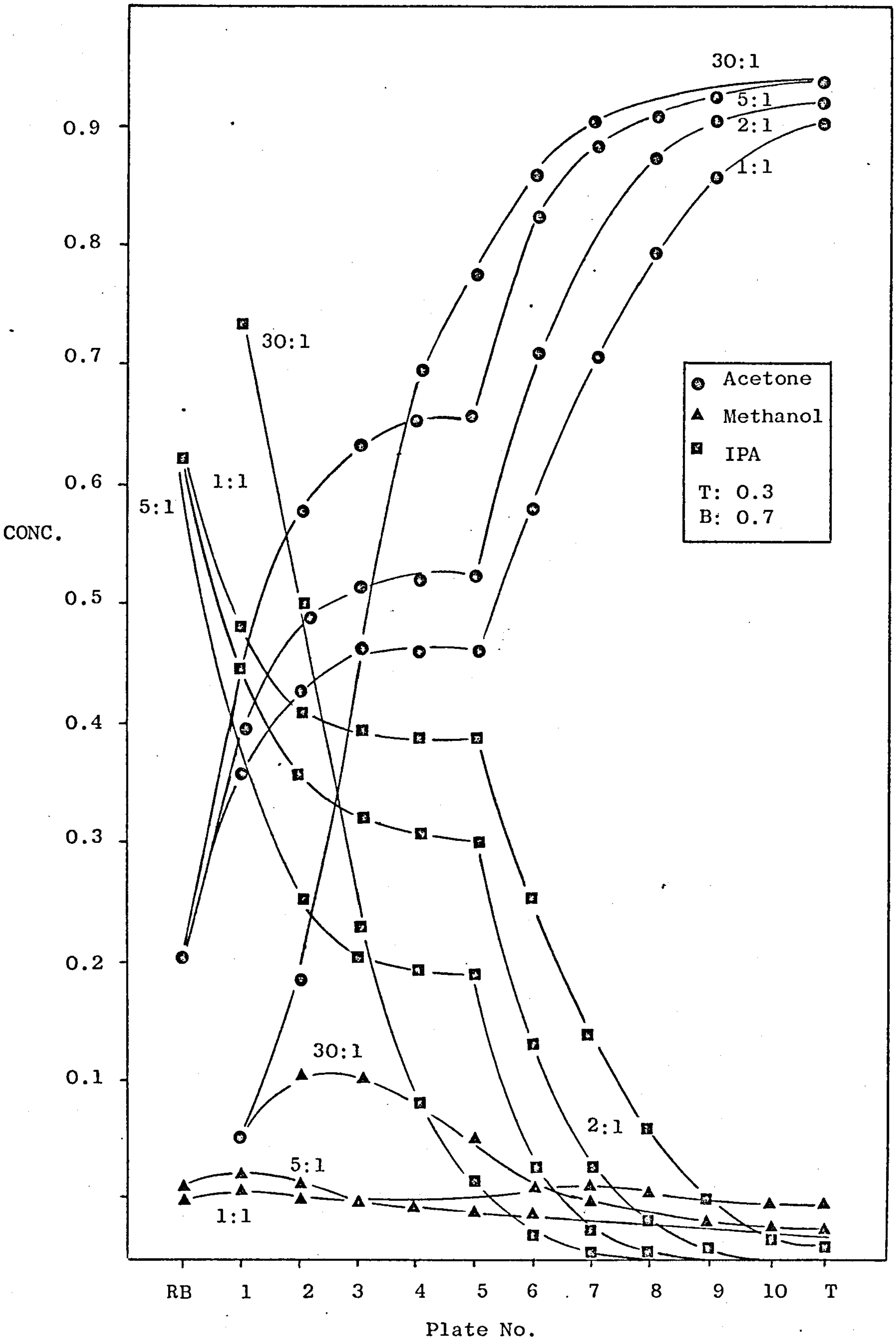

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
● Acetone
▲ Methanol
■ IPA
T: 0.3
B: 0.7
30:1
5:1
2:1
1:1
30:1
5:1
1:1
30:1
2:1
5:1
1:1

Fig.(1)

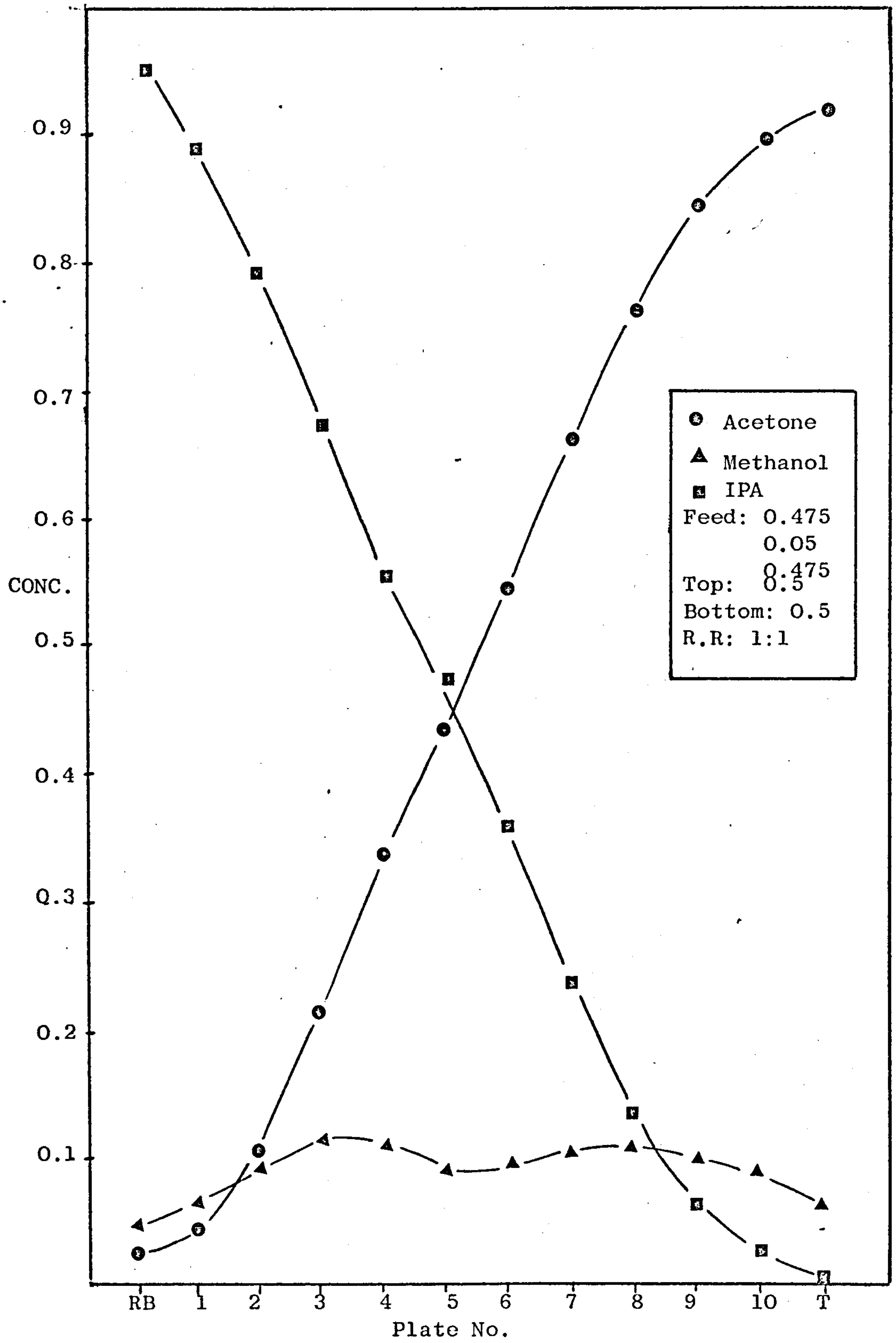

0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
● Acetone
▲ Methanol
■ IPA
Feed: 0.475
0.05
0.475
Top: 0.5
Bottom: 0.5
R.R: 1:1

Fig. (2)

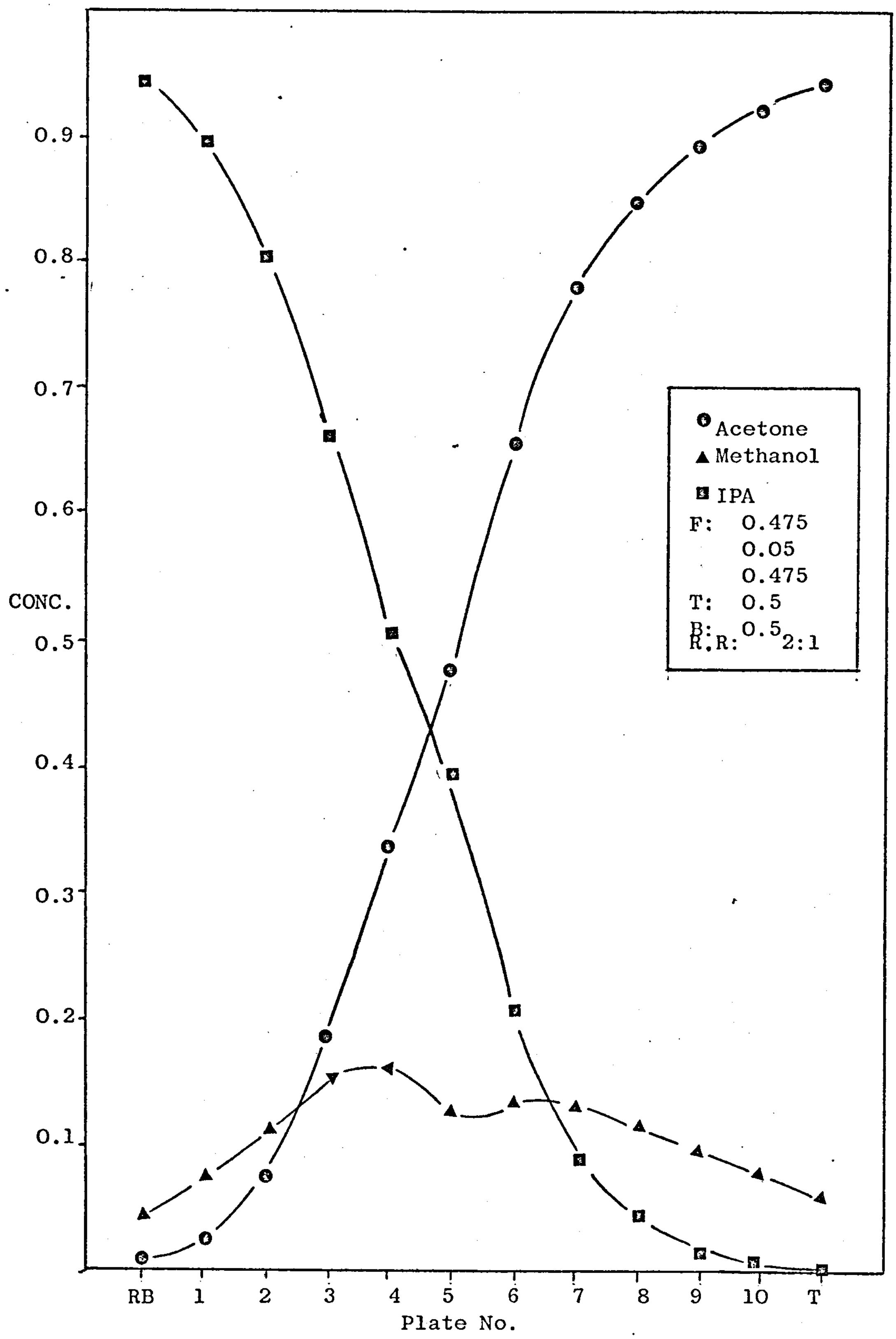

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
● Acetone
▲ Methanol
▣ IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 2:1

Fig.(3)

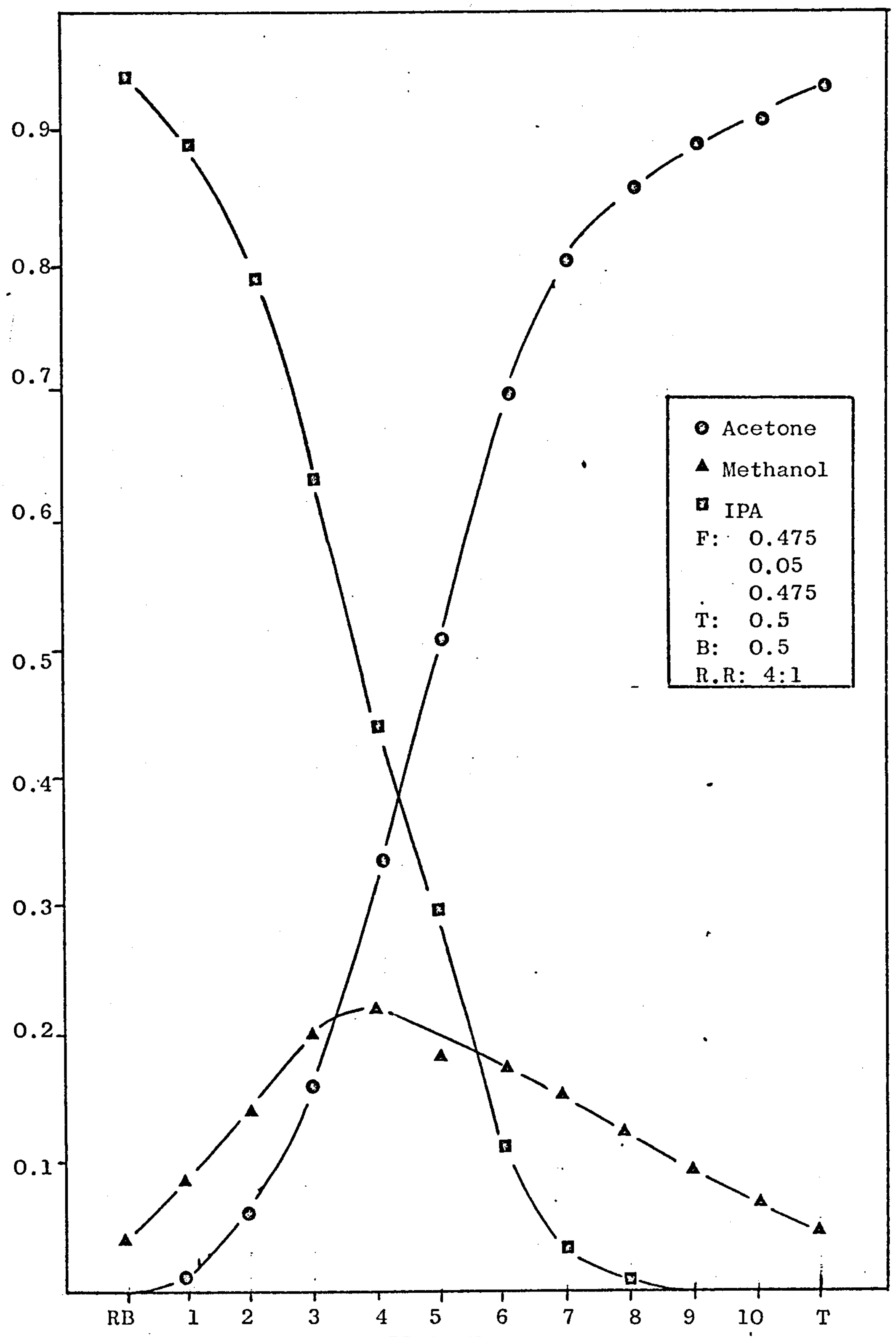
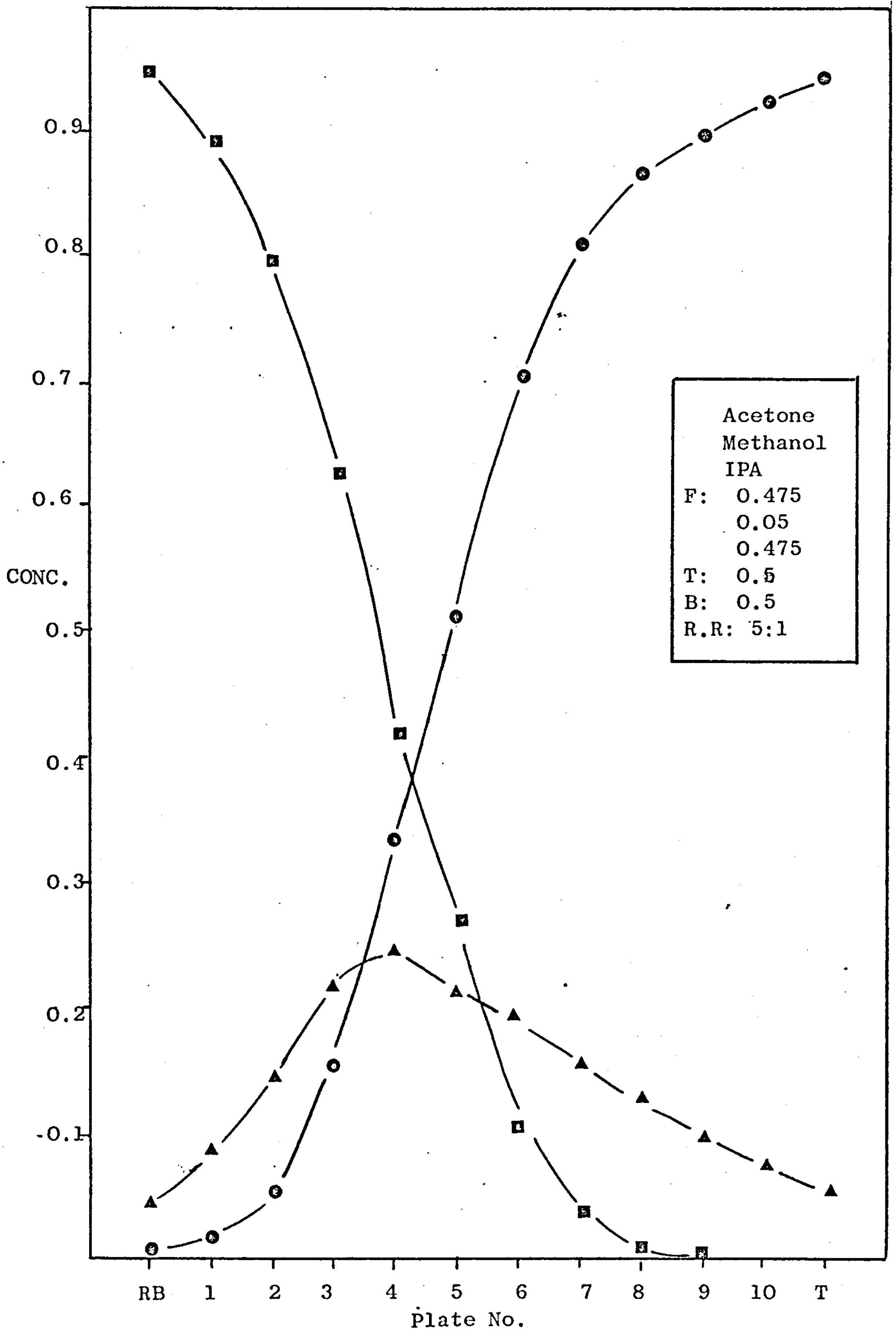

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
● Acetone
▲ Methanol
■ IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 4:1

Fig.(4)



0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
-0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
Acetone
Methanol
IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 5:1

Fig.(5)

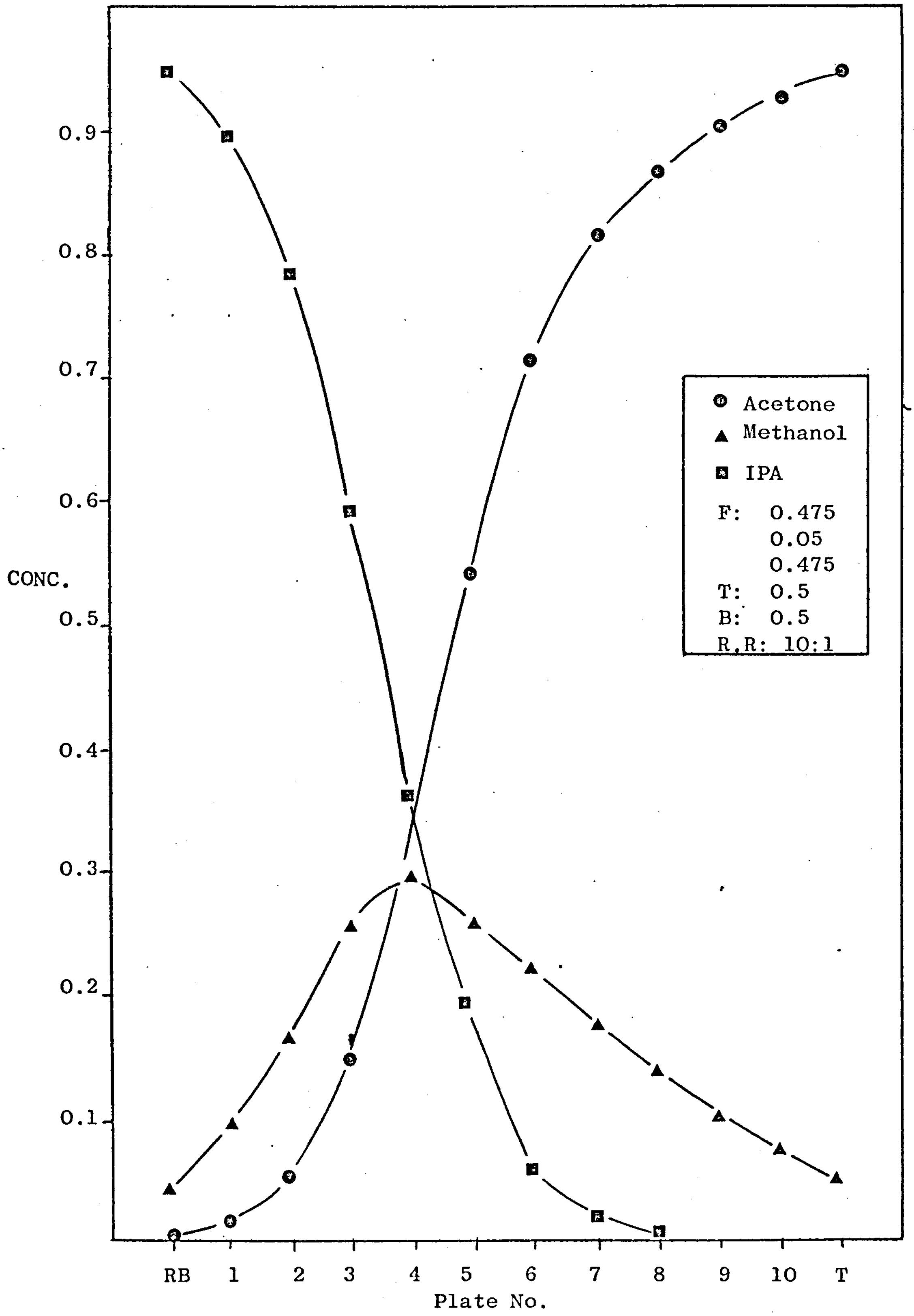

0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
● Acetone
▲ Methanol
▨ IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 10:1

Fig.(6)

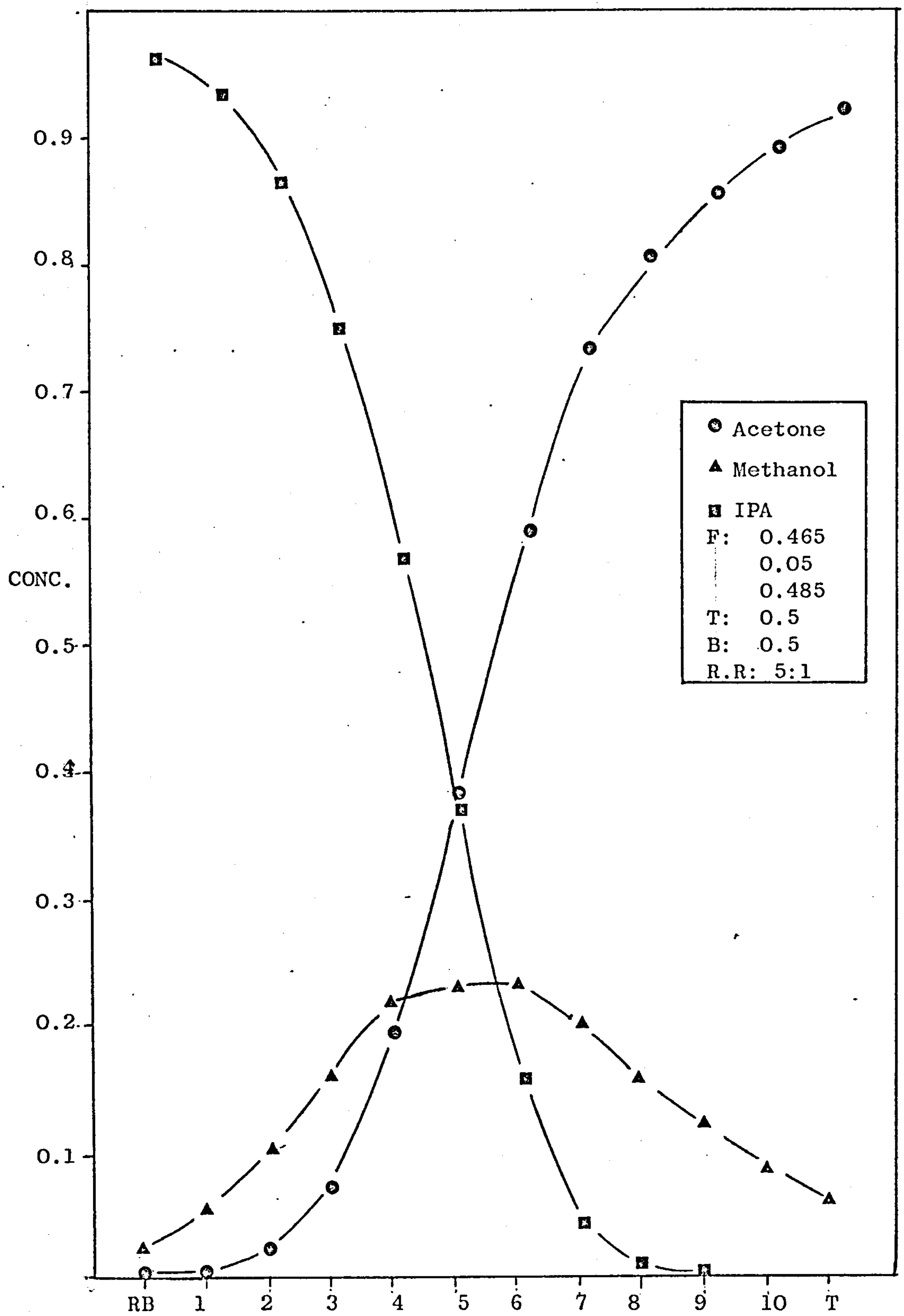
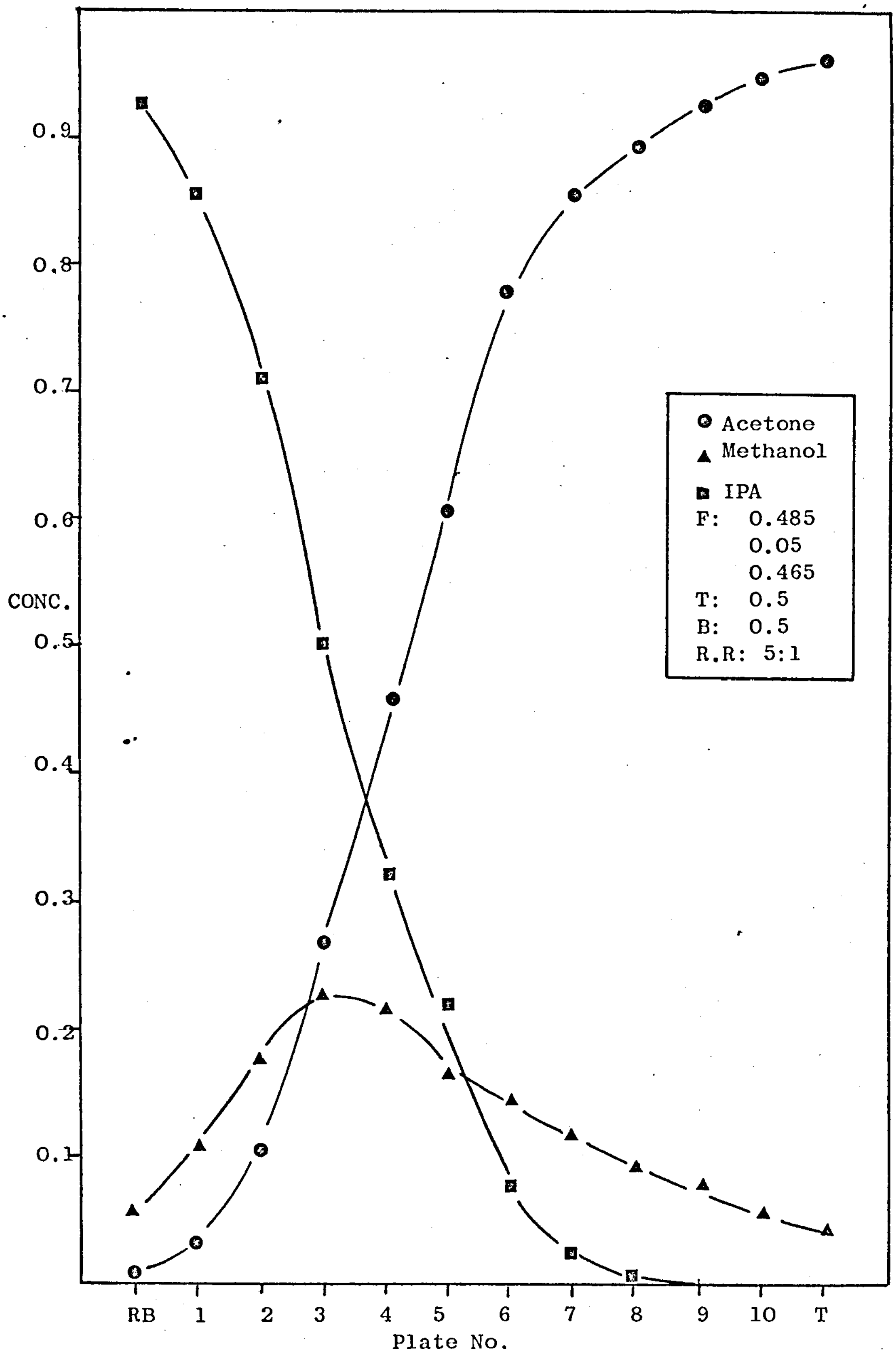


Plate No.

Fig. (7)



0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
● Acetone
▲ Methanol
■ IPA
F: 0.485
0.05
0.465
T: 0.5
B: 0.5
R.R: 5:1

Fig.(8)

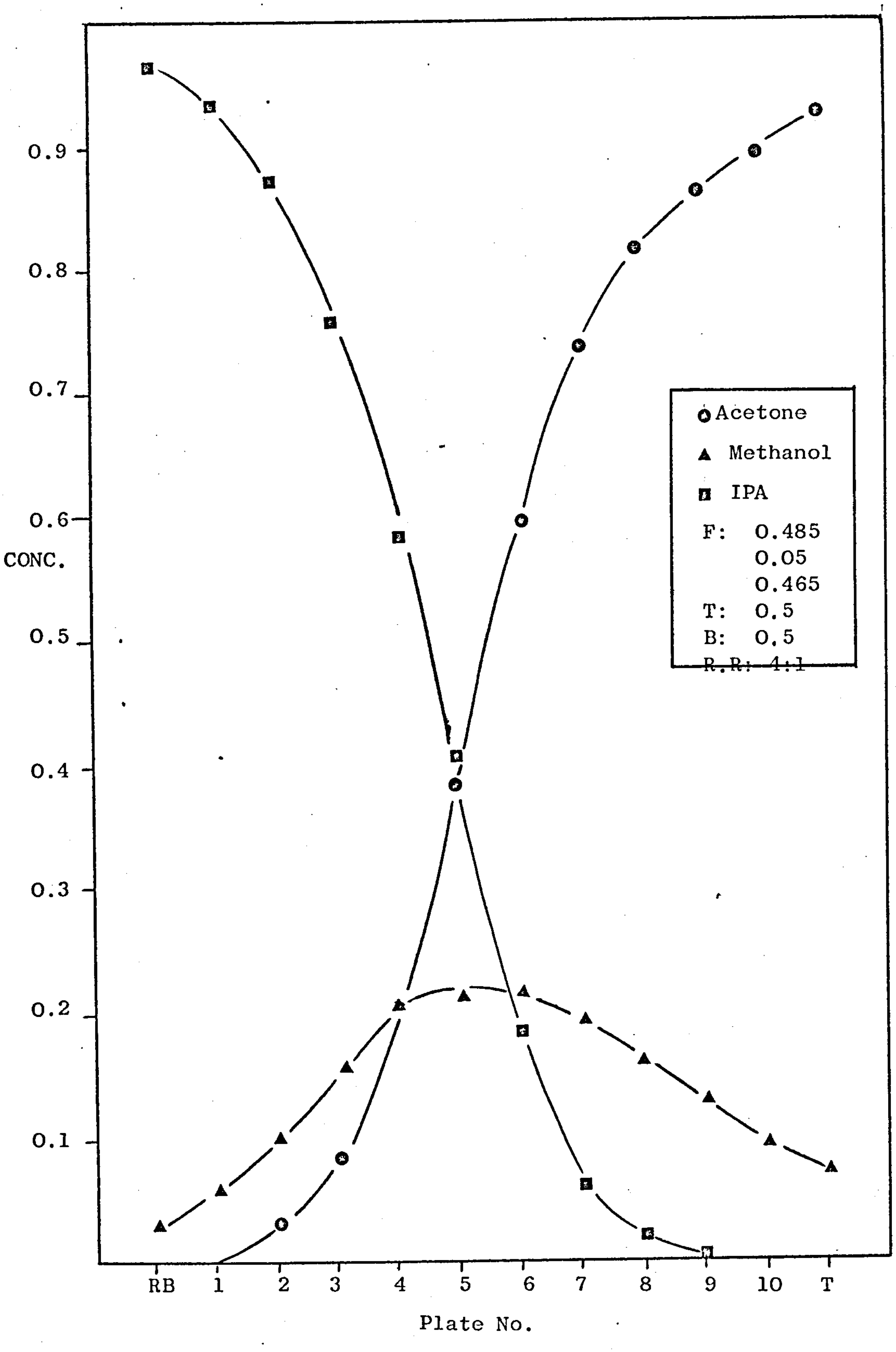
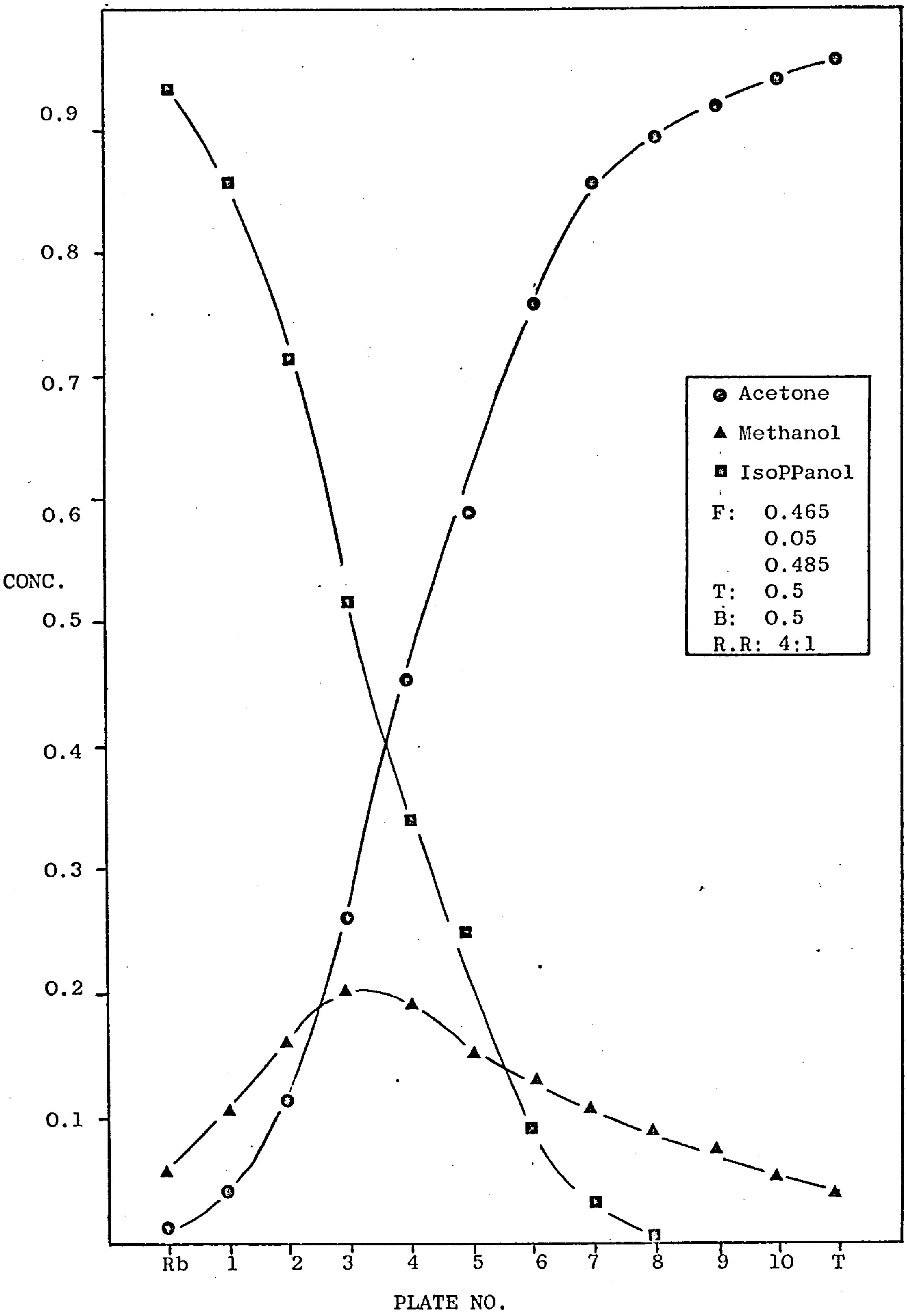

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
○ Acetone
▲ Methanol
■ IPA
F: 0.485
0.05
0.465
T: 0.5
B: 0.5
R.R: 4:1

Fig. (9)



CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Rb
1
2
3
4
5
6
7
8
9
10
T
PLATE NO.
Acetone
Methanol
IsoPPanol
F: 0.465
0.05
0.485
T: 0.5
B: 0.5
R.R: 4:1

Fig. (10)

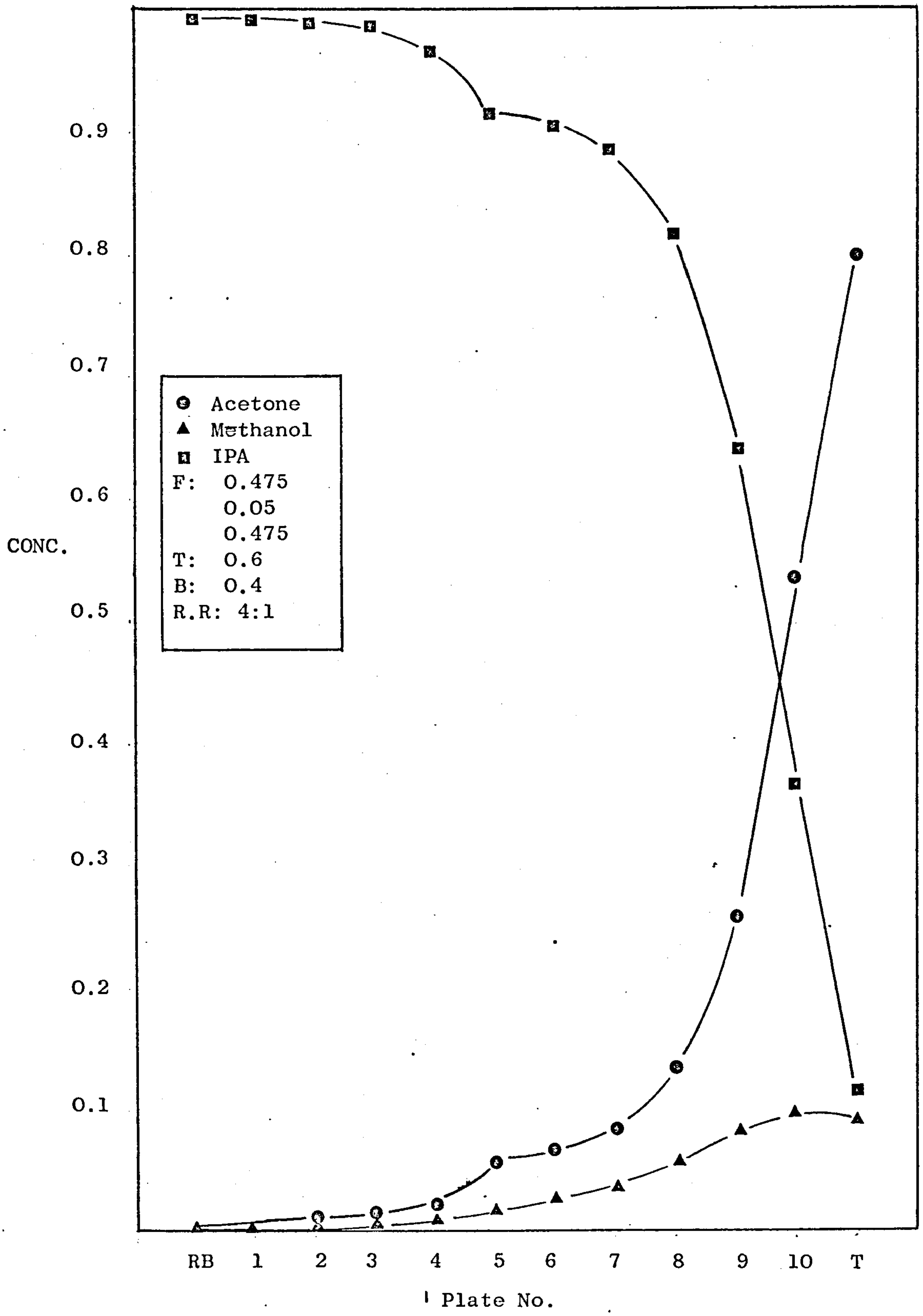

CONC.
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
● Acetone
▲ Methanol
■ IPA
F: 0.475
0.05
0.475
T: 0.6
B: 0.4
R.R: 4:1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.

Fig.(11)

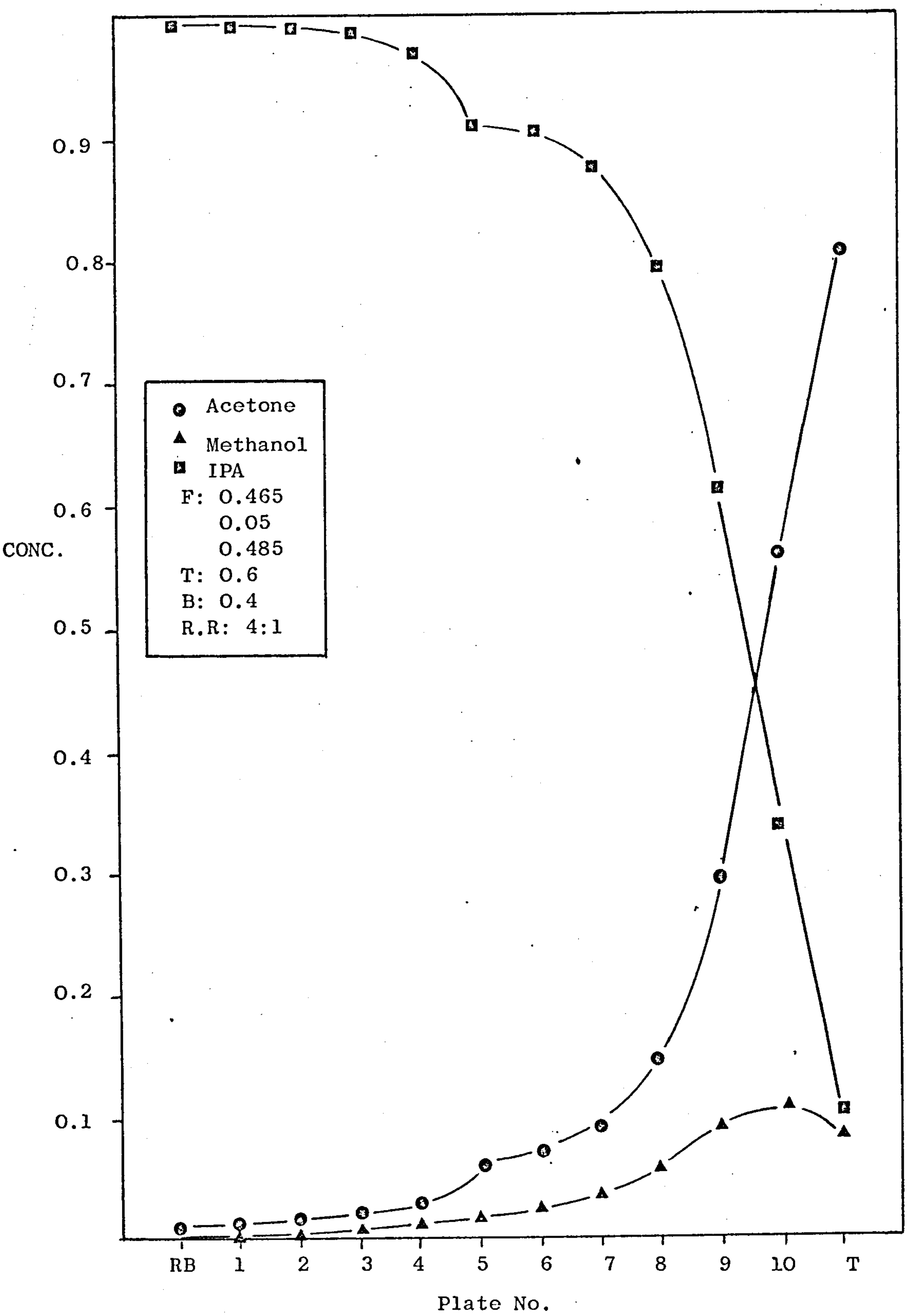

0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
0.1
● Acetone
▲ Methanol
▨ IPA
F: 0.465
0.05
0.485
T: 0.6
B: 0.4
R.R: 4:1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.

Fig.(12)

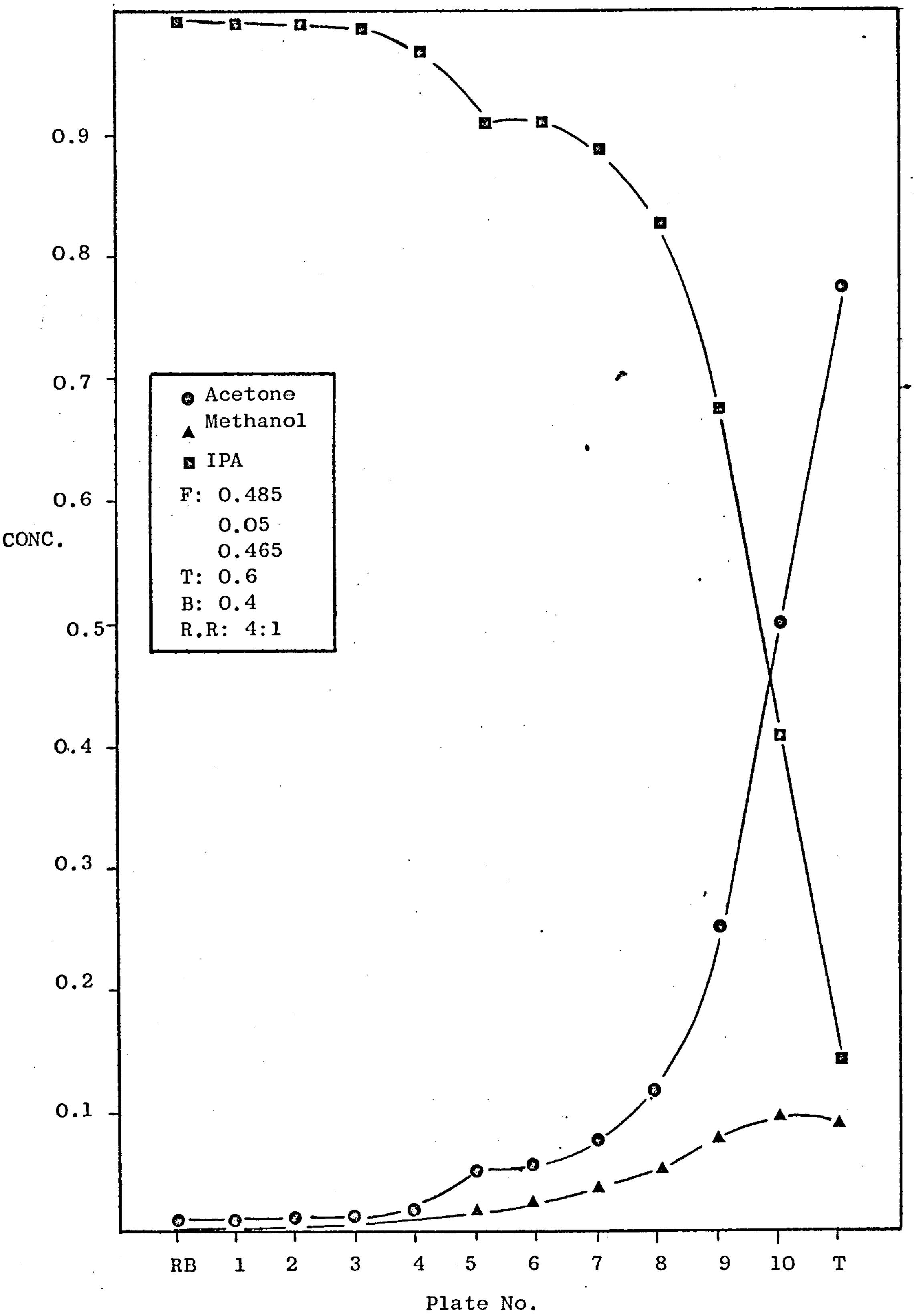

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
● Acetone
▲ Methanol
▨ IPA
F: 0.485
0.05
0.465
T: 0.6
B: 0.4
R.R: 4:1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.

Fig. (13)

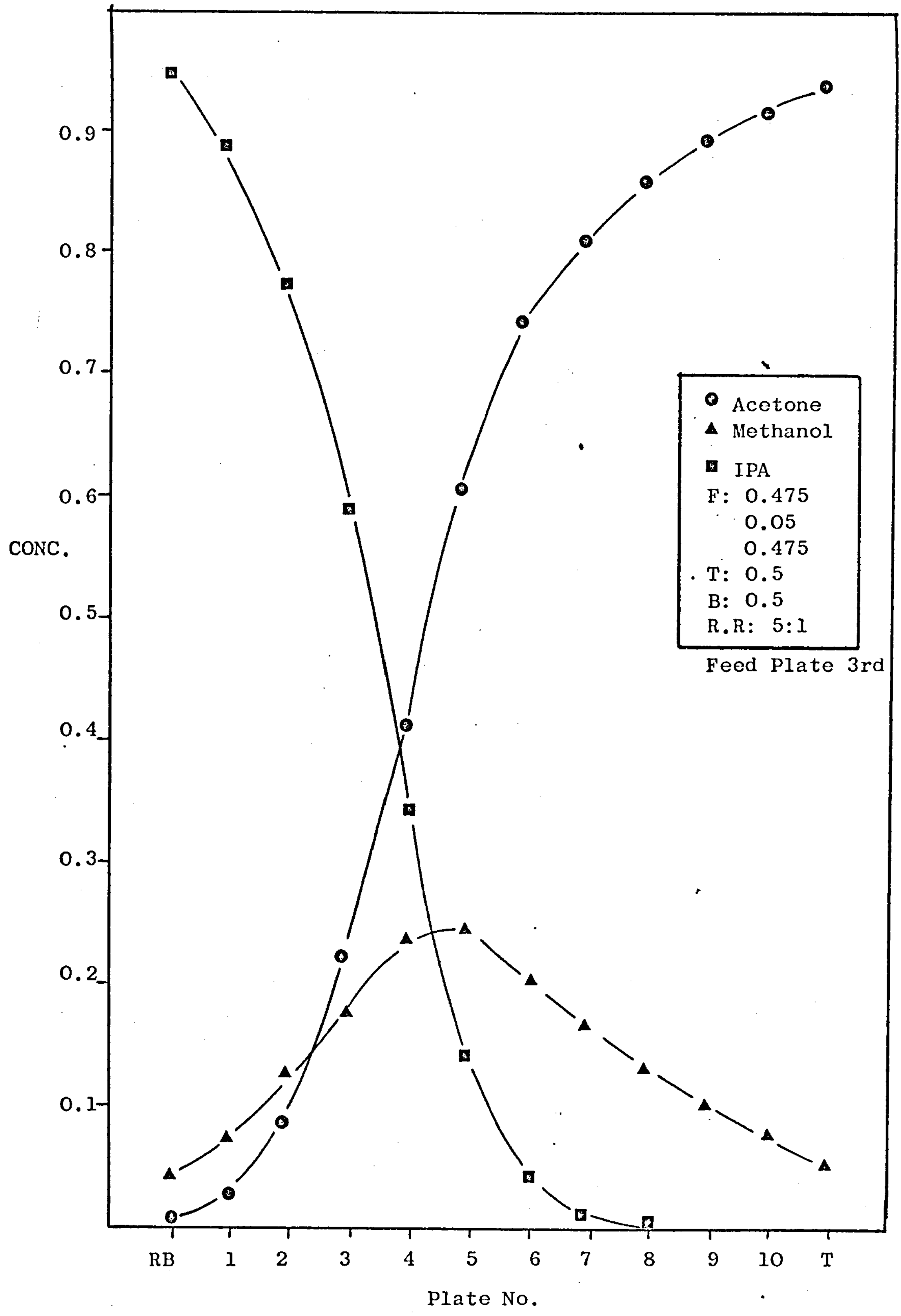

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
Acetone
Methanol
IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 5:1
Feed Plate 3rd

Fig. (14)

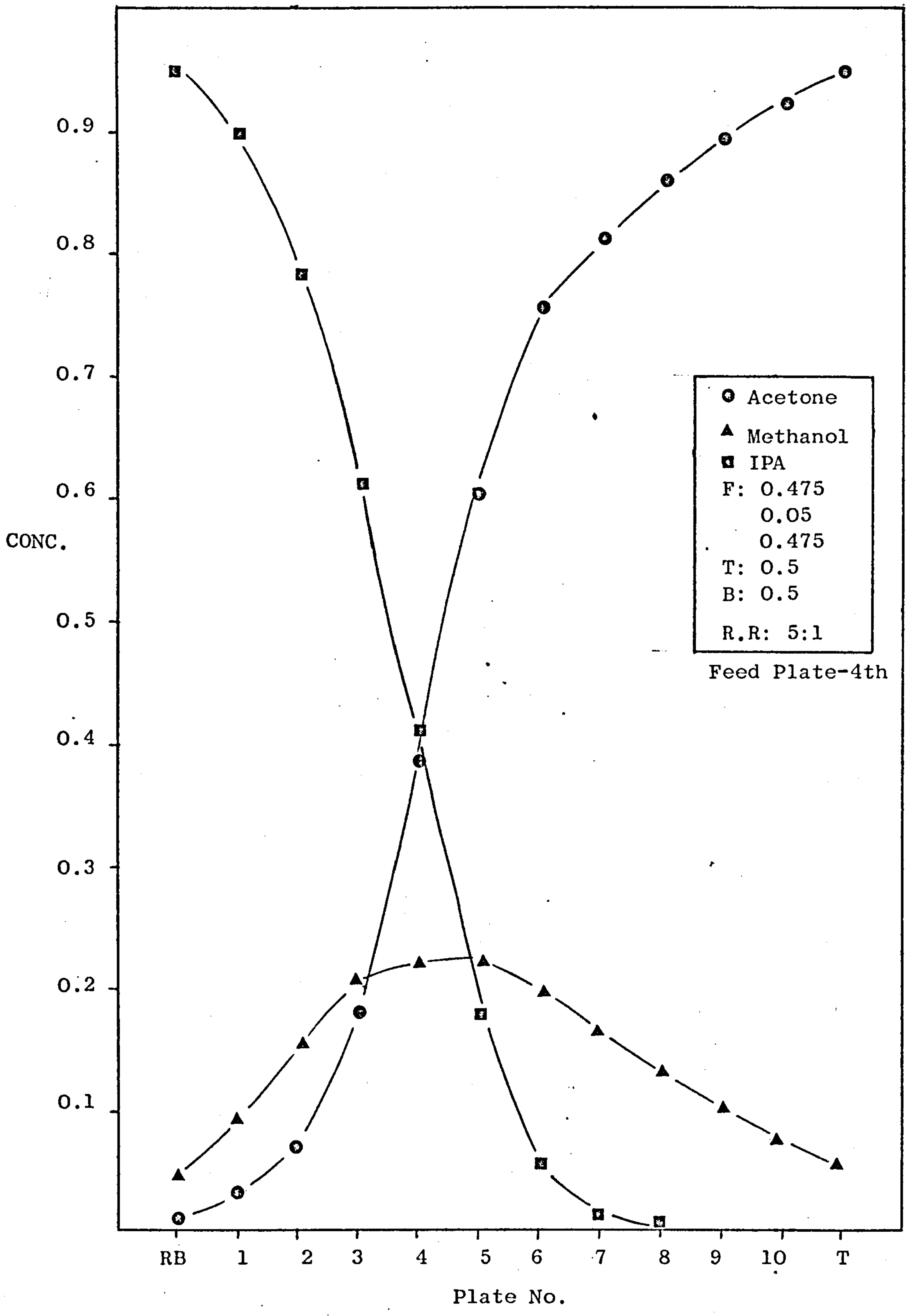

0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
○ Acetone
▲ Methanol
▣ IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 5:1
Feed Plate-4th

Fig. (15)

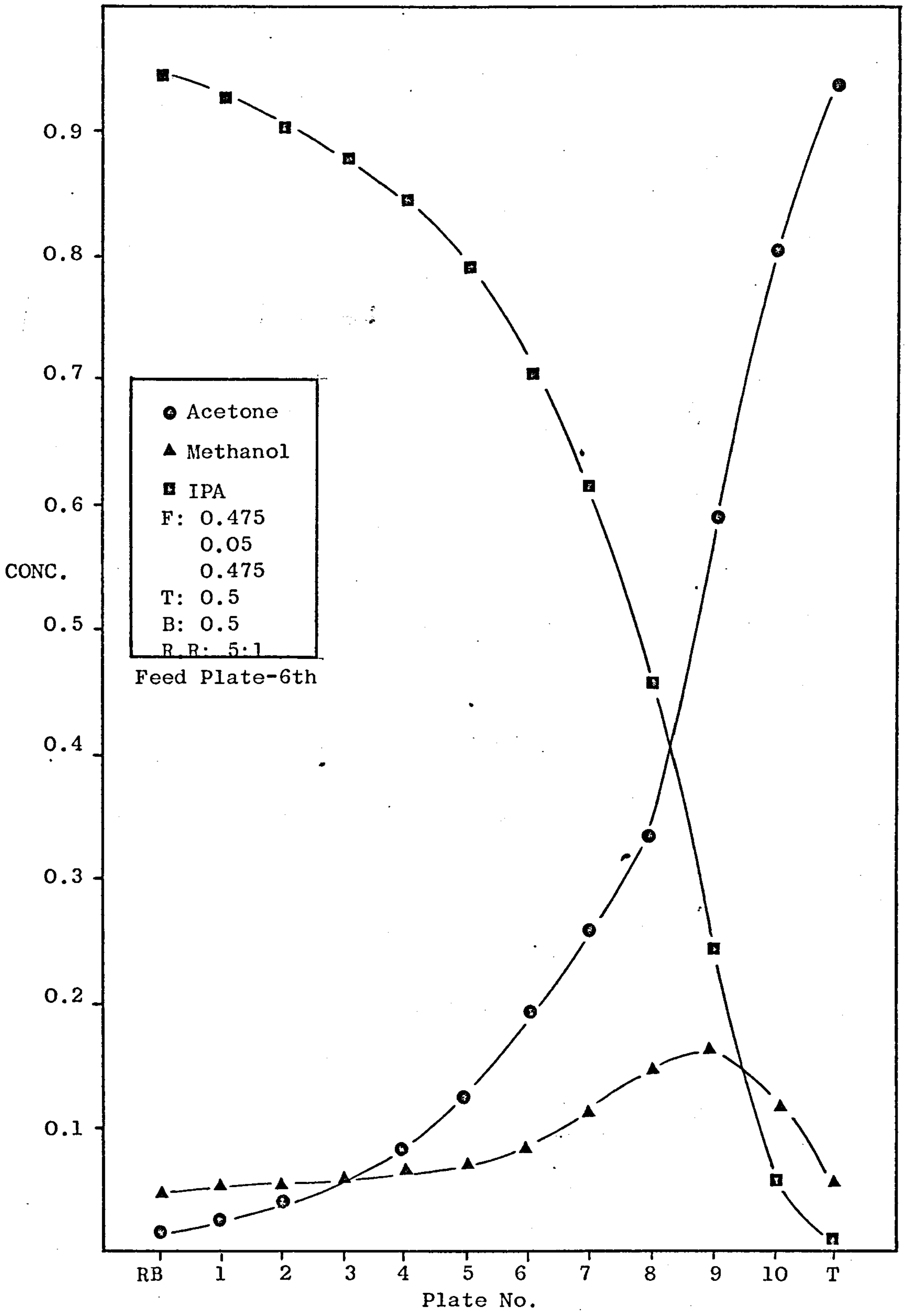

0.9
0.8
0.7
0.6
CONC.
0.5
0.4
0.3
0.2
0.1
● Acetone
▲ Methanol
■ IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 5:1
Feed Plate-6th
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.

Fig. 16

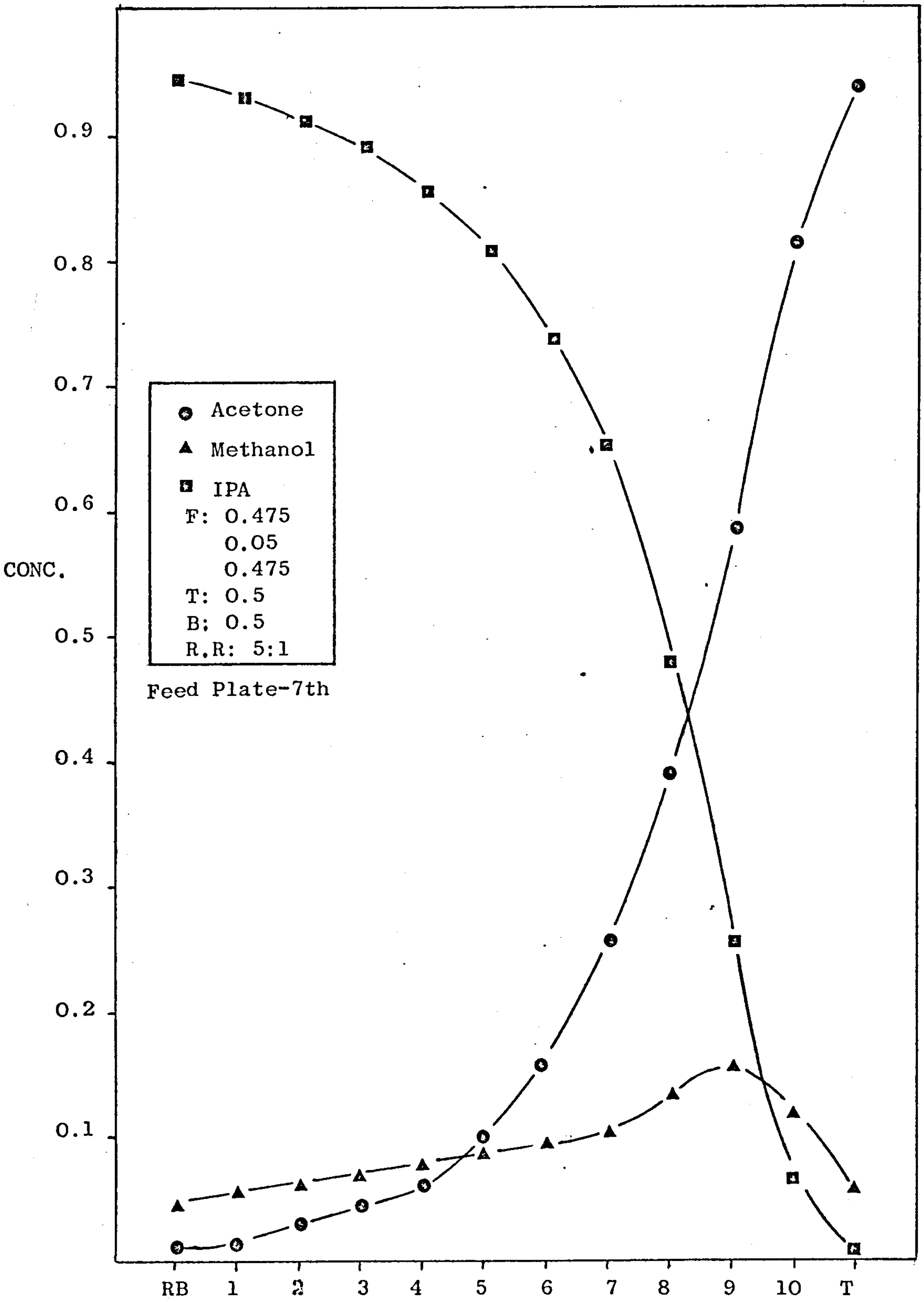

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
CONC.
● Acetone
▲ Methanol
▨ IPA
F: 0.475
0.05
0.475
T: 0.5
B: 0.5
R.R: 5:1
Feed Plate-7th
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.

Fig. (17)

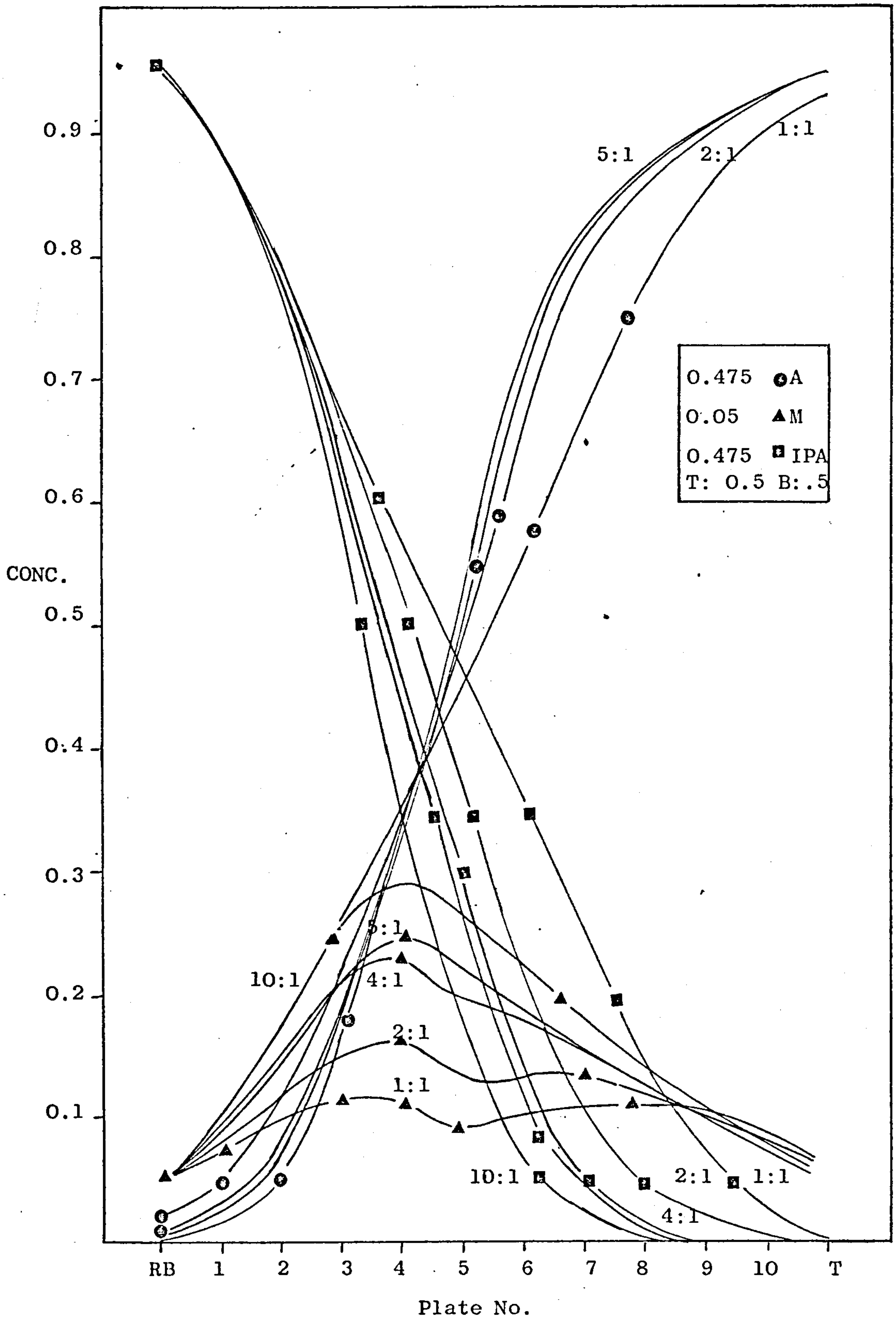

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
5:1
2:1
1:1
10:1
5:1
4:1
2:1
1:1
10:1
2:1
1:1
4:1
0.475 A
0.05 M
0.475 IPA
T: 0.5 B:.5

Fig.(18)

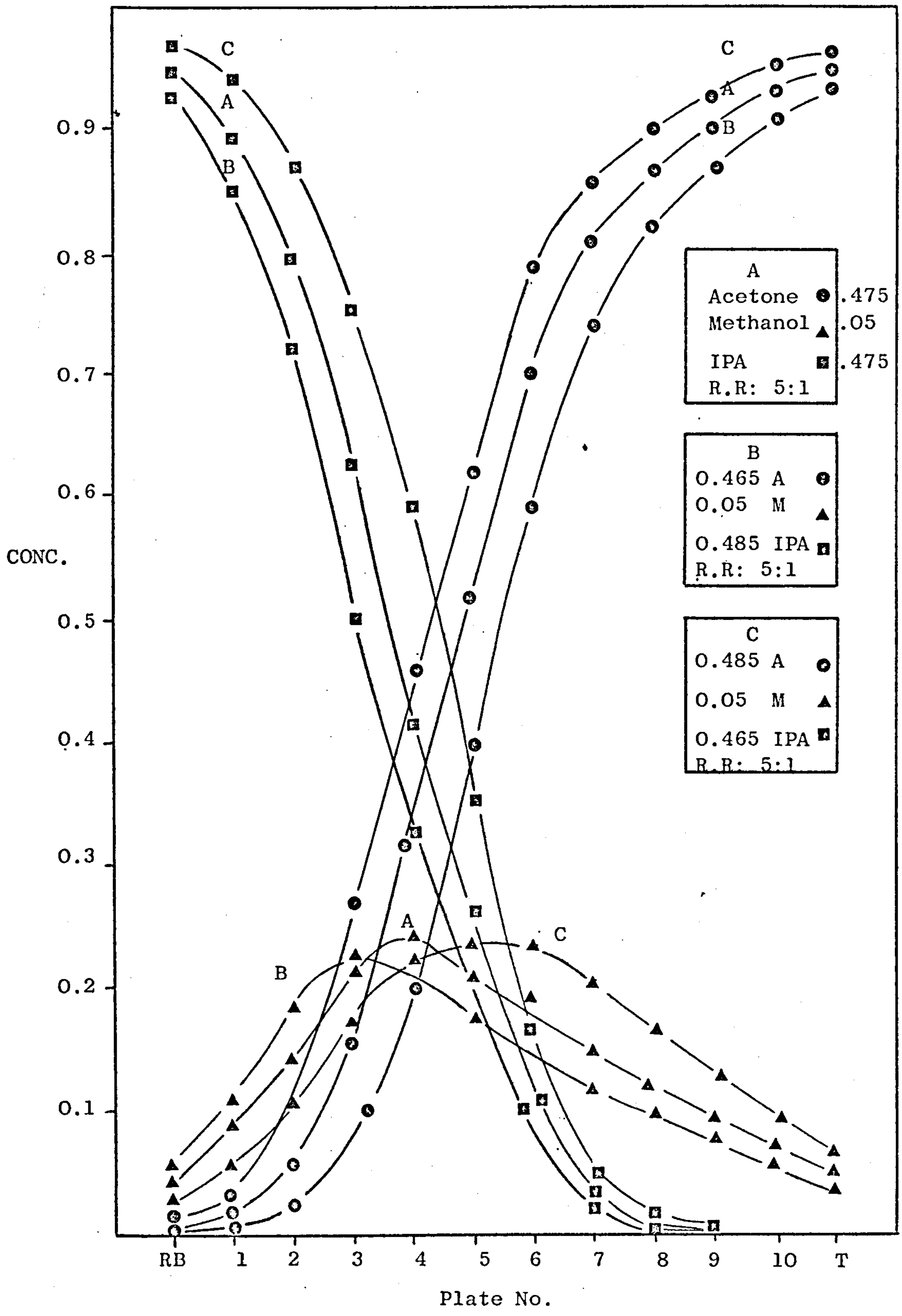

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
C
A
B
C
A
B
A
B
C
A
Acetone ● .475
Methanol ▲ .05
IPA ■ .475
R.R: 5:1
B
0.465 A ●
0.05 M ▲
0.485 IPA ■
R.R: 5:1
C
0.485 A ●
0.05 M ▲
0.465 IPA ■
R.R: 5:1

Fig.(19)

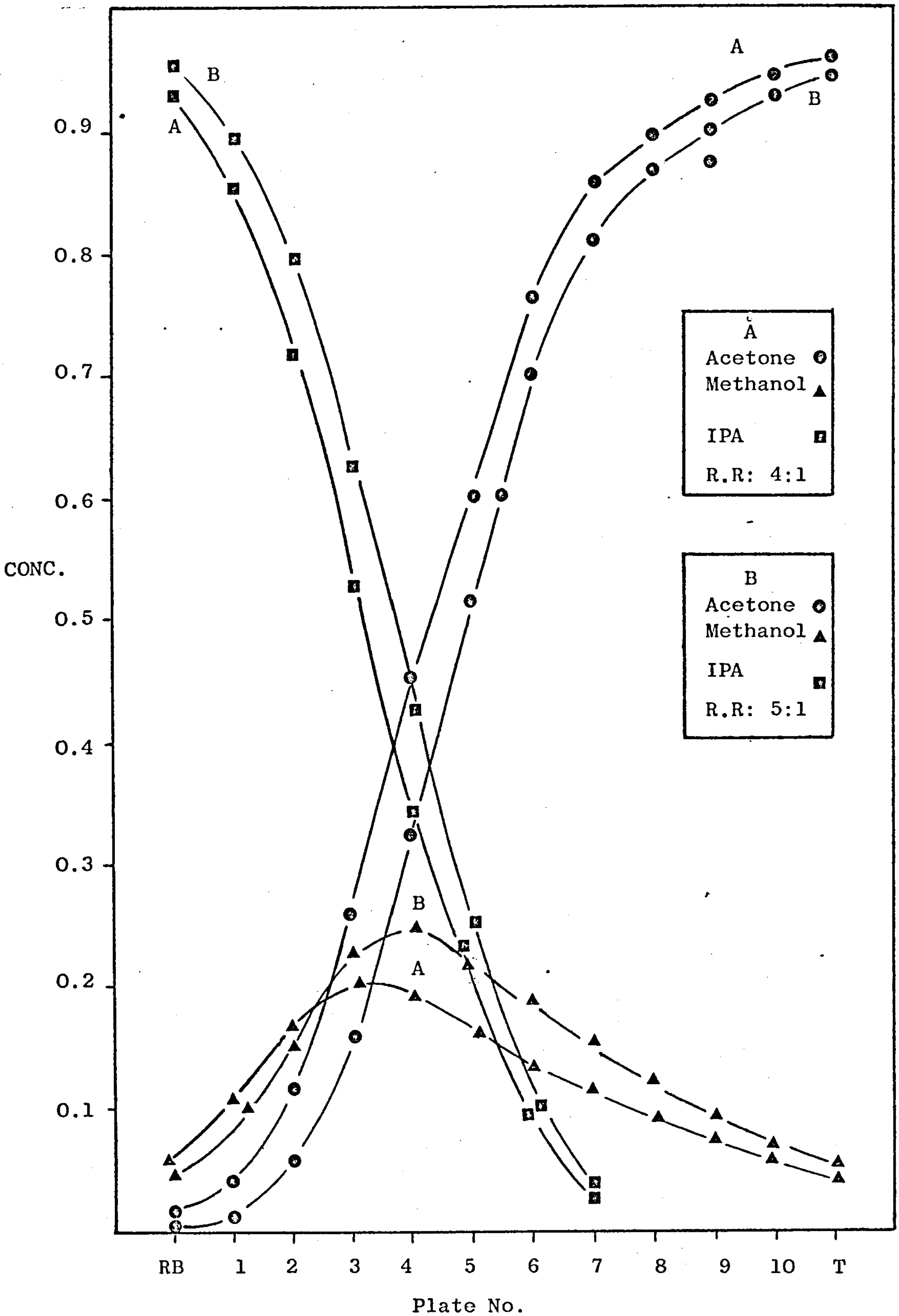

CONC.
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
A
B
A
B
B
A
RB
1
2
3
4
5
6
7
8
9
10
T
Plate No.
A
Acetone ●
Methanol ▲
IPA ■
R.R: 4:1
B
Acetone ●
Methanol ▲
IPA ■
R.R: 5:1

Fig. 20

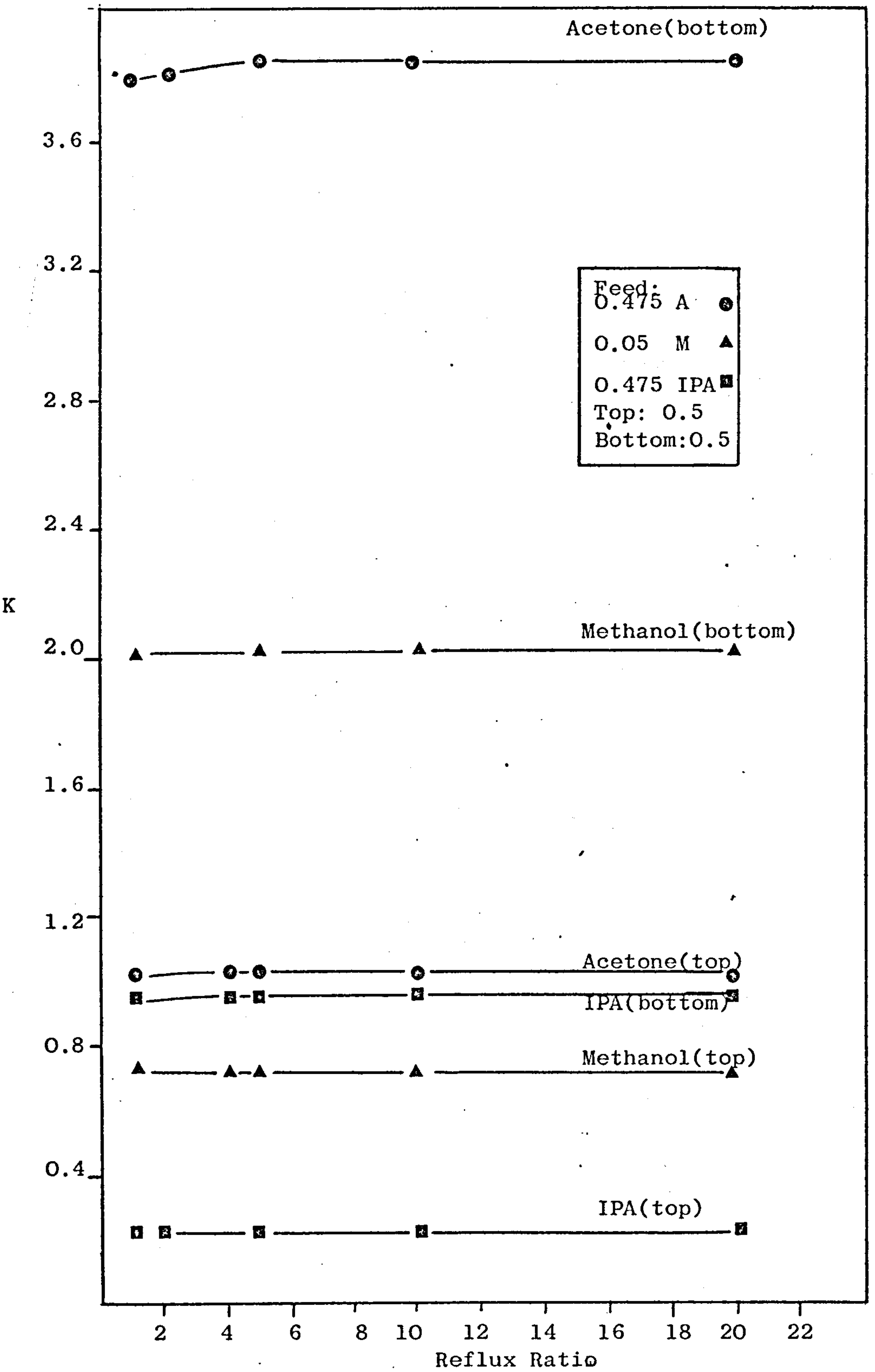


Fig.21) Effect of Reflux Ratio on Equilibrium Constants K.

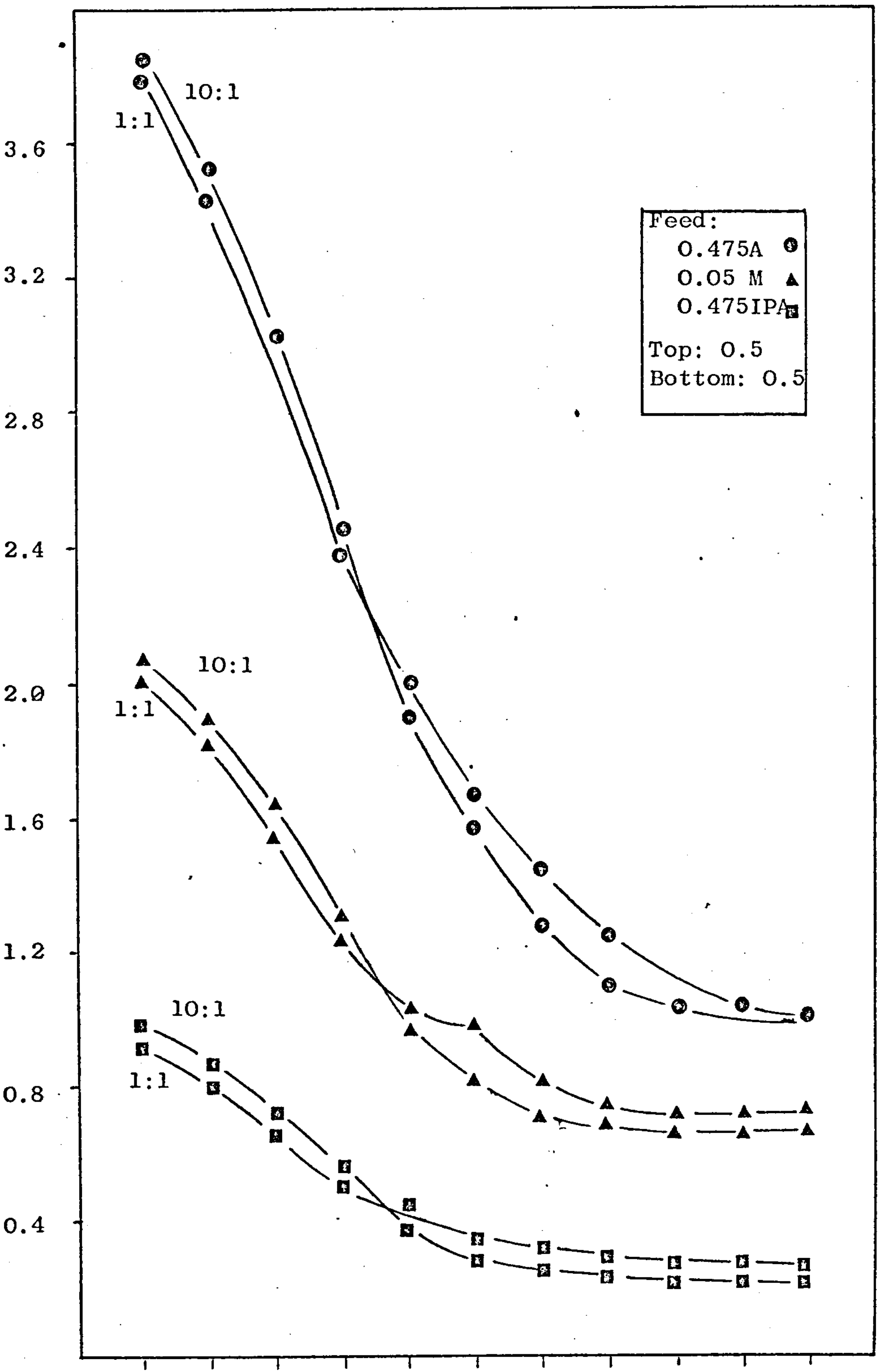


Fig.(11) Equilibrium Constants Profile at different R.R.

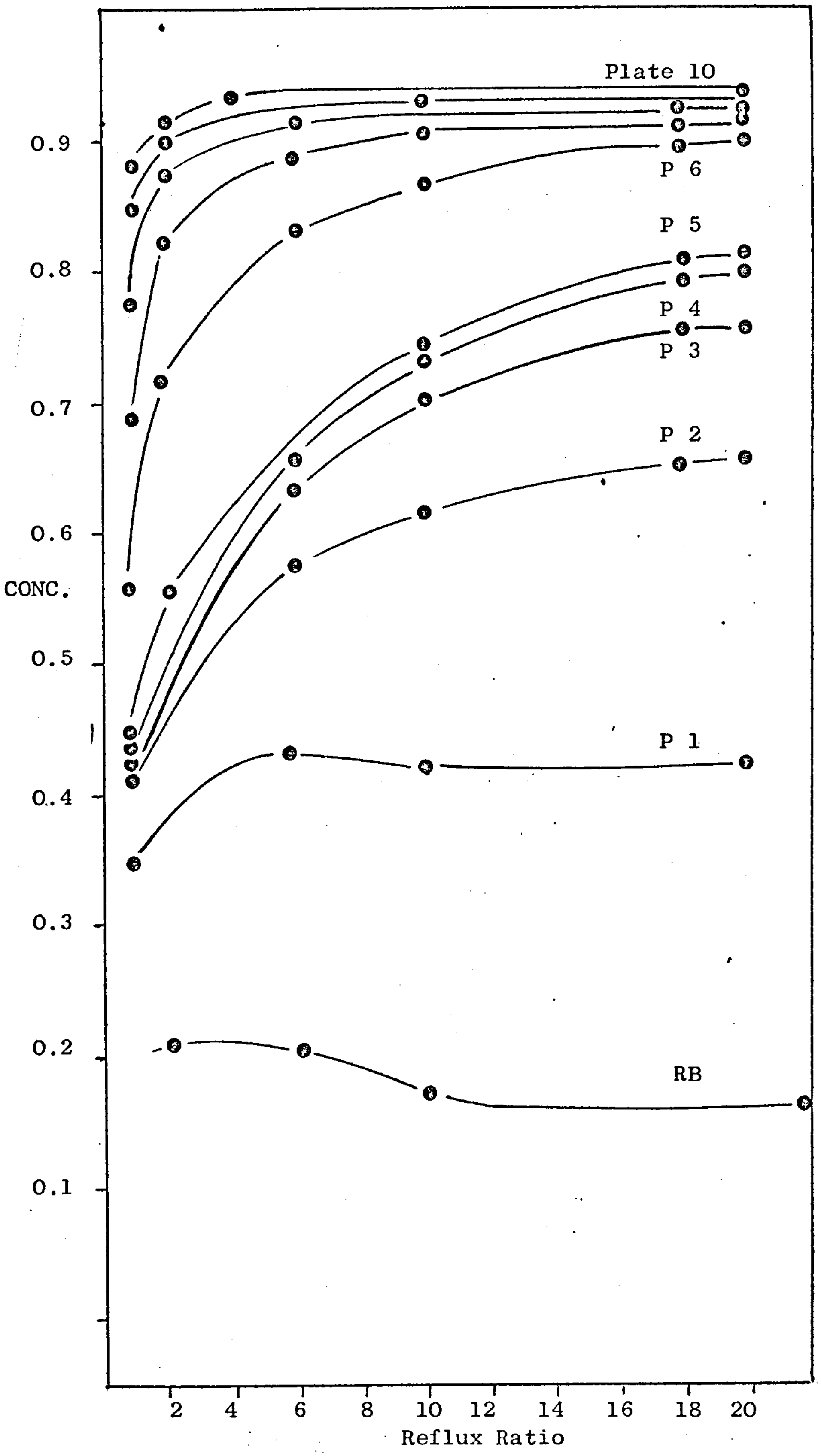


Fig.(13) Liquid Composition vs R.R. (Acetone).

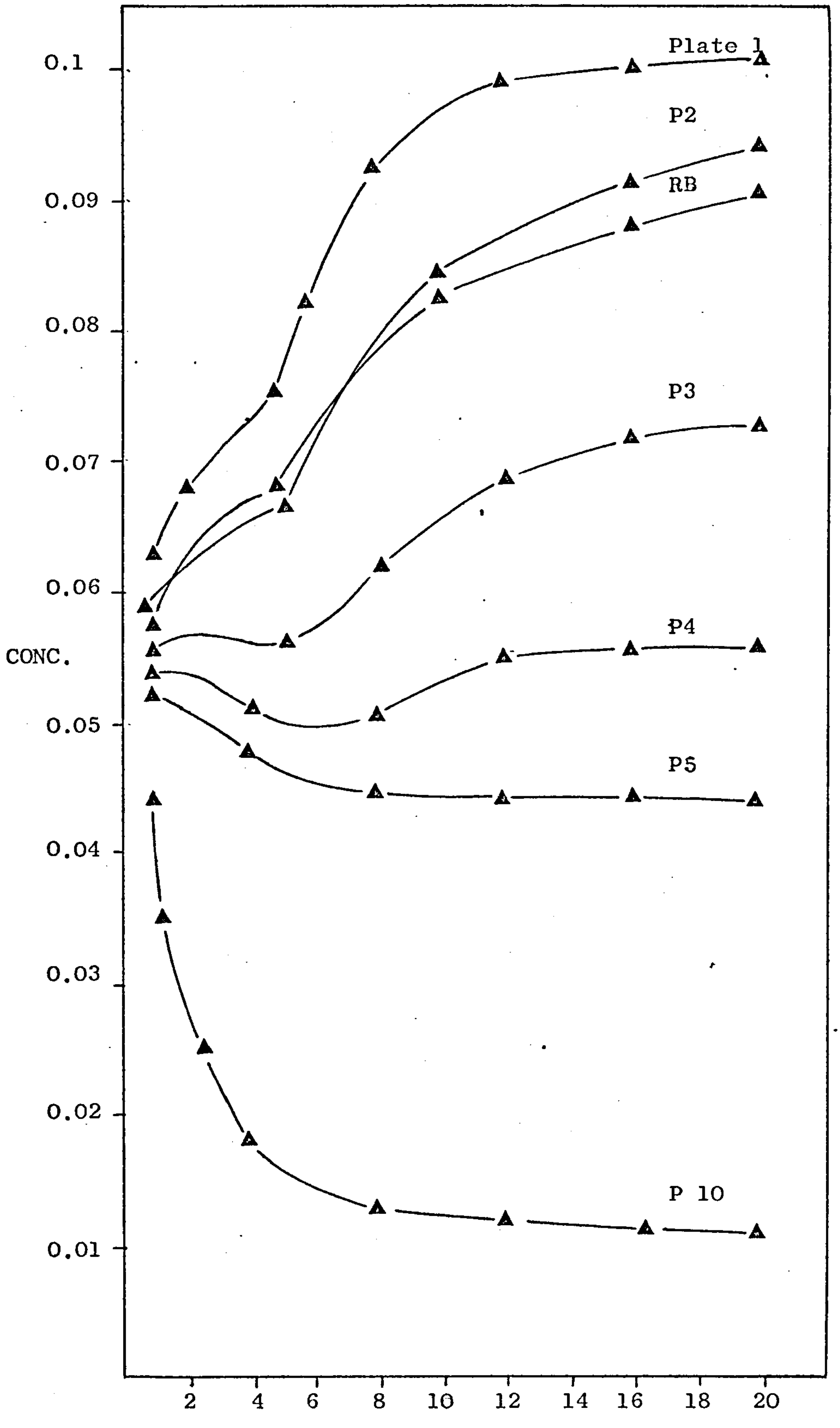


Fig. (23) Liquid composition vs R.R. (methanol).

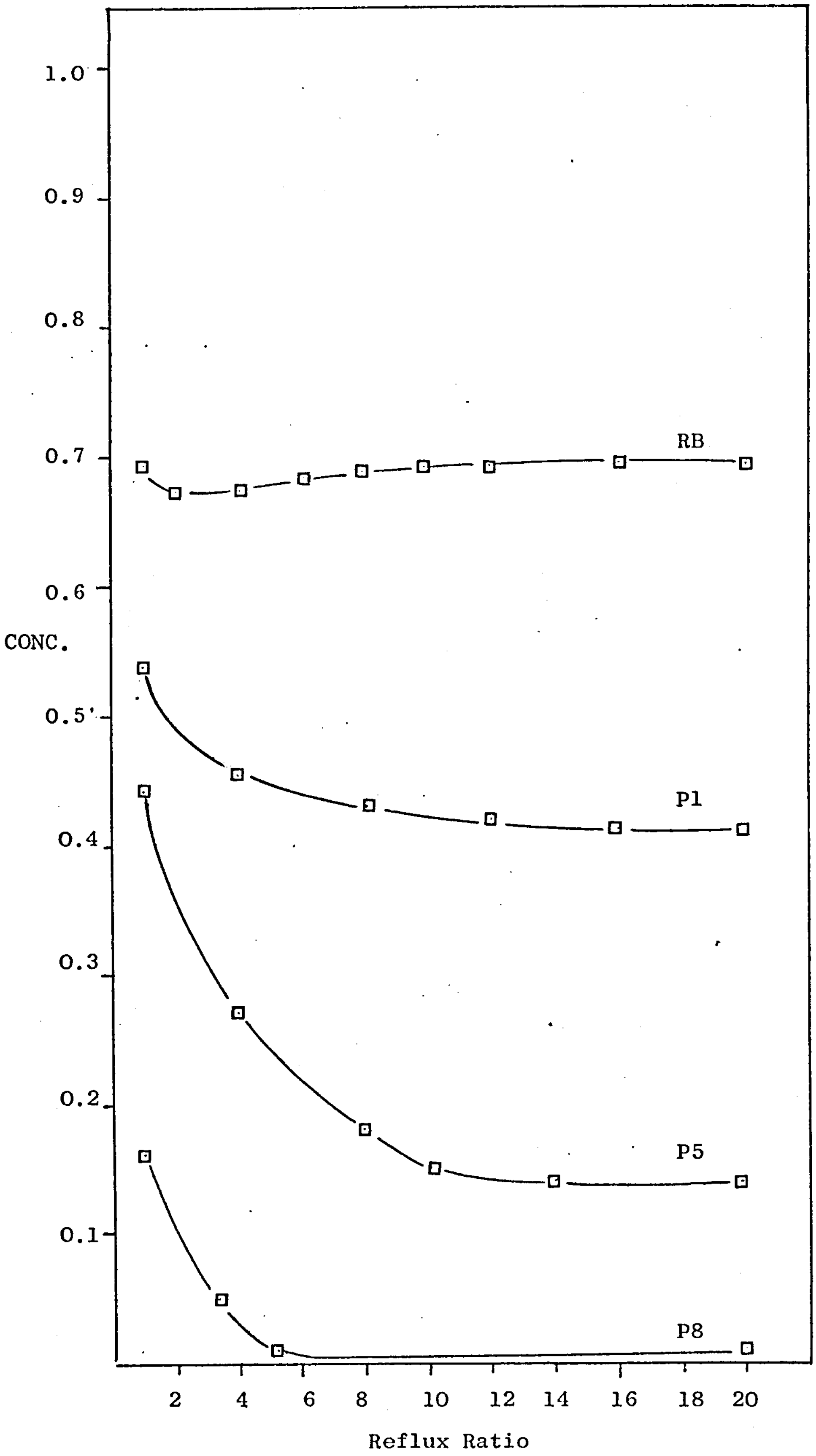


Fig. (23) Liquid composition vs R.R(IPA).

9.1.2. EXPERIMENTAL RUNS

Having obtained the knowledge about the sort of steady state profiles resulting from numerical runs, the next obvious step was to confirm these experimentally.

The experiments were performed on the distillation column described in chapter 7. Only a few of the runs are given here just to give the reader an idea about the sort of agreement between the numerical and experimental results. This not only provided a good cross cheque for the numerical and experimental runs, but also reassured about the fact that they were sound results to base the future dynamic runs. The authenticity of these results became even more critical, when it was no more feasible to perform dynamic runs on the column and all the dynamic runs had to be produced in a simulated version.

Feeds were made of the same compositions as for numerical runs and the column was operated as described in chapter 7 to reach a steady state. Which on the average took 2-4 hours. Then samples were taken and analysed as described fully in chapter 8. A typical chromatographic analysis of both top and bottom products can be seen in fig (24, 25). The actual results show the liquid concentrations for all the three components at varying feed composition, fixed top & bottom take off, and the reflux ratio varying from 1.1. to 5.1. The steady state runs (R.S.S. No.) have the same physical conditions as given in table (1). The results on the whole show a very good trend towards agreement with the numerically predicted results.

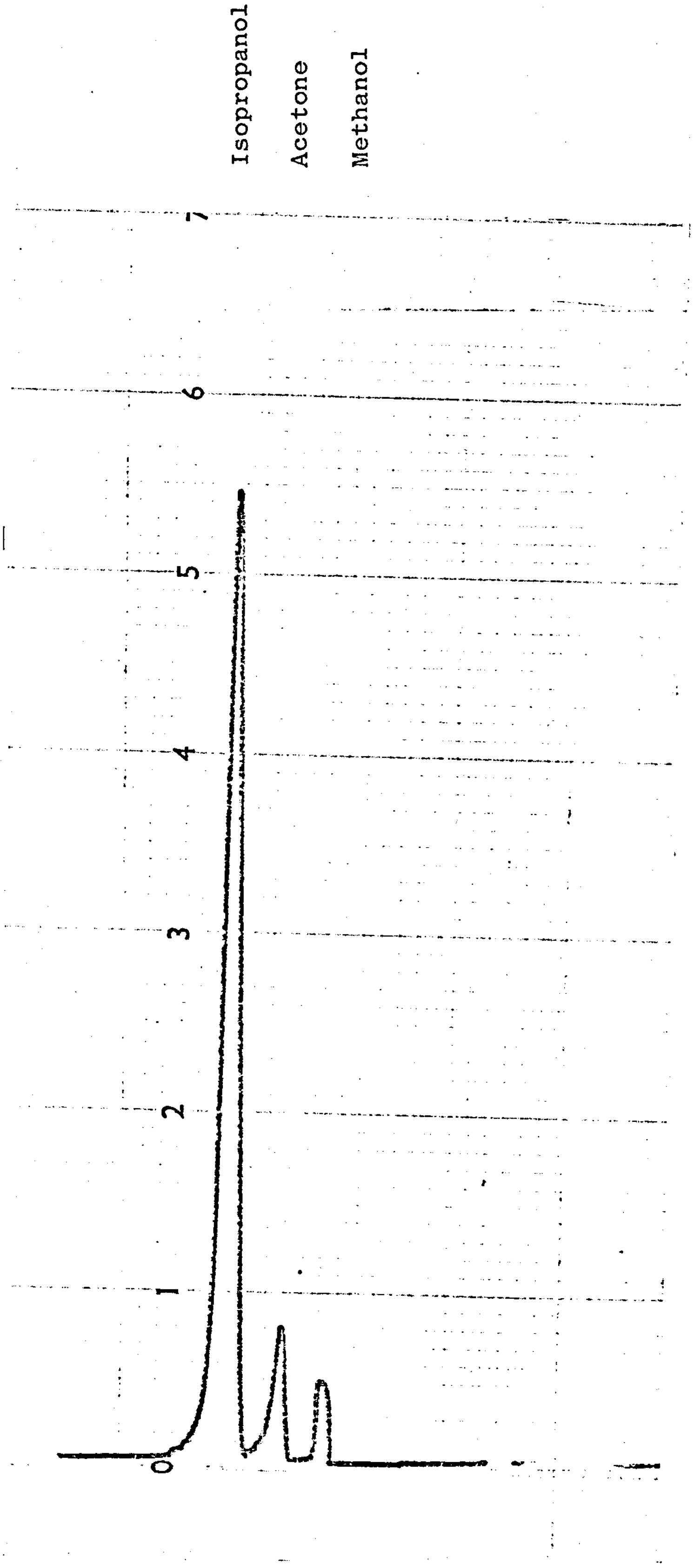


Fig.(24)
Bottom product analysis.

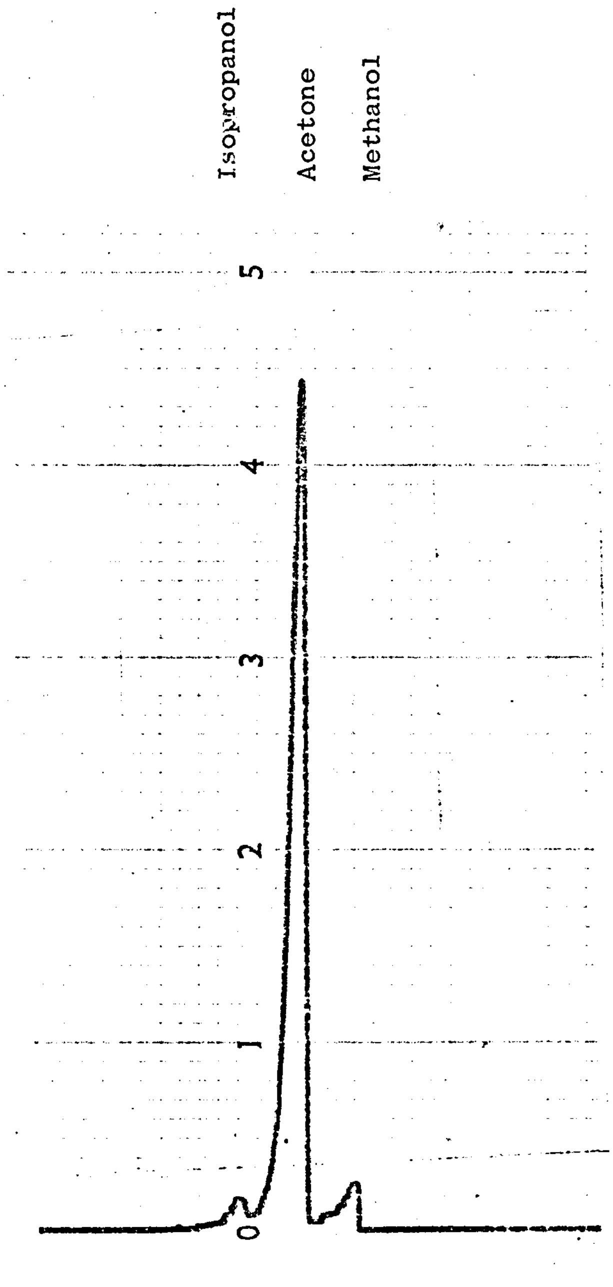


Fig.(25) Top product Analysis

TABLE (2)

STEADY STATE EXPERIMENTAL RUNS

RUN NO	EXPERIMENTAL			PREDICTED		
	ACETONE	METHANOL	IPA	ACETONE	METHANOL	IPA
	X1	X2	X3	X1	X2	X3
R.S.S.10 (top)	0.9153	0.0783.	0.000	0.9352	0.0583	0.0064
R.S.S.10 (bottom)	0.001	0,0400.	0.9510	0.0154	0.416	0.9432
R.S.S.11 (top)	0.9274	0.0786.	0.004	0.9421	0.0568	0.0009
R.S.S.11 (bottom)	0.03	0.02	0.9110	0.0088	0.0481	0.9483
R.S.S.13 (top)	0.9213	0.0687.	0.0	0.9447	0.055	0.0002
R.S.S.13 (bottom)	0.008	0.064.	0.928	0.0059	0.0449	0.9492
R.S.S.14 (top)	0.9261	0.0432.	0.0309	0.9452	0.0545	0.0002
R.S.S.14 (bottom)	0.0098	0.0534.	0.9368	0.0053	0.0454	0.9493
R.S.S.16 (top)	0.8658	0.1297	0.000	0.9287	0.0709	0.0003
R.S.S.16 (bottom)	0.077	0.1677	0.7545	0.0022	0.0291	0.9687
R.S.S.17 (top)	0.9428	0.0566	0.0000	0.9588	0.0409	0.0001
R.S.S.17 (bottom)	0.038	0.11	0.8471	0.011	0.0589	0.9299
R.S.S.18 (top)	0.8656	0.08	0.0	0.9284	0.0711	0.0004
R.S.S.18 (bottom)	0.06	0.04	0.981	0.0025	0.0289	0.9686
R.S.S.19 (top)	0.9428	0.0567	0.0	0.9581	0.0416	0.0002
R.S.S.19 (bottom)	0.05	0.06	0.9631	0.0121	0.0583	0.9296

9.2. TRANSIENTS BY SARGENT'S AND WOOD'S TECHNIQUES

The steady states at different conditions were made as the basis for the work in this phase of the investigation. Two different techinques of formulating a dynamic problem were investigated and shall be discussed appropriately when their respective usage is encountered. At this point it would be worth while saying something about the numerical techinque which was used in this project & has been fully described in chapter 6.

When using numerical integration techniques to solve multicomponent distillation equations, the following question always arises. Does one work with only C-l components and obtain the other by difference, or does one work with all C components and normalise the sum of the composition to equal one? The later was adopted in the present investigation for two reasons, first, because it is difficult, in a general program, to pick which C-l components to use (or which component should be obtained by difference); and second, because it is believed that the normalisation of the sum of the components to equal one acts as a damping device on small numerical errors.

The main criterion to use in the selection of a suitable numerical integration procedure for transient distillation calculations is the stability characteristics of the procedure. For example, given the choice between two methods, it is usually advantageous to use the one with the greater stability range, even at the expense of a large increase in the truncation error. The reason for this is that in problems of this nature the maximum step size for numerical integration is nearly always limited by the obsolute stability of the method. Therefore the step size required is usually so small that the truncation error is independent of the order of the method.

Stability problems are apparent when the maximum allowable step size is small compared with the time constant of the system, that is. When the maximum step size is sosmall that very little change takes place in the actual system over one integration step. Mahetal discussed the inabilities of numerical techinques when applied to continuous distillation calculation.

As previously tested by Gibilaro, Kropholler, (57) markov probabalistic procedure provides one with a very sophisticated numerical techinque which is quite stable as compared to other techinques.

A dimensionless time step of O.I was used in the numerical solution of the differential equations. This was found to be the largest time step that could be used without reducing the occuracy of the solutions significantly. Table (3) compares the response of the distillate composition to our impulse disturbance in feed composition computed with $\Delta T = 0.1$ with that computed with $\Delta T = 0.05$. If the area under the unit impulse response curue is used for compqrision, the error resulting from using $\Delta T = 0.1$. instead of $\Delta T = 0.05$ or less is 0.5%.

TABLE (3)

Comparison of Responses to Impulse Disturbance obtained by using different time steps

τ	$\Delta t = 0.05$ x d	$\Delta t = 0.1$ x d
0.0	0.0	0.0
2.0	0.1472	0.1472
4.0	0.2857	0.2858
6.0	0.3427	0.3429
8.0	0.3585	0.3586
10.0	0.3575	0.3577
20.0	0.3089	0.3091
30.0	0.2595	0.2598
60.0	0.1477	0.1478

9.2.1 Numerical Solution (MARKOV) using Sargents Method.

The changes in this case were made only in the feed composition and have been compared with results obtained by wood's method later on.

The intention was to see the effect of a step change in the feed composition on the middle component (methanol in this case) of a multi-component mixture. In fact the problem was to look for certain conditions which would give rise to limit cycling in a column separating a multicomponent mixture, when the product take off are at the top and bottom with very slight or no change at all in the middle component. This was the reason that most of the runs have been investigated around one main feed composition and that was a very high concentration of both very volatile and least volatile component and just a slight proportion of the third component (Methanol). By keeping its concentration constant it was decided to see the effects on the separation of the whole system.

A column with 10 plates plus a reboiler was made the test case and all the stages were assumed to be perfectly mixed stages. Markov method, as explained fully in chapter 6, was used to calculate the transients. Appropriate data was fed and results obtained are discussed below.

As a first case, taking steady state values for two cases, certain disturbance was made in the feed composition (each component separately) and studied the effect of the unit impulse and step response at the top and bottom of the column. Impulse responses for the plates 8, 9, 10 and the reboiler can be seen in Fig (26, 27, 28).

Fig (29) shows:

i) speed of response and time taken to reach a new steady state value of the M.V.C. (Acetone) and L.V.C. (IPA) is practically the same for both cases of feed composition.

ii) The speed of response of middle component (methanol) differs from one feed composition to another. It is opposite to the other two i.e., Acetone and IPA.

iii) There is more Acetone on the top, no IPA and an equal distribution of methanol throughout the column.

The response at the bottom of the column for the three components is exactly opposite to the one at the top as shown in Fig (30)

i) The speed of response for LVC & MVC is same but this time IPA replaces Acetone being the heavier component.

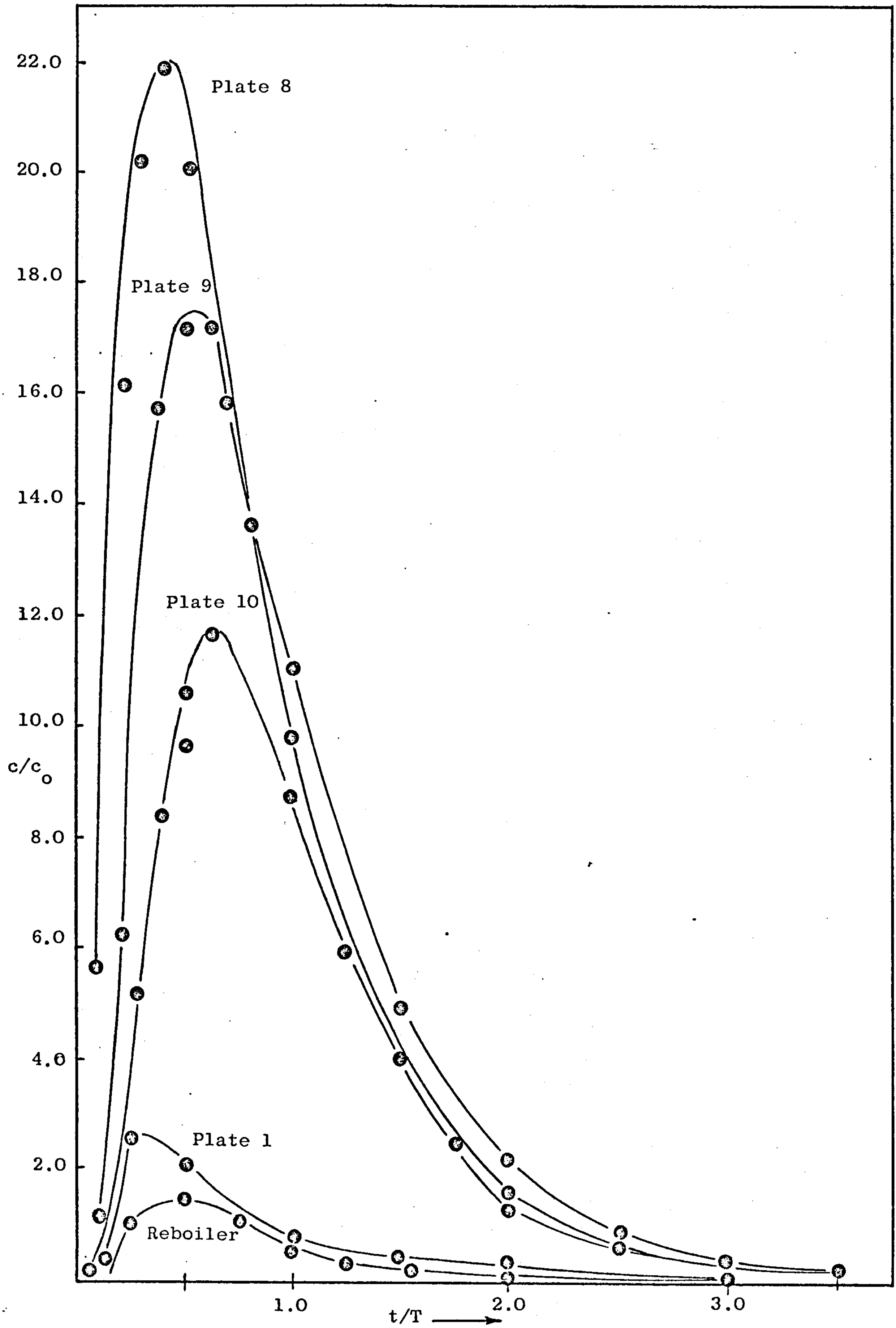


Fig.(26) Acetone Composition profiles to an Impulse Forcing In The Feed Composition.

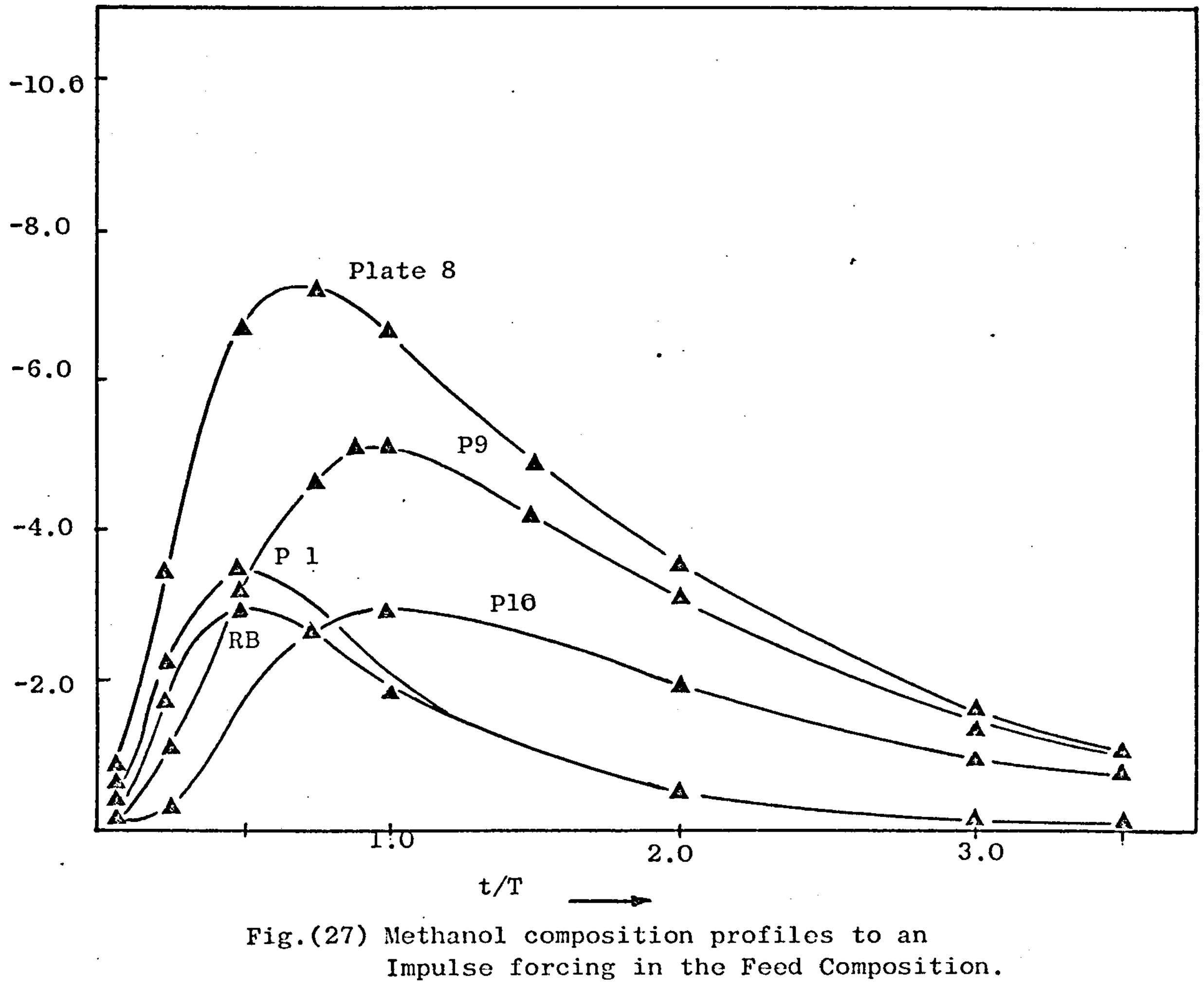


Fig.(27) Methanol composition profiles to an Impulse forcing in the Feed Composition.

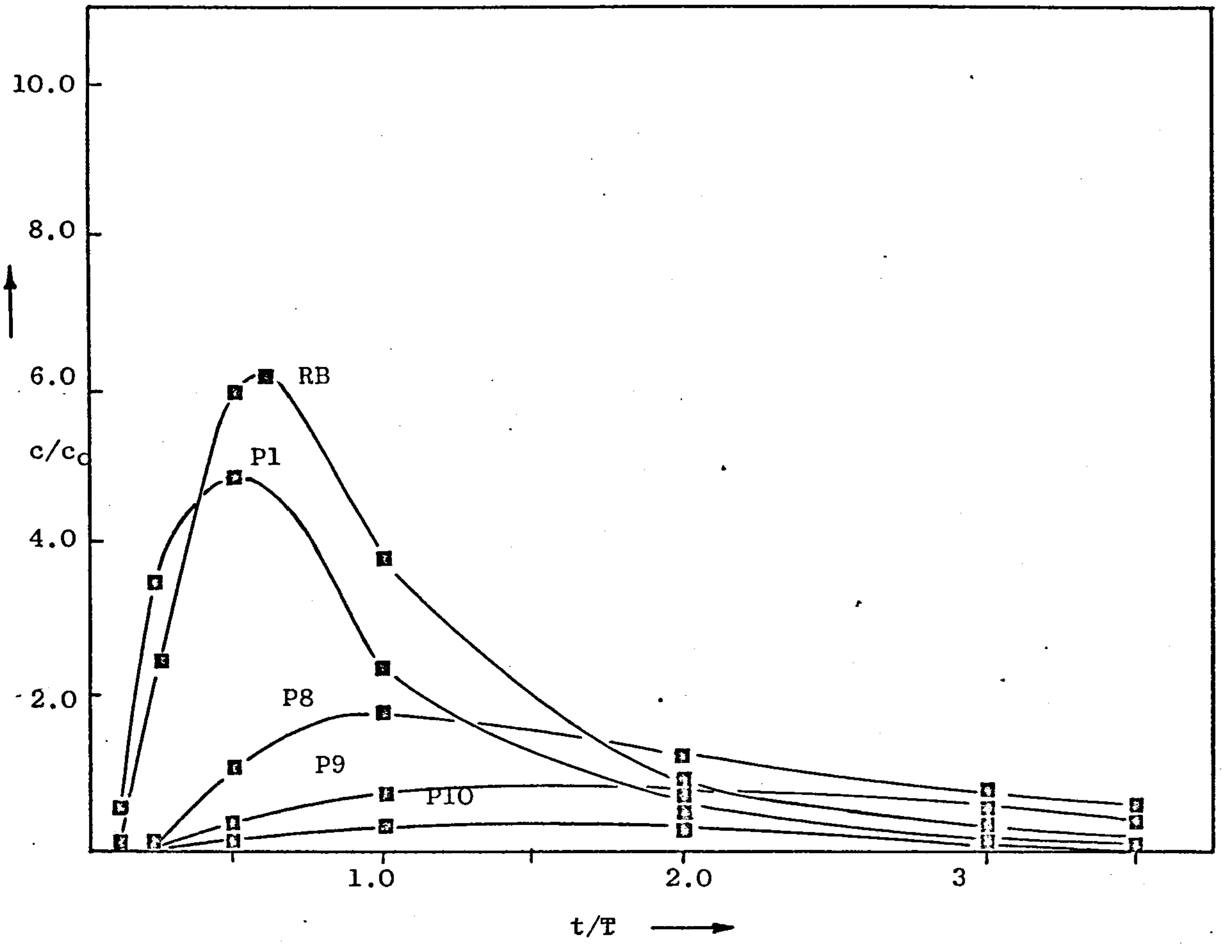


Fig.(28) Isopropanol composition profiles to a an Impulse forcing in the feed composition.

ii) The speed of response of methanol is different and it can be seen again that it is opposite to the other two and also apposite to that in Fig (29)

Step responses for one steady state with different reflux ratios is plotted in Fig 31).

It can be seen that

i) For Acetone (MVC), it takes more time to come to a new steady state with a reflux ratio of 5:1 than 1:1

ii) The speed of response for IPA (LVC) is practically the same for both reflux ratios.

iii) Methanol has the same magnitude, but has a quicker speed of response for a relux ratio of 1:1 as compared to 5:1

Till now the unit disturbance was being put in each component and the impulse or step response for individual components were being plotted. But this individual treatment did not provide with enough information of the whole system. So it was the next step to try to diffuse the unit disturbance in all the three components at one time. To meet this particular requirement, another technique (Wood's) was also used and shall be discussed in detail later.

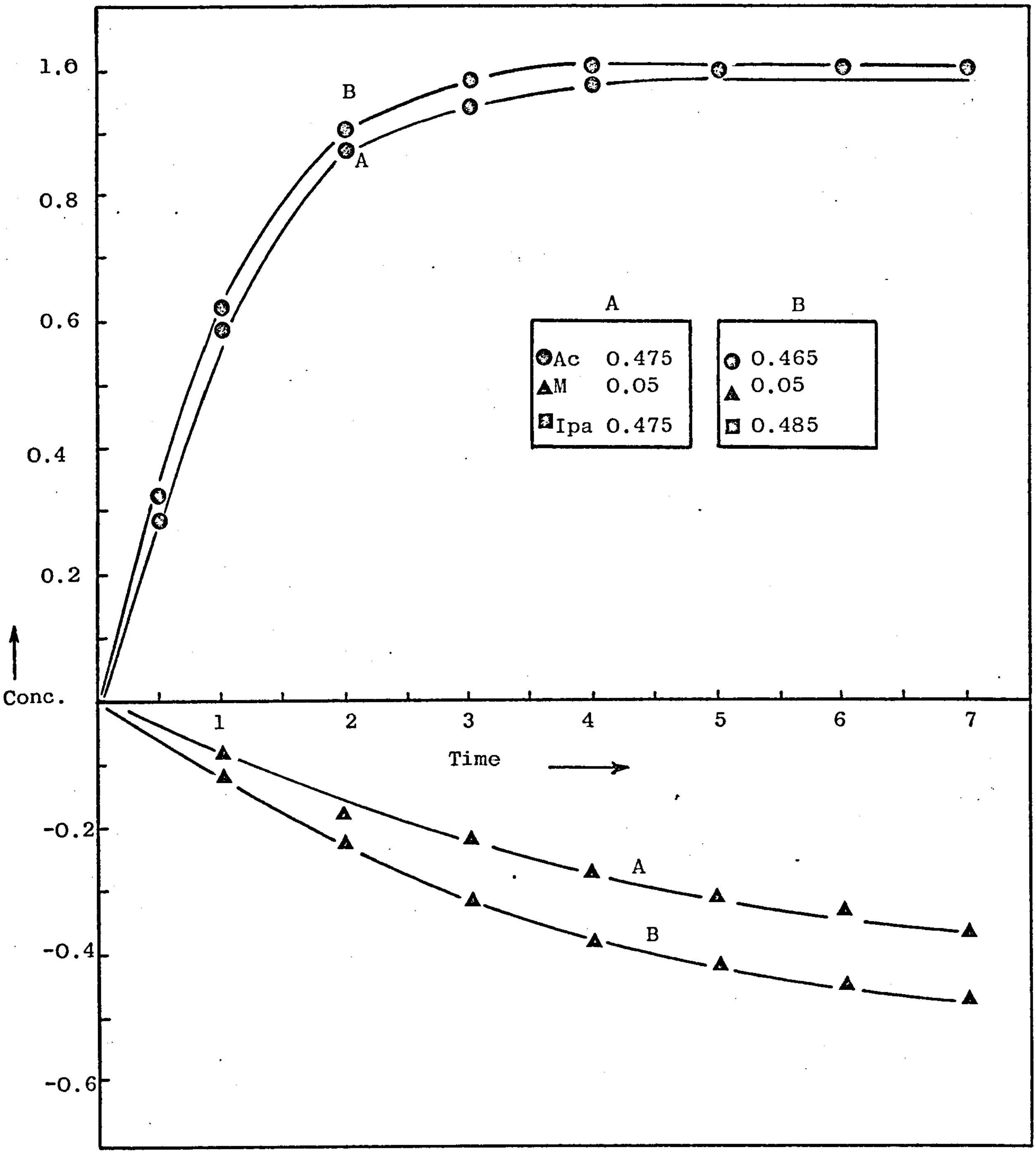


Fig.(29) Step responses at the top of the column to disturbances in two feed composition.

It was decided to make an actual step change from one steady state to another i.e.

0.475		0.465	Acetone
0.05	→	0.05	Methanol
0.475		0.485	IPA

In the physical system change corresponded to a change of 0.01 for Acetone, and - 0.01 for IPA, whilst methanol was not altered. This restricted our previous procedure to treat each component individually (because for Markov, we have to put the disturbance as a state vector and it would have been allright for Acetone and IPA both having a disturbance, but methanol response would be zero with a zero state vector). It was decided to make a modification in the original Markov program so that we were able to deal with all the three components in one matrix (Tri-diagonal form) and the disturbance applied to Acetone & IPA should also give us the relative effect on methanol without having to make any disturbance for that particular component initially.

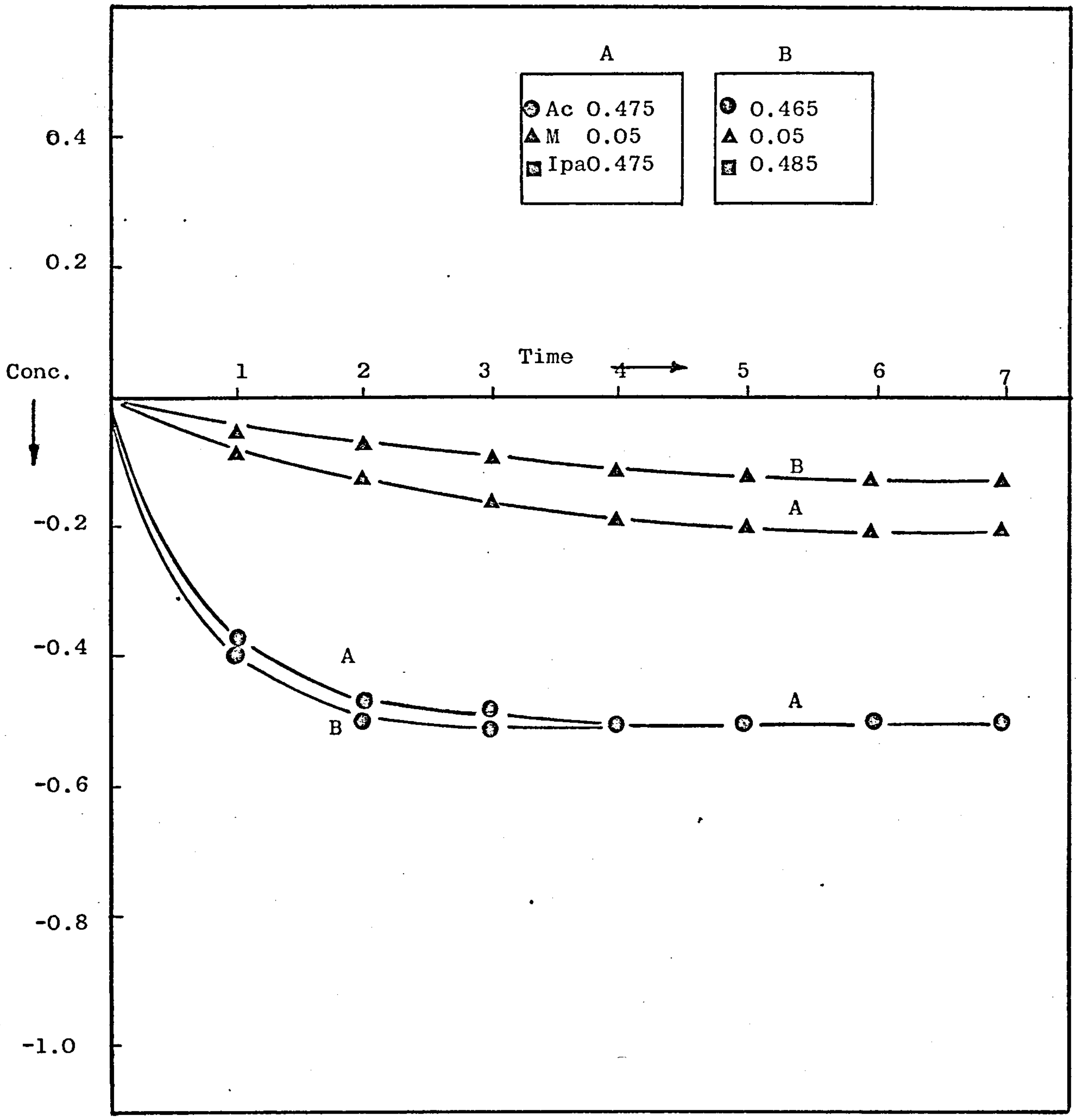


Fig.(30) Step responses at the bottom of the column to disturbances in two different feed composition.

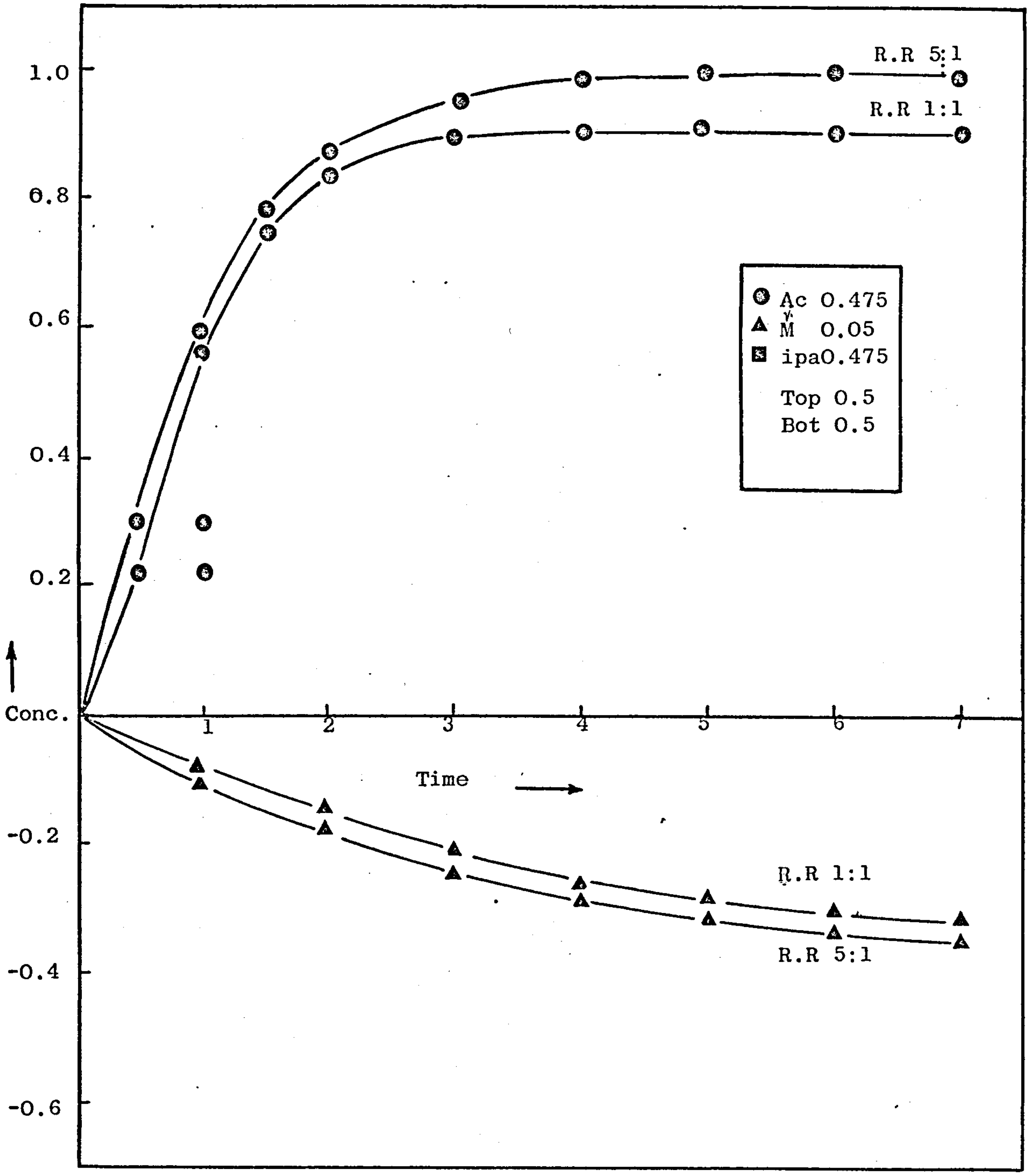
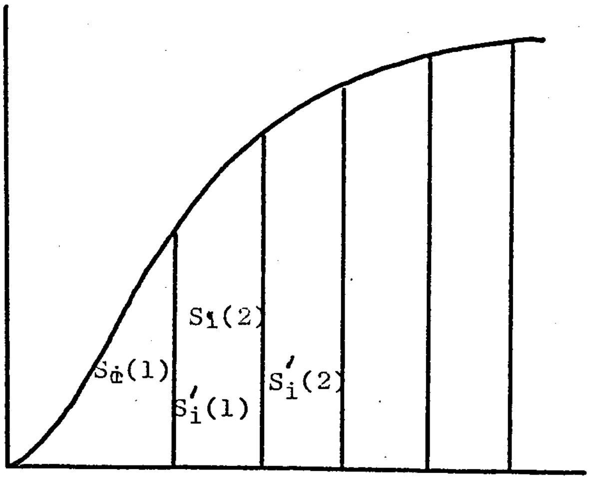


Fig.(31) Step responses at the top of the column to a disturbance in the feed composition.

Briefly, the modification was to read the initial state vector and then correct it to a new state vector by adding it to the steady state values and so on, till we get the required response. It can be represented as



$$\sum_{j=1}^{3}\left(S_{ij}(1) + x_{ij}(0)\right) = y_i = \sum_{j=1}^{3} y_{ij}$$

$$S'_i(1) = \frac{y_{ij}}{S_i} - x_i(0)$$

Fig (32) shows the response to a disturbances of 0.01 in Acetone and -0.01 in IPA. Taking the whole column, the step response for Acetone on the top is faster than IPA at the Bottom and all others are negligible as can be seen from fig (32) for R.T.S.1. This has been compared with the corresponding change under wood's technique.

9.2.2 Analytical Solution using Sargent's Method

The tridigional matrix for any feed charge can also be used as the system matrix to find its eigenvalues and eigenvectors, which could give as information about the transient behaviour. Eigenvalues and eigenvectors were found by technique described in chapter (6). The resulting time solutions agreed very well with the time solutions obtained by Numerical method. The eigenvalues have been listed in TABLE (17,18) and it may be noted that they are all distinct and negative.

The time solutions are approximately the reciprocals of the smallest eigenvalues. It was found that the time solutions were highly sensitive to any change in the feed composition. For a feed change the change in time constants is as follows :

Acetone	$e^{-t/4}$		$e^{-t/3}$
Methanol	$e^{-t/18}$	$\longrightarrow$	$e^{-t/15}$
1PA	$e^{-t/7}$		$e^{-t/8}$

That shows that the response of Acetone slightly, 1PA becomes slower - almost $\frac{1}{3}$rd of what it was before and Methanol remains very much the same. This indicates that the operation is a non-linear one and could be fairly consistant.

9.2.3 Numerical Solution (Markov) using Wood's Technique

Markov was used again to calculate the transients, but this time the dynamic formulation of the problem was done in Wood's technique, which has been fully explained in chapter 5.

Transient runs were made for feed changes, reflux change and boil up rate changes. All the transient runs for wood's case (R.T.W. No) and Sargent's case (R.T.S. No) are listed in Table 1. Forcing functions used as input disturbances have given in Tables 2, 3 and 4. These were calculated using the methods described in chapter 5. The responses have been plotted for the first 40 minutes time because after that the response tend to become constant. The responses are all plotted as step responses at the top and bottom of the column for all the three components and have been briefly given below.

i) The responses to all feed changes show a very similar trend. As a general inference Acetone (the most volatile component) responds at the top and IPA (the least volatile component) responds at the bottom. Methanol responds with a very even distribution throughout the column.

2) Responses, though similar in trend were not necessarily of the same magnitude. When a change was made towards the positive directions, the magnitude was more and reverse was the case when the change was made in the negative direction. This trend can be noticed in most of the responses. Fig 33 to fig 46.

3) The response of the system is much quicker when the change in feed was made in one direction as compared to the case when this direction was reversed. See R.T.W.1 & R.T.W.2

4) When the changes were made of equal magnitude from one feed in either direction of the responses were exactly the same, but of an opposite sign. See R.T.W.1 and R.T.W.3.

5) When the same feed change was made but at a different reflux ratio, the resulting responses were not effected appreciably. See R,T.W.1 and R.T.W.5.

6) Change in the top and bottom take off rate had very considerable effect on the response of the system. See R.T.W.1 and R.T.W.9. The system responded much quicker in this case both at the top and bottom of the column.

7) Keeping the feed fixed and changing the reflux ratio the responses were of higher magnitude as compared to feed changes. See R.T.W.11. The most effected section was the top of the column.

8) Responses obtained by changing the boil up rate were completely different as compared to either the feed changes or the reflux change. See R.T.W.12 and R.T.W.13. The system responded very quickly in the initial stages but drops down very readily.

9) It may be noted that all feed responses have been scaled down by a factor 10^2, for ease in plotting results. Tables of results are given in Appendix (A4).

TABLE ([illegible])
1

RUN NO	FEED CHANGE			REFLUX RATIO	TAKE OFFS	
					TOP	BOTTOM
R.T.W.1	0.475 0.05 0.475	→	0.465 0.05 0.485	5 : 1	0.5	0.5
R.T.W.2	0.465 0.05 0.485	→	0.475 0.05 0.475	5 : 1	0.5	0.5
R.T.W.3	0.475 0.05 0.475	→	0.485 0.05 0.465	5 : 1	0.5	0.5
R.T.W.4	0.485 0.05 0.465	→	0.475 0.05 0.475	5 : 1	0.5	0.5
R.T.W.5	0.475 0.05 0.475	→	0.465 0.05 0.485	4 : 1	0.5	0.5
R.T.W.6	0.465 0.05 0.485	→	0.475 0.05 0.475	4 : 1	0.5	0.5
R.T.W.7	0.475 0.05 0.475	→	0.485 0.05 0.465	4 : 1	0.5	0.5
R.T.W.8	0.485 0.05 0.465	→	0.475 0.05 0.475	4 : 1	0.5	0.5
R.T.W.9	0.475 0.05 0.475	→	0.465 0.05 0.485	4 : 1	0.4	0.6

RUN NO	FEED CHANGE			REFLUX RATIO	TAKE OFFS	
					TOP	BOTTOM
R.T.W.10	0.465 0.05 0.485	→	0.475 0.05 0.475	4 : 1	0.4	0.6
	FEED			REFLUX CHANGE		
R.T.W.11	0.475 0.05 0.475			4 : 1 → 5 : 1	0.5	0.5
				Boil up Ratecharge		
R.T.W.12	0.475 0.05 0.475			5 : 1 → 4 : 1	0.5	0.5
R.T.W.13	0.475 0.05 0.475			4 : 1 → 5 : 1	0.5	0.5

RUN NO	FEED CHANGE			REFLUX RATIO	TAKE OFFS	
					TOP	BOTTOM
R.T.S.1	0.475 0.05 0.475	→	0.465 0.05 0.485	5 : 1	0.5	0.5
R.T.S.2	0.465 0.05 0.485	→	0.475 0.05 0.475	5 : 1	0.5	0.5

TABLE 2

	FEED CHANGE			FORCING FUNCTION ON THE FEED PLATE
1.	0.475		0.465	-0.01
	0.05	→	0.05	0.0
	0.475		0.485	0.01
2.	0.465		0.475	0.01
	0.05	→	0.05	0.0
	0.485		0.475	-0.01
3.	0.475		0.485	0.01
	0.05	→	0.05	0.0
	0.475		0.465	- 0.01
4.	0.485		0.475	- 0.01
	0.05	→	0.05	0.0
	0.465		0.475	0.01

TABLE 3

PLATE NO.		FORCING FUNCTION FOR BOIL UP RATE CHANGE 5 : 1 → 4 : 1	FORCING FUNCTION FOR BOIL UP RATE CHANGE 4 : 1 → 5 : 1
Reboiler	A	0.0011	-0.0014
	M	0.0034	-0.0039
	IPA	- 0.0045	0.0053
1	A	0.0033	-0.0041
	M	0.0052	-0.0057
	IPA	- 0.0085	0.0098
2	A	0.0084	-0.0101
	M	0.0056	-0.006
	IPA	- 0.0140	0.0161
3	A	0.0148	-0.0173
	M	0.0021	-0.0019
	IPA	- 0.0169	0.0192
4	A	0.0154	-0.0176
	M	- 0.003	0.0035
	IPA	- 0.0124	0.0141
5	A	- 0.0231	0.0261
	M	- 0.0248	0.0266
	IPA	0.0479	- 0.0527
6	A	- 0.0084	0.0106
	M	0.0026	-0.0026
	IPA	0.0058	-0.008
7	A	- 0.0045	0.0055
	M	0.0026	-0.0028
	IPA	0.0018	-0.0027
8	A	- 0.0028	0.0034
	M	0.0023	-0.0026
	IPA	0.0005	-0.0008
9	A	- 0.0022	0.0025
	M	0.002	-0.0023
	IPA	0.0002	-0.0002
10	A	- 0.0017	0.0022
	M	0.0017	-0.002
	IPA	0.00005	-0.00015

TABLE 4

PLATE NO		FORCING FUNCTION FOR REFLUX CHANGE 5 : 1 → 4 : 1	FORCING FUNCTION FOR REFLUX CHANGE 4 : 1 → 5 : 1
Reboiler	A	- 0.013	0.0003
	M	- 0.0413	- 0.0007
	IPA	0.0544	- 0.001
1	A	- 0.0396	0.001
	M	- 0.0622	0.0015
	IPA	0.1018	- 0.0025
2	A	- 0.1	0.0037
	M	- 0.0677	0.0029
	IPA	0.1677	- 0.0066
3	A	- 0.1769	0.0131
	M	- 0.0258	0.0054
	IPA	0.2028	- 0.0185
4	A	- 0.1850	0.0435
	M	0.0362	0.0094
	IPA	0.1487	- 0.0529
5	A	- 0.1876	0.0045
	M	0.0151	0.0051
	IPA	0.1726	- 0.0096
6	A	- 0.1023	0.0149
	M	0.0322	0.0107
	IPA	0.0701	- 0.0256
7	A	- 0.0538	0.0488
	M	0.0316	0.0201
	IPA	0.0221	- 0.0689
8	A	- 0.0344	0.1379
	M	0.0279	0.028
	IPA	0.0065	- 0.1659
9	A	- 0.0260	0.2635
	M	0.0241	0.0145
	IPA	0.0019	- 0.2780
10	A	- 0.0213	0.2605
	M	0.0208	- 0.0163
	IPA	0.0005	- 0.2442

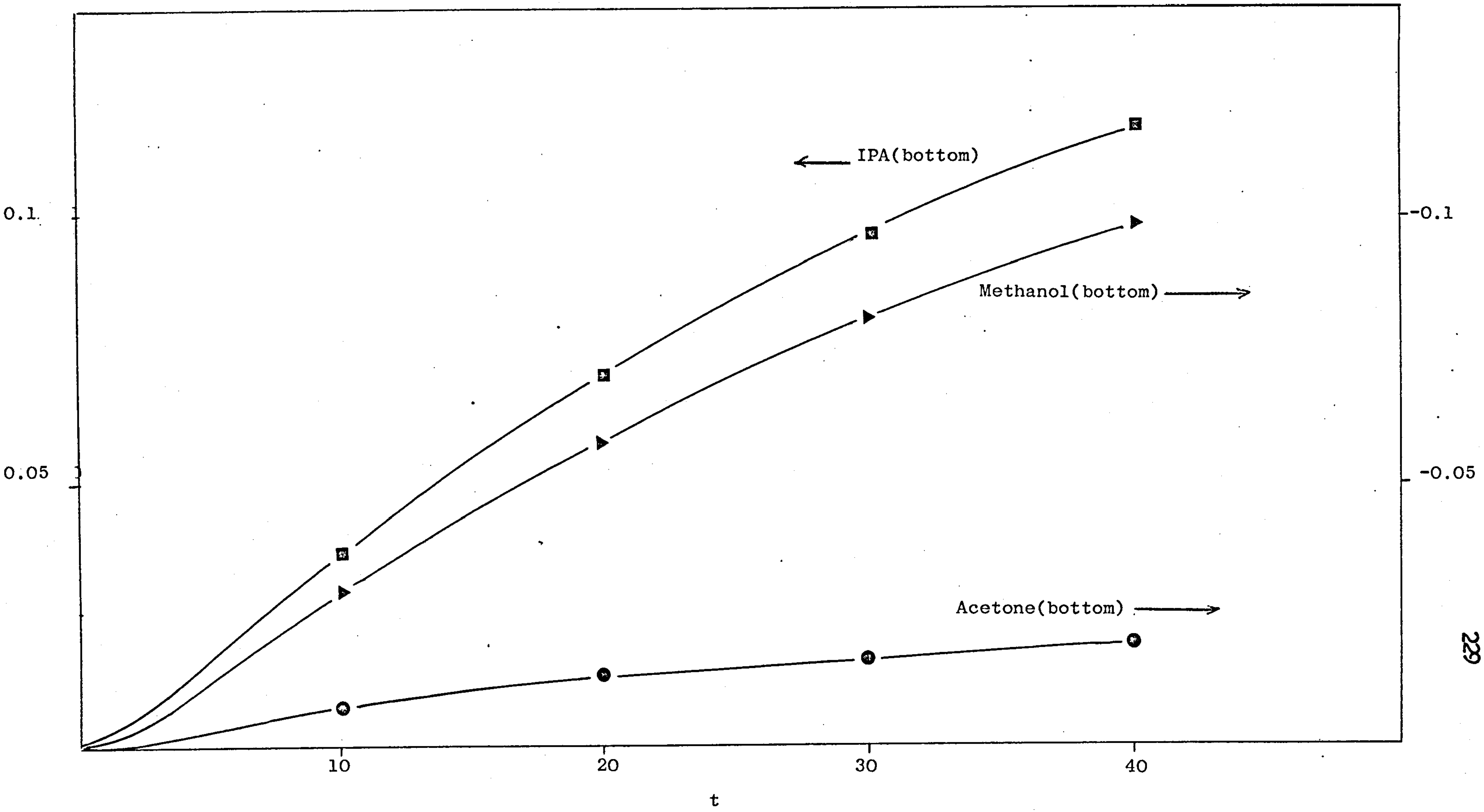

IPA(bottom)
Methanol(bottom)
Acetone(bottom)
0.1
0.05
-0.1
-0.05
10
20
30
40
t

Fig.(d1) R.T.W.1

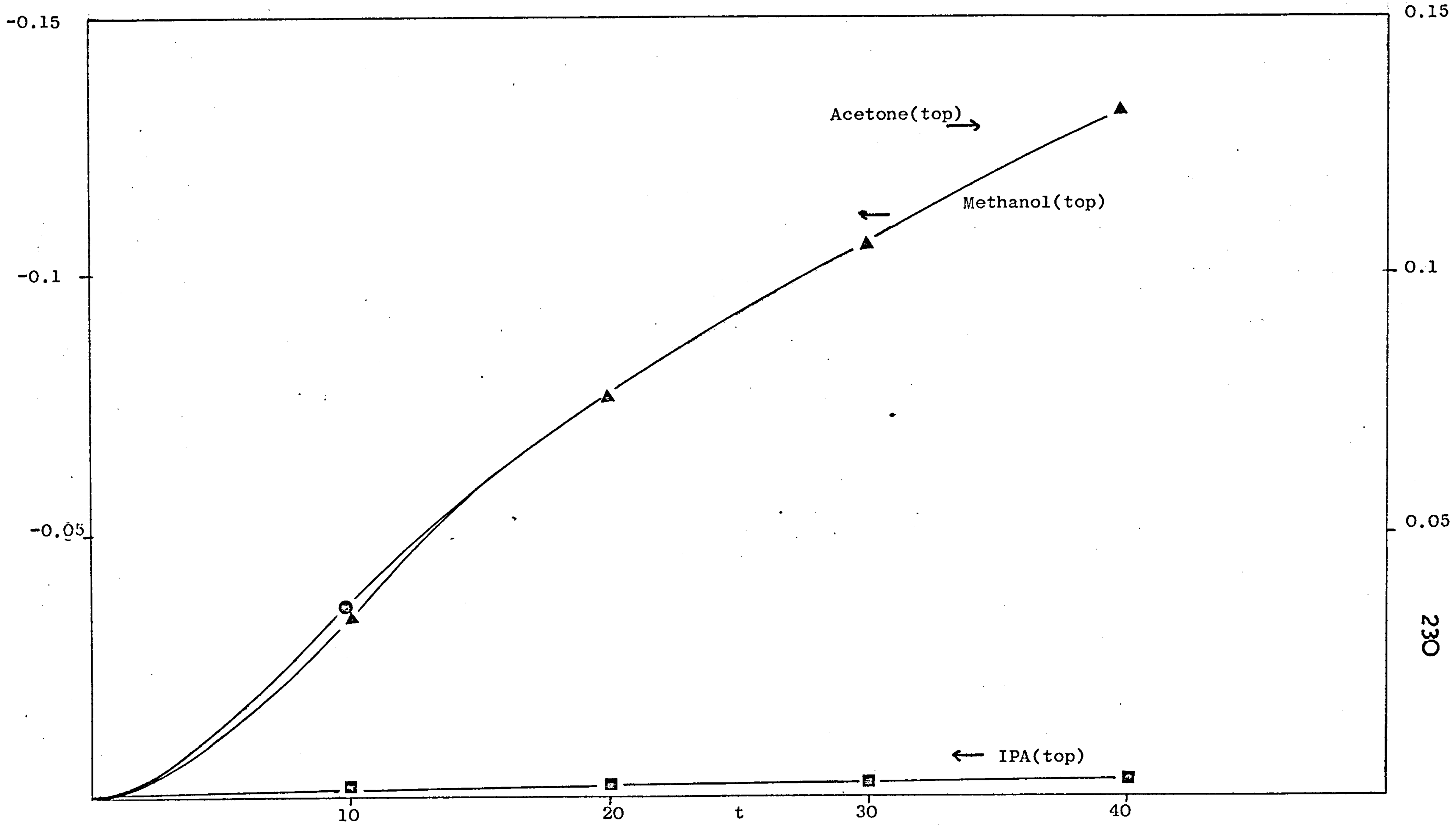

-0.15
-0.1
-0.05
0.15
0.1
0.05
Acetone(top)
Methanol(top)
IPA(top)
10
20
t
30
40

Fig.(23) R.T.W.2

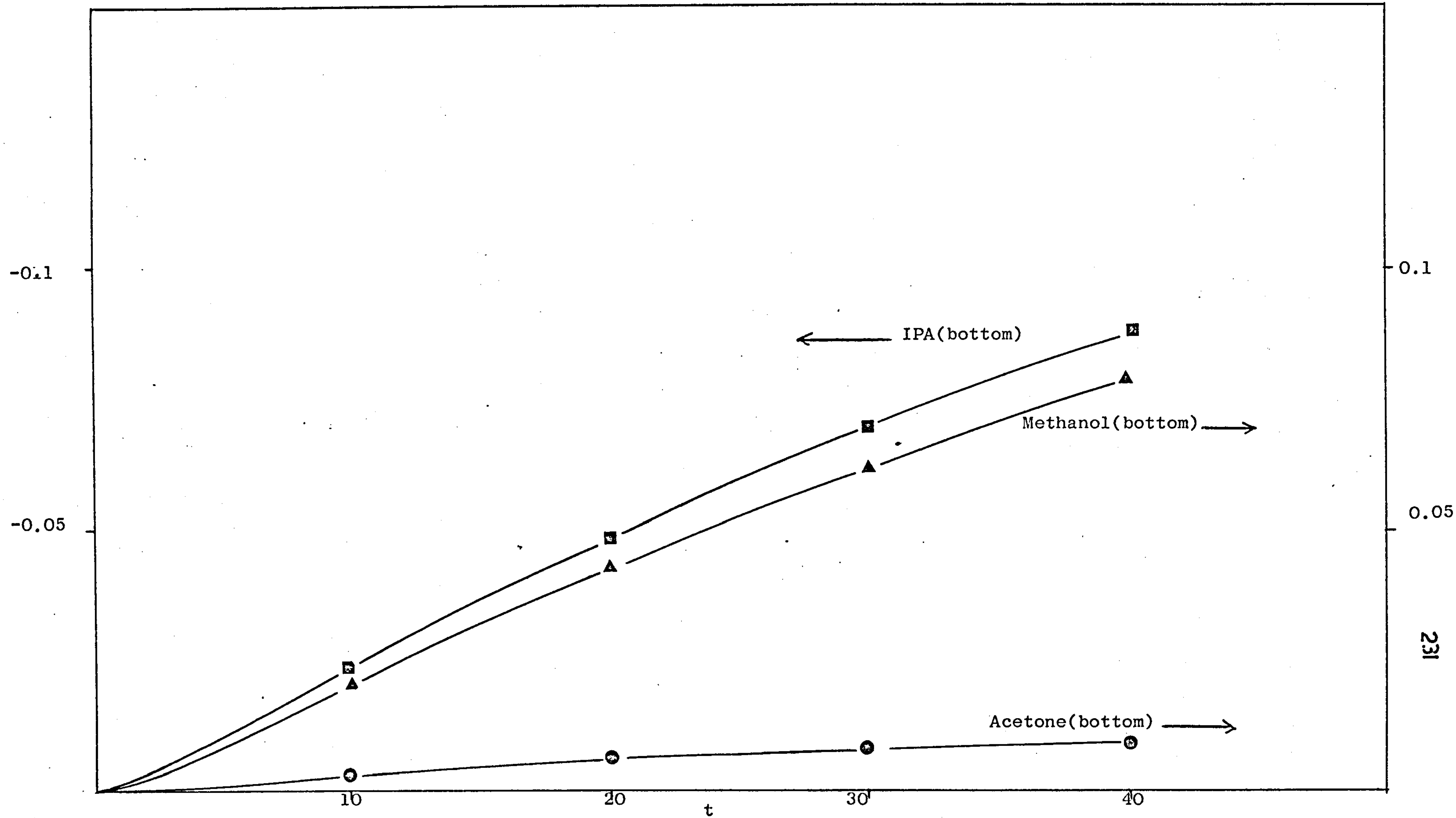

-0.1
-0.05
0.1
0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(33) R.T.W.2

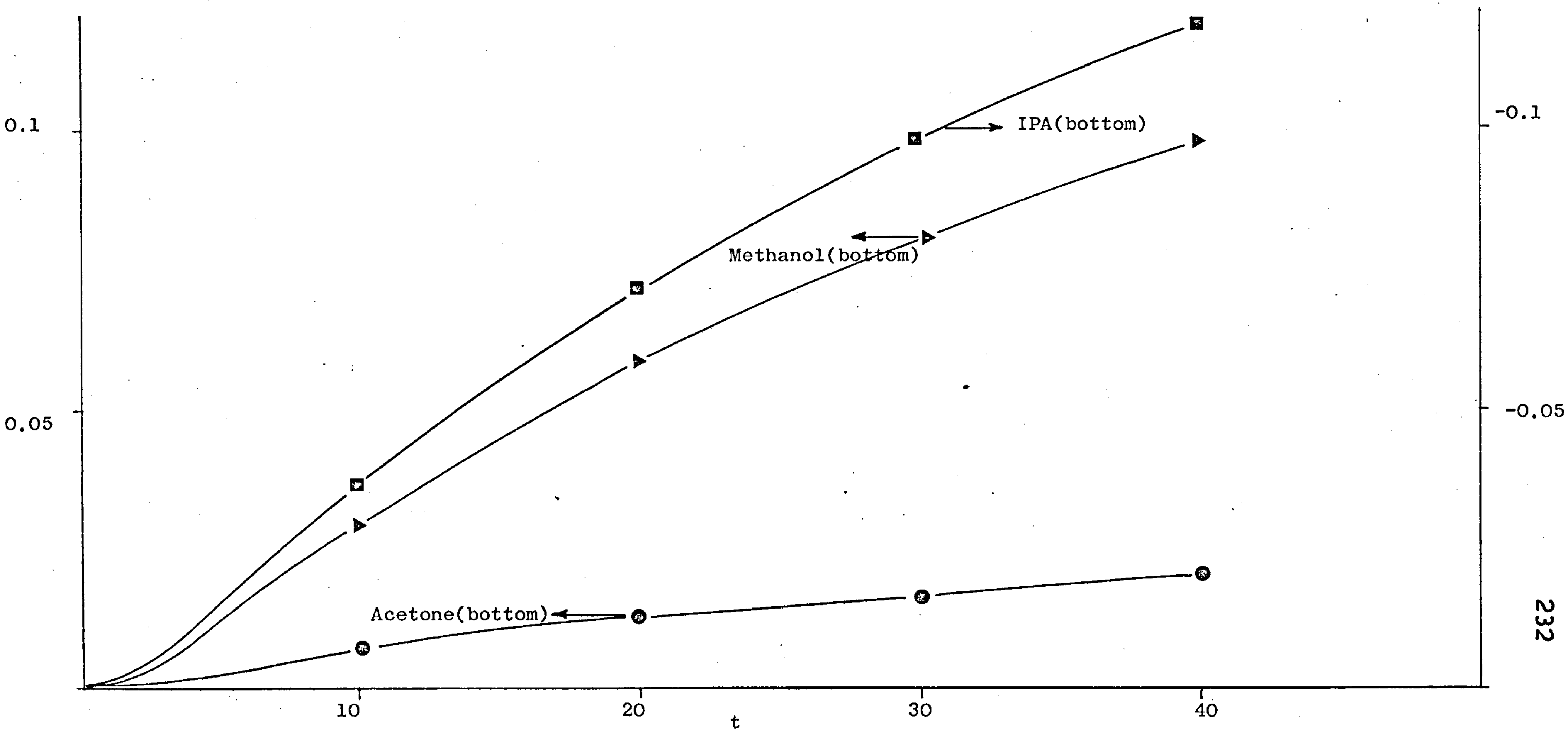

0.1
0.05
-0.1
-0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(34) R.T.W.3

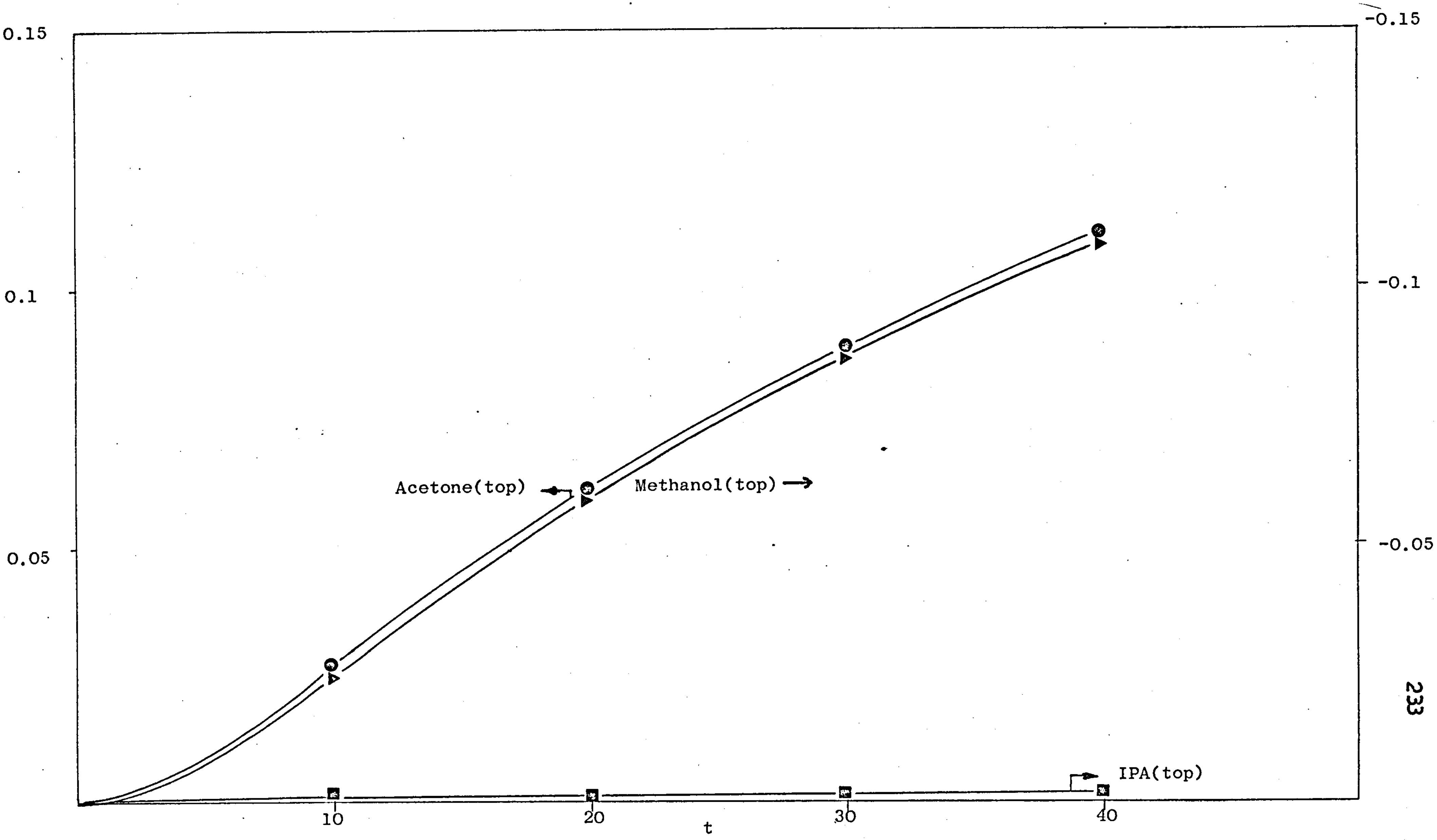

0.15
0.1
0.05
-0.15
-0.1
-0.05
Acetone(top)
Methanol(top)
IPA(top)
10
20
30
40
t

Fig.(34) R.T.W.3

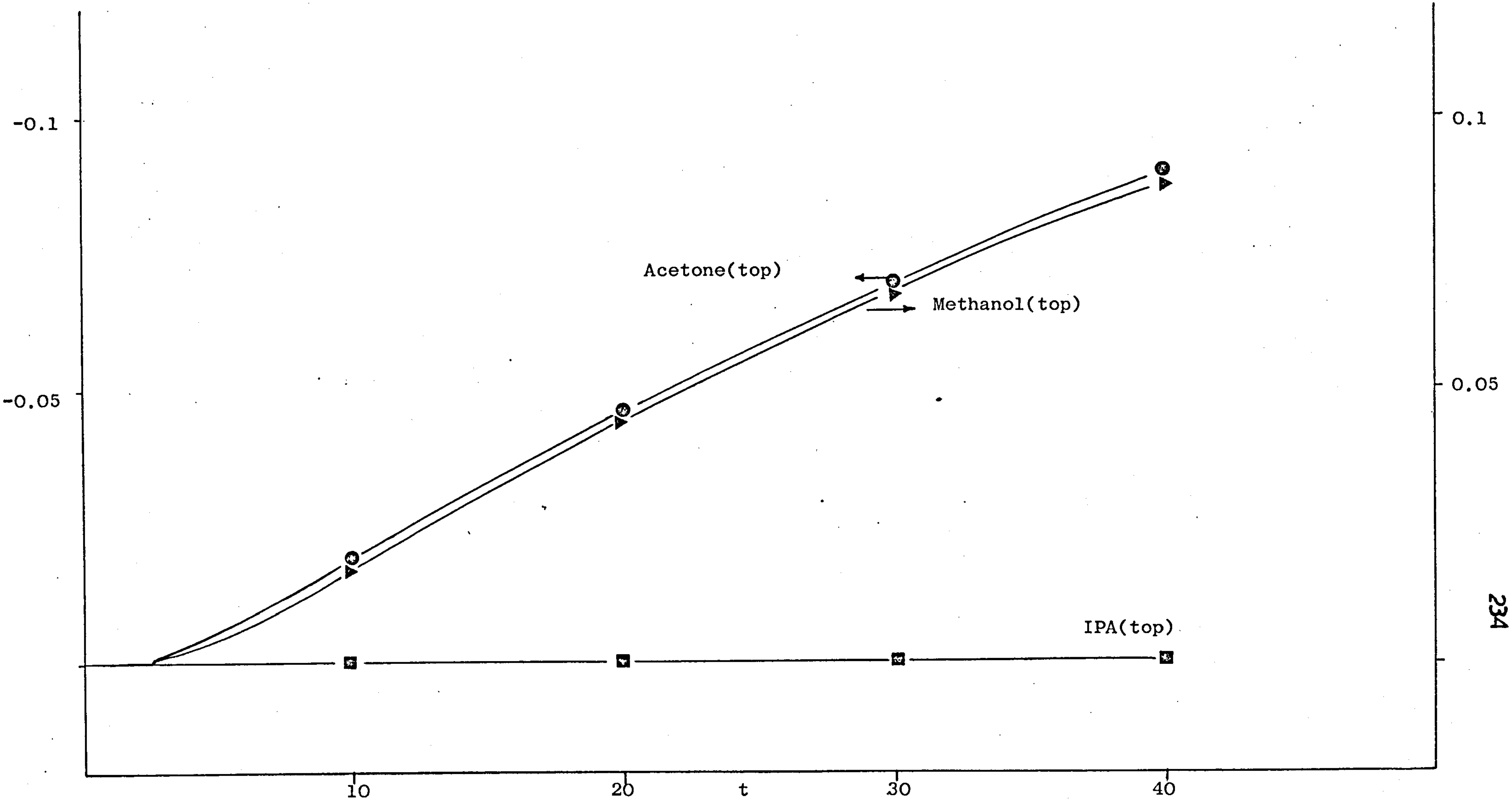


Fig.(35) R.T.W.4

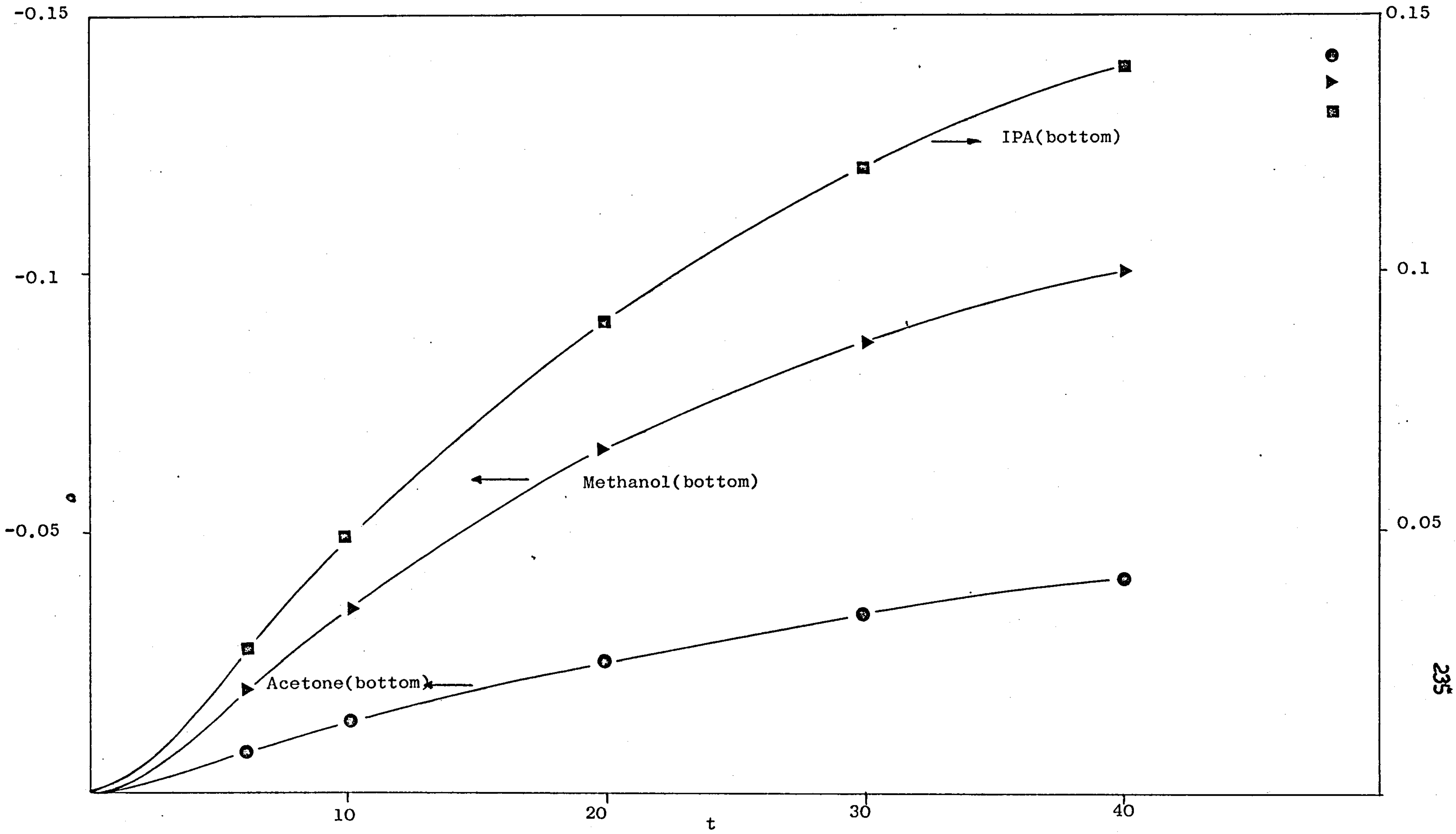

-0.15
-0.1
-0.05
0.15
0.1
0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(35) R.T.W.4

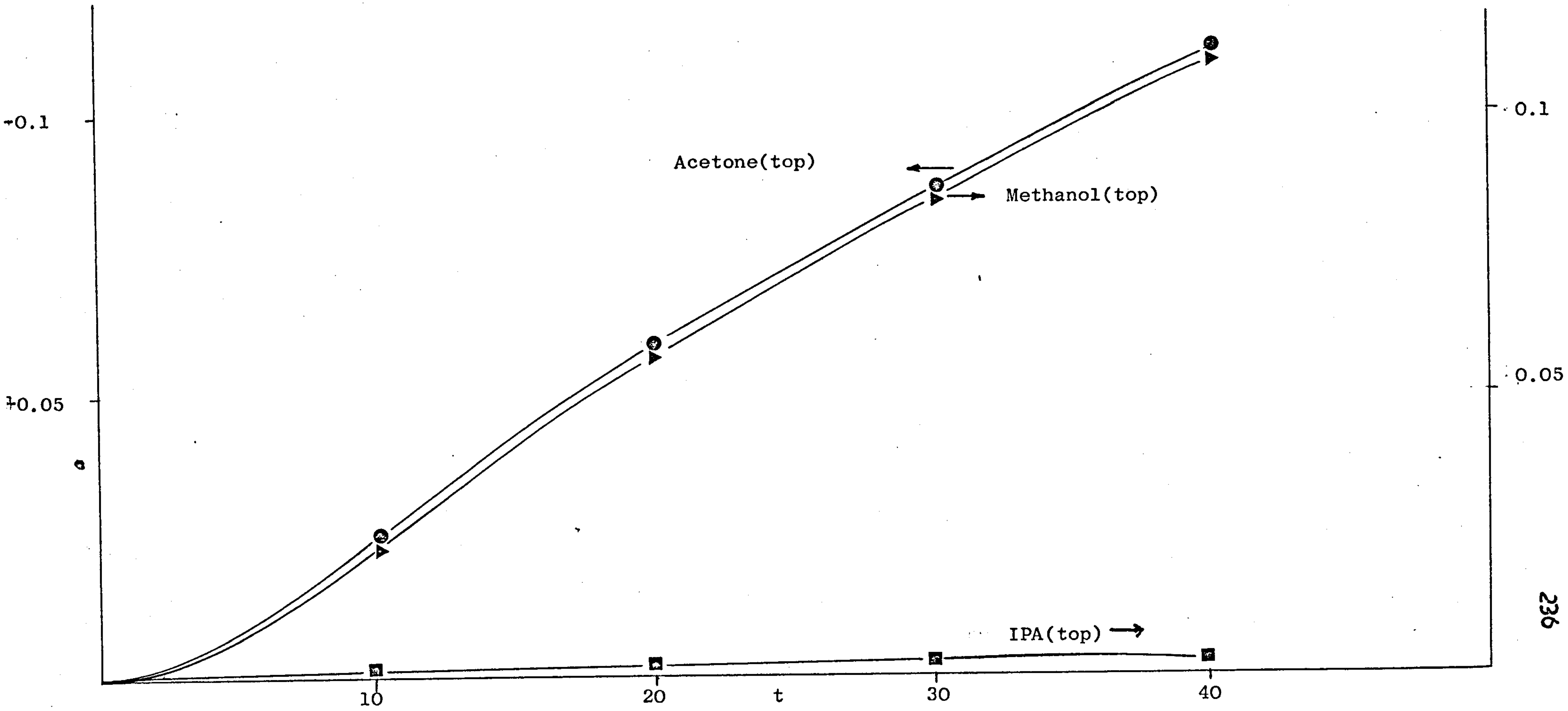


Fig.(36) R.T.W.5

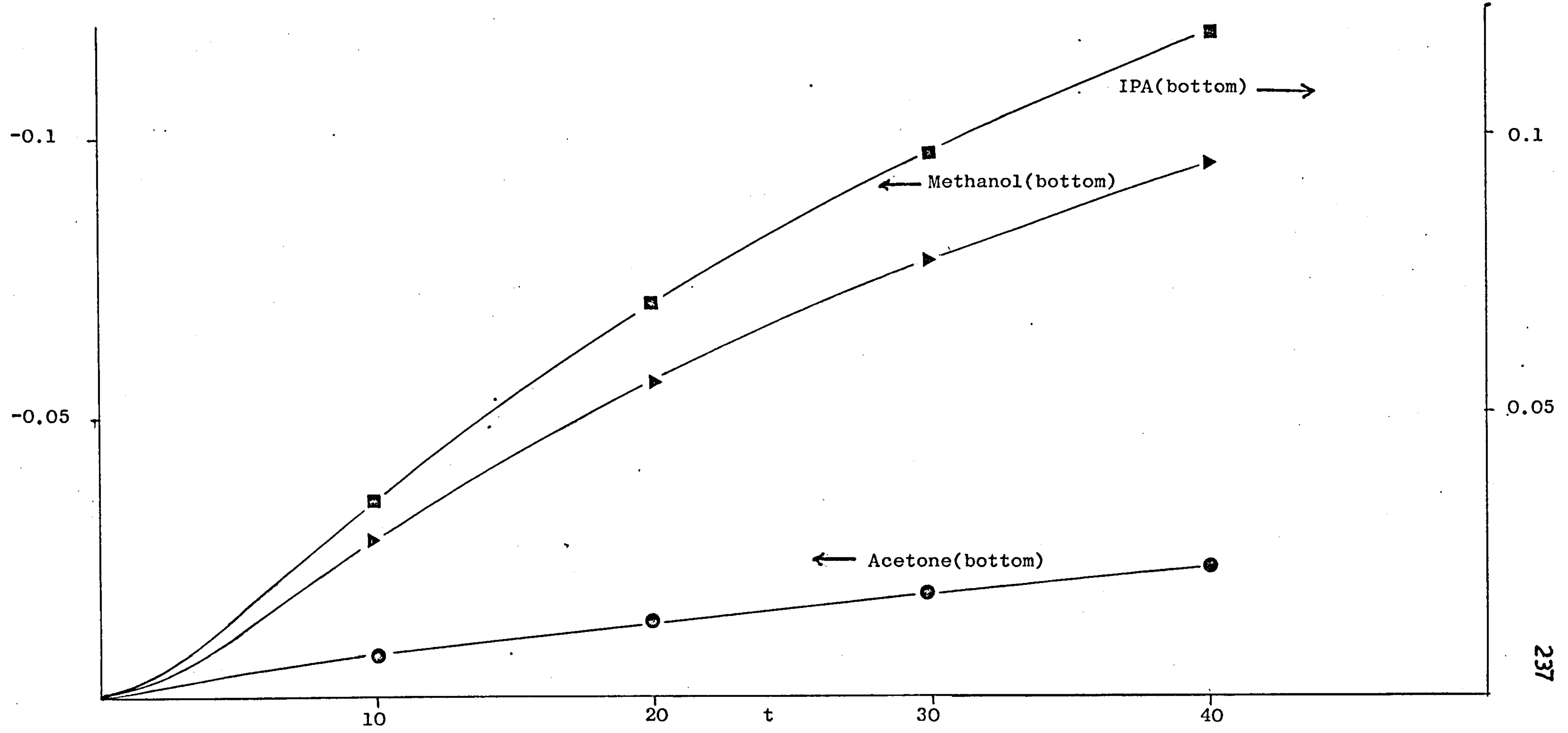

-0.1
-0.05
0.1
0.05
IPA(bottom) →
← Methanol(bottom)
← Acetone(bottom)
10
20
t
30
40

Fig.(36) R.T.W.5

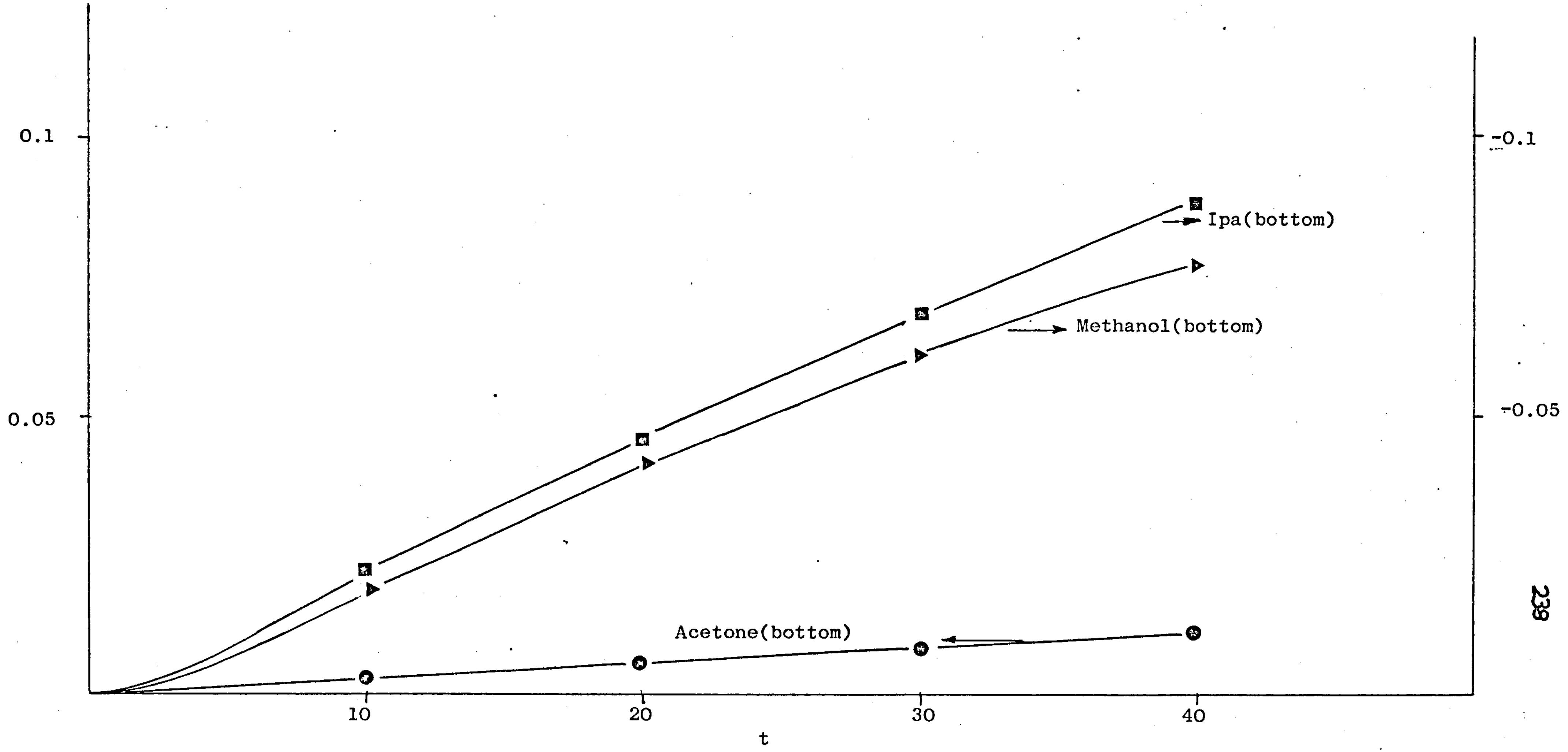

0.1
0.05
-0.1
-0.05
Ipa(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(57) R.T.W.6

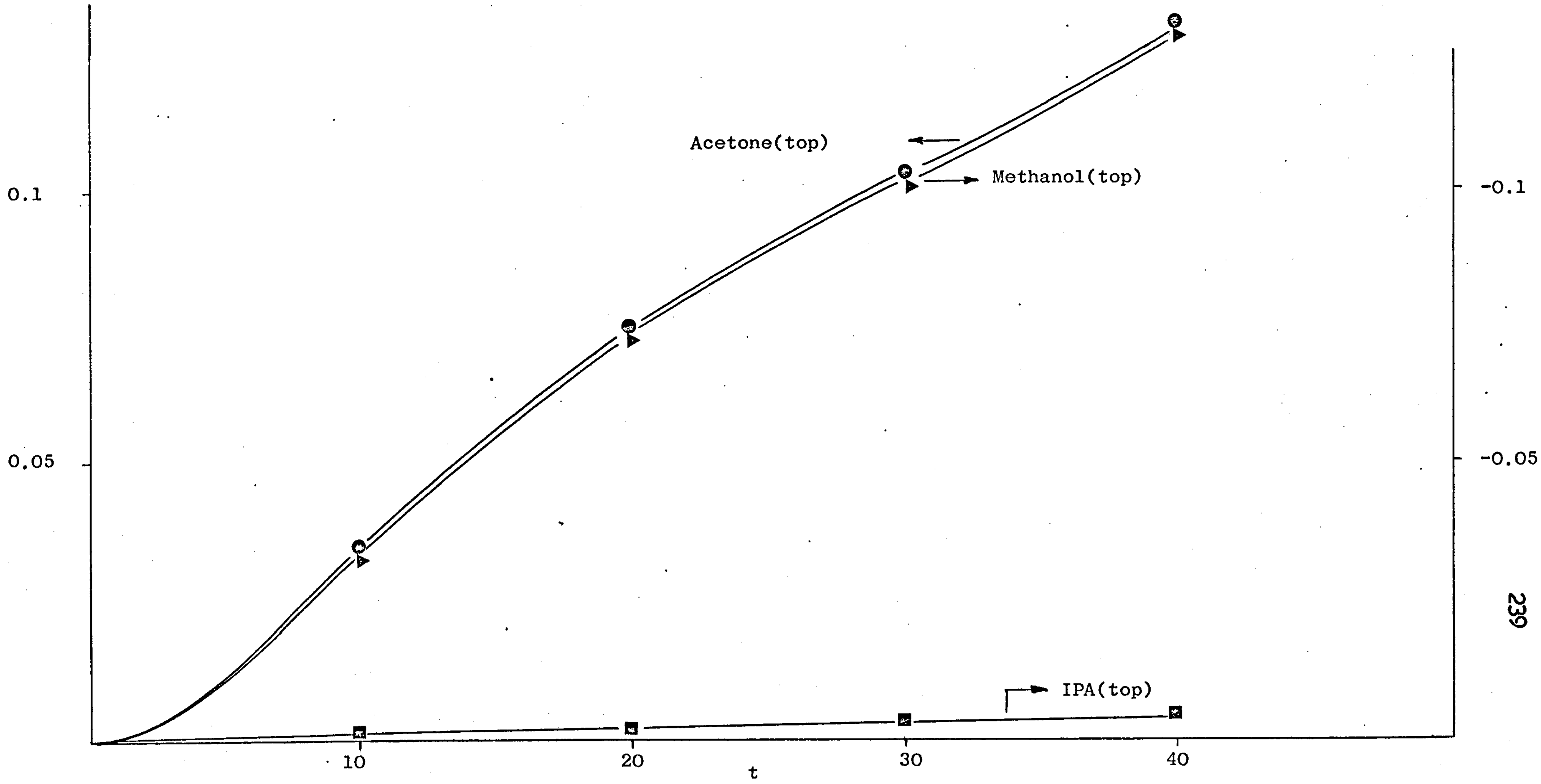


Fig.(37) R.T.W.6

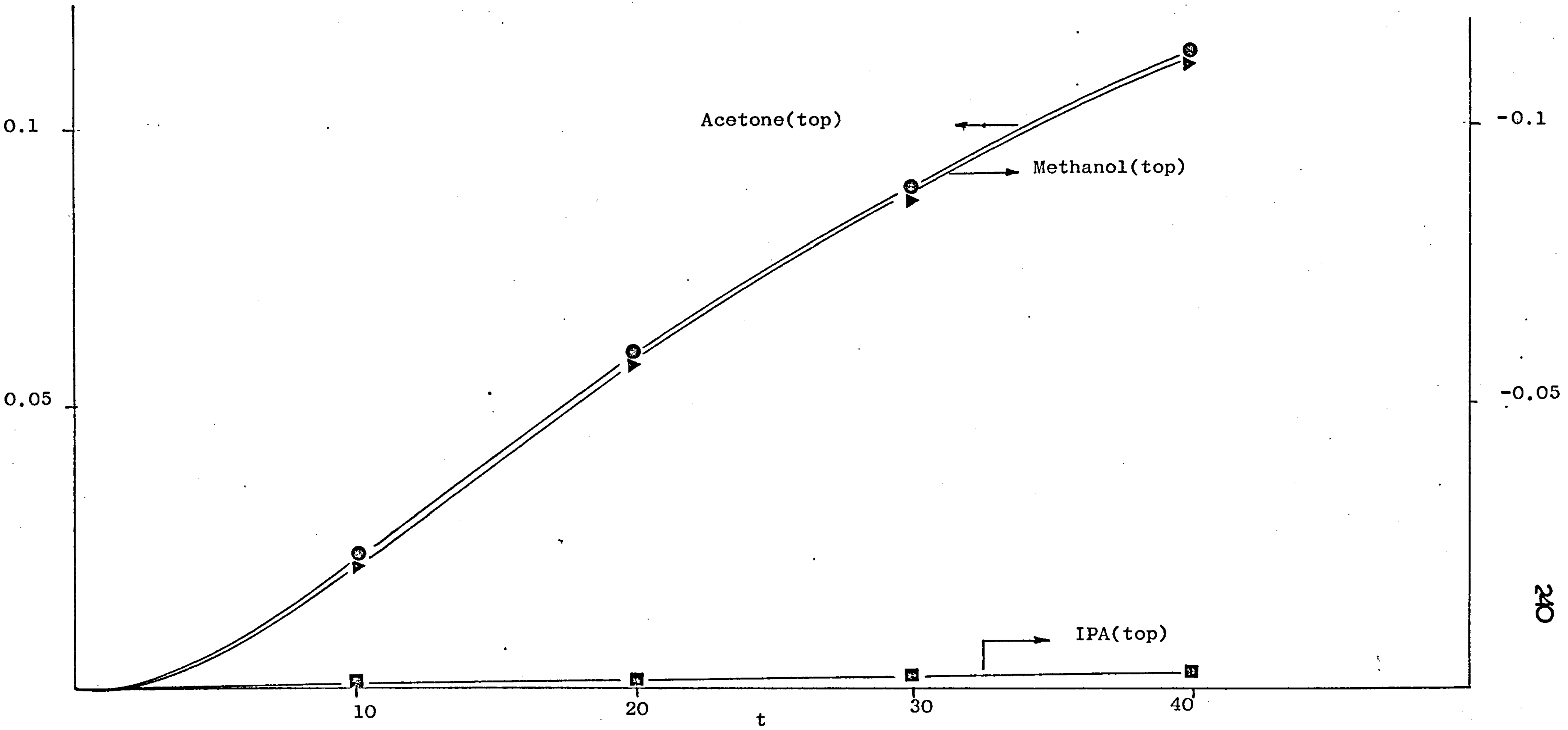


Fig.(33) R.T.W.7

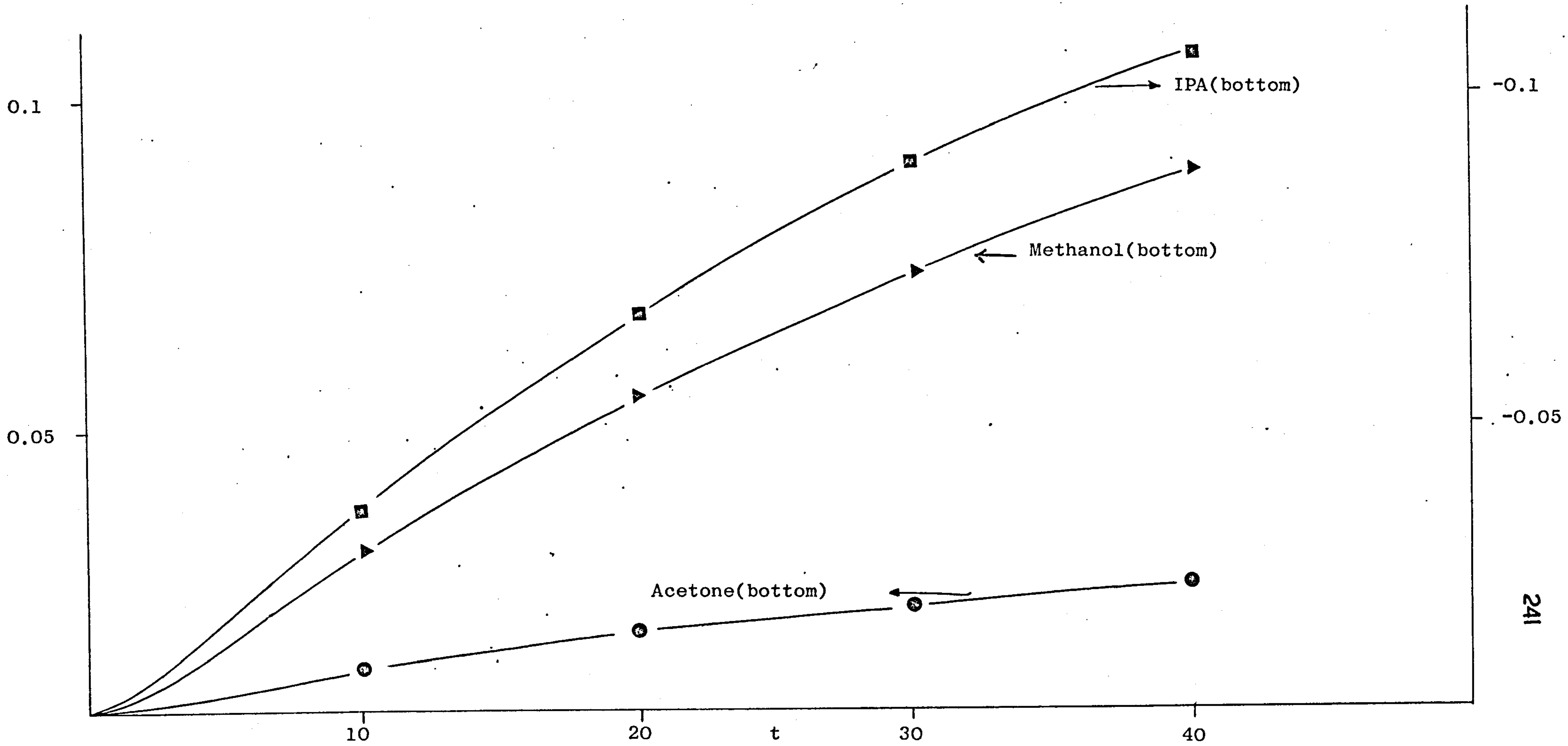

0.1
0.05
-0.1
-0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
t
30
40

Fig.(38) R.T.W.7

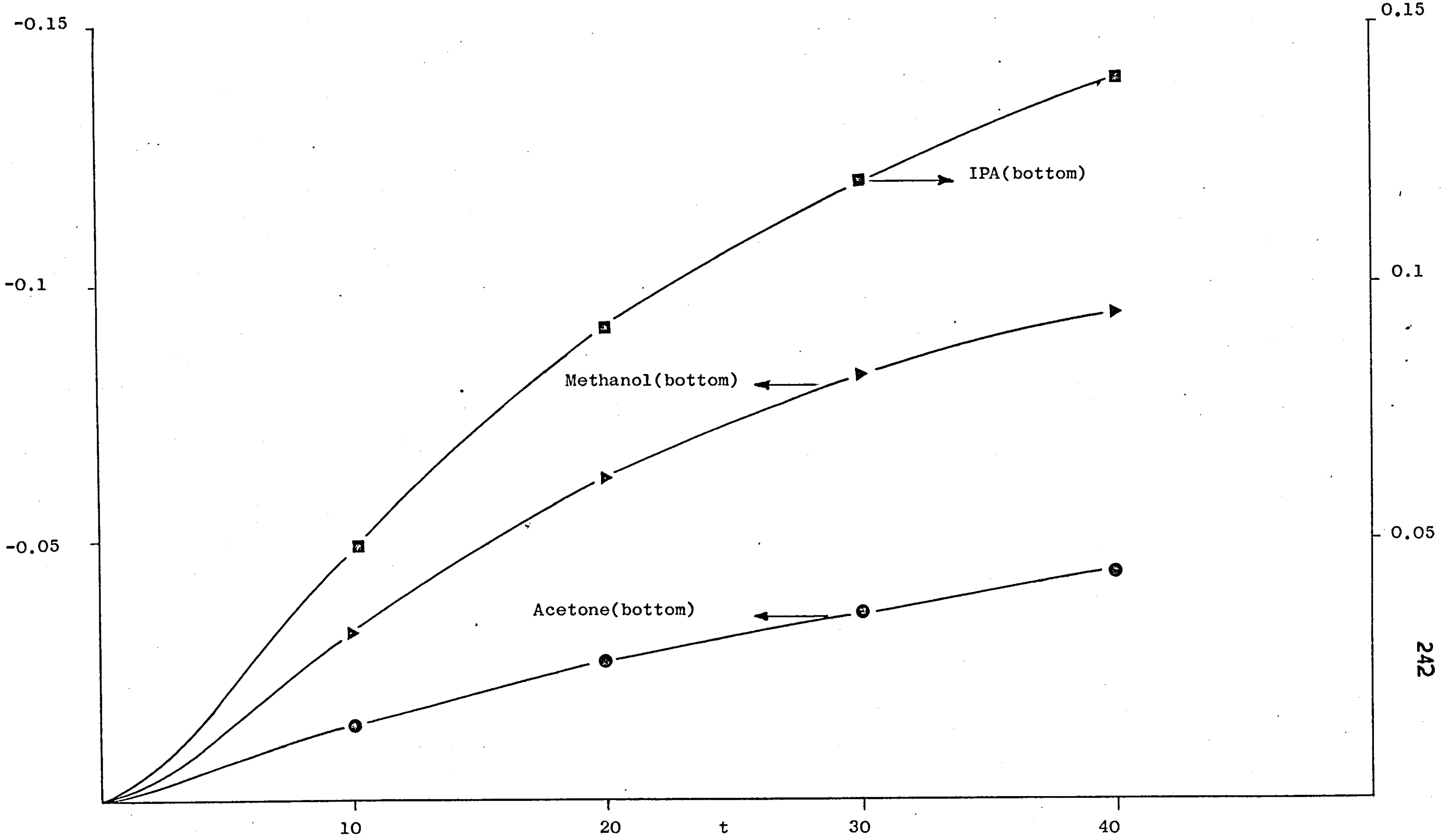

-0.15
-0.1
-0.05
0.15
0.1
0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(39) R.T.W.8

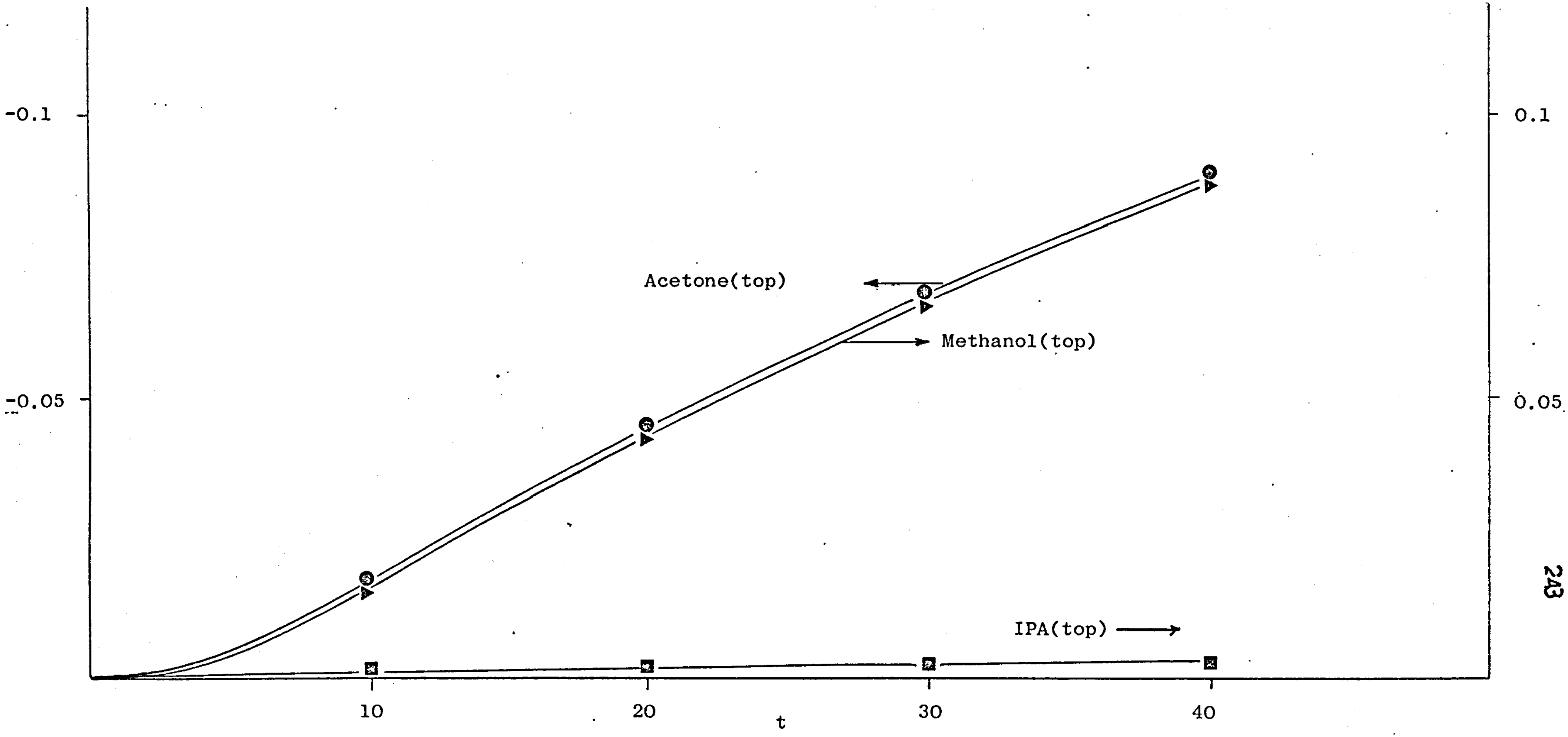


Fig.(39) R.T.W.8

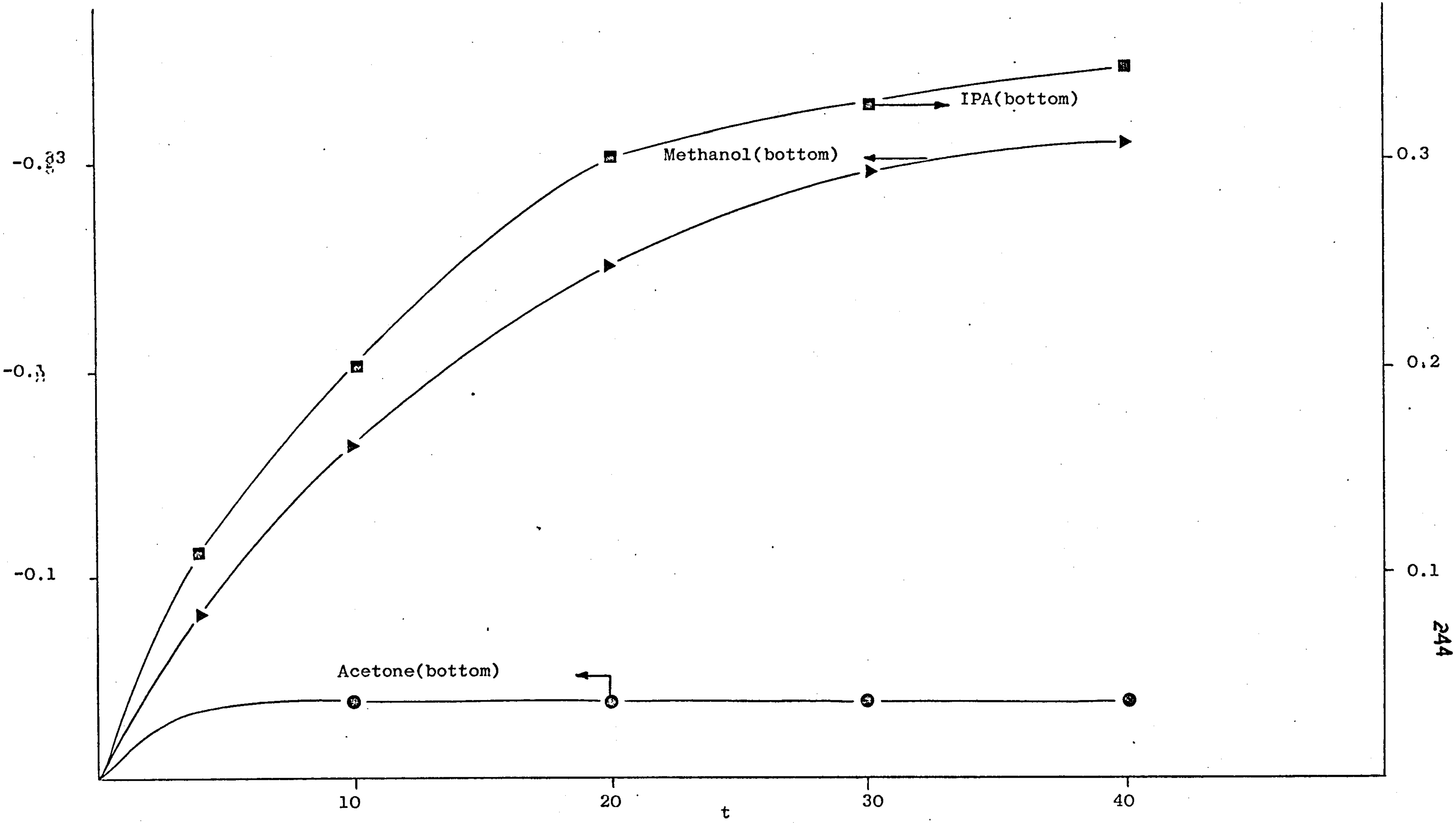

-0.03
-0.3
-0.1
0.3
0.2
0.1
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(40) R.T.W.9

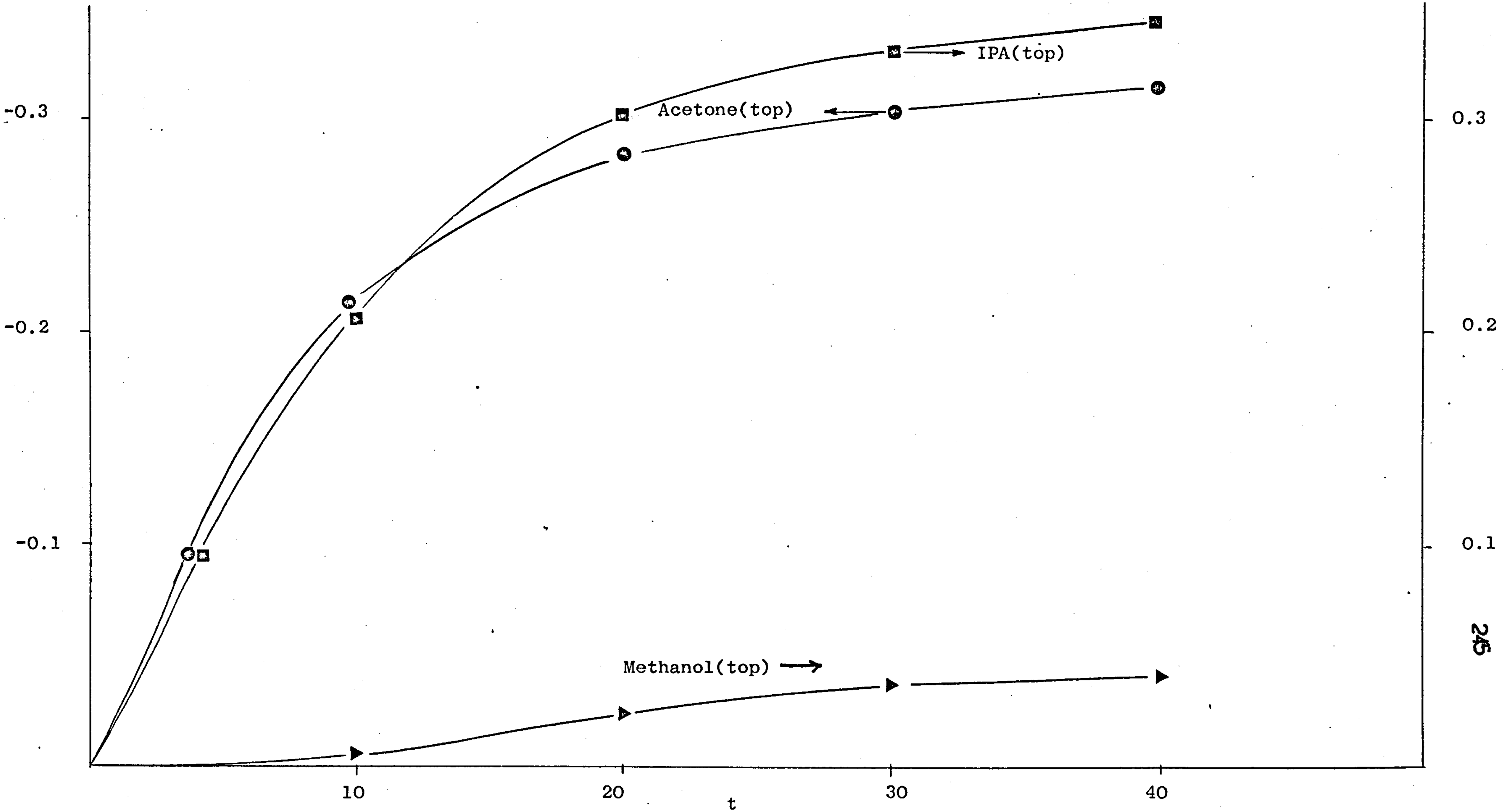


Fig. (40) R.T.W.9

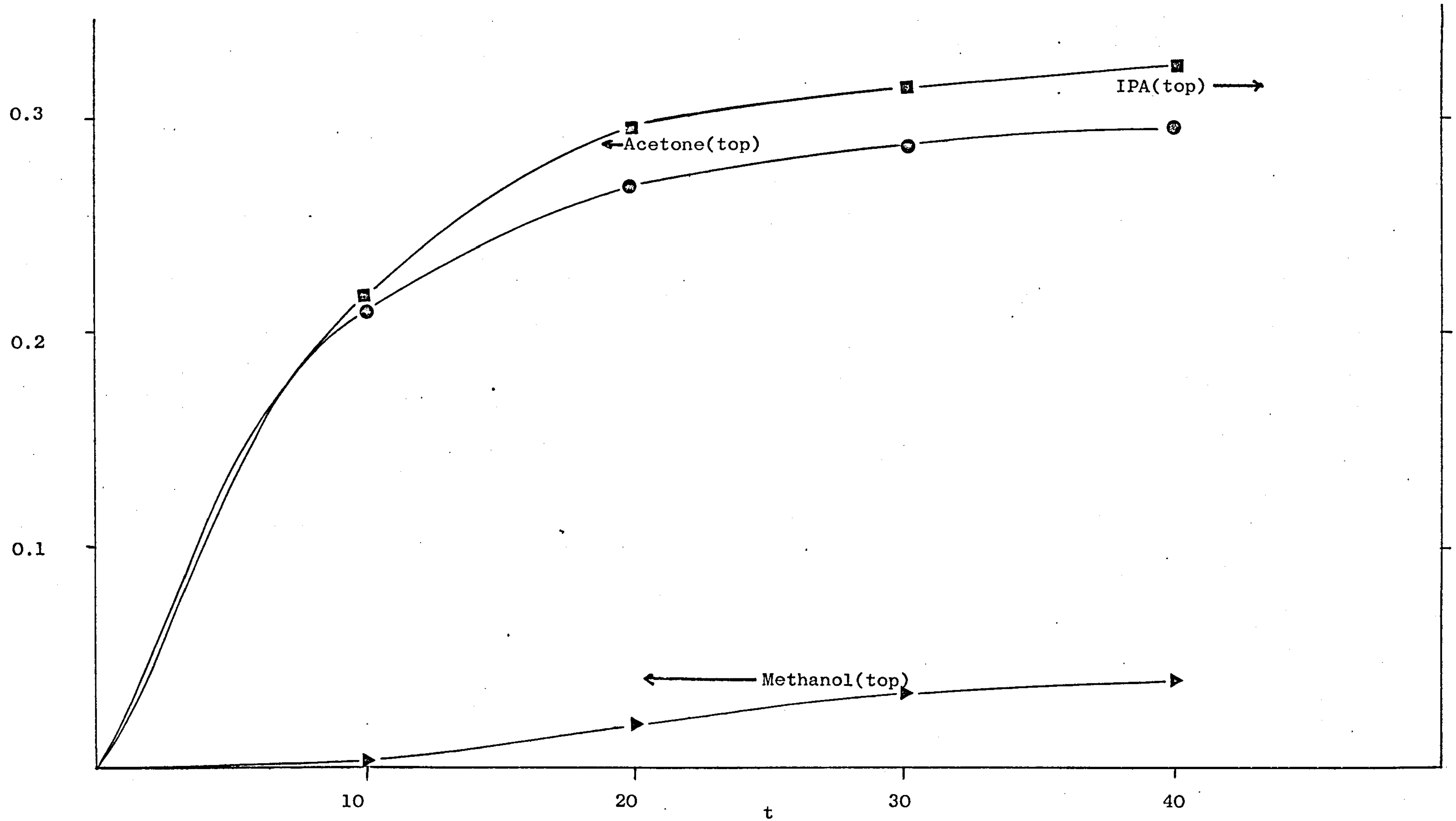


Fig.(41) R.T.W.10

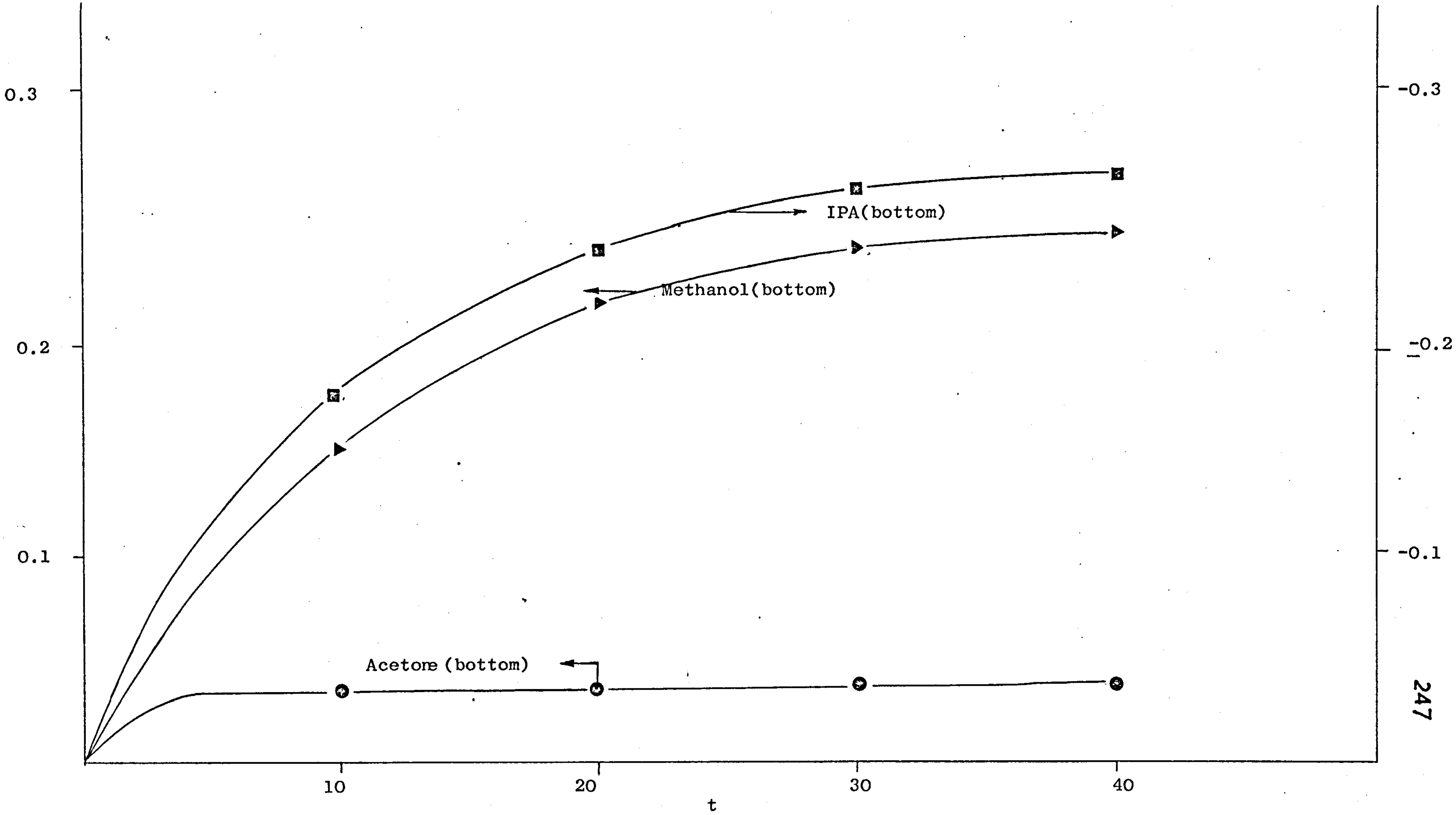

0.3
0.2
0.1
-0.3
-0.2
-0.1
IPA(bottom)
Methanol(bottom)
Acetone (bottom)
10
20
30
40
t

Fig.(41) R.T.W.10

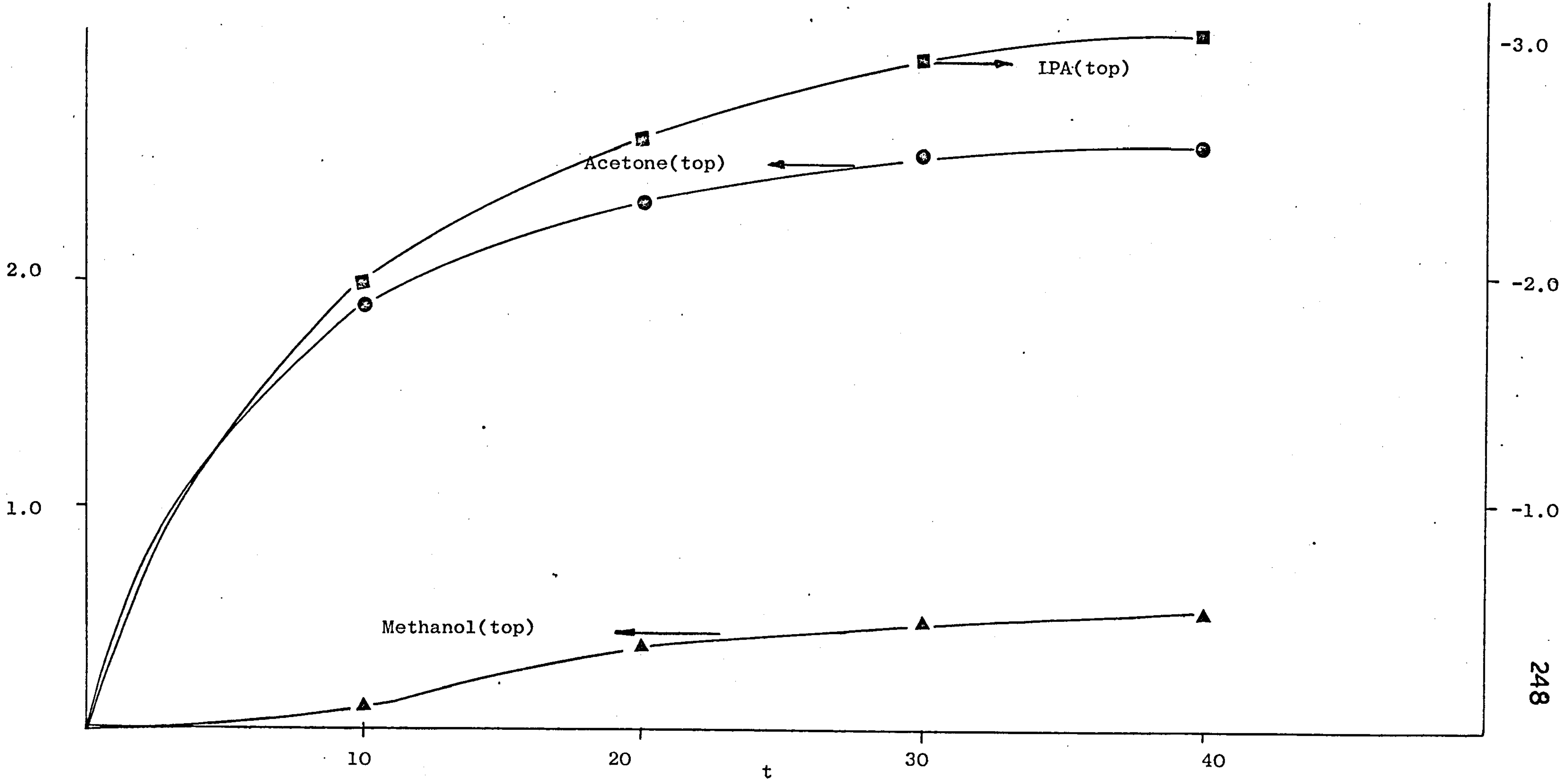


Fig.(42) R.T.W.11

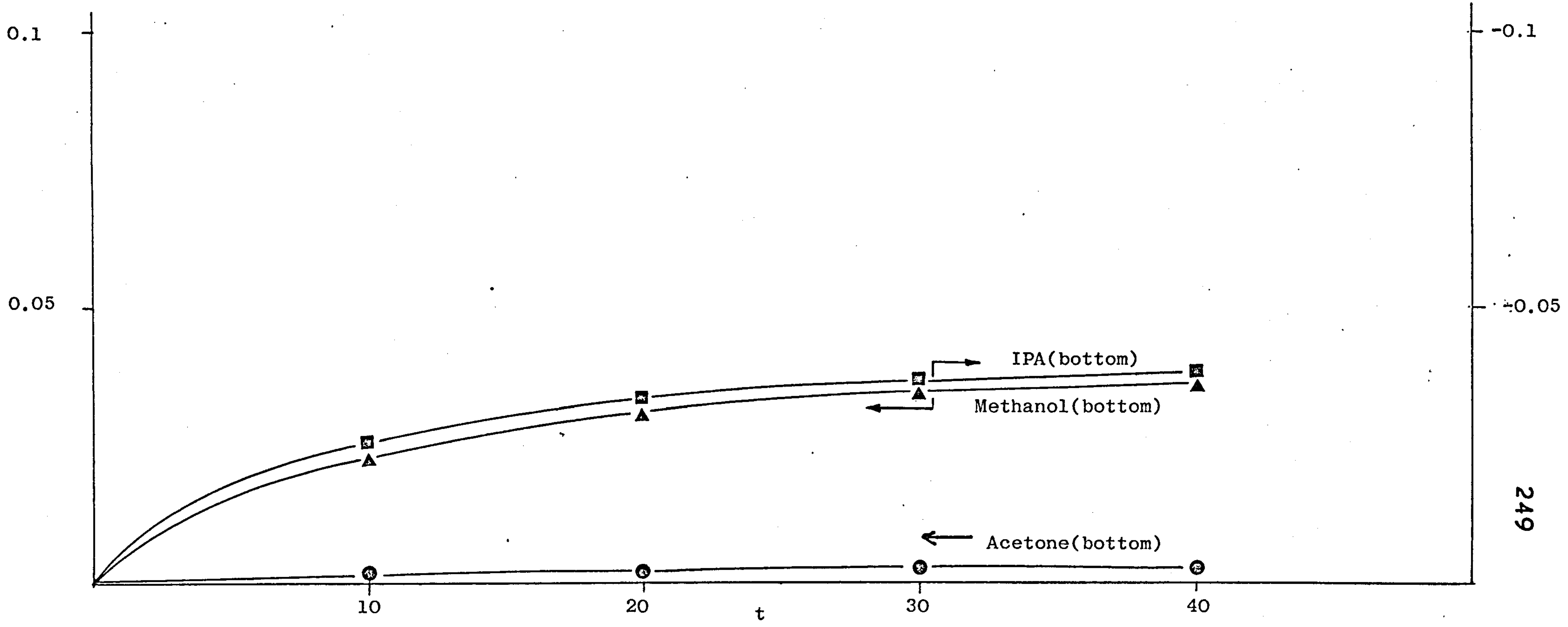

0.1
0.05
-0.1
-0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
30
40
t

Fig.(42) R.T.W.11

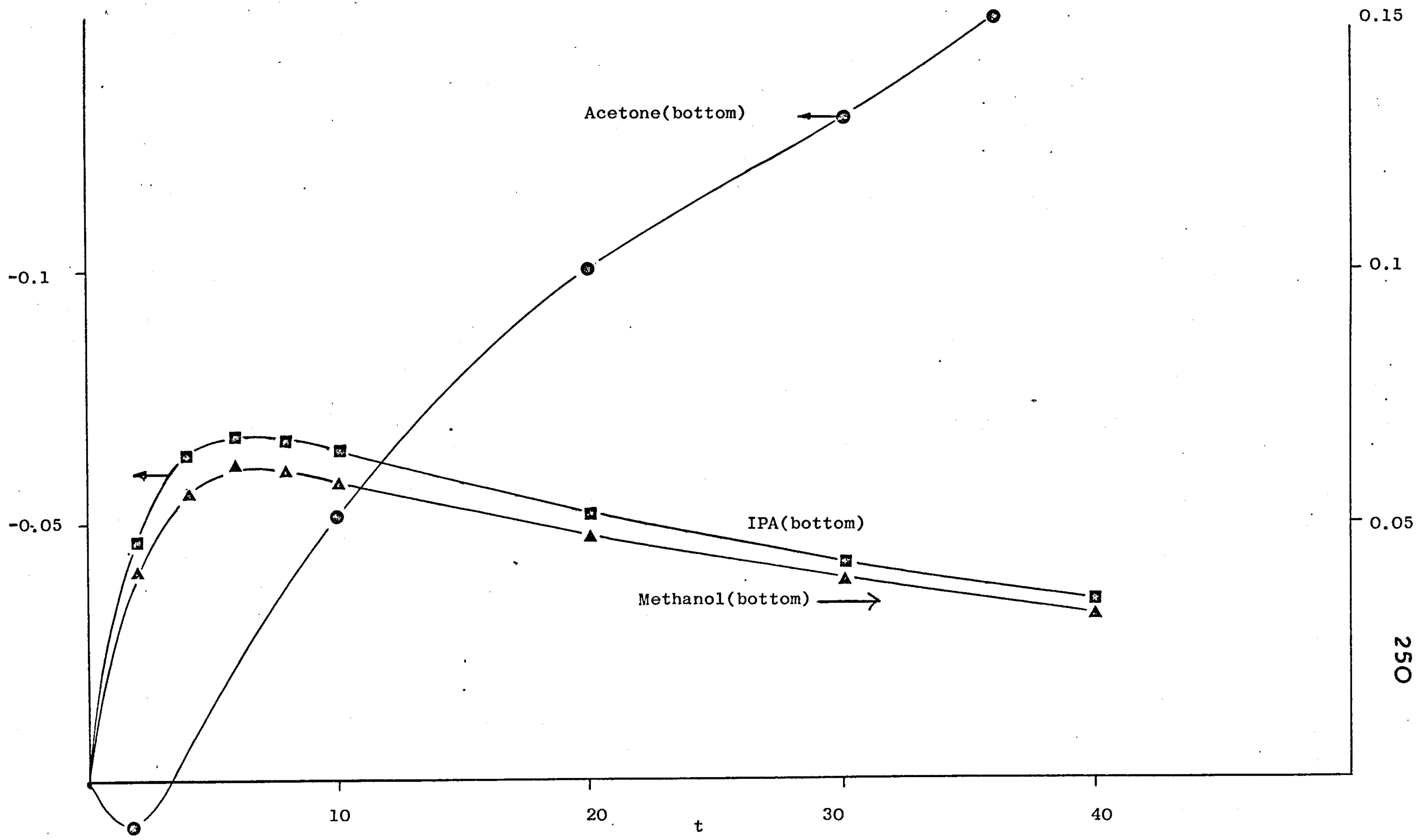

Acetone(bottom)
IPA(bottom)
Methanol(bottom)
-0.1
-0.05
0.15
0.1
0.05
10
20
30
40
t

Fig.(43) R.T.W.12

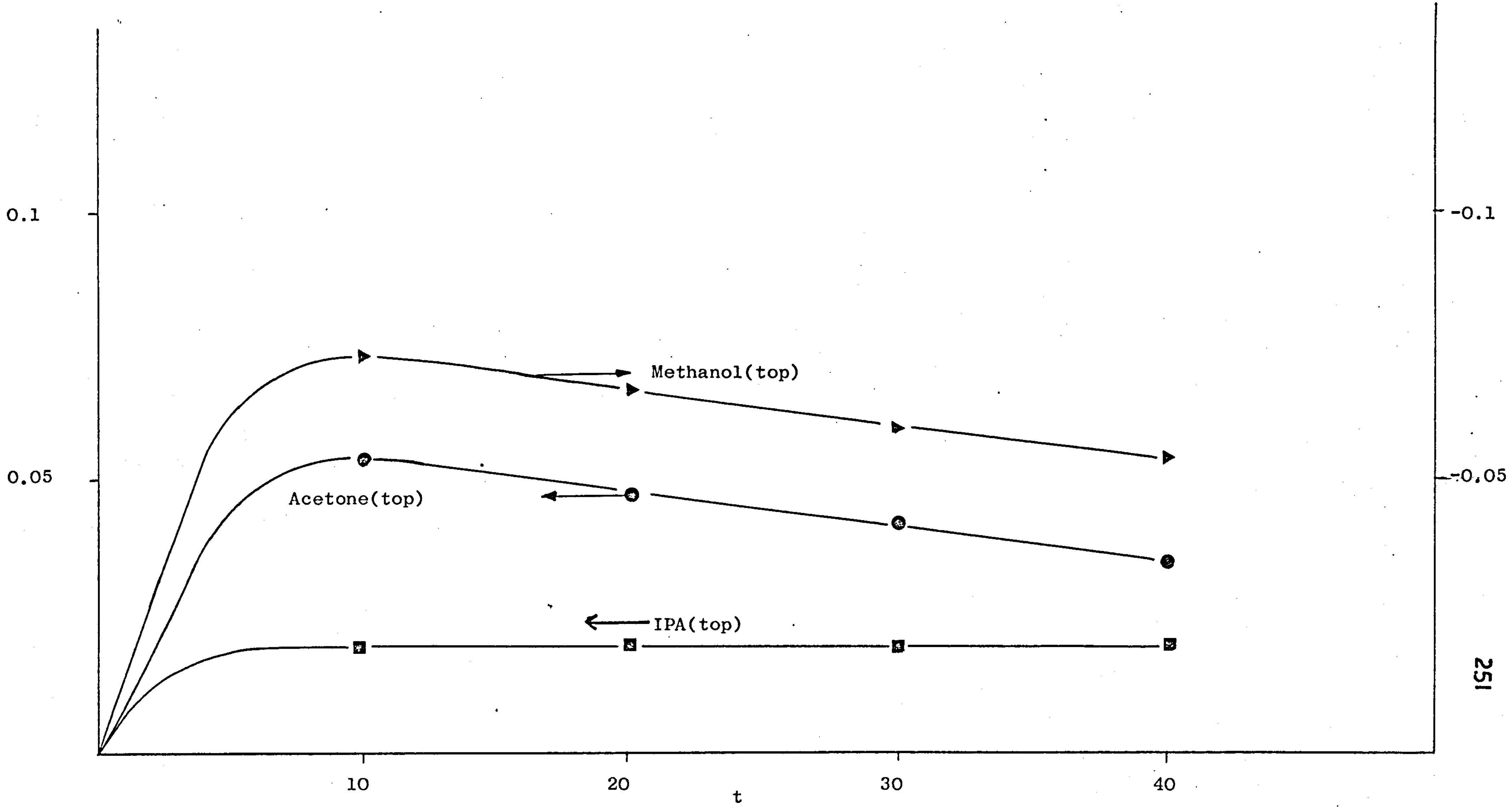


Fig.(43) R.T.W.12

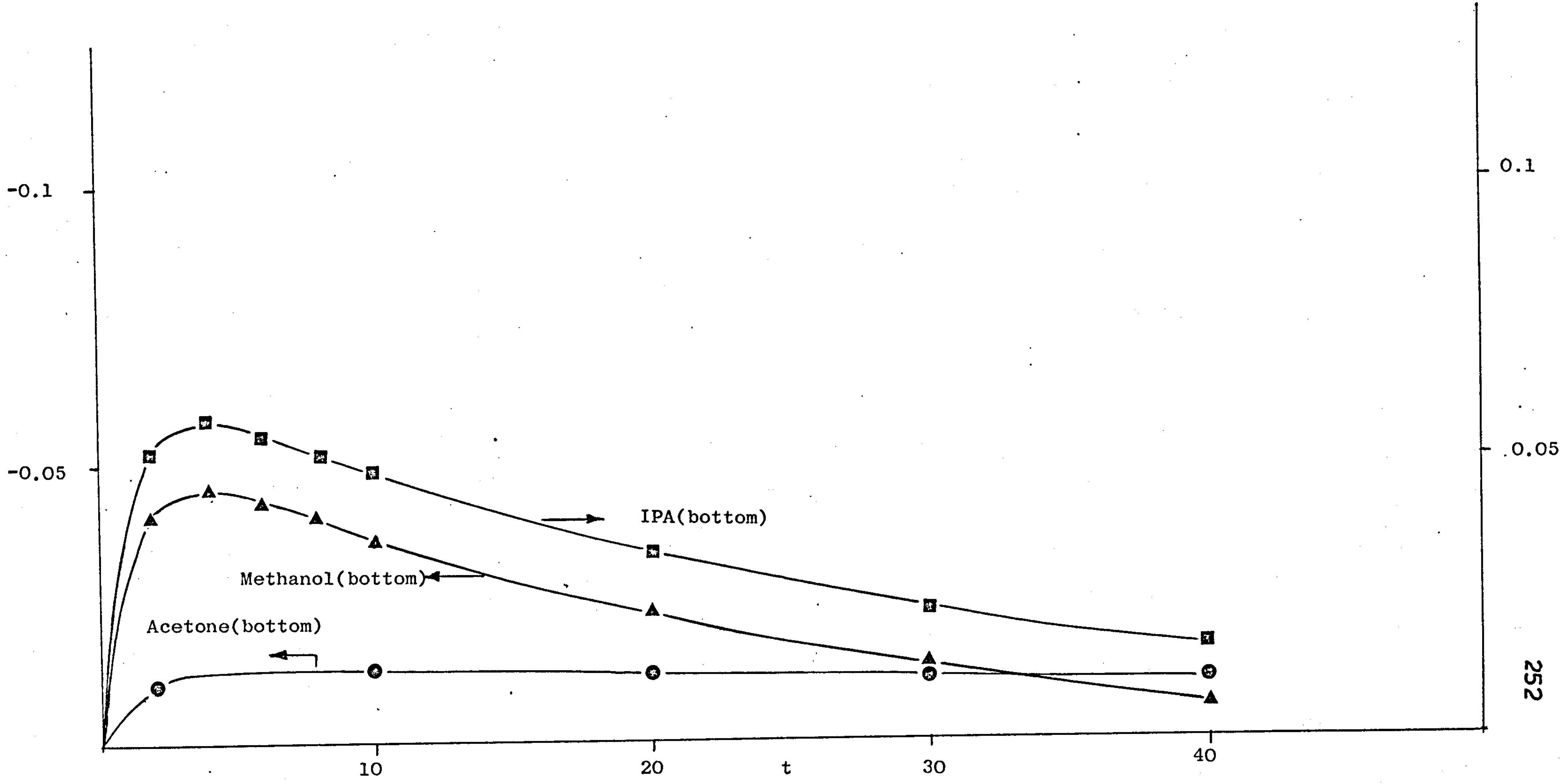

-0.1
-0.05
0.1
0.05
IPA(bottom)
Methanol(bottom)
Acetone(bottom)
10
20
t
30
40

Fig.(44) R.T.W.13

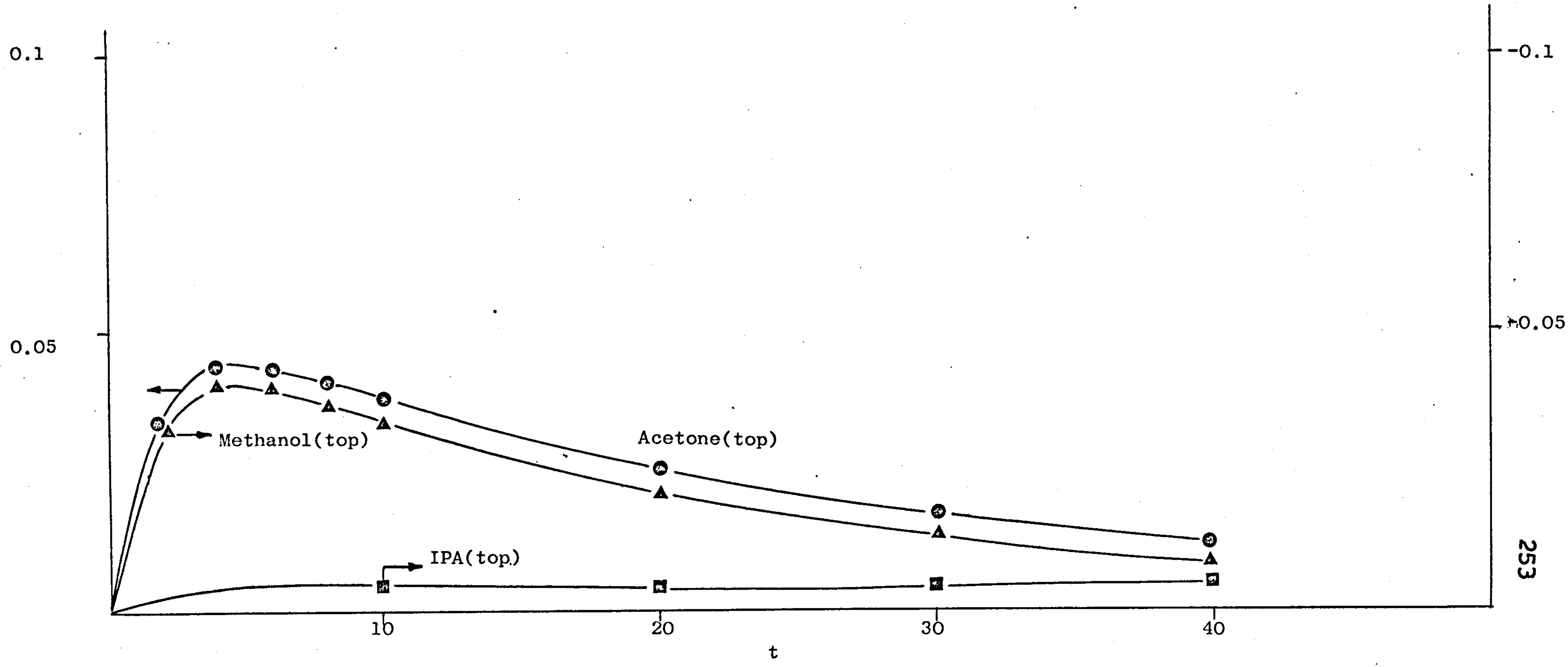


Fig.(44) R.T.W.13

9.2.4 Analytical Solution Using Wood's Method

The eigenvalues calculated for various step changes in feed, boil up rate and the reflux ratio are given in Tables (5 to 14). In all these cases, the matrices were based on Wood's formulation.

The following observations were made.

1) A step change in feed composition or a step change in reflux ratio does not have any apparent effect on the eigenvalues of the system.

2) Two cases can be made for a feed change
    - a) when a feed is changed in both directions (+tive or -tive) from a fixed feed composition, the eigenvalues remain the same see Tables(5,7) but the time solution depends on the sign of the forcing function and so does the resulting time solution.
    - b) when the above feed changes are reversed, the eigenvalues are effected in two ways, see Table (6)
        - i) the most significant eigenvalues increase in their value, and
        - ii) the complex pair, although occuring in the same place, changes in its value.

3) Similar changes may be seen, Tables(7,8), when the above procedure is tried for the same feed change at a different reflux ratio, say 4:1, as compared to 5:1 as in the previous case.

4) If the reflux ratio changes are compared separately the significant eigenvalues increase slightly with increase in reflux ratio and decrease with lowering the reflux ratio, Tables(13,14)

5) If the feed composition remains same as in (1), but the top and bottom product take-offs are altered, the resulting eigenvalues undergo a considerable change, Table (11). This is applicable to the reversal in this feed change, Table (12).

6) It may be interesting to note that for constant top and bottom take-offs, the fourth significant eigenvalue remains constant for nearly all the feed changes and reflux ratios. This could mean that the system behaves similarly for both conditions after the initial ossillations due to a slight change.

TABLE 5

	Feed Change		Take Offs		Reflux Change
			Top	Bottom	
Acetone	0.475	0.485			
Methnol	0.05	0.05	0.5	0.5	5:1
Isopropanol	0.475	0.465			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.02140	
-0.04009	
-0.4842	
-0.5000	
-0.7695	
-1.308	
-1.591	
-2.190	
-2.419	
-2.469	-0.07841
-2.469	+0.07841
-2.571	-0.05758
-2.571	+0.05758
-2.741	
-3.411	
-3.442	-0.04191
-3.442	+0.04191
-3.524	-0.06152
-3.524	+0.06152
-3.563	
-3.920	
-4.610	
-5.125	
-5.603	
-6.449	
-7.124	
-8.161	
-9.094	
-9.957	
-11.68	
-14.48	
-15.91	
-22.42	

TABLE 6

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.485	0.475			
Methnol	0.05	0.05	0.5	0.5	5:1
Isopropanol	0.465	0.475			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.02202	
-0.04994	
-0.4301	
-0.5000	
-0.7506	
-1.279	
-1.473	
-2.117	
-2.446	
-2.481	-0.05162
-2.481	+0.05162
-2.546	-0.03636
-2.546	+0.03636
-2.603	
-3.208	
-3.462	-0.02948
-3.462	+0.02948
-3.516	-0.04205
-3.516	+0.04205
-3.543	
-3.788	
-4.383	
-4.947	
-5.503	
-6.107	
-6.764	
-7.751	
-8.678	
-9.184	
-10.76	
-13.23	
-14.50	
-20.82	

TABLE 7

	Feed Change		Take Offs		Reflux Change
			Top	Bottom	
Acetone	0.475	0.465	0.5	0.5	
Methnol	0.05	0.05			4:1
Isopropanol	0.0475	0.485			

EIGENVALUES

DISTINCT	COMPEX PAIR
-0.02185	
-0.04248	
-0.3947	
-0.5000	
-0.6132	
-1.068	
-1.274	
-1.572	-0.2450
-1.572	+0.2450
-1.920	-0.4547
-1.920	+0.4547
-2.133	
-2.332	
-2.374	-0.4817
-2.374	+0.4817
-2.843	-0.4997
-2.843	+0.4997
-3.198	-0.4031
-3.198	+0.4031
-3.419	-0.1492
-3.419	+0.1492
-3.774	
-4.242	
-4.583	
-5.346	
-5.981	
-6.787	
-7.513	
-8.423	
-9.827	
-12.20	
-13.37	
-18.83	

TABLE 8

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.465	0.475			
Methnol	0.05	0.05	0.5	0.5	4:1
Isopropanol	0.485	0.475			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.01634	
-0.04214	
-0.4491	
-0.5000	
-0.6537	
-1.095	
-1.421	
-1.906	
-1.965	-0.02268
-1.965	+0.02268
-2.012	-0.04362
-2.012	+0.04362
-2.047	
-2.353	
-2.960	
-2.986	-0.03606
-2.986	+0.03606
-3.025	-0.02994
-3.025	+0.02994
-3.041	
-3.333	
-4.005	
-4.402	
-4.770	
-5.634	
-6.543	
-7.064	
-8.018	
-9.495	
-10.86	
-13.17	
-14.84	
-19.99	

TABLE 9

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.475	0.485			
Methnol	0.05	0.05	0.5	0.5	4:1
Isoporpanol	0.475	0.465			

EIGENVALUES

DISTINCT	COMPEX PAIR
-0.02185	
-0.04248	
-0.3947	
-0.5000	
-0.6132	
-1.068	
-1.274	
-1.572	-0.2450
-1.572	+0.2450
-1.920	-0.4547
-1.920	+0.4547
-2.133	
-2.332	
-2.374	-0.4817
-2.374	+0.4817
-2.843	-0.4997
-2.843	+0.4997
-3.198	-0.4031
-3.198	+0.4031
-3.419	-0.1492
-3.419	+0.1492
-3.774	
-4.242	
-4.583	
-5.346	
-5.981	
-6.787	
-7.513	
-8.423	
-9.827	
-12.20	
-13.37	
-18.83	

TABLE 10

	Feed Change		Take Offs Top	 Bottom	Reflux Ratio
Acetone	0.485	0.475			
Methnol	0.05	0.05	0.5	0.5	4:1
Isopropanol	0.465	0.475			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.02303	
-0.05102	
-0.3519	
-0.5000	
-0.5863	
-1.053	
-1.196	
-1.629	
-1.886	-0.3598
-1.886	+0.3598
-1.998	-0.00338
-1.998	+0.003338
-2.004	
-2.145	
-2.617	-0.6087
-2.617	+0.6087
-2.660	
-3.160	
-3.260	-0.5125
-3.260	+0.5125
-3.587	-0.06533
-3.587	+0.06533
-4.102	
-4.515	
-5.071	
-5.674	
-6.478	
-7.178	
-7.738	
-9.061	
-11.14	
-12.20	
-17.44	

TABLE II

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.475	0.465			
Methnol	0.05	0.05	0.4	0.6	4:1
Isopropanol	0.475	0.485			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.09406	
-0.2435	
-0.4000	
-0.8616	
-1.860	
-2.329	
-2.374	-0.06972
-2.374	0.06972
-2.389	
-2.464	-0.05085
-2.464	0.05085
-3.105	
-3.341	-0.04739
-3.341	0.04739
-3.425	-0.06402
-3.425	0.06402
-3.466	
-3.694	
-4.849	
-5.433	
-6.687	
-7.567	
-8.823	
-10.13	
-11.02	
-12.65	
-12.91	
-15.47	
-15.85	
-18.19	
-18.37	
-22.50	
-26.73	

TABLE 12

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.465	0.475			
Methnol	0.05	0.05	0.4	0.6	4:1
Isopropanol	0.485	0.475			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.1071	
-0.2613	
-0.4000	
-0.8686	
-1.883	
-2.351	
-2.384	-0.04823
-2.384	0.04823
-2.428	
-2.449	
-2.449	
-3.143	
-3.358	-0.03272
-3.358	0.03272
-2.418	-0.04740
-3.418	0.04740
-3.449	
-3.763	
-4.914	
-5.495	
-6.788	
-7.673	
-8.936	
-10.26	
-11.12	
-12.82	
-13.03	
-15.50	
-16.02	
-18.23	
-18.45	
-22.56	
-26.74	

TABLE 13

	Feed Change		Take Offs		Reflux Change	
			Top	Bottom		
Acetone	0.475	0.475				
Methnol	0.005	0.005	0.5	0.5	5:1	4:1
Isopropanol	0.475	0.475				

EIGENVALUES

DISTINCT	COMPEX PAIR
-0.02140	
-0.04009	
-0.4842	
-0.5000	
-0.7695	
-1.308	
-1.591	
-2.190	
-2.419	
-2.469	-0.07841
-2.469	+0.07841
-2.571	-0.05758
-2.571	+0.05758
-2.741	
-3.411	
-3.442	-0.04191
-3.442	+0.04191
-3.524	-0.06152
-3.524	+0.06152
-3.563	
-3.920	
-4.610	
-5.125	
-5.603	
-6.449	
-7.124	
-8.161	
-9.094	
-9.957	
-11.68	
-14.48	
-15.91	
-22.42	

TABLE 14

	Feed Change		Take Offs		Reflux Change	
			Top	Bottom		
Acetone	0.475	0.475				
Methnol	0.05	0.05	0.5	0.5	4:1	5:1
Isoproponal	0.475	0.475				

EIGENVALUES

DISTINCT	COMPEX PAIR
-0.02185	
-0.04248	
-0.3947	
-0.5000	
-0.6132	
-1.068	
-1.274	
-1.572	-0.2450
-1.572	+0.2450
-1.920	-0.4547
-1.920	+0.4547
-2.133	
-2.332	
-2.374	-0.4817
-2.374	+0.4817
-2.843	-0.4997
-2.843	+0.4997
-3.198	-0.4031
-3.198	+0.4031
-3.419	-0.1492
-3.419	+0.1492
-3.774	
-4.242	
-4.583	
-5.346	
-5.981	
-6.787	
-7.513	
-8.423	
-9.827	
-12.20	
-13.37	
-18.83	

CHAPTER 10

DISCUSSIONS AND CONCLUSIONS

DISCUSSION AND CONCLUSIONS

Work in this thesis helps in its own way towards better understanding of the dynamics of a column, so that full control of distillation columns by computer is expected.

The steady state model used in this project was based on the model suggested by Hanson (67), but modified to suit the problem being investigated. Although Hanson's model was not very efficient, as was found out by another worker[68] in the department, who used θ - method, yet when it was used, did provide with the relevant information which was needed for the purposes of the work being carried out in this thesis. As the prime object was to investigate the transient compositions between steady states, it was not necessary to have a very high powered steady state model. What was needed was steady states at different operating conditions, from which disturbances could be made in one direction or the other and the resulting transients investigated.

The various steady states are illustrated in figs (1-23) and Appendix (A4). The next and the main object was to develop a dynamic model. The equations describing the transient behaviour may be formulated in two different ways. Sargents and Woods' techniques have been investigated and the comparison between the two has been discussed later on in detail. It was also decided to get to the predicted transients both analytically and numerically. The purpose for this was, apart from providing a useful cross check for each technique, to make use of two very useful techniques such as eigenvectors and eigenvalues and a numerical method called Markov probabilistic method. After a successful application of this technique to mixing in stirred vessels (57), it was thought worthwhile to see its application to mixing in continuous counter current vessels which depicts a distillation column adequately.

In this investigation Matrix techniques have been fully utilized to describe the formulation of the problems both analytical and numerical. As the matrices used in both analytical and numerical, Sargent and Wood were same for any given particular situation, it reduced the work to quite an extent, specially in case of multi-component mixtures.

As mentioned earlier two different methods of formulating the dynamic equations have ~~were~~ been tried. Sargents method was a bit earlier then Wood's. Formulating in Sargents' method, the equations form a tridiagonal matrix, for each component separately. In a multi-component system this may not be good enough as the interactions between the different components is a very important feature. Moreover as all the K's are composition dependent, temperature is a valid parameter to be added into the equations. Adding a temperature term to Sargent's equation did increase the matrix elements but it no more remained a tridiagonal matrix.

Wood's method was tried as the equations are composition based and the components are interrelated by the relative volatilities. As this provided a scope for ~~of~~ more interaction between components, more stress was laid on this technique to investigate a multi-component system.

The analytical method handles both real eigenvalues and the complex conjugate columns in the trans~~p~~for~~t~~mation matrix. This wastes computer storage so the method was modified based on the fact that one of a pair of complex conjugate vector contains all of the essential information of the pair. The method is discussed in detail in Chapter 4.

Next it would be worthwhile to mention point by point the essential differences in Sargents' method and Woods' method.

COMPARISON OF SARGENT AND WOOD'S METHODS

1. Wood determines the transient response of a column in the frequency response domain, whereas Sargent studies the dynamic behaviour of multistage systems without any reference to frequency domain.

2. The matrix formulation for the two are quite different as shown in figs 5.7.1 FIG(5.7.2) Sargent's is a tridiagonal matrix whereas Wood's is a band matrix.FIG(5.7.3)represents the difference adequately. FIG5.7.3)also indicates that Sargent's method involves less number of interactions than Wood's which could contribute towards misrepresenting or underrepresenting the actual problem by Sargent.

3. Sargent can deal with only one component at a time, whereas Wood deals with all the components' in the same matrix.

SARGENT

$$\begin{matrix}\dot{\underline{x}}_1\\ \dot{\underline{x}}_2\\ \dot{\underline{x}}_3\end{matrix} = \begin{matrix} A_1 & o & o\\ o & A_2 & o\\ o & o & A_3\end{matrix} \quad \begin{matrix}\underline{x}_1\\ \underline{x}_2\\ \underline{x}_3\end{matrix} + F \tag{1}$$

WOOD

$$\dot{\underline{x}} = B\underline{x} + F \tag{2}$$

4. In Sargent's method, disturbance in one component does not have any effect on the other components whereas in Wood's technique disturbance is equally distributed through all the components which is more consistent with the physical system of disturbance in a distillation column.

5. Method proposed by Sargent uses an approximating system which reproduces correctly the complete qualitative behaviour of the real system, and further does not depend on estimates of the x_j to determine the dx_i/dt. On the other hand in Wood's method the slopes $g_{n,i}$ for multi-component mixtures depend on all the perturbations in composition on plate n, this is because the slope of the equilibrium data is no longer a line of fixed gradient but is a line in a vector space. In order to determine the direction of a line in such a space it is necessary for the liquid compositions to be specified, i.e., $x_{n,i}$ must be known. It is evident that as $g_{n,i}$ are functions of $x_{n,j}$ with $j = 1 \dots k$, that it will be necessary to solve the equations for all K components simultaneously. In other words, it will be impossible to obtain a solution for the transient behaviour of one component in isolation.

6. The assumptions made by Wood are :

   i) composition changes are sufficiently small so that the equations which determine the transient behaviour of the column may be linearised. This in itself is a big assumption,

   ii) the plates are ideal stages and any time dependent variable may be set equal to its steady state value plus a small perturbation.

Sargent assumed that each stage behaved as a theoretical plate, the vapor holdup was negligible and the mixture obeyed the ideal solution laws in both phases.

7. Sargent's equilibrium relationship depend on K (equilibrium constant) which are dependent on temperature at each plate. Wood on the other hand makes use of relative volatility and assumes it constant throughout (in our case, the relative volatility was calculated at each stage for the sake of greater accuracy and rigorous apprehension of the problem involved).

8. Wood's matrix is more time consuming than Sargent's in terms of computation.

9. Sargent's eigenvalues are real and negative with no complex pair, whereas eigenvalues found in Wood's case have a real negative part and a complex pair.

10. As the basic forms of characteristic equations roots in the two cases are different, their representation on complex plane, and their nature of effect on transient response are quite different. However both represent stable systems which decrease with time in Sargent's case and decays with time in Wood's method.

TABLE 15

	Feed Change		Take Offs		Reflex Change
			Top	Bottom	
Acetone	0.475	0.465			
Methnol	0.05	0.05	0.5	0.5	5:1
Isopropanol	0.475	0.485			

EIGENVALUES

DISTINCT	COMPEX PAIR
-0.02140	
-0.04009	
-0.4842	
-0.5000	
-0.7695	
-1.308	
-1.591	
-2.190	
-2.419	
-2.469	-0.07841
-2.469	+0.07841
-2.571	-0.05758
-2.571	+0.05758
-2.741	
-3.411	
-3.442	-0.04191
-3.442	+0.04191
-3.524	-0.06152
-3.524	+0.06152
-3.563	
-3.920	
-4.610	
-5.125	
-5.603	
-6.449	
-7.124	
-8.161	
-9.094	
-9.957	
-11.68	
-14.48	
-15.91	
-22.42	

TABLE 17

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.475	0.465			
Methanol	0.05	0.05	0.5	0.5	5:1
Isopropanol	0.475	0.485			

EIGENVALUES

ACETONE	METHANOL	ISOPROPANOL
-0.2668	-0.0557	-0.1456
-1.130	-0.6274	-0.7584
-2.547	-1.595	-1.314
-4.143	-2.668	-1.863
-5.783	-4.097	-2.826
-7.694	-5.598	-3.614
-9.389	-6.985	-4.543
-10.81	-8.402	-5.234
-13.21	-9.384	-6.178
-17.57	-12.10	-7.966
-23.36	-15.89	-10.46

TABLE 16

	Feed Change		Take Offs		Reflux Ratio
			Top	Bottom	
Acetone	0.465	0.475			
Methnol	0.05	0.05	0.5	0.5	5:1
Isopropanol	0.485	0.475			

EIGENVALUES

DISTINCT	COMPLEX PAIR
-0.01603	
-0.04030	
-0.5000	
-0.5549	
-0.8328	
-1.334	
-1.758	
-2.302	
-2.467	
-2.488	
-2.502	-0.03765
-2.502	+0.03765
-2.540	
-2.859	
-3.440	
-3.485	-0.05573
-3.485	+0.05573
-3.545	-0.03066
-3.545	+0.03066
-3.668	
-4.033	
-4.859	
-5.337	
-5.765	
-6.859	
-7.812	
-8.569	
-9.721	
-11.24	
-13.05	
-15.63	
-17.91	
-23.98	

TABLES 18

	Feed Changes		Take Offs Top	Take Offs Bottom	Reflux Ratio
Acetone	0.465	0.475			
Methanol	0.005	0.005	0.5	0.5	5:1
Isoproponal	0.485	0.475			

EIGENVALUES

ACETONE	METHANOL	ISOPROPANOL
-0.3090	-0.0662	-0.0543
-1.36	-0.6847	-0.6837
-2.773	-1.668	-1.232
-4.405	-2.732	-1.846
-6.052	-4.261	-2.842
-7.994	-5.771	-3.738
-9.778	-7.229	-4.612
-11.11	-8.511	-5.272
-14.356	-9.875	-6.569
-19.052	-12.96	-8.640
-24.409	-16.64	-10.91

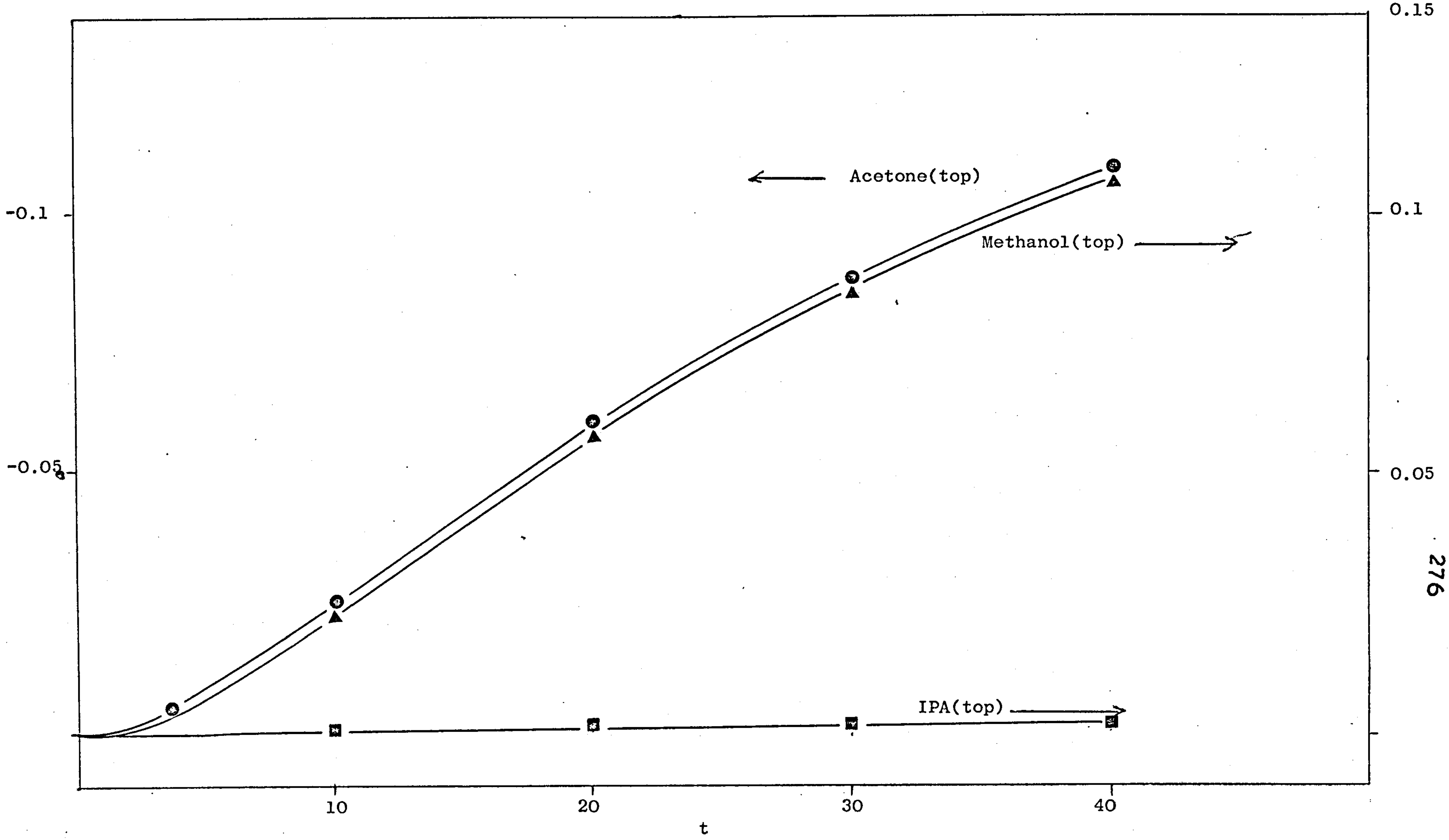


Fig.(31) R.W.T.1

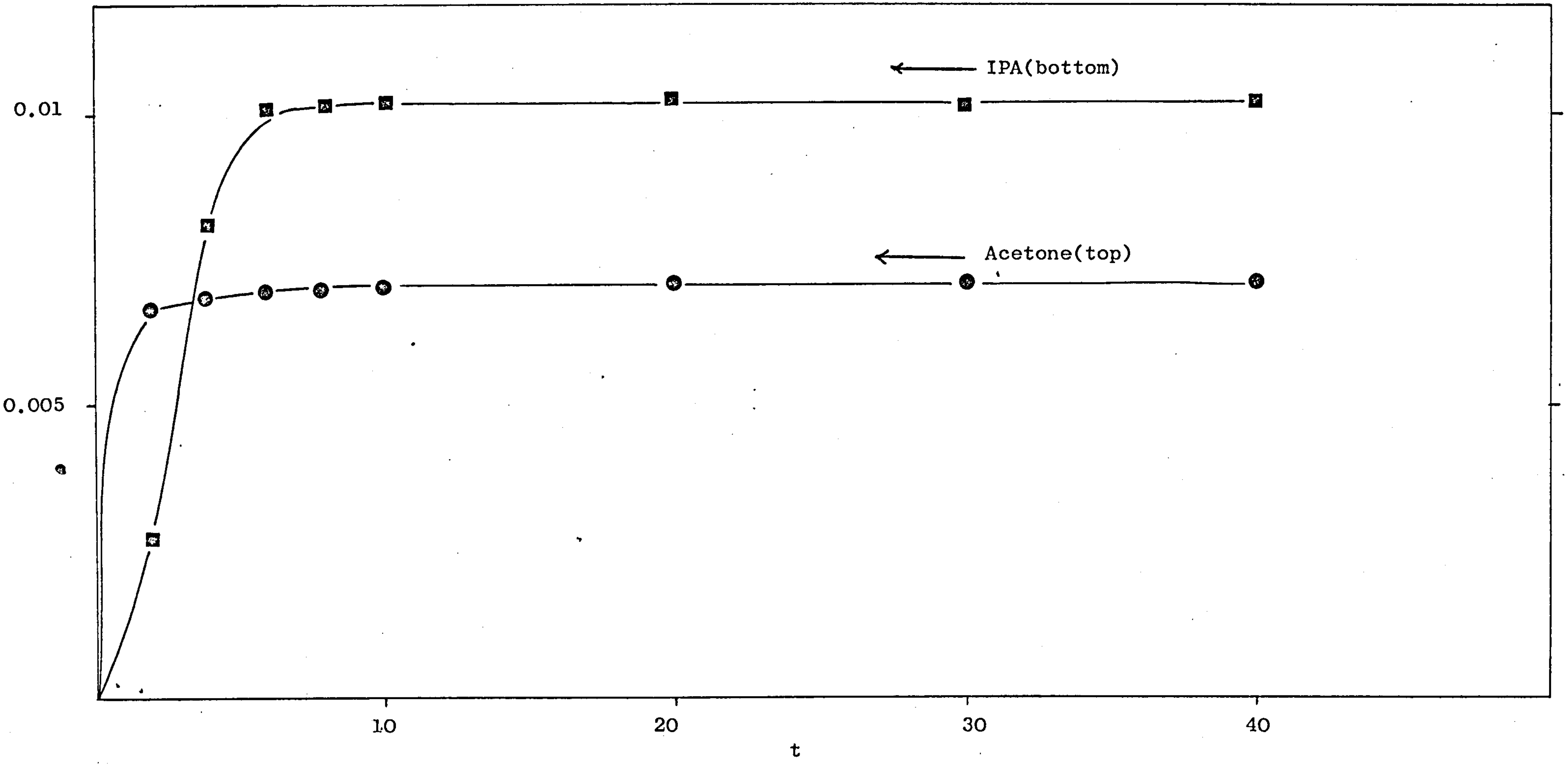


Fig.(32) R.T.S.1

Caping up the comparison between the two techniques, it can be concluded that Sargent's technique although relatively simpler to use, does not define a multi-component system fully as compared to Wood's technique which uses more interactions than Sargent's to define the same problem.

It was noticed that the discrepancy between the two techniques was quite large and needed probing into. The idea was to see which of the two was better or at least was able to define specifically about the type of case where one or the other technique may be applied advantageously.

This discrepancy, it was felt, was due to the fact that the number of equations used by Wood were more than Sargent's. Sargent's, admittedly has its advantage in its simplicity and the ease with which the three components can be handled separately, independent of each other, but it falls down if the components are to be handled jointly or if the intention is to see the effect of disturbance in one component transmitted to the rest of the system. Wood's technique handles this situation very adequately. It can tackle all the components and all the plates and a disturbance in one component is equally distributed in the rest of the components. In other words, disturbance in each component equals the total disturbance. Whereas, in Sargent's method the total disturbance equals only to the one component in which the disturbance is made at one particular time. Individual disturbances in each components are shown in section 9.2.3. Attempt was also made to combine all the three matrices for three components in one matrix to study the resulting transients which could be compared with Wood's technique. It is given in Section 9.2.1.

Another worth noting feature of Wood's technique is that it furnishes besides the distinct negative eigenvalues some complex pair, which not only illustrates that the system is oscillatory, but has the potentialities of rendering more information regarding the non-linearity of the system.

Although the eigenvalues obtained by the Wood's method are complex, thereby showing the oscillatory tendency of the system, yet it was observed that the complex eigenvalues do not have an appreciable effect on the dynamics. The reason being that the ratio of the most significant eigenvalue and the eigenvalue just before the complex pair occurs, is more than 100:1 to cause the system to oscillate significantly. It could be more appreciable if there were more than three components or even if the concentration of the middle component was more than what was used in the present investigation.

The responses obtained for one particular feed change for both techniques illustrates the difference very well. Comparison has been made both analytically and numerically. Both numerical responses and the eigenvalues which give the analytical solution are given in fig. R.T.W.I. and R.T.S.I. and Tables (15-18). It can be seen that the responses obtained by Wood's technique provide more information regarding the system as compared to Sargent's technique.

Some of the other results are briefly summarised as follows:

The quasi-linearisation technique described in this work has been shown to give good approximation to the dynamic characteristics of a distillation column.

The responses of a distillation column to reflux disturbances generally follows the same pattern as in the case of feed composition disturbances. In case of reflux changes, the shape of the impulse response curve for reflux disturbance was the same whether the disturbance is expressed in terms of reflux ratio disturbance, ΔR, or in terms of reflux rate disturbances, ΔL. The only difference is that for the system considered, ΔR was larger than ΔL. In other words, the impulse response curves in terms of reflux ratio disturbance are lower than those obtained in terms of reflux flow rate disturbance. In practical terms this amounts to setting the appropriate values (ΔR or ΔL) on the proportional controller.

When a digital computer is employed for the analysis, simultaneous determination of the impulse response to feed composition disturbance and that to reflux disturbance is not recommended because of the effect of non-linearities and because of the almost two fold increase in sample length required for an accurate determination of the responses.

CHAPTER 11

SUGGESTIONS FOR FURTHER WORK

11. FUTURE WORK

A logical continuation of the present work is to compare the cost integral approach with the minimum start up time approach on a more realistic distillation column model. On-line feed back and feed forward control schemes are required for practical application and in order to do this, methods of generating simplified modes which preserve the important features of the dynamic behaviour of the process are required.

Another important class of end point problems which have not been solved numerically here are those for which the final state variables are constrained. For example, if there is only a limited amount of feed material available, the integral of the feed rate over the operating period must not be greater than a given value.

Effect of nonlinerarity on the dynamics of a distillation column is another worth investigating subject. This particular suggestion has been discussed in detail in the next section. A complete method of Analysis is also suggested.

11.1 Introduction

Another objective of this investigation is to study the effect of nonlinearities on the response of a distillation column to feed composition disturbances and reflux disturbances.

The transient behaviour of a plate-type distillation column can be described by a set of nonlinear, first order, ordinary differential equations. The nonlinearity of the equations is due to the nonlinear relationships between the equilibrium vapour compositonand the liquid composition. In their general form, these equations cannot be solved analytically. To obtain an approximate solution and also for the sake of simplicity in the analysis, many investigators (4) (5) (33) (35) (36) (38) (53) (54) resort to the technique of linearization. Linearisation is a valuable tool in the analysis of many physical problems of interest. However, there are many phenomena peculiar to nonlinear systems, such as the existence of the limit cycles, which cannot be explained by the analysis of the linear approximation to the original system. Furthermore, linearization is a valid approximation to the actual system only for small departures from equilibrium. The purpose of this research is, therefore, to investigate the manner in which the solution to the linearized equations may differ from the solution to the original set of nonlinear equations after disturbances have been introduced into the system.

The most important property of a linear system is that the principle of superposition applies. The sum of any two solutions of a linear system is also a solution, and any constant multiple of a solution is also a solution. The response of a constant coefficient linear system to a unit impulse disturbance, the impulse response, and its Laplace transform, the transfer function, are the characteristics of the system. The importance of the impulse response comes from the fact that once the impulse response of any linear system is known, the response of that system to any arbitrary inputs is also known. The relationship of the output of a linear system with constant coefficients, Y (t), to the unit impulse response, g(t), and any arbitrary input, X(t), is given by the superposition integral.

$$Y(t) = \int_0^\infty g(t-\tau)\, X(\tau)\, d\tau$$

The integral $g(t-\tau)\,X(\tau)$ has the signigicance of being the output of the system at time t for an impulse of magnitude $X(\tau)$ applied at time τ As a consequence of the validity of the principle of superposition, certain test signals such as the step function, the impulse function, or the sinusoidal function with variable frequency can be used to measure the transient characteristics, that is the impulse response or the transfer function, of a linear system; the magnitude of the signal is immaterial.

In the case of nonlinear systems, none of the properties mentioned above need to be true. The principle of superposition does not apply. The transient bahaviour of a nonlinear system frequently depends on the initial conditions, the type of input, and its magnitude. Therefore, in the investigation of the transient behaviour of a nonlinear system, the input employed should be the one which actually occurs in practice or a time function which approximates it as closely as possible. Since the distrubances which occur in practice are more or less tandom, therefore, in this investigation, emphasis should be placed on the study of the response of the distillation system to random disturbance in feed composition and reflux rate, although system response to step and impulse disturbances have also been investigated already.

Objective is to investigate the use of a technique with random input for the analysis when the response of the distillation system to random disturbance in feed composition or reflux rate is investigated. One such technique is Booton's(69)quasi-linearization technique with random input and involves the fitting of an equivalent linear system in the form of an equivalent impulse response to a given set of input-output data by the least mean square error criterion. The equivalent impulse response obtained is a function of the mean square magnitude of the random disturbance. By varifying the mean square magnitude of the input, a set of equivalent impulse responses are obtained. These are then compared with the impulse response of the linearized system, which is independent of the mean square magnitude of the input, to determine the effect of nonlinearity.

11.1.1 Method of Analysis

A. Determination of Equivalent Linear System

In this investigation, a least mean square quasi linearization technique with random inputs is employed for the analysis of the non linear control system in question. The technique involves the fitting of a physically realiable equivalent linear system (usually defined either by a unit impulse response or a transfer function) to a given set of input and output data. The best equivalent linear system is defined as the one which gives the minimum mean square error between the output and the actual output of the non-linear system, since such a criterion is the simplest to handle mathematically.

Let the input to a nonlinear system be a stationery random time function X(t) and the output by Y(t). An attempt will be made to find

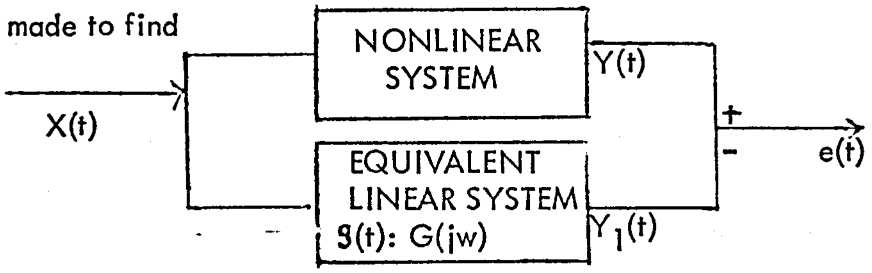


FIG. 1 EQUIVALENT LINEAR SYSTEM

an equivalent linear system which will give the minimum mean square error between its output $Y_1(t)$ and the actual output $Y(t)$ for the input $X(t)$ as shown in Figure 1.

The output of the equivalent linear system is related to the input by the integral equation

$$Y_1(t) = \int_0^{\infty} g(\tau)\, X\,(t-\tau)\,d\,\tau \qquad (1)$$

where $g(\tau)$ is the unit impulse response of the equivalent linear system. The difference $Y(t) - Y_1(t)$ between the actual output $Y(t)$ and the output $Y_1(t)$ of the equivalent linear system is the error $e(t)$ resulting from the approximation Hence.

$$Y(t) = e(t) + \int_0^{\infty} g(\tau)\, x\,(t-\tau)\,d\,\tau \qquad (2)$$

Minimization of the mean square error between $Y(t)$ and $Y_1(t)$ means that the expression

$$\overline{e^2(t)} = \lim_{T\to\infty} \frac{1}{2T} \int_0^{\infty} e^2(t)\,dt$$

$$= \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} \left[Y(t) - \int_0^{\infty} g(\tau)\, x\,(t-\tau)\,dr\right]^2 dt \qquad (3)$$

is to be minimum. It can be shown(70)(71)(72) that the necessary and sufficient condition for the expression (3) to be a minimum is that the equivalent impulse response $g(t)$ be a solution of the integral equation

$$R_{xy}(\tau) = \int_o^{\infty} g(t)\, R_{xx}(\tau - t)dt \; ; \quad \tau > o \qquad (4)$$

where $R_{xx}(t)$ and $R_{xy}(\tau)$ are correlation functions defined by

$$R_{xx}(\tau) = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} X(t)\, X(t - \tau)\, dt \qquad (5)$$

$$R_{xy}(\tau) = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} Y(t)\, X(T - \tau)\, dt \qquad (6)$$

In this investigation, the random input can be obtained by generating a random number at the beginning of each time interval, and the system output can be obtained by solving the set of differential equations which describes the transient behaviour of the column by finite difference method.

According to the finite difference scheme(56), the input during an interval of integration is

$$Z(n\Delta t) = \frac{X^{(n-1)} + X^{(n)}}{2} \qquad (7)$$

where $X^{(n-1)}$ and $X^{(n)}$ denotes the random number generated at $t = (n-1)\Delta t$ and $t = n\Delta t$ respectively. It can be shown that the autocorrelation function $R_{zz}(\tau)$ decreases linearly from $R_{zz}(\upsilon) = \frac{1}{2} R_{xx}^{(o)}$ to $R_{zz}(2\Delta t) = o$ as τ changes from $\tau = o$ to $\tau = 2\Delta t$.

The autocorrelation function for $R_{zz}(\tau)$ is shown in Fig:2.

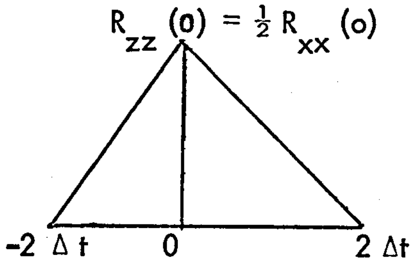


FIG:2 AUTOCORRELATION FUNCTION

It can also be shown that when $N = T/\Delta t$ is large and when the time increment Δt is small in comparison with the effective memory time of the system, the crosscorrelation function $R_{zy}(\tau)$ is approximately equal to $R_{xy}(\tau)$ for the system investigated. Hence,

$$R_{zy}(\tau) = R_{xy}(\tau) = \int_{\tau - 2\Delta t}^{\tau + 2\Delta t} g(\tau)\ R_{zz}(\tau - t)\, dt, \quad \tau > 0 \tag{8}$$

Since the interval of integration is very small, $g(t)$ can be considered to have a constant value $g(\tau)$ within the internal of integration and taken outside of the integral. Thus

$$R_{zy}(\tau) = R_{xy}(\tau) = g(\tau) \int_{T-2\Delta t}^{T+2\Delta t} \cancel{g(t)}\ R_{zz}(\tau - t)\, dt,$$

$$= g(\tau)\ R_{xx}(o)\, \Delta t \tag{9}$$

and

$$g(\tau) = \frac{R_{xy}(\tau)}{R_{xx}(o)\ \Delta t} \tag{10}$$

The de$\overset{r\,v}{v}$iation of equation ($\overset{9}{\cancel{10}}$) from equation (8) is based on the assumption that the impulse response $g(t)$ can be considered to have a constant value $g(\tau)$ within the interval of integration $[\tau - 2\Delta t,\ \tau + 2\Delta t]$. The discussion of the error in the calculated value of $g(\tau)$ resulting from making such an assumption is given in the following paragraphs.

Since R_{zz} $(\tau - t)$ does not change its sign in the interval τ-2Δt] and g(t) is continuous therefore on the basis of the mean value theorem of integral calculus

$$\int_{\tau-2\Delta t}^{\tau+2\Delta t} g(t)\, R_{zz}\, (\tau - t)\, dt = g(\bar{t}) \int_{\tau-2\,\Delta t}^{\tau+2\Delta t} R_{zz}\, (\tau - t)\, dt \qquad (11)$$

where $(\bar{t})$ is some unknown point in the interval $\tau - 2\,\Delta\, t,\ \tau\,]$ or in the interval $\tau,\ \tau+2\Delta t]$. Comparison of equations (11) on with equation (9) shows that it is $g(\bar{t})$ instead of $g(\tau)$ that was actually being evaluated.

From the mean value therom, $g(\bar{t})$ can be expressed as

$$g(\bar{t}) = g(\tau) + \dot{g}(\bar{t})\ (\bar{t} - T) \qquad (12)$$

where $\bar{t}$, is some unknown point in the interval $\tau, \bar{t} - T]$. Substitution of this expression in the right hand side of equation (11) yields

$$g(\bar{t}) \int_{\tau-2\Delta t}^{T+2\Delta T} R_{zz}\, (\Delta - t)\, dt = g(\Delta) \int_{\tau-2\Delta t}^{\tau+2\Delta t} R_{zz}(\tau - t)\, dt$$

$$+ \int_{\tau-2\,\Delta t}^{\tau+2\Delta t} \dot{g}\,(\bar{t}_1)\, (\bar{t} - \tau)\, R_{zz}\, (\tau - t)\, dt \qquad (13)$$

The error is therefore

$$\epsilon = g\ (\bar{t}) - g(\tau) = \frac{\displaystyle\int_{\tau-2\Delta t}^{\tau+2\Delta t} \dot{g}\,(\bar{t}_1)\, (\bar{t} - \tau)\, R_{zz}\, (\tau - t)\, dt}{R_{zz}\ (o)\ \ 2\,\Delta\, t} \qquad (14)$$

and the maximum absolute error is

$$| \epsilon | \leq \frac{| \dot{g}(t) |_{max} \int_{T-2\Delta t}^{T+2\Delta t} |(\bar{t}-\tau) R_{zz} (\tau-t)| dt}{R_{zz} (o) 2 \Delta t}$$

$$= \frac{| \dot{g} (t) |_{max} 4/3 (\Delta t)^2}{2 \Delta t}$$

$$= | \dot{g} (t) |_{max} \tfrac{2}{3} \Delta t \qquad (15)$$

where $| \dot{g} (t) |_{max}$ is the maximum absolute value of the slope of $g(t)$. it could be that equation 15 gives a conservative error estimate. A less conservative error estimate can be obtained if the impulse response $g(t)$ is expanded in terms of a Taylor's series with remainder term instead of making use of the mean value theorem. Let

$$g^{\cdot} (t) = g(\tau) + \dot{g}^{(1)} (\tau) (t - \tau) + R^{(2)} \qquad (16)$$

where

$$R^{(2)} = \dot{g} \; (2) \; (\lambda) \frac{(t - \tau)^2}{2\,!} \qquad \lambda - \tau > t - \tau$$

Substituion of this expression into the integral on the right hand side of equation (8) yields

$$\int_{\tau-2 \Delta t}^{\tau + 2\Delta t} g (t) R_{zz} (\tau-t) \, dt = \dot{g}(\tau) \int_{\tau-2\Delta t}^{T+ 2 \Delta t} R_{zz} (\tau-t) \, dt$$

$$+ \dot{g}^{(1)}(\tau) \int_{\tau-2 \Delta t}^{\tau+2\Delta t} (t-\tau) R_{zz} (\tau-t) \, dt + \int_{\tau-2\Delta t}^{\tau+2\Delta t} R^{(2)} (\tau) R_{zz} (\tau-t) \, dt$$

(17)

The second integral on the right hand side vanishes, hence

$$\int_{\tau-2\Delta t}^{\tau+2\Delta t} g\ (t)\, R_{zz}\ (\tau-t)\ dt = g(\tau) \int_{\tau-2\Delta t}^{\tau+2\Delta t} R_{zz}\ (\tau-t)\ dt$$

$$+\int_{\tau-2\Delta t}^{\tau+2\Delta t} R^{(2)}\ R_{zz}\ (\tau-t)\ dt \qquad (18)$$

Apply the mean value theorem of integral calculus to the left hand side and rearrange to obtain

$$e = g(\bar{t}) - g\ (\tau) = \frac{\int_{\tau = 2-\Delta t}^{\tau+2\Delta t} R^{(2)} R_{zz}\ (\tau - t)\ dt}{\underline{R_{zz}\ (o)\ 2\ \Delta\ t}} \qquad (19)$$

The absolute error is

$$|e| = |\ g\ (\bar{t})\ -\ g\ (\tau)\ | = \frac{\left| \int_{\tau-2\Delta t}^{\tau+2\Delta t} R^{(2)} R_{zz}\ (\tau-t)\ dt\ \right| \leq}{R_{zz}\ (o)\ 2\ \Delta\ t}$$

$$|\ R^{(2)}|_{max} \frac{\int_{\tau-2\Delta t}^{\tau+2\Delta t} R_{zz}\ (\tau-t)\ dt}{R_{zz}\ (o)\ 2\Delta t} = |\ R^{(2)}\ |_{max}\ , \qquad (20)$$

where

$$|\ R^{(2)}\ |_{max} = \frac{|\ g^{(2)}(\tau)\ |_{max}\ (2\Delta\ t)^2}{2\ !}$$

$$= |\ g^{(2)}\ (\tau)\ |_{max}\ 2\ (\Delta t)^2$$

Equation (19) shows that the error is positive or negative, depending on whether the second derivative of g(t) is positive or negative at the point in question. Thus, for any two impulse response curves which have approximately the same geometrical shape such as the equivalent impulse response of the nonlinear system and the impulse response of the linear system, the error at corresponding points on the two curves such as the peaks should be in the same direction. Equation (19) shows that if g(t) can be assumed to vary linearly with t inside the interval $(\tau-2\Delta t,\ \tau+2\Delta t)$, that is $R^{(2)}$ can be considered to be negligible, then $\bar{t}$ coincides with τ and the error $e = g(\bar{t}) - g(\tau)$ becomes zero. This ought to be verified experimentally from the impulse responses which have been obtained on the present multicomponent system for disturbances in feed comp.

Nomenclature:

e = error between the output of the nonlinear system and that if the equivalent linear system.

G(S) = closed loop transfer function connecting distillate comp. deviation to feed composition disturbance.

g(t) = closed loop unit impulse response connecting distillate comp. deviation to feed composition disturbance

$R_{xx}(\tau)$ = autocorrelation function of random disturbances

$R_{xy}(\tau)$ = cross correlation between disturbance and output.

N = Total number of plate or numerical factor.

T = Total length of sample in time unit.

t = time

τ = dimensionless time = F_t / H_c^o

B. THE CLOSED LOOP

Use can be made of the open loop impulse responses obtained from the open loop computation. The entire control system can be represented by the block diagram as shown in Fig. 4. The closed loop transfer function for the control system may be synthesized according to the block diagram and the closed loop impulse response can then be obtained by taking inverse Laplace transfomation of the closed loop transfer function. A brief description of the method of closed loop synthesis is given in the following paragraphs.

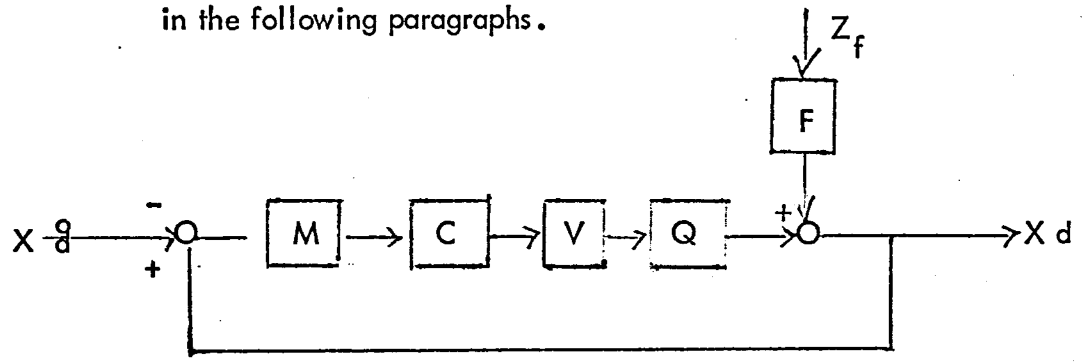


FIGURE 4

EQUIVALENT BLOCK DIAGRAM OF THE CONTROL SYSTEM.

The transfer function of a linear system, which is equal to the laplace transform of the impulse response, is defined as the ratio of the Laplace transform of the output of the system to the laplace transform of the input. Let F(s) be the open loop transfer function of the equivalent linear system connecting the change in distillate composition to feed composition disturbance, and Q (S) that connecting the change in distillate composition to change in reflux rate. Also, let M(S), C(S), and V(S) be the transfer function for the measuring unit, the controlling, and the reflux value, respectively. If the disturbance entering the column is in the form of feed composition disturbance, and if the reflux rate to the top plate is used as the control medium, then the equivalent block diagram of the whole control system is as shown in Figure 4.

According to Figure 4, the closed loop transfer function connecting the change in distillate composition with the change in feed composition is

$$G(S) = \frac{Xd(S)}{Zf(S)} = \frac{F(S)}{1 + M(S)C(S)V(S)Q(S)} \qquad (21)$$

If a proportional controller is used and if M(S) and V(S) are assumed to be pure gains then Equation (21) becomes.

$$G(S) = \frac{F\,(S)}{1 + KQ\,(S)} \qquad \text{———} \qquad (22)$$

where K is a constant. The equivalent closed loop impulse response can be obtained by taking inverse laplace transform of G(S).

Equation (22) shows that the synthesis of the closed loop equivalent transfer function requires the knowledge of the equivalent open loop transfer function for feed composition disturbance and that for reflux distrubance The equivalent open loop impulse responses obtained by open loop computation are in the form of sets of data. To facilitate the synthesis of the closed loop transfer function and the subsequent inversion of the

Laplace transform to obtain the equivalent closed loop impulse response, it is desirable to represent each equivalent open loop impulse response by an orthonormal expansion that transforms into rational functions when it is subjected to Fourier or laplace transformation. When the impulse response is aperiodic, the more common practice is to express it either in terms of Lagandre polynomials or in terms of Laguerre functions. To a given circumstance on or the other of these two methods may be preferred. In this investigation, the latter is preferrable because when the data are of limited accuracy the inversion of the laplace transformation to restore the indical function can be accompalished more accurately in terms of laguerre functions than in terms of legendre polynomials, especially when the terms in the expansion is large. Although discussion of the merits of various ways to carry out the inverse laplace transform can be found in reference (73). In general, when the equivalent open loop impulse response is obtained by taking inverse laplace transform of the equivalent closed loop transfer function by Laguerre functions, it is given in the form

$$g(t) = C_o \phi_o(2t) - C_1 \phi_1(2t) + C_2 \phi_2(2t) \text{ ------(23)}$$

where

$$\phi_k(t) = \frac{e^{-t/2} \, l_k(t)}{K!}$$

$$l_k(t) = e^{t} \frac{d^k}{dt^k} (t^k e^{-t})$$

$$l_k(2t) = e^{2t} \frac{d^k}{dt^k} (t^k e^{-2t})$$

when the closed loop impulse response is obtained in the form of Equation (23), the mean square deviation of the distillate composition from the steady state value, $\overline{(\delta X d)^2_s}$, for the closed loop system can be calculated with the equation

$$\overline{(\delta X d)^2_S} = \frac{1}{2\propto} R_{xx}(o) \, \Delta\tau \, \Sigma C_n^2 + \left[(X_d)_m - X_d^o \right]^2 \quad - (24)$$

where

C_n = the coefficients in Equation (23)

R_{xx} = the auto correlation of the feed composition disturbance with zero time leg

$\overline{(\delta Xd)^2_s}$ = the mean square deviation of the distillate composition from the steady state value X_d^o

$(Xd)_m$ = mean distillate composition

$\Delta\tau$ = size of the time step

Equation (24) can be derived in the following manner:

Let X(t) and Y(t) be the feed composition disturbance and the deviation of the distillate composition from the mean value, respectively. Making use of the superposition integral, Y (t) can be expressed as

$$Y(t) = \int_o^\infty g(t) \; X \; (t-\lambda) \, d\lambda \;\; \tau \qquad (25)$$

The mean square deviation is

$$\overline{Y(t)^2} = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} \left[\int_o^\infty g(\lambda) \; x \, (t-\lambda) d\overset{\lambda}{\cancel{X}} \int_o^\infty g(\sigma) \; x \, (t-\sigma) d\sigma \right] dt$$

change the order of integration to obtain

$$\overline{Y(t)^2} = \int_0^\infty \int_0^\infty g(\lambda)\, g(\sigma) \left[\lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} x(t-\lambda)\, x(t-\sigma)\, dt \right] d\lambda d\sigma$$

$$= \int_0^\infty \int_0^\infty g(\lambda)\, g(\sigma)\, R_{xx}(\lambda-\sigma)\, d\, x\, d\, \sigma$$

$$= \int_0^\infty g(\lambda) \left[\int_0^\infty g(\sigma)\, R_{xx}(\lambda-\sigma)\, d\sigma \right] d\lambda$$

Using the same argument as that employed in deriving Equation (9) from Equation (8) yields

$$\overline{Y(t)}^2 = \int_0^\infty g(\lambda)\, g(\lambda) \left[\int_{\lambda-\Delta t}^{\lambda+\Delta t} R_{xx}(\lambda-\sigma)\, d\sigma \right] d\lambda$$

$$= R_{xx}(o)\, \Delta t \int_0^\infty g(\lambda)\, g(\lambda)\, d\lambda$$

Substitution of the expression $g(\propto \lambda \cdot) = \Sigma C_n\, \Phi_n(2\propto\lambda)$ into the above equation and making use of the orthogonal property of $\Phi_n(2\propto\lambda)$ results in

$$\overline{Y(t)}^2 = \frac{1}{2\propto} R_{xx}(o)\, \Delta t\, \Sigma C_n^2 \tag{26}$$

where α is the scale factor in the transformation $\tau = \alpha t$.

To obtain the expression for $\overline{(\delta Xd)_3^2}$ it is necessary to correct for the difference between the mean distillate composition and the steady state distillate composition. Thus

$$\overline{(\delta X d)_3^2} = \frac{1}{N} \Sigma (Xd - X_d^o)^2$$

$$= \frac{1}{N} \Sigma \left[X_d - (X_d)_m + (X_d)_m - X_d^o\right]^2$$

$$= \frac{1}{N} \Sigma \left\{Y(t)^2 - 2Y(t)\left[(X_d)_m - X_d^o\right]^{\cancel{2}} + \left[(X_d)_m - X_d^o\right]^2\right\}$$

$$= \overline{Y(t)^2} + \left[(X_d)_m - X_d^o\right] \qquad (27)$$

σ = Standard deviation of disturbance

Z_f = feed composition

X_d = distillate composition

S = Laplace transform variable

$l_n(t)$ = Laguerre function of n the order is defined by eq ~~54(5~~ 23)

k = system gain

$\phi_n(t)$ = Laguerre function.

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APPENDICES

A1: LISTING OF THE STEADY STATE PROGRAM

NO MENCLATURE

AS IT APPEARS IN THE FORTRAN LISTING

GENX (I,J) = liquid mole fraction of any component I on any stage J.
GENY (I,J) = vapour mole fraction of any component I on any stage J.
SUMX (J) = liquid mole fraction summation at each stage J.
SUMY (J) = vapour mole fraction summation at each stage J.
TEMP (J) = temperature at each stage J.
VAPOR (J) = total vapour flow from each stage J - moles
QUID (J) = total liquid flow from each stage J - moles
FD1LIQ (I) = moles of component I in liquid position of feed 1.
FD1VAP (I) = moles of component I in vapor position of feed 1
FD2LIQ (I) = moles of component I in liquid position of feed 2.
FD2VAP (I) = moles of component I in vapor position of feed 2.
FD3LIQ (I) = moles of component I in liquid position of feed 3.
FD3VAP (I) = moles of component I in vapor position of feed 3.

A(I) COMPOSITION DEPENDENT CONSTANTS APPEARING IN
B(I) = THE EQUILIBRIUM RELATION (EQUILKF) APPEARING
C(I) = BELOW.

FD(J-1) = vector set aside for feed flows at each stage.
SFM(J-1) = vector set aside for modified stripping factor at each stage.
EQK(J-1) = vector set aside for modified equilibrium constant at each stage.

TS(10) = ten position vector for erasable or temporary storage

RFBOT(I) = vector set aside for bottom product recovery fraction of each component I.

RFTOP(I) = vector set aside for top product recovery fraction of each component I.

RFSUM(I) = vector set aside for sum of recovery fractions of each component I.

BOTP (I) = composition of bottom product - moles of component I.

TOPP (I) = composition of top product - moles of component I.

QUIDX (I) = erasable vector set aside for stage liquid compositions.

VAPY (I) = erasable vector set aside for stage vapour compositions.

GAMMA (I) = erasable vector set aside for stage activity coefficients.

EQUILUF (A, B, C, I) = equilibrium function defined by the equation.

L = actual components used in a given calculation
- $(2 < L < I)$ - limit for DO loops.

M = number of plates in column between raboiler and feed 1.

M1 = number of plates in column between feed 1 and feed 2.

M2 = number of plates in column between feed 2 and feed 3.

N = number of plates in column between feed 3 and top of column.

JT = total number of stages in column plus 1 for equilibrium reboiler
=(M+M1+M2+N+1)

JC = total number of stages in column plus 1 for equilibrium reboiler
plus 1 for partial condenser = (JT +1).

JD = total number of stages in column plus 3 = (JC+1)

JMIN = total number of stages in column only = (JT-1)

FD1LIS = total feed 1 liquid flow - moles.

FD1VAS = total feed 1 vapor flow - moles.

FD2LIS = total feed 2 liquid flow - moles.

FD2VAS = total feed 2 vapor flow - moles.

FD3 LIS = total feed 3 liquid flow - moles.

FD3VAS = total feed 3 vapor flow - moles

SUMERR = arbitrarily small number for acceptable limit of error in stage summations.

RFERR = arbitrarily small number for acceptable limit of errror in bubble point calculation.

SUBRTG = counter used by activity coefficient sub-routine to determine which pate to follow.

ITERAT = counter used by main program to tally the iterations.

SUMFDL = total feed liquid to the column.

SUMFDV = total feed vapour to the column.

T = counter set to current value of stage temperature.

J = counter set to various values depending on number of stages.

BOT PS = summation of bottom products.

TOPPS = summation of top products.

SUMFD = total feed to column

ACTCO = SUBROUTINE FOR DETERMINING ACTIVITY Coefficients using multicomponent Margules equation.

BUBPTG = bubble point subroutine using activity coefficients.

ACTO

TERMS USED IN THE ACTIVITY COEFFICIENT SUBROUTINE, WHICH DO NOT APPEAR IN THE LISTING OF THE MAIN PROGRAM.

AVAL (I,J) = two dimensional array of binary interaction constants.

ASTAR (I,J,K) = three dimensional array of A^* value already defined by eq ( )

RHO (I) = one dimensional array of P, defined by eq ( ).

JMAX = maximum value of J index

KMIN = minimum value of K index

TAU = τ as defined by eq ( ).

THETA = θ as defined by eq ( ).

TSTO = temporary storage counter

OMEGA = ω_1 as defined by eq ( ).

PSI = Ψ_1 as defined by eq ( ).

BUBPT G

SUMY = Summation of vapour compositions

SUMYO = old value of summation of vapour compositions

TO = old value of stage temperature

TN = new value of stage temperature.

```
LIST(LP)
SEND TO (ED,FORTCOMPAREA ONE)
PROGRAM(GP11)
INPUT1=CR0
OUTPUT2,(MONITOR)=LP0
TRACE
END
MASTER SHAHID
```

```
C
C BASIC PROGRAM FOR NON'IDEAL DISTILLATION WITH TOTAL CONDENSER
C
C
C MIXTURE BEING USED  ACETONE   METHANOL   ISOPROPANOL
C
      DIMENSION GENX(10,103),GENY(10,103),SUMX(103),SUMY(103),TEMP(103),
     1VAPOR(103),QUID(103),FD1LIQ(10),FD1VAP(10),FD2LIQ(10),FD2VAP(10),F
     2D3LIQ(10),FD3VAP(10),A(10),B(10),C(10),GAML(10,103),FD(102),SFM(10
     32),EQK(102),TS(10),RFBOT(10),RFTOP(10),RFSUM(10),BOTP(10),TOPP(10)
     4,QUIDX(10),VAPY(10),GAMMA(10)
      COMMON GENX,GENY,SUMX,SUMY,TEMP,VAPOR,QUID,FD1LIQ,FD1VAP,FD2LIQ,FD
     12VAP,FD3LIQ,FD3VAP,A,B,C,GAML.FD,SFM,EQK,TS,RFBOT,RFTOP,RFSUM,BOTP
     2,TOPP,QUIDX,VAPY,GAMMA
      EQUILK(A,B,C,T)=EXP(A-B/(.555*T+212.3)+C*(.555*T+212.3)-5.487)
    3 FORMAT (5I3)
 1000 READ(1,3),L,M,M1,M2,N
      JT=M+M1+M2+N+1
      JC=JT+1
      JD=JC+1
      JMIN=JT-1
    4 FORMAT(9F8.0)
      READ(1,4),(TEMP(J),J=1,JD)
      READ(1,4),(VAPOR(J),J=1,JD)
      READ(1,4),(QUID(J),J=1,JD)
      READ(1,4),(FD1LIQ(I),I=1,L)
      READ(1,4),(FD1VAP(I),I=1,L)
```

```
      READ(1,4),(FD3VAP(I),I=1,L)
      READ(1,4),(A(I),I=1,L)
      READ(1,4),(B(I),I=1,L)
      READ(1,4),(C(I),I=1,L)
      READ(1,4),FD1LIS,FD1VAS,FD2LIS,FD2VAS,FD3LIS,FD3VAS
      READ(1,4),SUMERR,RFERR,BPERR
5     FORMAT(49H1INPUT DATA FOR PROB. NO.    USING PROGRAM (GP11))
      WRITE(2,5)
    6 FORMAT (116H0NO. OF COMPONENTS      PLATES IN SECTION M      PLATES
     1IN SECTION M1      PLATES IN SECTION M2      PLATES IN SECTION N/I10
     2,I23,I24,I25,I25)
      WRITE(2,6),L,M,M1,M2,N
    7 FORMAT (50H0FEED FLOWS IN ORDER OF LOWEST ENTERING TO HIGHEST/38H0
     1MOLES FEED LIQUID     MOLES FEED VAPOR/(E16.8,F21.8))
      WRITE(2,7),FD1LIS.FD1VAS,FD2LIS.FD2VAS,FD3LIS.FD3VAS
    8 FORMAT(23H0COMPONENT FEED AMOUNTS/95H                         LOWEST FEED
     1                      INTERMEDIATE FEED                      HIGHEST FEED
     2/99H              LIQUID              VAPOR              LIQUID            VA
     3POR             LIQUID              VAPOR/(6E17.8))
      WRITE(2,8),(FD1LIQ(I),FD1VAP(I),FD2LIQ(I),FD2VAP(I),FD3
     1LIQ(I),FD3VAP(I),I=1,L)
    9 FORMAT(85H0EQUILIBRIUM CONSTANTS A       EQUILIBRIUM CONSTANTS B
     1       EQUILIBRIUM CONSTANTS C/(E19.8,2E29.8))
      WRITE(2,9),(A(I),B(I).C(I),I=1,L)
   10 FORMAT(98H0ERROR LIMIT ON SUMMATION      ERROR LIMIT ON RECOVERY F
     1RACTION SUM     ERROR LIMIT ON BUBBLE POINT/E20.8,F35.8,F36.8)
      WRITE(2,10),SUMERR,RFERR,BPERR
```

```
      SUBRTG=0.0
      SUBRT=0.0
      CHECK=0.0
      ITERAT=0
      DO 12 I=1,L
   12 TS(I)=FD1LIQ(I)+FD1VAP(I)+FD2LIQ(I)+FD2VAP(I)+FD3LIQ(I)+FD3VAP(I)
      SUMFDL=FD1LIS+FD2LIS+FD3LIS
      SUMFDV=FD1VAS+FD2VAS+FD3VAS
      IF (SUMFDL) 13,13,17
   13 IF (SUMFDV) 57,57,14
   14 DO 15 I=1,L
   15 VAPY(I)=(FD1VAP(I)+FD2VAP(I)+FD3VAP(I))/SUMFDV
      T=TEMP(1)
      CALL DEWPT (VAPY,T,A,B,C,L,BPERR)
      DO 16 I=1,L
   16 QUIDX(I)=VAPY(I)/EQUILK(A(I),B(I),C(I),T)
      GO TO 23
   17 IF (SUMFDV) 18,18,21
   18 DO 19 I=1,L
   19 QUIDX(I)=(FD1LIQ(I)+FD2LIQ(I)+FD3LIQ(I))/SUMFDL
      T=TEMP(1)
      CALL BUBPT (QUIDX,T,A,B,C,L,BPERR)
      DO 20 I=1,L
   20 VAPY(I)=QUIDX(I)*EQUILK(A(I),B(I),C(I),T)
      GO TO 23
   21 DO 22 I=1,L
   22 VAPY(I)=(FD1VAP(I)+FD2VAP(I)+FD3VAP(I))/SUMFDV
      QUIDX(I)=(FD1LIQ(I)+FD2LIQ(I)+FD3LIQ(I))/SUMFDL
   23 DO 24 J=1,JC
      DO 24 I=1,L
```

```
   GENX(I,J)=QUIDX(I)
   GENY(I,J)=VAPY(I)
24 GAML(I,J)=1.0
```

```
C
C CALCULATION OF PLATE COMPOSITIONS
C
   25 DO 29 I=1,L
      DO 26 J=1,JC
      EQK(J)=GAML(I,J)*EQUILK(A(I),B(I),C(I),TEMP(J))
      SFM(J)=VAPOR(J)*EQK(J)+QUID(J)
   26 FD(J)=0.0
      J=M+1
      FD(J)=FD1LIQ(I)+FD(J)
      J=M+2
      FD(J)=FD1VAP(I)+FD(J)
      J=M+M1+1
      FD(J)=FD2LIQ(I)+FD(J)
      J=M+M1+2
      FD(J)=FD2VAP(I)+FD(J)
      J=M+M1+M2+1
      FD(J)=FD3LIQ(I)+FD(J)
      J=M+M1+M2+2
      FD(J)=FD3VAP(I)+FD(J)
      GENX(I,1)=(GENX(I,2)*QUID(2)+FD(1))/SFM(1)+1.0E-20
      GENY(I,1)=GENX(I,1)*EQK(1)
      DO 27 J=2,JT
      GENX(I,J)=(GENX(I,J+1)*QUID(J+1)+GENY(I,J-1)*VAPOR(J-1)+FD(J))/SF
     1M(J)+1.0E-20
   27 GENY(I,J)=GENX(I,J)*EQK(J)
      GENX(I,JC)=GENY(I,JT)
      GENX(I,JD)=GENY(I,JT)
      J=JT
      DO 28 K=2,JT
```

```
      GENX(I,J)=(GENX(I,J+1)*QUID(J+1)+GENY(I,J-1)*VAPOR(J-1)+FD(J))/SFM
     1(J)+1.0E-20
      GENY(I,J)=GENX(I,J)*EQK(J)
   28 J=J-1
      GENX(I,J)=(GENX(I,2)*QUID(2)+FD(1))/SFM(1)+1.0E-20
   29 GENY(I,1)=GENX(I,1)*EQK(1)
```

```
C
C PRODUCT AMOUNTS     RECOVERY FRACTIONS     SUMMATIONS
C
      BOTPS=0.0
      TOPPS=0.0
      SUMFD=0.0
      DO 30 I=1,L
      SUMFD=SUMFD+TS(I)
      TOPP(I)=QUID(JD)*GENX(I,JD)
      RFTOP(I)=TOPP(I)/TS(I)
      BOTP(I)=QUID(1)*GENX(I,1)
      RFBOT(I)=BOTP(I)/TS(I)
      RFSUM(I)=RFTOP(I)+RFBOT(I)
      BOTPS=BOTPS+BOTP(I)
   30 TOPPS=TOPPS+TOPP(I)
      DO 31 J=1,JD
      SUMX(J)=0.0
      SUMY(J)=0.0
      DO 31 I=1,L
      SUMX(J)=SUMX(J)+GENX(I,J)
   31 SUMY(J)=SUMY(J)+GENY(I,J)
```

```
C
C OUTPUT
C
      ITERAT=ITERAT+1
      GO TO 32
   32 DO 34 J=1,JT
      IF (ABS(SUMX(J)-1.0)-SUMERR) 33,33,58
   33 IF (ABS(SUMY(J)-1.0)-SUMERR) 34,34,58
   34 CONTINUE
      DO 35 I=1,L
      IF (ABS(RFSUM(I)-1.0)-RFERR) 35,35,58
   35 CONTINUE
   36 FORMAT(12H1PROBLEM NO./15H0ITERATION NO.=I3/49H0MOLE FRACTIONS
     1LISTED AS COMPONENTS PER PLATE)
   37 WRITE(2,36),ITERAT
   38 FORMAT(21H0          BOTTOM PRODUCT/(5E20.8))
      WRITE(2,38),(GENX(I,1),I=1,L)
   39 FORMAT(21H0          REBOILER VAPOR/(5E20.8))
      WRITE(2,39),(GENY(I,1),I=1,L)
      JPLATE=0
      DO 42 J=2,JT
      JPLATE=JPLATE+1
   40 FORMAT(17H0          PLATE NO.=I3/7H0LIQUID/(5E20 8))
      WRITE(2,40),JPLATE,(GENX(I,J),I=1,L)
   41 FORMAT(6H0VAPOR/(5E20 8))
42    WRITE(2,41),(GENY(I,J),I=1,L)
   43 FORMAT(13H0          REFLUX/(5E20.8))
      WRITE(2,43),(GENX(I,JC),I=1,L)
   44 FORMAT(18H0          TOP PRODUCT/(5E20.8))
      WRITE(2,44),(GENX(I,JD),I=1,L)
```

```
45 FORMAT(34H0BOTTOM PRODUCT RECOVERY FRACTIONS/(5E20.8))
   WRITE(2,45),(RFBOT(I).I=1,L)
46 FORMAT(31H0TOP PRODUCT RECOVERY FRACTIONS/(5E20.8))
   WRITE(2,46),(RFTOP(I),I=1,L)
47 FORMAT(32H0SUMMATION OF RECOVERY FRACTIONS/(5E20.8))
   WRITE(2,47),(RFSUM(I).I=1,L)
48 FORMAT(27H0MOLES OF FEED AND PRODUCTS)
   WRITE(2,48)
49 FORMAT(75H0          COMPONENT        FEED        BOTTOM PRODUCT
  1        TOP PRODUCT/(I11,E22.8,2E19.8))
   WRITE(2,49),(I,TS(I),BOTP(I),TOPP(I),I=1,L)
50 FORMAT(2H  /E33.8,2E19.8)
   WRITE(2,50),SUMFD,BOTPS,TOPPS
51 FORMAT(16H0PLATE VARIABLES)
   WRITE(2,51)
52 FORMAT(99H0       LIQUID SUMMATIONS       VAPOR SUMMATIONS      TEMP
  1ERATURES      LIQUID FLOWS      VAPOR FLOWS/(5E20.8))
   WRITE(2,52),(SUMX(J),SUMY(J),TEMP(J),QUID(J),VAPOR(J),J=1,JD)
   DO 54 J=1,JT
   IF (ABS(SUMX(J)-1.0)-SUMERR) 53,53,58
53 IF (ABS(SUMY(J)-1.0)-SUMERR) 54,54,58
54 CONTINUE
   DO 55 I=1,L
   IF (ABS(RFSUM(I)-1.0)-RFERR) 55,55,58
55 CONTINUE
   IF (CHECK) 1000,58,1000
57 END FILE 2
   PAUSE
   GO TO 1000
```

```
C
C NORMALIZATION AND CALCULATION OF ACTIVITY COEFFICIENTS
C
   58 DO 59 J=1,JT
      DO 59 I=1,L
      GENX(I,J)=GENX(I,J)/SUMX(J)
   59 GENY(I,J)=GENY(I,J)/SUMY(J)
      DO 60 I=1,L
      GENX(I,JC)=GENX(I,JC)/SUMX(JC)
   60 GENX(I,JD)=GENX(I,JC)
      DO 62 J=1,JC
      DO 61 I=1,L
   61 QUIDX(I)=GENX(I,J)
      CALL ACTO (SUBRTG,QUIDX,GAMMA,L)
      DO 62 I=1,L
   62 GAML(I,J)=GAMMA(I)
```

```
C
C CORRECTION OF TEMPERATURES
C
      DO 64 J=1,JC
      DO 63 I=1,L
      QUIDX(I)=GENX(I,J)
   63 GAMMA(I)=GAML(I,J)
      CALL BUBPTG (QUIDX,GAMMA,TEMP(J),A,B,C,L,BPERR)
   64 CONTINUE
      TEMP(JD)=TEMP(JC)
      GO TO 25
      END
```

```
C SUBROUTINE FOR ACTIVITY COEFFICIENTS THREE SUFFIX MARGULES EQUATION
C
C
      SUBROUTINE ACTO (SUBRTG,X,GAMMA,L)
      DIMENSION X(10),GAMMA(10),AVAL(10,10),ASTAR(10,10,10),RHO(10)
    3 FORMAT(9F8.0)
      IF (SUBRTG) 11,4,11
    4 DO 5 I=1,L
      READ(1,3),(AVAL(I,J),J=1,L)
    5 CONTINUE
      DO 10 I=1,L
      JMAX=L-1
      DO 9 J=1,JMAX
      IF (J-1) 6,9,6
    6 KMIN=J+1
      DO 8 K=KMIN,L
      IF (K-1) 7,8,7
    7 ASTAR(I,J,K)= 5*(AVAL(I,J)+AVAL(J,I)+AVAL(I,K)+AVAL(K,I)+AVAL(J,K)
     1+AVAL(K,J))
    8 CONTINUE
    9 CONTINUE
   10 CONTINUE
      SUBRTG=SUBRTG+1.0
   11 TAU=0.0
      DO 16 I=1,L
      RHO(I)=0.0
      JMAX=L-1
      DO 15 J=1,JMAX
      IF (J-I) 12,15,12
   12 KMIN=J+1
```

```
      DO 14 K=KMIN,I
      IF (K-1) 13,14,13
   13 RHO(I)=RHO(I)+(X(J)+1.0E-10)*(X(K)+1.0E-10)*ASTAR(I,J,K)
   14 CONTINUE
   15 CONTINUE
   16 TAU=TAU+(X(I)+1.0E-10)*RHO(I)
      TAU=TAU/3.0
      THETA=0.0
      DO 18 I=1,L
      TSTO=0.0
      DO 17 J=1,L
   17 TSTO=TSTO+(X(J)+1.0E-10)*AVAL(I,J)
   18 THETA=THETA+TSTO*(X(I)+1.0E-10)*(X(I)+1.0E-10)
      DO 20 I=1,L
      OMEGA=0.0
      PSI=0.0
      DO 19 J=1,L
      OMEGA=OMEGA+(X(J)+1.0E-10)*AVAL(J,I)
   19 PSI=PSI+(X(J)+1.0E-10)*(X(J)+1.0E-10)*AVAL(I,J)
      GAMMA(I)=EXP(2.0*X(I)*OMEGA+PSI+RHO(I)-2.0*THETA-2.0*TAU)
   20 CONTINUE
      RETURN
      END
```

```
C SUBROUTINE FOR DEW POINTS
C
C
      SUBROUTINE DEWPT (VAPY,T.A,B,C,L,BPERR)
      DIMENSION VAPY(20),A(20).B(20),C(20)
      EQUILK(A,B,C,T)=EXP(A-B/(.555*T+212.3)+C*(.555*T+212.3)-5.487)
      KTIMES=1
    3 SUMX=0.0
      DO 4 I=1,L
      X=VAPY(I)/EQUILK(A(I).B(I),C(I),T)
    4 SUMX=SUMX+X
      IF (ABS(SUMX-1.0)-BPERR) 8,8,5
    5 KTIMES=KTIMES-1
      IF (KTIMES) 7.6,6
    6 SUMXO=SUMX
      TO=T
      T=T+10.0
      GO TO 3
    7 SLOPE=(SUMX-SUMXO)/(T-TO)
      TN=((1.0-SUMX)/SLOPE)+T
      SUMXO=SUMX
      TO=T
      T=TN
      GO TO 3
    8 RETURN
      END
C SUBROUTINE FOR BUBBLE POINT
C
```

```
C
      SUBROUTINE BUBPT (QUIDX,T,A,B,C,L,BPERR)
      DIMENSION QUIDX(20),A(20),B(20),C(20)
      EQUILK(A,B,C,T)=EXP(A-B/(.555*T+212.3)+C*(.555*T+212.3)-5.487)
      KTIMES=1
    3 SUMY=0.0
      DO 4 I=1,L
      Y=EQUILK(A(I),B(I),C(I),T)*QUIDX(I)
    4 SUMY= SUMY+Y
      IF (ABS(SUMY-1.0)-BPERR) 8,8,5
    5 KTIMES=KTIMES-1
      IF (KTIMES) 7,6,6
    6 SUMYO=SUMY
      TO=T
      T=T+10.0
      GO TO 3
    7 SLOPE=(SUMY-SUMYO)/(T-TO)
      TN=((1.0-SUMY)/SLOPE)+T
      SUMYO=SUMY
      TO=T
      T=TN
      GO TO 3
    8 RETURN
```

```
      END
C SUBROUTINE FOR NON'IDEAL BUBBLE POINTS
C
C
      SUBROUTINE BUBPTG (QUIDX.GAMMA,T,A,B,C,L,BPERR)
      DIMENSION QUIDX(10),GAMMA(10).A(10),B(10),C(10)
      EQUILK(A,B,C,T)=EXP(A-B/(.555*T+212.3)+C*(.555*T+212.3)-5.487)
      KTIMES=1
    3 SUMY=0.0
      DO 4 I=1,L
      Y=EQUILK(A(I).B(I).C(I),T)*GAMMA(I)*QUIDX(I)
    4 SUMY= SUMY+Y
      IF (ABS(SUMY-1.0)-BPERR) 8,8,5
    5 KTIMES=KTIMES-1
      IF (KTIMES) 7,6,6
    6 SUMYO=SUMY
      TO=T
      T=T+10.0
      GO TO 3
    7 SLOPE=(SUMY-SUMYO)/(T-TO)
      TN=((1.0-SUMY)/SLOPE)+T
      SUMYO=SUMY
      TO=T
      T=TN
      GO TO 3
    8 RETURN
      END
      FINISH
```

```
  3  7        3
125.     121.     118      116.     114.     112.     111.     110.     107.
103       97.      88       88.
3.0      3.0      3.0      3.0      3.0      3.0      3.0      3.0      3.0
3.0      3.0
 .5      3.5      3.5      3.5      3.5      3.5      3.5      3.5      2.5
2.5      2.5      2.5       .5
.475      050     .475


16.4603 18.0958 19.2578
2813.4733377.4523942.131

1.0
.001      .001    .0001
.2343    -.0469
.2468             -.0305
          .2740   .2572
```

A3: LISTING OF THE ANALYTICAL PROGRAM.

```
LIST(LP)
SEND TO(ED,FORTCOMPAREA.ONE)
LIBRARY(ED,SUBGROUPFSCE)
PROGRAM(G086)
INPUT1=CR0
OUTPUT2,(MONITOR)=LP0
NO TRACE
END
```

```
C
C     THIS PROGRAM CALCULATES THE ANALYTICAL SOLUTION OF THE EQUATIONS
C     CHARACTERISING THE TRANSIENT CONDITIONS OF A CONTINUOUS
C     DISTILLATION COLUMN . . ... VIA EIGENVALUES AND EIGENVECTORS
C
      MASTER EIGEN
      DIMENSION A(33,33),AA(33,33),ITS(40),X(40),Y(40),INT(40),T(1880),G
     1(33,33),IL(40),B(33,33),REINT(7,7),YY(40),Z(40),BB(33,33)
      EQUIVALENCE(A(1,1),G(1,1)),(B(1,1),T(1))
      READ(1,50)NT
      DO 12 L=1,NT
      READ(1,50) M
      DO 1 J=1,M
      READ(1,54)(A(J,I),I=1,M)
1     CONTINUE
      READ(1,50)J
      IF(J.GT.M)GO TO 2
      READ(1,54)(A(I,J),I=1,M)
2     DO 28 I=1,M
28    WRITE(2,52)I,(A(I,J),J=1,M)
52    FORMAT(6H0ROW =,I3,7G16.6/(9X,7G16.6))
50    FORMAT(I3                   )
54    FORMAT(1600F0.0)
51    FORMAT(10F8.4)
      IVS=1
      M1=M*M+7*M
      CALL F4DIRHESSE(M,A,INT)
      CALL F4QRHESSE(M,A,ITS,X,Y,AA,IVS)
      CALL F4QRVS(M,M1,A,AA,X,Y,T)
      CALL F4BACK(M,A,AA,Y,INT)
```

```
      WRITE(2,53)((X(I),Y(I)),I=1,M)
53    FORMAT(/9H  EIGEN  2G14.4)
      DO 100 I=1,M
100   WRITE(2,52)I,(AA(I,J),J=1,M)
      DO 40 I=1,M
      DO 40 J=1,M
40    B(I,J)=AA(I,J)
      NA=M*33
      NB=M*33
      IN=1
      DO 29 I=1,M
      DO 29 J=1,M
      IF (I-J) 30,31,30
30    G(I,J)=0.0
      GO TO 29
31    G(I,J)=1.0
      GO TO 29
29    CONTINUE
      CALL F4SOLVE(B,G,M,NA,NB,IN,D,ID,IT,REINT)
      DO 116 I=1,M
116   WRITE(2,52)I,(G(I,J),J=1,M)
      WRITE(2,55)IT
55    FORMAT(1H0,I3)
250   READ(1,50) MK
      IF (MK) 251,251,252
252   READ(1,54)(YY(I),I=1,M)
      DO 118 I=1,M
      DUM=0.
      DO 117 J=1,M
117   DUM=DUM+G(I,J)*YY(J)
```

```
118    Z(I)=DUM
       DO 101 I=1,M
       IF(Y(I).LT.1.0E-10) GO TO 102
       IL(I)=I
       GO TO 101
102    IF(Y(I).LT.-1.0E-10)GO TO 103
       IL(I)=0
       GO TO 101
103    IL(I)=-I
101    CONTINUE
       DO 105 J=1,M
       IF(IL(J)) 108,107,106
106    GO TO 105
107    DO 111 I=1,M
111    B(I,J)=AA(I,J)*Z(J)
       GO TO 105
108    DO 113 I=1,M
       B(I,J)=AA(I,J)*Z(J)+AA(I,J+1)*Z(J+1)
113    B(I,J+1)=AA(I,J+1)*Z(J)-AA(I,J)*Z(J+1)
105    CONTINUE
       DO 115 I=1,M
115    WRITE(2,52)I,(B(I,J),J=1,M)
       GO TO 250
12     CONTINUE
251    STOP
       END
       FINISH
```

```
  1
 33
-12.78 0.003 0.001 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0.02 -7 046 0.005 0  3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0.
12.36 6 643 -0.406 0. 0. 3.4 0  0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0.
12.38 -0.003 -0.001 -15.74 0.01 0.005 3.4 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
-0.02 6 646 -0.005 0.04 -10.02 0.01 0. 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
-12.36 -6.643 0.006 12.3 6.61 -3.415 0. 0. 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0.
0. 0. 0  12.34 -0.01 -0.005 -15.62 0.04 0.018 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  -0.04 6.62 - 01 .08 -9.97 0.02 0. 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  -12.30 -6.61 0.015 12 14 6.53 -3.438 0. 0. 3.4 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 12.22 -0.04 -0.018 -15.26 0.136 0.06 3.4 0. 0. 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0.
0. 0. 0  0. 0. 0. - 08 6.57 -0 02 0.16 -9.827 0.04 0. 3.4 0. 0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. -12.14 -6.53 0.038 11.7 6.291 -3.5 0. 0. 3.4 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 11.86 -0.136 -0.06 -14.16 0.44 0.19 3.4 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. -0.16 6.427 -0.04 0.28 -9.48 0.07 0. 3.4 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
```

```
0. 0. 0  0. 0. 0. 0  0. 0. -11.7 -6.291 0.1 10.48 5.64 -3.66 0. 0. 3.4 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 10.76 -0.44 -0.19 -11.54 1.16 0.52 2.4 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0  0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. -0.28 6.08 -0.07 0.39 -8.64 0.09 0. 2.4 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. -10.48 -5.64 0.26 7.75 4.08 -4.01 0. 0. 2.4
 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 8.14 -1.16 -0.52 -10.29 1.2 0.54
 2.4 0  0. 0. 0. 0. 0. 0. 0  0. 0. 0.
0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. -0.39 5.24 -0.09 0.47 -7.5 0.11 0.
 2.4 0. 0. 0. 0. 0. 0. 0. 0  0  0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. -7.75 -4.08 0.61 7.42 3.9 -3.05 0.
 0. 2.4 0. 0. 0. 0, 0. 0. 0  0  0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 7.89 -1 2 -0.54 -0.57 1.34
 0.6 2.4 0. 0. 0. 0  0. 0. 0. 0.
0  0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. -0.47 5 1 -.11 .61 -7.17
 0.14 0  2.4 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. -7.42 -3.9 0.65 6.56 3.43
 -3.14 0. 0. 2.4 0. 0  0. 0. 0  0
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  7.17 -1.34 -0.6
 -7.78 1.66 0.75 2.4 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0  -0.61 4.77 -0.14
 0.72 -6.48 0.16 0. 2.4 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  -6.56 -3.43 0.74
 4.66 2.42 -3.31 0. 0. 2.4 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 5.38
 -1.66 -0.75 -5.12 2.0 0.86 2.4 0. 0.
0  0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0.
-0.72 4.08 -0.16 0.63 -5.5 0.14 0. 2.4 0.
```

```
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. -4.66
 -2.42 0.91 2.09 1.1 -3.4 0. 0  2.4
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0.
 0. 2.72 -2.0 -0.86 -2.585 0.40 0.159
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0.
 0. -0.63 3.1 -0.14 0.074 -2.86 0.017
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0.
 0. -2.09 -1.1 1.0 0.111 0.06 -2.576
 40
  1
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0.   -.01 0.  0.01
0  0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0.       0. 0. 0. 0. 0. 0
```

A3: LISTING OF THE MARKOV PROGRAM.

```
LIST(LP)
SEND TO(ED,FORTCOMPAREA.ONE)
PROGRAM(G303)
INPUT1=CR0
OUTPUT2=LP0
NO TRACE
END
```

```
C
C      THIS PROGRAM DESCRIBES A NUMERICAL METHOD TO CALCULATE THE
C      TRANSIENTS OF A CONTINUES DISTILLATION COLUMN AND IS BASED
C      ON THE MARKOV PROBABILISTIC TECHNIQUE
C
       MASTER MARGOT BABY
       DIMENSION Q(40,40),D(40),IV(40),V(40),F(40,40,2),R(40,40)
       EQUIVALENCE (Q(1),F(1601)),(R(1),F(1))
       NZ=0
 98    READ(1,101) N,NR,(IV(I),I=N-NR+1,N),NTR
       CALL ITIME(I1)
       IF(NTR+1)30,99,0
 101   FORMAT(900I0)
       NT=N+NTR
       NI=NT-N-1
C       DATA  N IS NUMBER OF STAGES(WITHOUT INTEGRATION STATES)
C       NR IS THE NUMBER OF STAGE RESPONSES REQUIRED AND THE VECTOR IV
C      HOLDS THE NUMBERS OF THOSE STAGES, ALL INTEGRATION STATES ARE OUTPUT
C      TO TERMINATE JOB USE CARD PUNCHED  1 1 1 -1
C      FLOW MATRIX Q, VOLUME VECTOR V
C      H IS PRINTOUT INTERVAL, TMAX IS MAX TIME VALUE, QTHRO IS VOL. THROUGHPUT
C      VTOT IS THE TOTAL SYSTEM VOLUME, STAYP IS THE MINIMUM PROBABILITY
C      OF AN ELEMENT REMAINING IN ANY STAGE DURING TIME DT, E.G. STAYP=0.94
       READ (1,104)((Q(I,J),J=1,N),I=1,N),(V(I),I=1,N),H,TMAX,QTHRO,VTOT
      1,STAYP
104    FORMAT(1600F0.0)
52     FORMAT(6H0ROW =,I3,8G14.4/(9X,8G14.4))
       DO 100 I=1,N
100    WRITE(2,52)I,(Q(I,J),J=1,N)
       IF(NTR.EQ.0) GO TO 203
```

```
      READ(1,104) ((Q(I,J),J=1,N),I=N+1,NT)
      DO 201 J=N+1,NT
201   IV(J)=J
 203  CC=1.0E+76
      DO 1 I=1,N
      D(I)=-Q(I,I)
C     CC IS MINIMUM STAGE TIME CONSTANT
C     POSITIVE STAGE THROUGH FLOWS IN D, DIAGONALS OF Q MADE ZERO
      IF(ABS(V(I)).GE.1.0E-10) CC=AMIN1(CC,V(I)/D(I))
    1 Q(I,I)=0.
C     CALCULATION OF TIME INCREMENT
C     CONSTRAIN DT TO FIT IN WITH NORMALISED TIME PRINT OUT INTERVAL
      IX=(1.+DIM (ALOG(H*VTOT/(-ALOG(STAYP)*CC*QTHRO))/ALOG(2.),0.))
      DT=H/(2.**IX)*VTOT/QTHRO
      STAYP=EXP(-DT/CC)
C     IF V IS ZERO MAKE EXP(-D/V*DT) ZERO,  (1-EXP(-D/V*DT/2))/D IS PUT IN D
      DO 5 I=1,N
      IF(ABS(V(I)).GE.1.0E-10)  V(I)=EXP(-D(I)*DT/(2.*V(I)))
    5 D(I)=(1.-V(I))/D(I)
C     MAKE TRANSITION MATRIX, CC IS (1.0-EXP(-D/V*DT/2.))/D
      DO 4 I=1,NT
      IF(I-N-1)9,8,10
      CC=(1.0+V(I))*D(I)
      GO TO 9
 8    CC=DT
 10   R(I,I),V(I)=1.0
    9 DO 5 J=1,N
      CD=0.
      DO 6 K=1,N
    6 CD=CD+D(K)*Q(I,K)*Q(K,J)
```

```
    3 R(I,J)=CC*(CO+V(J)*Q(I,J))
    4 R(I,I)=R(I,I)+V(I)*V(I)
C     FINDING THE 2**M TH POWER OF THE TRANSITION MATRIX R IN F
      L=1
      DO 57 M=1,IX
      L=3-L
      L1=3-L
      DO 57 I=1,NI
      AIR=FLOAT((I+NL)/NI)
      DO 57 J=1,N
      CA=0.
      DO 58 K=1,N
   58 CA=CA+F(I,K,L1)*F(K,J,L1)
   57 F(I,J,L)=CA+AIR*F(I,J,L1)
      NS=N-NK+1
C     READ INITIAL STATE VECTOR INCLUDING INTEGRATION STATES
C     WRITE OUT COLUMN HEADINGS
50    CONTINUE
      READ(1,104)(V(I),I=1,NT)
      NZ=NZ+1
      WRITE(2,103) NZ,QTHRO,VTOT,STAYP,IX,(IV(I),I=NS,NT)
 103  FORMAT(1H1,8H CASE NO,I3//17H THROUGHPUT RATE=,G12.4/
     1  14H TOTAL VOLUME=,G12.4/7H STAYP=,G12.4////
     2  3H M=,I3//5H TIME,25X,21H STAGE CONCENTRATIONS/
     3  10X,10(5X,I2,5X)/)
      TIME=0.
   97 WRITE(2,102) TIME,(V(IV(I)),I=NS,NT)
  102 FORMAT(F8.2,4X,9G12.4/(12X,9G12.4))
      IF(TIME.GE.TMAX) GO TO 151
C     CALCULATE RESPONSES
```

```
      DO 42 I=1,NT
      CB=0.
      DO 43 J=1,N
   43 CB=CB+V(J)*F(I,J,L)
   42 D(I)=CB+FLOAT((I+NL)/NT)*V(I)
      DO 45 I=1,NT
   45 V(I)=D(I)
      TIME=TIME+H
      GO TO 97
  151 CALL ITIME(I2)
      I2=I2-I1
      WRITE(2,150) NZ,I2
  150 FORMAT(1H0,23H TIME TAKEN FOR CASE NO,I2,2H =,I4,5H SECS)
107   WRITE(2,102) TIME,(V(I),I=1,NT)
      GO TO 98
 99   CONTINUE
      STOP
      END
      FINISH
```

```
33 6 1 2 3 31 32 33 6
-12.77 0.003 0.001 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0 02 -7 045 0.005 0  3.4 0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0.
12.35 6 642 -0.406 0. 0. 3.4 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0.
12.37 -0.003 -0.001 -15.74 0.01 0.005 3.4 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0.
 0. 0  0. 0. 0. 0. 0. 0  0. 0. 0. 0  0.
-0.02 6 645 -0.005 0.05 -10.02 0.011 0. 3.4 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0.
-12.35 -6.642 0.006 12.29 6.61 -3 416 0. 0. 3.4 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0.
 0. 0  0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  12.34 -0.01 -0.005 -15.61 0.04 0.02 3.4 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0
0. 0. 0  -0.05 6.62 -0.011 0.08 -9.96 0 02 0. 3.4 0  0. 0. 0. 0. 0. 0  0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0.
0. 0. 0  -12.29 -6.61 0.016 12 13 6.52 -3.44 0. 0. 3.4 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 12.21 -0.04 -0.02 -15.24 0.14 0.06 3.4 0. 0  0. 0. 0. 0. 0. 0.
 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0
0. 0. 0  0. 0. 0. -0.08 6.56 -0.02 0.17 -9.82 0.04 0. 3.4 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. -12 13 -6 52 0.04 11.67 6.28 -3.5 0. 0. 3.4 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0.
0  0. 0  0. 0. 0. 0  0. 0. 11.84 -0.14 -0.06 -14.16 0.45 0.2 3.4 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. -0.17 6.42 -0.04 0.29 -9 45 0.07 0  3.4 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0. 0. 0. -11 67 -6.28 0.1 10.47 5 6 -3.67 0  0. 3.4 0. 0. 0.
```

```
0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 10.76 -0.45 -0.2 -11.43 1 2 0.53 2.4 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. -0.29 6.05 -0.07 0.4 -8.6 0.1 0. 2.4 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. -10.47 -5.6 0.27 7.63 4.0 -4.03 0. 0. 2.4 0.
 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 8.03 -1.2 -0.53 -10.14 1.23 0.55
2.4 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0  0. 0. -0.4 5.2 -0.1 0.49 -7.45 0.12 0.
2.4 0  0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. -7.63 -4.0 0.63 7.25 3.82 -3.07 0.
0. 2.4 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 7.74 -1 23 -0.55 -9.32
1.39 0.62 2.4 0. 0. 0  0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. -0.49 5 05 -0.12 0.63
-7.08 0 15 0. 2.4 0  0. 0  0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. -7.25 -3.28 0.67 6.29
3.29 -3 17 0. 0. 2.4 0. 0. 0. 0. 0. 0
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  6.92 -1.39 -0.62
-7.4 1.71 0.77 2.4 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  -0.63 4.68 -0.15
0.73 -6 33 0.17 0. 2.4 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  -6.29 -3 29 0.77
4.27 2.22 -3.34 0. 0. 2.4 0. 0. 0.
0  0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 5.0
-1.71 -0.77 -4.8 2.0 0.86 2.4 0. 0.
0  0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. -0.73
3.93 -0 17 0.61 -5.34 0.14 0. 2 4 0.
0  0. 0  0. 0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. -4.27
```

```
-2.22 0 94 1.79 0.94 -3.4 0. 0. 2.4
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0.
 2.4 -2 0 -0.86 -2.56 0.396 0.158
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0.
 -0 61 2 94 -0.14 0 07 -2.849 0.016
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0. 0. 0. 0. 0.
 -1 79 -0 94 1.0 0.09 0 053 -2 574
1  1. 1  1. 1. 1. 1  1. 1. 1. 1. 1. 1  1. 1. 1. 1. 1. 1. 1.
1. 1. 1  1. 1. 1. 1  1. 1. 1. 1. 1. 1.
2. 400. 1. 1. 0.98
1  0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0..0. 0
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0.
0. 1. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0.
0. 0. 1  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0  0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 1. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 1. 0
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 1.
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0.  -0.01 0. 0.01
0. 0. 0  0. 0. 0. 0  0. 0. 0. 0. 0. 0. 0. 0.
0. 0. 0  0. 0. 0.
```

A 2: LISTING OF THE ANALYSIS PROGRAM

```
IF(TIME-859.)34,35,35
35 SUM3=SUM3*DT/3.
TOTAL=SUM1+SUM2+SUM3
P1=(SUM1/TOTAL)*100.
P2=(SUM2/TOTAL)*100.
P3=(SUM3/TOTAL)*100.
PRINT,P1,P2,P3
END
XXXXXXX*XXXXXXXXXXXXX
```

TOTAL PEAK AREAS

PERCENTAGE OF EACH COMPONENT IN THE MIXTURE.

APPENDIX 'B'

```
READ,COUNT                        CONSTANT FOR A VARIABLE TIME BASE
40 READ,S
IF (S+1.0)40,40,43                TEST LOOP FOR MARKER VOLTAGE
43 DT=60./COUNT                   TIME BASE CALCULATED
TIME=0.
4 READ,A                          SPACE SETTING ROUTINE
TIME=TIME+DT
IF (TIME-1.)4,5,5
5 SUM=0.
8 READ,B
TIME=TIME+DT
IF (TIME-171.)6,7,7
6 SUM=SUM+B                       FIRST BASE LINE CALCULATION
GO TO 8
7 SUM=SUM+B
AV1=SUM/((TIME-1.)/DT)
SUM1=0.
15 READ,C,D
TIME=TIME+2.*DT
IF (C-AV1)51,51,12
12 C=(C-AV1)*4.                   ACETONE PEAK AREA ROUTINE
SUM1=SUM1+C+(D-AV1)*2.
51 CONTINUE
IF (TIME-400.)15,16,16
16 SUM1=SUM1*DT/3.
SUM=0.
20 READ,E
TIME=TIME+DT
IF (TIME-410.)18,19,19            SECOND BASE LINE CALCULATION
18 SUM=SUM+E
GO TO 20
19 SUM=SUM+E
AV2=SUM/((TIME-400.)/DT)
SUM2=0.
24 READ,F,G
TIME=TIME+2.*DT
IF (F-AV2)52,52,23                ISO PROPANOL PEAK AREA ROUTINE
23 F=(F-AV2)*4.
SUM2=SUM2+F+(G-AV2)*2.
52 CONTINUE
IF (TIME-543.)24,25,25
25 SUM2=SUM2*DT/3.
SUM=0.
30 READ,H
TIME=TIME+DT
IF (TIME-553.)27,28,28            THIRD BASE LINE CALCULATION
27 SUM=SUM+H
GO TO 30
28 SUM=SUM+H
AV3=SUM/((TIME-543.)/DT)
SUM3=0.
34 READ,P,Q
TIME=TIME+2.*DT
IF (P-AV3)53,53,33
33 P=(P-AV3)*4.                   METHANOL PEAK AREA ROUTINE
SUM3=SUM3+P+(Q-AV3)*2.
53 CONTINUE
35(SUMB-859.)34,35,35
```

A4: TABLES OF RESULTS.

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.475	0.0076	0.467
x_2	0.05	0.021	0.029
x_3	0.475	0.471	0.0030

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION			EQUILIBRIUM CONSTANT		
	x_1	x_2	x_3	y_1	y_2	y_3	k_1	k_2	k_3
REBOILER	0.01514	0.0416	0.9432	0.05735	0.08377	0.8589	3.794	2.01	0.910
1	0.04328	0.0697	0.8870	0.1497	0.1267	0.7235	3.465	1.817	0.815
2	0.1048	0.09836	0.7968	0.3092	0.1505	0.5401	2.942	1.531	0.678
3	0.2112	0.1143	0.6746	0.5002	0.1401	0.3596	2.369	1.225	0.533
4	0.3384	0.1073	0.5542	0.6514	0.1088	0.2397	1.926	1.015	0.432
5	0.4393	0.08644	0.4743	0.7395	0.07866	0.1817	1.683	0.909	0.383
6	0.5439	0.0989	0.3570	0.7987	0.08192	0.1193	1.469	0.827	0.334
7	0.6623	0.1055	0.2321	0.8505	0.08113	0.06824	1.283	0.768	0.294
8	0.7659	0.1039	0.13	0.8882	0.07684	0.03488	1.16	0.739	0.268
9	0.8412	0.0954	0.0633	0.9144	0.0694	0.01612	1.086	0.727	0.254
10	0.8936	0.08049	0.0258	0.9352	0.0583	0.0064	1.074	0.724	0.248
TOP PRODUCT	0.9352	0.0583	0.0064						

TABLE R.S.S.10

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.475	0.0044	0.471
x_2	0.05	0.022	0.028
x_3	0.475	0.474	0.0005

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION			EQUILIBRIUM CONSTANT		
	x_1	x_2	x_3	y_1	y_2	y_3	k_1	k_2	k_3
REBOILER	0.0088	0.0431	0.9483	0.0339	0.08802	0.8781	3.845	2.044	0.926
1	0.0276	0.0768	0.8956	0.0989	0.1446	0.7564	3.577	1.885	0.844
2	0.0764	0.1192	0.8044	0.2366	0.1919	0.5713	3.097	1.609	0.71
3	0.1796	0.1547	0.6657	0.441	0.1962	0.3626	2.455	1.267	0.545
4	0.3329	0.1578	0.5092	0.6304	0.1579	0.2116	1.894	1.0	0.415
5	0.4748	0.1292	0.3959	0.7486	0.1121	0.1391	1.576	0.868	0.352
6	0.652	0.1397	0.2083	0.8331	0.1072	0.0591	1.278	0.766	0.286
7	0.7787	0.1322	0.08903	0.88	0.0969	0.0229	1.130	0.733	0.257
8	0.8491	0.1169	0.03386	0.9068	0.08476	0.0084	1.068	0.725	0.246
9	0.8892	0.0986	0.01205	0.9256	0.07136	0.0029	1.04	0.722	0.244
10	0.9174	0.0786	0.0039	0.9421	0.0568	0.0009	1.027	0.723	0.244
TOP PRODUCT	0.9421	0.0568	0.0009						

TABLE (   ) R.S.S.11

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.475	0.0029	0.472
x_2	0.05	0.022	0.027
x_3	0.475	0.4746	0.0001

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION		
	X_1	X_2	X_3	Y_1	Y_2	Y_3
REBOILER	0.0059	0.0449	0.9492	0.0227	0.0925	0.8847
1	0.0199	0.0846	0.8955	0.0722	0.1617	0.7660
2	0.06118	0.1422	0.7966	0.1933	0.2333	0.5733
3	0.1620	0.2019	0.6360	0.4002	0.2571	0.3426
4	0.3344	0.2217	0.4438	0.6117	0.2152	0.1729
5	0.5107	0.1868	0.3024	0.7492	0.1545	0.0962
6	0.7004	0.1795	0.1201	0.8348	0.1336	0.0315
7	0.8075	0.1532	0.0393	0.8791	0.1112	0.0096
8	0.8627	0.1252	0.0119	0.9066	0.0905	0.00289
9	0.8971	0.0993	0.00355	0.9272	0.0718	0.00086
10	0.9229	0.0759	0.00101	0.9447	0.05496	0.0002
TOP PRODUCT	0.9447	0.055	0.0002			

TABLE ( ) R.S.S.13

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.475	0.0026	0.473
x_2	0.05	0.0227	0.0272
x_3	0.475	0.4746	0.00009

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION			EQUILIBRIUM CONSTANT		
	x_1 Mol.Fr	x_2 Mol.Fr	x_3 Mol.Fr	y_1 Mol.Fr	y_2 Mol.Fr	y_3 Mol.Fr	k_1	k_2	k_3
REBOILER	0.0053	0.0454	0.9493	0.0205	0.0936	0.8858	3.877	2.061	0.933
1	0.0183	0.0867	0.8949	0.0666	0.1662	0.7670	3.635	1.916	0.857
2	0.0579	0.1489	0.7931	0.1834	0.2451	0.5714	3.167	1.646	0.720
3	0.1579	0.2166	0.6254	0.3898	0.2753	0.3348	2.468	1.271	0.535
4	0.3349	0.2424	0.4226	0.6056	0.2330	0.1613	1.808	0.961	0.381
5	0.5198	0.2062	0.2739	0.7470	0.1684	0.0845	1.437	0.816	0.308
6	0.7075	0.1911	0.1013	0.8323	0.1416	0.0261	1.176	0.74	0.256
7	0.8098	0.1589	0.03123	0.8871	0.1152	0.0076	1.083	0.724	0.243
8	0.8636	0.1273	0.00907	0.9058	0.0919	0.0022	1.048	0.722	0.241
9	0.8979	0.0994	0.00258	0.9275	0.0718	0.0006	1.033	0.722	0.241
10	0.9239	0.0753	0.0007	0.9452	0.0545	0.0002	1.023	0.772	0.244
TOP PRODUCT	0.9452	0.0545	0.0002						

TABLE (   ) R.S.S.14

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.465	0.0011	0.464
x_2	0.05	0.0145	0.0354
x_3	0.485	0.484	0.00015

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION			EQUILIBRIUM CONSTANT		
	x_1	x_2	x_3	y_1	y_2	y_3	k_1	k_2	k_3
REBOILER	0.0022	0.0291	0.9687	0.0086	0.0615	0.9298	3.954	2.111	0.959
1	0.0077	0.0569	0.9354	0.02955	0.1153	0.8552	3.818	2.025	0.914
2	0.0256	0.1029	0.8714	0.0905	0.1908	0.7187	3.529	1.853	0.825
3	0.0778	0.1677	0.7545	0.2331	0.2596	0.5073	2.991	1.548	0.672
4	0.2001	0.2267	0.5733	0.4543	0.2659	0.2796	2.272	1.173	0.487
5	0.3897	0.2321	0.3782	0.6546	0.2107	0.1345	1.679	0.907	0.355
6	0.5999	0.2387	0.1613	0.7726	0.1833	0.04395	1.287	0.768	0.272
7	0.7415	0.2058	0.0527	0.8367	0.1502	0.0129	1.123	0.729	0.245
8	0.8185	0.1661	0.0154	0.8762	0.1199	0.0037	1.071	0.722	0.239
9	0.8658	0.1297	0.00437	0.9052	0.0936	0.001	1.045	0.722	0.239
10	0.9006	0.09817	0.0012	0.9287	0.07092	0.0003	1.031	0.722	0.243
TOP PRODUCT	0.9287	0.07092	0.0003						

TABLE ( ) R.S.S.16

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.485	0.006	0.479
x_2	0.05	0.029	0.021
x_3	0.465	0.4649	0.00007

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION			EQUILIBRIUM CONSTANT		
	x_1	x_2	x_3	y_1	y_2	y_3	k_1	k_2	k_3
REBOILER	0.0110	0.0589	0.9299	0.0416	0.1181	0.8402	3.781	2.005	0.903
1	0.0373	0.1097	0.8531	0.1272	0.1960	0.6768	3.410	1.788	0.793
2	0.1106	0.1764	0.7129	0.3072	0.2527	0.4401	2.776	1.432	0.617
3	0.2649	0.2250	0.5101	0.5392	0.2391	0.2218	2.036	1.062	0.434
4	0.4637	0.2134	0.3229	0.7123	0.1818	0.1059	1.536	0.852	0.328
5	0.6122	0.1643	0.2236	0.8071	0.1279	0.06503	1.318	0.778	0.290
6	0.7767	0.1453	0.078	0.8738	0.1063	0.0198	1.125	0.731	0.253
7	0.8569	0.1194	0.0237	0.9078	0.0864	0.0058	1.059	0.729	0.244
8	0.8976	0.0955	0.00694	0.9293	0.069	0.0017	1.035	0.722	0.243
9	0.9234	0.0746	0.002	0.9454	0.0539	0.0005	1.023	0.723	0.245
10	0.9428	0.0566	0.0006	0.9588	0.0409	0.0001	1.016	0.724	0.246
TOP PRODUCT	0.9588	0.0409	0.0001						

TABLE ( ) R.S.S.17

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.465	0.0012	0.464
x_2	0.05	0.0145	0.0355
x_3	0.485	0.484	0.0002

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION		
	X_1	X_2	X_3	Y_1	Y_2	Y_3
	Mol.Fr	Mol. Fr	Mol. Fr			
REBOILER	0.0025	0.0289	0.9686	0.0098	0.0611	0.9291
1	0.0086	0.0557	0.9356	0.0328	0.1128	0.8544
2	0.0277	0.0989	0.8735	0.0976	0.1828	0.7196
3	0.0817	0.1572	0.7612	0.2441	0.2431	0.5127
4	0.2038	0.2074	0.5888	0.4648	0.2445	0.2906
5	0.3877	0.2085	0.4037	0.6610	0.1916	0.1473
6	0.5943	0.2216	0.1841	0.7769	0.1716	0.0514
7	0.7391	0.1967	0.0641	0.8400	0.1439	0.0159
8	0.8180	0.1622	0.0197	0.8779	0.1172	0.0048
9	0.8654	0.1288	0.0058	0.9056	0.0929	0.0014
10	0.8999	0.09842	0.0016	0.9284	0.0711	0.0004
TOP PRODUCT	0.9284	0.0711	0.0004			

TABLE ( ) R.S.S.18

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.485	0.006	0.479
x_2	0.05	0.0292	0.208
x_3	0.465	0.465	0.000099

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION		
	X_1 Mol.Fr	X_2 Mol.Fr	X_3 Mol.Fr	Y_1	Y_2	Y_3
REBOILER	0.0121	0.0583	0.9296	0.0456	0.1165	0.8379
1	0.04002	0.1068	0.8532	0.1361	0.1899	0.6741
2	0.1154	0.1679	0.7167	0.3189	0.2395	0.4414
3	0.2678	0.2093	0.5228	0.5471	0.2233	0.2296
4	0.4579	0.1958	0.3463	0.7148	0.1687	0.1165
5	0.5976	0.1503	0.2520	0.8059	0.1184	0.0755
6	0.7680	0.1376	0.0943	0.8745	0.1011	0.0243
7	0.8536	0.1159	0.0304	0.9085	0.0839	0.0075
8	0.8961	0.0946	0.0093	0.9293	0.0684	0.0023
9	0.9222	0.0751	0.0028	0.9449	0.0543	0.0007
10	0.9417	0.0575	0.0008	0.9581	0.0416	0.0002
TOP PRODUCT	0.9581	0.0416	0.0002			

TABLE ( ) R.S.S.19

MOLES OF FEED & PRODUCT

	Feed	Bottom	Top
x_1	0.475	0.00004	0.475
x_2	0.05	0.00031	0.049
x_3	0.475	0.399	0.075

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION		
	X_1	X_2	X_3	Y_1	Y_2	Y_3
REBOILER	0.00011	0.0008	0.9992	0.0004	0.0017	0.9979
1	0.0004	0.0016	0.9980	0.0016	0.0034	0.9949
2	0.0015	0.0031	0.9954	0.00586	0.0067	0.9873
3	0.0052	0.006	0.9887	0.0207	0.0128	0.9664
4	0.0183	0.0114	0.9703	0.0701	0.0234	0.9065
5	0.06183	0.02074	0.9174	0.2113	0.03728	0.7514
6	0.0663	0.0259	0.9078	0.2233	0.0458	0.7308
7	0.0812	0.0366	0.8822	0.2624	0.0619	0.6757
8	0.1300	0.05668	0.8133	0.3726	0.08432	0.5429
9	0.2679	0.0846	0.6474	0.5834	0.09596	0.3205
10	0.5314	0.0992	0.3693	0.7918	0.0829	0.1251
TOP PRODUCT	0.7981	0.0829	0.1251			

TABLE (   ) R.S.S.20

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.465	0.00004	0.465
x_2	0.05	0.0003	0.0497
x_3	0.485	0.3996	0.0851

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION		
	X_1	X_2	X_3	Y_1	Y_2	Y_3
REBOILER	0.0001	0.0007	0.9992	0.00043	0.0016	0.9979
1	0.00038	0.0015	0.9981	0.00157	0.00329	0.9951
2	0.0014	0.0029	0.9956	0.0056	0.0065	0.9878
3	0.00501	0.0058	0.9892	0.02	0.012	0.9675
4	0.0177	0.011	0.9713	0.0679	0.0227	0.9094
5	0.0599	0.0201	0.9199	0.2059	0.0363	0.7577
6	0.0637	0.0246	0.9117	0.2162	0.0439	0.7398
7	0.0765	0.0342	0.8893	0.2503	0.0586	0.6910
8	0.1192	0.0525	0.8283	0.3503	0.0803	0.5693
9	0.2442	0.07963	0.6762	0.5553	0.0939	0.3507
10	0.5004	0.0967	0.4029	0.7752	0.0829	0.1418
TOP PRODUCT	0.7752	0.0829	0.1418			

TABLE (   ) R.S.S.21

MOLES OF FEED & PRODUCTS

	Feed	Bottom	Top
x_1	0.485	0.00004	0.485
x_2	0.05	0.0003	0.0497
x_3	0.465	0.399	0.065

PLATE NO.	LIQUID COMPOSITION			VAPOUR COMPOSITION		
	X_1	X_2	X_3	Y_1	Y_2	Y_3
REBOILER	0.0001	0.0008	0.9991	0.0005	0.0017	0.9978
1	0.0004	0.00164	0.9979	0.00168	0.0036	0.9949
2	0.0015	0.0032	0.9952	0.00606	0.00702	0.9868
3	0.0054	0.0063	0.9883	0.0214	0.0134	0.9651
4	0.01887	0.0119	0.9692	0.7232	0.02434	0.9033
5	0.0638	0.0216	0.9146	0.2169	0.0386	0.7444
6	0.0691	0.0275	0.9033	0.2311	0.0482	0.7206
7	0.08079	0.0396	0.8135	0.2764	0.06593	0.6576
8	0.1433	0.0617	0.7949	0.3984	0.0889	0.5126
9	0.2960	0.0905	0.6135	0.6137	0.09797	0.2882
10	0.5652	0.1017	0.3331	0.8085	0.08287	0.1084
TOP PRODUCT	0.8085	0.0828	0.1084			

TABLE (   ) R.S.S.22

R.T.W.1

TIME	ACETONE$_B$	MENTHOL$_B$	IPA$_B$	ACETONE$_T$	MENTHOL$_T$	IPA$_T$
	CONCENTRATIONS					
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	-0.1023E-03	-0.2580E-03	0.3603E-03	-0.1145E-03	0.1120E-03	0.4230E-05
4.0	-0.2559	-0.9065	0.1163E-02	-0.5764	0.5597	0.1663E-04
6.0	-0.4006	-0.1606E-02	0.2007	-0.1227E-02	0.1198E-02	0.2842
8.0	-0.5376	-0.2294	0.2832	-0.1943	0.1904	0.3911
10.0	-0.6681	-0.2955	0.3623	-0.2670	0.2621	0.4912
20.0	-0.1239E-02	-0.5298	0.6433	-0.6062	0.5969	0.9267
30.0	-0.1696	-0.8029	0.9725	-0.8934	0.8806	0.1278E-03
40.0	-0.2064	-0.9756	0.1182E-01	-0.1134E-01	0.1118E-01	0.1561
50.0	-0.2359	-0.1111E-01	0.1347	-0.1333	0.1315	0.1789
60.0	-0.2596	-0.1217	0.1477	-0.1498	0.1478	0.1974
100.0	-0.3165	-0.1463	0.1779	-0.1909	0.1885	0.2419

NOTE: This table applies to R.T.W.3 with reversed signs.

R.T.W.2

CONCENTRATIONS

TIME	BOTTOM			TOP		
	ACETONE	METHANOL	IPA	ACETONE	METHANOL	IPA
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	0.4744E-04	0.1764E-03	-0.2238E-03	0.1893E-03	-0.1833E-03	-0.6017E-05
4.0	0.1080E-03	0.6059	-0.7140	0.8965	-0.8700	-0.2650E-04
6.0	0.1645	0.1079E-02	-0.1243E-02	0.1806E-02	-0.1757E-02	-0.4865
8.0	0.2186	0.1555	-0.1774	0.2748	-0.2678	-0.6980
10.0	0.2707	0.2026	-0.2297	0.3666	-0.3576	-0.9000
20.0	0.5060	0.4223	-0.4729	0.7657	-0.7477	-0.1805E-03
30.0	0.7059	0.9153	-0.6859	0.1077E-01	-0.1052E-01	-0.2568
40.0	0.8751	0.7836	-0.8711	0.1323	-0.1291	-0.3212
50.0	0.1019	0.9296	-0.1031E-01	0.1520E-01	-0.1482E-01	-0.3758
60.0	0.1141	0.1056	-0.1170	0.1679	-0.1637	-0.4220
100.0	0.1472	0.1406	-0.1553	0.2076	-0.2022	-0.5469

R.T.W.4

CONCENTRATIONS

TIME	BOTTOM			TOP		
	ACETONE	METHANOL	IPA	ACETONE	METHANOL	IPA
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	-0.1898E-03	-0.3210E-03	0.5109E-03	-0.7363E-04	0.7039E-04	0.3241E-05
4.0	-0.5115	-0.1147	0.1658E-02	-0.3753E-03	0.3636E-03	0.1167E-04
6.0	-0.8176	-0.2013	0.2831	-0.8236	0.8050	0.1859
8.0	-0.1105E-02	-0.2838E-02	0.3943	-0.1341E-02	0.1316E-02	0.2447
10.0	-0.1375	-0.3605	0.4981	-0.1834	0.1854	0.2987
20.0	-0.2519	-0.6626	0.9145	-0.4552	0.4499	0.5316
30.0	-0.3392	-0.8324	0.1202E-01	-0.6921	0.6850	0.7170
40.0	-0.4067	-0.9966	0.1403	-0.8952	0.8865	0.8050
50.0	-0.4591	-0.1088E-01	0.1547	-0.1066E-01	0.1056E-01	0.9832
60.0	-0.5002	-0.1152	0.1653	-0.1208	0.1197	0.1078E-03
100.0	-0.5943	-0.1273	0.1868	-0.1560	0.1547	0.1302

R.T.W.5

TIME	CONCENTRATIONS					
	BOTTOM			TOP		
	ACETONE	METHANOL	IPA	ACETONE	METHANOL	IPA
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	-0.1020E-03	-0.2062E-03	0.3082E-03	-0.8315E-04	0.7968E-04	0.3411E-05
4.0	-0.2733	-0.8067	0.1080E-02	-0.4728E-03	0.4554E-03	0.1708E-04
6.0	-0.4363	-0.1483E-02	0.1919	-0.1067E-02	0.1034E-02	0.3192
8.0	-0.5905	-0.2158	0.2748	-0.1754	0.1708	0.4560
10.0	-0.7370	-0.2812	0.3548	-0.2493	0.2414	0.5832
20.0	-0.1375E-02	-0.5655E-02	0.7024E-02	-0.5909	0.5794	0.1129E-03
30.0	-0.1884	-0.7855	0.9730	-0.8829	0.8670	0.1566
40.0	-0.2291	-0.9563	0.1184E-01	-0.1126E-01	0.1107E-01	0.1917
50.0	-0.2617	-0.1090E-01	0.1350	-0.1326	0.1305	0.2200
60.0	-0.2877	-0.1194	0.1480	-0.1492	0.1467	0.2427
100.0	-0.3496	-0.1434	0.1782	-0.1899	0.1869	0.2969

NOTE: This table applies (with reversed signs) to R.T.W.7

R.T.W.6

TIME	CONCENTRATIONS					
	BOTTOM			TOP		
	ACETONE	METHANOL	IPA	ACETONE	METHANOL	IPA
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	0.5200E-04	0.1427E-03	-0.1947E-03	0.1360E-03	-0.1303E-03	-0.5654E-05
4.0	0.1249E-03	0.5413	-0.6663	0.7382	-0.7072	-0.3102E-04
6.0	0.1924	0.9976	-0.1190E-02	0.1583E-02	-0.1521E-02	-0.6236
8.0	0.2567	0.1465E-02	-0.1722	0.2497	-0.2404	-0.9343
10.0	0.3184	0.1930	-0.2249	0.3408	-0.3285	-0.1233E-03
20.0	0.5967	0.4115	-0.4712	0.7425	-0.7169	-0.2561
30.0	0.8319	0.6034	-0.6866	0.1056E-01	-0.1020E-01	-0.3672
40.0	0.1031E-02	0.7704	-0.8735	0.1304	-0.1258	-0.4606
50.0	0.1200	0.9148	-0.1035E-01	0.1502	-0.1418	-0.5393
60.0	0.1342	0.1039E-01	-0.1173	0.1662	-0.1602	-0.6057
100.0	0.1727	0.1382	-0.1555	0.2063	-0.1984	-0.7836

R.T.W.8

CONCENTRATIONS

TIME	BOTTOM ACETONE	 METHANOL	 IPA	TOP ACETONE	 METHANOL	 IPA
0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	-0.1815E-03	-0.2487E-03	0.4348E-03	-0.5268E-04	0.4981E-04	0.2875E-05
4.0	-0.5299	-0.9974	0.1541E-02	-0.3019E-03	0.2885E-03	0.1345E-04
6.0	-0.8684	-0.1818E-02	0.2708	-0.6988	0.6752	0.2358
8.0	-0.1187E-02	-0.2611	0.3830	-0.1181E-02	0.1148E-02	0.3215
10.0	-0.1485	-0.3352	0.4886	-0.1704	0.1664	0.3983
20.0	-0.2742	-0.6264	0.9147	-0.4372	0.4300	0.7208
30.0	-0.3691	-0.8155	0.1208E-01	-0.6769	0.6672	0.9749
40.0	-0.4418	-0.9396	0.1412	-0.8819	0.8702	0.1176E-03
50.0	-0.4978	-0.1022E-01	0.1557	-0.1054E-01	0.1040E-01	0.1336
60.0	-0.5413	-0.1079	0.1663	-0.1169	0.1155	0.1462
100.0	-0.6392	-0.1180	0.1875	-0.1540	0.1523	0.1756