THE SEPARATION OF ^{15}N AMMONIA BY A GAS-LIQUID PROCESS IN A PACKED COLUMN

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ABSTRACT

A study was conducted of a process to concentrate ^{15}N, from its natural abundance, by exchange between ammonia and ammonia solutions in packed columns.

The theoretical part of the investigation covered the gas-liquid transfer process and the packed column dynamics. Equilibrium data were available in literature for a variety of solvents and these data suggested a new interpretation for the transfer process. The dynamic studies consisted of the development of a mathematical model for the unsteady and steady operation of a packed column, covering both total and partial reflux operation. Steady-state solutions were obtained by direct integration for the non-linear and for a linearized equilibrium relation. The unsteady-state analysis was restricted to the linearized case and solutions were obtained by the Laplace transform method. The model uses a generalized type of boundary conditions, which take into account the dynamic behaviour of the reflux equipment at both ends of the column. Particular cases and approximate solutions are also discussed. Two immediate application areas of this model are proposed. They are the estimation of the column separation performance using the operation start-up data and the simulation of the start-up when the feed and product flow-rates are not constant.

The experimental part of the study consisted of the design, construction and operation of a pilot plant to implement the process. Measurements of packing pressure drop and liquid hold-up were undertaken. Performance data were then obtained from transient runs at total reflux, the isotopic content of samples

being determined by mass-spectrometry. These results and similar data available in the literature were treated by the model, and a correlation for the overall mass transfer coefficient was obtained. The results suggest that the transfer process is gas-phase controlled, thus confirming published qualitative evidence.

A meus Pais

À Milú e à Sophia.

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CHAPTER ONE

INTRODUCTION

The separation of isotopes is an intrinsically difficult process, because the physical and chemical properties of isotopic compounds are very similar. In other words, the mass transfer driving force is in general so small, that the "single stage separation factor" (which is a measure of the separation achieved in an equilibrium stage) is very close to unity.

The influence of the separation factor on the economic viability of any separation process can hardly be exaggerated. Under the same conditions, processes with small separation factors require a large number of separation stages and/or a high reflux ratio, thus affecting the plant size and/or the operating costs. This influence is specially critical when a large "separative duty" is required (i. e. when a very pure product is sought from a depleted feed). In the field of isotope separations this has almost invariably been the case, since the natural abundances of the isotopes of interest are generally small and, for most applications, a very concentrated product is required. It is not surprising, therefore, that a great deal of research has been devoted over the past four decades to the study of any new small difference in the properties of isotopic compounds in an attempt to devise new and more favourable separation methods.

However, in the case of ^{15}N, there is now reason to believe that a process which was originally devised in 1936 (25,43) (but was never implemented because of its small separation factor), may have regained economic competitiveness. This process involves a gas-liquid contact between a saturated solution of ammonia in a certain type of solvents and a gas phase containing ammonia and

solvent vapour. The heavy component ($^{15}NH_3$) is found to concentrate in the liquid phase, even at room temperature when the saturation vapour pressures of ^{14}N and ^{15}N ammonias are the same. The separation factor varies with the solvent employed, but is generally smaller than the separation factor of the currently used Nitrox process. The gas-liquid and liquid-gas refluxes are performed in absorption and desorption columns and only involve the withdrawal and supply of heat.

The present renewed interest (53-60) in this process may be understood in the light of specific new applications for ^{15}N and also because of the recent drastic increase in utilities costs. The small separation factor seems to have acquired a less critical role because there is now a growing demand for large quantities of moderatly enriched (5-10% in ^{15}N) ammonium compounds for agricultural research (9,10). Also, the supply of heat needed to perform the liquid-gas reflux in this process is of low energy content and can be eventually recovered in part from the highly exotermic absorption of ammonia taking place in the top reflux section (gas-liquid reflux). In contrast, in the Nitrox process (which produces ^{15}N in the form of HNO_3 and would require, for the above mentioned application, an additional reactor), the liquid-gas and gas-liquid refluxes are chemically obtained, consuming large quantities of sulphur and oxygen (38).

These qualitative arguments suggest that a reassessement of the present economic viabilities of ^{15}N separation methods is imperative. The last known cost analyses (30,33,38) are outdated, not only because of the above mentioned change in general economic conditions and in ^{15}N market needs, but also because of technological innovations (new materials, more efficient packings, etc.) not

available at that time. In order to include the ammonia/ammonia solution process in such comparative analysis, updated column performance data of this process are needed.

In this context, the work now being reported attempted to model the process, to gain practical experience from the design and operation of a pilot plant and to collect data of plant performance.

CHAPTER TWO

LITERATURE SURVEY

2.1 The separation of isotopes

The discovery of isotopes - atoms of the same element with different masses - was a direct consequence of two lines of research being conducted at the end of the 19th century:

(a) The discovery of natural radioactive salts and the chemical analysis of their decay products - Becquerel (1896), P. and M. Curie (1896) and Rutherford (1902) (1);

(b) The studies on the conduction of electricity through rarefied gases - Goldstein (1886), J. J. Thomson (1894) (2) and Roentgen (1895).

The identification of the same types of radiation in both natural and artificially induced phenomena led to the concept of the isotope, and later made possible the dispersion studies which were to be of great importance in establishing the basic features of the structure of the atom. The concept of the isotope in itself had also profound effects on modern chemistry, ranging from the reformulation of the Periodic Table and the use of new scales of atomic weights, to tracer chemistry (3-5) and to its well-known structural and mechanism applications.

A very accurate measurement of atomic masses was made possible by the development of "mass-spectrographs"-Aston(1918) (6) - and these mass measurements were, strictly speaking , "isotope separations".

The physical and chemical properties of isotopic compounds started being systematically determined as soon as

sufficient amounts of enriched material were obtained in the laboratory, and the observed small differences in these properties suggested, in turn, new isotope separation methods.

By the end of the 1930's, the atomic energy applications of ^{235}U and/or ^{2}H were established, and war-time priorities imposed a quick extrapolation of laboratory-scale units into huge plants (7). Very large amounts of very pure material were needed in a short period of time, and economic implications were relatively unimportant compared with these objectives. This large scale production was, however, to be generally discontinued at the end of the war when, for instance, several deuterium plants were shut down (7).

Since then, there has been an increasing interest in the uses and separation of stable isotopes. This shift from radioactive towards stable isotopes was partly made possible by the development of new analytical techniques such as the optical spectroscopic analysis of ^{15}N (8,9) and the nuclear magnetic resonance spectroscopy of nuclei with non-zero spin quantum number (e.g. ^{13}C, ^{15}N and ^{18}O). In addition, there is an increasing research effort in fields such as biology, medicine and agriculture (10), and the elements N and O, which are abundantly present in living matter, have no sufficiently long-lived alternative radioisotopes.

Nevertheless, the separation of isotopes remains a "marginal" field in a chemical industry context, and can be characterized by relatively small capital investments, extremely small production levels, very high unit costs (e.g. the market price of one mole of 99.9% ^{15}N is of the order of

US $ 6000.), and a fairly elastic demand, particularly for isotopes exclusively used in research.

2.2 Special uses of ^{15}N

The separation of ^{15}N followed the general pattern outlined above, i.e., has been almost exclusively oriented towards small-scale production for laboratory research.

Two particular uses which could eventually lead to large-scale production will now be mentioned:

(a) A few years ago there was some interest in the possible use of ^{15}N as thorium nitrate solution in homogeneous nuclear reactors (7,38). ^{15}N is of interest in this respect because it has a cross-section for thermal neutron capture of 2.4×10^{-5} am^2 compared with 1.81 am^2 for ^{14}N (81). Comparative economic analysis of different separation methods were made (30,33) but were not very encouraging;

(b) Recently there is interest in the use of moderatly enriched (5-10% in ^{15}N) ammonium fertilizers for agriculture field research (9,10). This large-scale application seems to have been enhanced by the development of the previously mentioned optical analysis of ^{15}N, which requires less sophisticated equipment than the traditional mass spectroscopy, while still having a reasonable accuracy ($\simeq$ 1%).

2.3 The separation of ^{15}N

A large variety of methods for the separation of ^{15}N have been proposed or actually used in laboratory or industrial scale. A list of these methods is presented in Table 2.1.

Table 2.1 ^{15}N separation methods

METHOD	CHEMICALS	SEPARATION FACTOR	REFERENCES
Gaseous diffusion	N_2	1.018 (calc.)	11,12
Thermal diffusion	N_2	1.009	13,14
Sorption on zeolites	N_2	1.030 (78K)	15
Electrolysis	NH_4^+	1.008 (303K)	16
Ion exchange	NH_4^+	-	17
Distillation	NH_3	1.0024(10^5N m^{-2})	18,19
Distillation	N_2	1.0047(10^5N m^{-2})	20-22
Distillation	NO	1.026 (b.p.)	23,24,38
Exchange	HCN/CN^-	1.003 (298K)	25,26
Exchange	NO/NO_2	1.006 (773K)	27-29
Exchange	NO/N_2O_3	1.031 (264K)	30,31
Exchange	NO/HNO_3	1.055 (10M sol.)	32-42
Exchange	NH_3/NH_4^+	1.031 (.058M sol.)	25,43-51
Exchange	$NH_3(g)/NH_3(sol.)$	1.004-1.011	43-60

Although their separation factors are very small, the distillations of liquid nitrogen and ammonia were industrially used owing to the availability and low costs of the raw materials and to the traditional character of the required "know-how".

The distillation of nitrogen oxide has a much larger separation factor and although no pilot-plant studies are yet known, it seems rather promising, at least for the laboratory scale production of highly enriched material.

The vapour pressures of these nitrogen compounds were experimentally determined and correlated by

$$\log (p_l^o/p_h^o) = A/T - Bx10^{-3} \qquad (2.1)$$

where the subscripts l and h denote the light and heavy components. The constants A and B are given in Table 2.2.

Table 2.2 Vapour pressures of N compounds

LIGHT/HEAVY	A(K)	B	$T_{p_l^o=p_h^o}(K)^*$	REFERENCES
$^{14}N_2/^{15}N_2$	.7974	6.91	115.4	23
$^{14}N_2/^{15}N^{14}N$	.3985	3.43	116.2	23
$^{14}N^{16}O/^{15}N^{16}O$	3.0230	13.40	225.6	23
$^{14}NH_3/^{15}NH_3$	1.3665	4.632	295.0	19

(*-extrapolated)

These ratios of vapour pressures are plotted, within the experimental temperature ranges, in Figure 2.1.

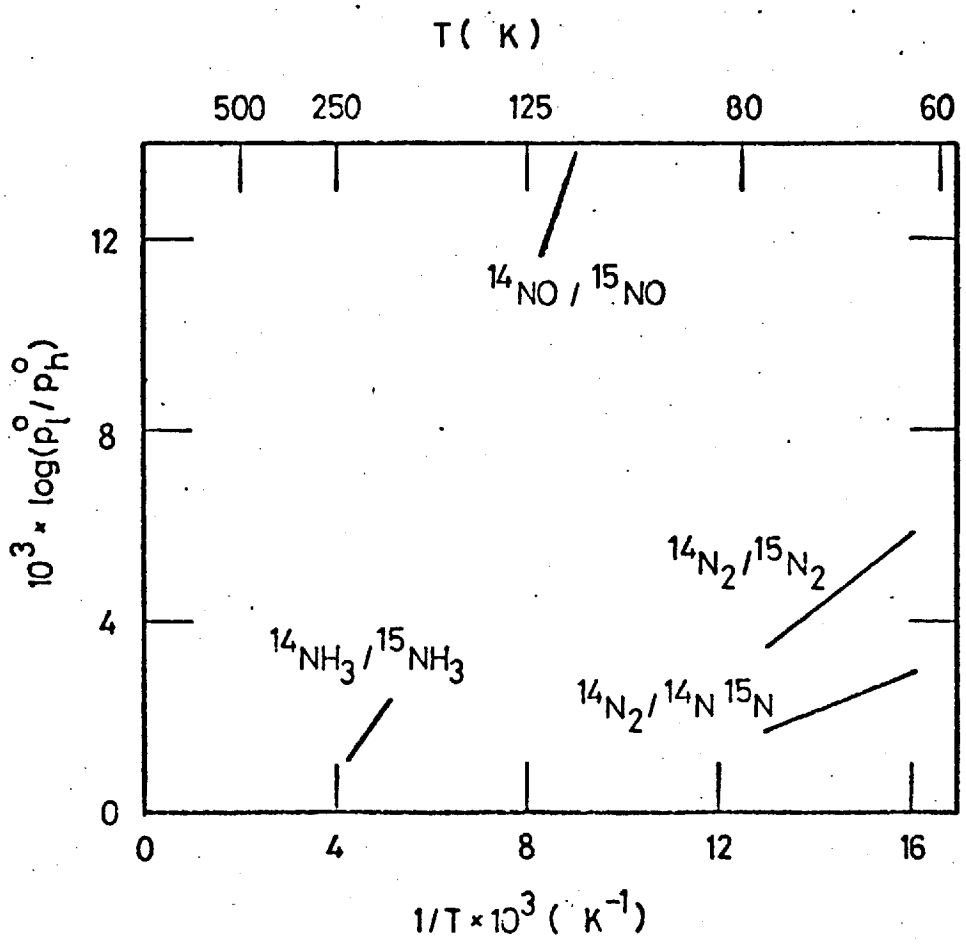


Figure 2.1 Vapour pressures of N compounds

The liquid nitrogen sorption on CaA type zeolites (15) also has a large separation factor, and the development of a mobile-bed column for continuous operation seems perfectly justifiable.

Two exchange processes will be reviewed in greater detail:

(a) The Nitrox process (32-42) which is very widely used at present;

(b) The $NH_3(g)/NH_3(soln)$ process (43-60) which will be the subject of the present work and is closely related to the NH_3/NH_4^+ exchange.

2.3.1 The Nitrox process

The method was originally developed by Spindel and Taylor (32,34), who obtained 99.8% ^{15}N in a two-column plant. The gas phase contains a mixture of nitrogen oxides (NO, NO_2, N_2O_4, N_2O_3) and the liquid phase is a solution of nitric and nitrous acids. The concentration of ^{15}N in the liquid phase was attributed to the principal equilibrium reaction

$$^{15}NO(g) + H^{14}NO_3(aq.) \rightleftarrows {}^{14}NO(g) + H^{15}NO_3(aq.) \qquad (2.2)$$

the equilibrium constant being greater than one. The conversion of $HNO_3(aq.)$ to $NO(g)$ at the bottom end of the column was performed by adding $SO_2(g)$, according to the overall reaction

$$2HNO_3 + 3SO_2(g) + 2H_2O \rightleftarrows 2NO(g) + 3H_2SO_4 \qquad (2.3)$$

Reflux at the top end of the columns was not envisaged.

As the preliminary experiments were very promising, a cost estimate was made (33). With some optimistic assumptions, (material losses were neglected, the separation plant was assumed to be located near a SO_2 plant and the by-product H_2SO_4 was assumed to be produced in concentrated form - $60^{o}Be$ -), the net cost (after crediting for the by-products) of 95% ^{15}N at a production rate of 5.3×10^{-3} g s^{-1} was estimated at US \$4200 kg^{-1} (1955 prices), which was about 50% of the $NH_3/NH_4^+(CO_3^=)$ process costs.

The separation factor was later determined by single-stage equilibrations (35-37) and from column operation data (37),

and was found to depend on the HNO_3 concentration in the liquid phase. The proposed operating conditions were 298K, $1x10^5$ N m^{-2} and 10M HNO_3, in which case the separation factor was found to be 1.055 ± .005 (average of the values given by the two methods).

In 1961 Gowland and Johns (38) introduced a waste end reflux to oxidize NO to HNO_3, by feeding oxygen according to the overall reaction

$$4NO(g) + 3O_2(g) + 2H_2O \rightleftarrows 4HNO_3 \qquad (2.4)$$

the strength of the acid being controlled by the water and oxygen flow rates. A pilot plant capable of producing $3.5x10^{-6}$ g s^{-1} of 99.8% ^{15}N was installed and construction details were described.

A two-stage reflux reactor for the total reduction of HNO_3 into pure NO was later introduced by Mahenc and Pompidor (39), since when pure NO is fed to the column, the exchange reaction (2.3) is accompanied by a partial oxidation of NO into NO_2, and this favours the ^{15}N transfer into the liquid phase (30,42). The separation factor was estimated from column start-up data and was found to agree with the value previously referred to.

More detailed experiments were recently performed on a similar plant by Guernier and co-workers (40-42), who obtained the following empirical relation between the number of theoretical plates and the liquid flow-rate, for steady-state and total reflux conditions

$$N_p = .52\, h^{1.23} (9.62\, L_v^2 - 25.96\, L_v + 30.47) \qquad (2.5)$$

where N_p is the number of theoretical plates, h is the height of packing (m) and L_v is the volumetric liquid flow rate(cm^3s^{-1}). The separation factor estimated from production data was 1.055 ± .008 for a 57wt% acid strength.

In conclusion, the Nitrox process has a very favourable separation factor and has therefore received considerable attention. It is very widely used, and relatively large-scale columns (5 cm i.d. and 20 m height) are known to be in operation. The main relative disadvantages are:

(a) An absolute need for strict safety precautions due to the use of SO_2 (toxic) and NO_2 (poisonous);

(b) The very large consumption of S (estimated (38) at 25 kg per gram of ^{15}N produced);

(c) The very low commercial value of a diluted by-product (H_2SO_4).

2.3.2 The ammonia exchange processes

The ^{15}N exchanges between ammonia and ammonia solutions in water and in methanol, and between ammonia and ammonium salts (nitrate and sulphate) solutions, were originally investigated by Urey et.al. (25,43) in 1936. The separation apparatus consisted of a large steel column 10.5 m high and 15 cm i.d., containing 621 pairs of alternate stationary and rotating cones (61). The conversion of NH_3(soln) or NH_4^+ into NH_3(g) was performed by adding Na^+OH^- solution and by steam stripping.

The separation factor for the system NH_3(g)/NH_3(soln) was taken as 1.006 (25), and the number of theoretical plates obtained with this system for given operating conditions, was

used under the same conditions to estimate the separation factor for the system $NH_3(g)/NH_4^+(SO_4^{2-})$. The obtained value (1.021 for a 31% NH_4^+ solution) was confirmed by analysing samples of the gas leaving the column and the top reflux section (differing by one equilibrium stage). The separation factors for the systems $NH_3(g)/NH_3(CH_3OH)$ and $NH_3(g)/NH_4^+(NO_3^-)$ were assumed by comparison to be 1.006 and 1.021 respectively.

The authors conclusions on the relative merits of the two basic processes were:

"...It would be most desirable from the standpoint of operation and expense, to use $NH_3(g)/NH_3(H_2O)$ in concentrating ^{15}N, since no sodium hydroxide would be necessary and a considerable fraction of the NH_3 could be refluxed at the top of the column. These advantages, however, are more than compensated by the much higher fractionation factor found for the concentrated salt solutions...".

More detailed studies of the system $NH_3(g)/NH_4^+(NO_3^-)$ were later performed by Kirshenbaum et. al. (47), who were able to correlate the separation factor with the NH_4^+ concentration in the solution. It was assumed that two isotopic equilibria were present

$$^{14}NH_4^+ + {}^{15}NH_3(g) \rightleftarrows {}^{15}NH_4^+ + {}^{14}NH_3(g) \qquad (2.6)$$

$$^{14}NH_3(soln) + {}^{15}NH_3(g) \rightleftarrows {}^{15}NH_3(soln) + {}^{14}NH_3(g) \qquad (2.7)$$

the equilibrium constants being,

$$K_1 = C.D / (A.B) \qquad K_2 = D.F / (B.E) \tag{2.8}$$

where,

$$A = (^{14}NH_4^+) \quad B = (^{15}NH_3) \quad C = (^{15}NH_4^+)$$
$$D = (^{14}NH_3) \quad E = (^{14}NH_3\text{soln.}) \quad F = (^{15}NH_3\text{soln.}) \tag{2.9}$$

The separation factor is given by

$$\alpha = (D/B)/\{(A+E)/(C+F)\} \tag{2.10}$$

and the ratio of moles of ammonia in solution to moles of ammonia plus ammonium ion (M) was defined as

$$M = (E+F)/(A+C+E+F) \tag{2.11}$$

For small ^{15}N enrichments F<<E and C<<A. Thus

$$M \simeq E / (A+E) \tag{2.12}$$

and from (2.8), (2.10) and (2.12)

$$\alpha = M (K_2 - K_1) + K_1 \tag{2.13}$$

Equation (2.13) was fitted by a least-squares technique to experimental data, and K_1 and K_2 were found to be (see Figure 2.2),

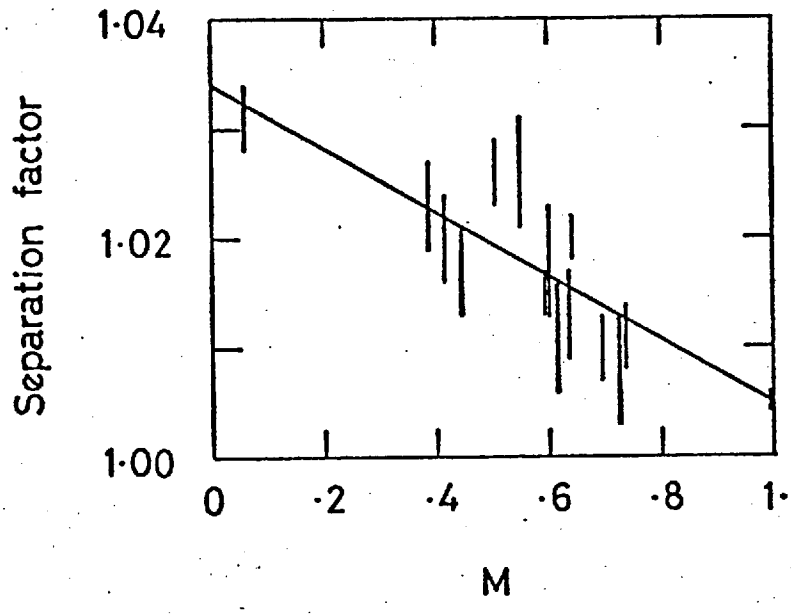


Figure 2.2 Separation factor as a function of M

$$K_1 = 1.034 \qquad (2.14)$$

$$K_2 = 1.005 \qquad (2.15)$$

In 1951 Sugimoto et.al. (48) studied the $NH_3(g)/NH_4^+(NO_3^-)$ system and obtained a 9.3% ^{15}N product. The plant consisted of two packed columns and was operated at 9.3×10^3 N m^{-2}. The gas--liquid reflux was obtained, in both columns, by adding HNO_3. The packing consisted of Fenske type helixes of 2 mm and 2.4 mm in diameter made up of aluminium wire, and was previously treated by boiling it in a $Na^+ CO_3^{2-}$ solution. This treatment covered the packing surface with Al_2O_3 crystals which were claimed to be virtually corrosion free.

In 1952 Nakane (49,50) determined the temperature dependence of K_1 and K_2 (see Table 2.3). In addition, the steady--state total separation S_∞ (ratio of liquid concentrations in the top and bottom of the column) was correlated by,

$$S_{\infty} = \exp \{97.8\ (ha_s/L_v)\ \frac{p_{NH_3}}{(p_{NH_3}+p_{H_2O})^{-.7}}\ \frac{\alpha - 1}{(NH_4^+)+(NH_3)}\} \qquad (2.16)$$

where h is the column height(cm), a_s is the interfacial area/ /length of bed(cm), L_v is the liquid flow-rate ($cm^3\ s^{-1}$), α is the separation factor, p are partial pressures (atm.) and the NH_3 and NH_4^+ concentrations are in mol l^{-1}. The process was assumed to be gas-phase controlled and the gas-phase mass transfer coefficient was expressed by

$$K_G = 1.22 \times 10^{-3}\ (p_{NH_3} + p_{H_2O})^{-.7}\ . \qquad (2.17)$$

Table 2.3 Temperature dependence of K_1 and K_2 (49)

TEMPERATURE (K)	K_1	K_2
278	1.038	1.006
283	1.037	1.006
288	1.036	1.005
293	1.035	1.005
298	1.034	1.005
303	1.033	1.005
308	1.032	1.005

A closed-cycle variation of the ammonia/ammonium ion exchange process was developed in 1956 by Palko et.al.(51).The basic difference consisted in the use of ammonium carbonate instead of ammonium nitrate (see Figure 2.3).

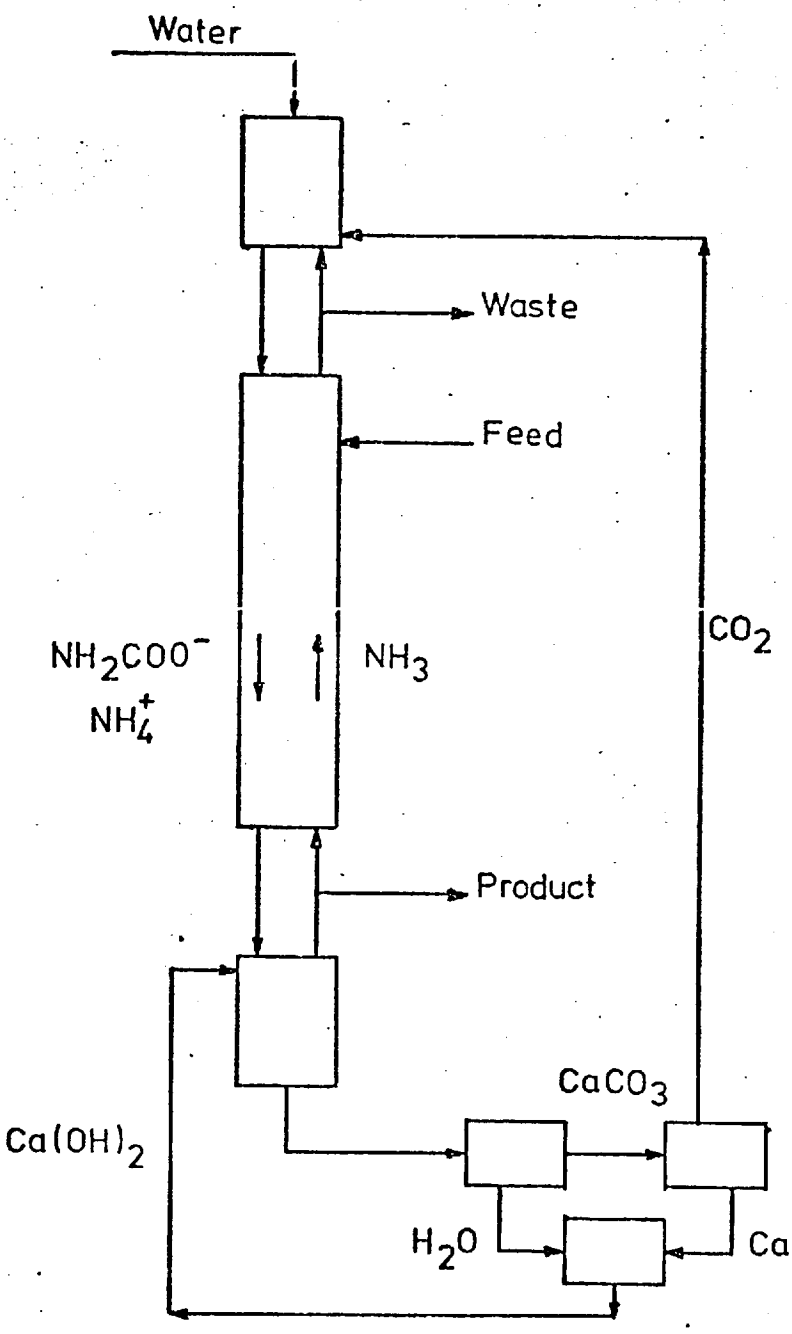


Figure 2.3 Flow diagram of the carbonate system

The $NH_4^+ \rightarrow NH_3$ reflux was obtained by adding $Ca(OH)_2$ to the solution, thus producing $CaCO_3$. This was then calcinated to give CO_2 and CaO. The carbon dioxide was used to convert NH_3 to NH_4^+ at the top of the column, and the calcium oxide was mixed with water to regenerate $Ca(OH)_2$.

The chemical composition of the liquid phase is more complex than can be deduced from the above description,because it contains hydrogencarbonate (HCO_3^-) and carbamate (NH_2COO^-) ions. Since the later contains N atoms, it is also involved in the ^{15}N isotopic exchange according to the reaction

$$^{14}NH_2COO^- + {}^{15}NH_3(g) \rightleftarrows {}^{15}NH_2COO^- + {}^{14}NH_3(g) \qquad (2.18)$$

The equilibrium constant is

$$K_3 = D.H/(G.B) \qquad (2.19)$$

where

$$G = (^{14}NH_2COO^-) \qquad (2.20)$$

$$H = (^{15}NH_2COO^-) \qquad (2.21)$$

and the concentrations B and D were defined in (2.9). Thus the exchange equilibria (2.6), (2.7) and (2.18) are all simultaneously contributing to the gas-liquid transfer of ^{15}N.

Using a treatment similar to that of Kirshenbaum et. al. (47) previously discussed, Palko and coworkers (51) expressed the separation factor in terms of K_1, K_2 and K_3 by

$$(\alpha-1) = M_1(K_1-1) + M_2(K_2-1) + M_3(K_3-1) \qquad (2.22)$$

where

$$M_1 = (A+C)/(A+C+E+F+G+H) \simeq A/(A+E+G) \qquad (2.23)$$

$$M_2 = (E+F)/(A+C+E+F+G+H) \simeq E/(A+E+G) \qquad (2.24)$$

$$M_3 = (G+H)/(A+C+E+F+G+H) \simeq G/(A+E+G) \qquad (2.25)$$

The separation factor was experimentally determined in the temperature range 289-317 K, and using the temperature dependence of K_1 and K_2 reported by Nakane (49) it was possible to estimate the temperature dependence of K_3. The values of K_1, K_2 and K_3 and the isotopic fractions M_1, M_2 and M_3 are shown in Table 2.4 for four different temperatures.

Table 2.4 Temperature dependence of α (51)

TEMP(K)	M_1	M_2	M_3	K_1	K_2	K_3	α
288.8	.213	.595	.192	1.036	1.005	1.023	1.015±.003
299.0	.325	.385	.290	1.034	1.005	1.021	1.019±.002
309.6	.399	.269	.332	1.032	1.005	1.021	1.021±.003
317.5	.477	.147	.376	1.030	1.004	1.019	1.022±.004

Although the values of K_1, K_2 and K_3 are seen to decrease with increasing temperature, the separation factor seems to increase,

this being due to the decreasing isotopic fraction of dissolved ammonia (M_2).

In conclusion, the essencial features of the ammonia--ammonium ion processes can be summarized as follows:

(a) The separation factors for these systems are large, although smaller than the separation factor of the Nitrox process;

(b) The $NH_3(g)/NH_4^+(NO_3^-)$ and the $NH_3(g)/NH_4^+(SO_4^{2-})$ processes consume large quantities of chemicals on the refluxes $NH_3(g) \rightarrow NH_4^+$ and $NH_4^+ \rightarrow NH_3(g)$;

(c) The closed-cycle carbonate system does not possess this disadvantage but the capital investment is high (it was estimated (33) to be approximately four times the investment on a Nitrox plant for equal production);

(d) The corrosion on common stainless steels is considerable.

The original $NH_3(g)/NH_3(soln)$ method of Urey and co--workers (25,43) was recently the subject of extensive research by Kuznetsov and Panchenkov (53-60), following the development of similar systems for the separation of ^{10}B, ^{13}C, ^{17}Cl and ^{34}S (reference 55 lists twelve references on these systems). A wide range of solvents and operating conditions were covered, and this work will now be reviewed.

The first system to be studied was $NH_3(g)/NH_3(1\text{-}C_3H_7OH)$ (54) in a 1.4 m height 1.6 cm i.d. column, packed with 2 mm stainless steel wire rings and operating at atmospheric pressure. A total separation of $S_\infty = 1.49$ was obtained at 279 K and with a liquid flow-rate of 16.7 $mm^3\ s^{-1}$.

Similar experiments using the same apparatus (54) with straight-chain and branched-chain alcohols (55) and with acetone and water (56) were later reported. In the case of acetone no separation was detected.

Qualitative conclusions on the influence of column temperature (278-333 K) and liquid flow-rate (8.3-50 mm^3 s^{-1}) on the total separation and on the time to reach steady state were reported (57):

"...When the process temperature is reduced the total separation S_∞ tends to increase slightly, but there is at the same time a marked increase in the time required for the attainment of the steady state".

A tentative investigation (58) of the kinetics of the gas-liquid transfer process, suggested that the transfer is "very rapid" and that "...the rate-limiting stage is not the isotope exchange itself but the mixing of ^{14}N and ^{15}N ammonias... in the gas stream".

The separation factors of the systems under study were later experimentally determined (59) by single-stage equilibrations, and the separation factors and the HETP were calculated from the column experimental data. The results are summarized in Table 2.5.

These results suggest that:

(a) The calculated values of the separation factors are within the experimental error involved in the single-stage equilibrations method;

(b) The separation factors for the alcohol solvents investigated are of the order of magnitude of the

Table 2.5 Kuznetsov and Panchenkov results (59,60)

SOLVENTS	TEMP(K)	$L_v(mm^3s^{-1})$	S_∞	HETP(cm)	α_{calc}	α_{exp}
Methanol	293	16.7	1.8	3.1	1.0135	1.011±.004
Ethanol	293	16.7	1.8	1.6	1.0067	1.008±.003
1-Propanol	288	8.3	2.5	.8	1.0055	1.007±.002
2-Propanol	293	20.0	1.57	1.8	1.0062	1.007±.002
1-Butanol	293	8.3	2.6	1.3	1.009	1.007±.002
2-Butanol	293	17.5	1.47	2.4	1.007	-
3-Pentanol	284	20.0	1.33	2.7	1.0057	1.004±.002
Water	293	11.7	1.65	1.6	1.006	-

separation factor of the $NH_3(g)/NH_3(H_2O)$ system (the α for methanol being the exception and consistently higher);

(c) The separation factors seem to increase when the length of the hydrocarbon group of the alcohol decreases;

(d) Apparently there is no correlation between HETP and the liquid flow-rate (L_v), but S_∞ seems to increase when L_v decreases.

In conclusion, the basic features of the $NH_3(g)/NH_3(soln)$ systems are:

(a) Their separation factors are small compared with the Nitrox process, but still slightly larger than the separation factors of the distillations of liquid nitrogen and ammonia;

(b) The gas-liquid and liquid-gas refluxes do not consume any additional chemicals and only involve the supply and withdrawl of heat;

(c) The chemicals used in the process are cheap and do not require any special handling care;

(d) The separation plant is simple and can be operated at atmospheric pressure and room temperature.

2.4 Dynamic behaviour of mass transfer columns

A common feature of all the isotope separation processes reviewed in section 2.1, is that they lead to long column start-up periods. This feature is by no means characteristic of isotope separations. Indeed, it is well known that separation systems with a small driving force, large material hold-ups and /or exacting product specifications usually show a slow column start-up. In extreme cases, this non-productive period can take several years (62), but even the more common order of magnitude of months is sufficient to illustrate the economic implications of the problem and the need for accurate descriptions of the phenomenon.

The dynamic behaviour of mass transfer columns has been extensively studied in the last four decades, particularly in the context of process control, i.e., with emphasis on small

perturbations around the steady-state. The intrinsically transient batch operations, where there is no steady-state, have also been widely investigated. These two dynamic situations lie outside the scope of the present investigation and will thus not be specifically covered here. In addition, plate columns are also excluded, since the mathematical modelling of processes taking place in stagewise equipment is different from the treatment of packed columns. Literature surveys on these topics can be found elsewhere (63,66).

The basic principles of isotope separations are treated in books by Cohen (64) and Rozen (65), and a less formal account of unsteady behaviour in continuous countercurrent separations can be found, for instance, in reference (66).

The first attempt to model the transient start-up of a separation column with two moving phases seems to be due to Urey et.al. (43,61). Assuming an infinite reservoir at one end of the column (the concentration at that point was taken as time-independent), a relation between concentration and time was derived for total reflux conditions, which in the present notation is

$$(1-x)\ \ln\left(\frac{1-x}{1-x_o}\right) + x\ \ln(x/x_o) = (\alpha-1)\ \ln(\alpha)\ xL_vN_pt/(AHh) \qquad (2.26)$$

where x(t) is the liquid mole fraction of the heavy component at one end of the column, x_o is the constant mole fraction at the other end, α is the separation factor, L_v is the volumetric liquid flow-rate, N_p is the number of theoretical plates, t is the time variable, A is the column cross-sectional area, H is

the liquid hold-up in the column per unit volume of bed and h is the column height. Equation (2.26) was used to estimate N_p from start-up data.

A different mathematical approach was later used by Cohen in 1940 in a much quoted paper (67). The use of a continuous height variable led to a second-order partial differential equation. Both exact and approximate (for linear equilibrium relation) steady-state solutions were obtained by direct integration, for production conditions. A transient series solution for total reflux conditions was obtained by the use of Laplace transforms. The reverse transformation was based on the "Heavyside expansion theorem" and the series of transient terms was found to converge very rapidly. The concentration at one end of the column was assumed constant with time throughout the derivation, and the interfacial mass transfer flux was expressed as the rate of a "bimolecular reversible reaction" (the separation process under study was the concentration of ^{13}C by exchange between HCN and CN^-).

This treatment was later used by Dostrowski et.al. (68) to cover the transient operation with a "finite supply reservoir without production" and with a "infinite supply with production from the boiler", and was applied by Nakane (69) to the $NH_3(g)/NH_4^+$ ^{15}N separation process.

In 1956, Rozen (70) published a more comprehensive treatment of the unsteady-state operation of packed columns, for a variety of boundary conditions. Solutions were obtained by the Laplace transform method and by separation of variables.

The similarity conditions

$$\frac{x(z,t) - x(z,0)}{x(z,\infty) - x(z,0)} = f(t) \qquad (2.27)$$

and

$$\frac{x(z,t) - x(0,t)}{x(1,t) - x(0,t)} = g(z) \qquad (2.28)$$

where $x(z,t)$ is the liquid mole fraction of heavy component, t is the time variable and z is the height variable (0 at the top of the column and 1 at the bottom), were shown to be a good approximation to the exact solution, near the steady state or when the material hold-up in the column is small. This asymptotic character of solution (2.28) was experimentally confirmed by several authors (39,41,71).

In 1962, Babkov et.al.(71) developed a model for the total reflux transient operation of a packed column, assuming that the degree of approach to the steady state was the same at all levels in the column (condition (2.27)) and using the HETP concept (which leads to an ordinary differential equation instead of a partial differential equation). The model was applied to published data (30) on the Nitrox process.

The same basic assumptions were recently used by Guernier et.al. (41), who extended Babkov's model to cover the operation with draw-off. The HETP was assumed independent of height, time and of the column mode of operation, and the model

represented well the authors's results on the Nitrox process.

In all the models so far mentioned, the equilibrium distribution relationship was linearised assuming small enrichments. A linearisation near the steady state was used by Heinke and Wagner (73) who obtained a series solution with separated variables.

A similar perturbation method was used by Elliev et. al. (72), who also considered the effect of small changes in the feed mixture composition after the attainment of a steady state. The solution of the model was consistent with experimental results of the distillation of mixtures of organic compounds with similar vapour pressures (e.g. n-heptane / methylcyclohexane and benzene/dichloroethane).

A method to estimate the steady-state overall separation in a given column, from unsteady-state data, was proposed in 1967 by Zhavoronkov et.al. (74). The solution of the model was obtained by separation of variables and yielded the relation

$$1/\log S_t = c/(t \log S_\infty) + 1/\log S_\infty \qquad (2.29)$$

where S_t is the ratio of the concentrations at both ends of the column at time t, S_∞ is the same ratio at steady state, t is the time variable and c is an empiric constant. Given a set of data points S_t vs. t, S_∞ can be obtained by linear extrapolation from a plot of $1/\log S_t$ as a function of 1/t.

Finally, the ten models that were briefly mentioned in this section suggest the following comments:

(a) The formulation of mathematical models for the unsteady operation of packed columns is highly diversified, both in terms of physical concepts and of methods of solution;

(b) In several models (41,61,70,71,74) the gas-phase hold-up was neglected and the transient behaviour was assumed exclusively due to liquid - phase accumulation;

(c) Different types of boundary conditions were covered. However, the reflux equipment was always assumed to behave like a well-stirred tank;

(d) The initial condition was always taken as constant (independent of height).

More general formulations of the initial and boundary conditions will be proposed in Chapter Three, where the need and applications of these improvements are mentioned.

CHAPTER THREE

MODELLING OF THE PROCESS

3.1 The gas-liquid transfer of ^{15}N ammonia

The literature search on the $NH_3(g)/NH_3(soln)$ processes (see section 2.3.2) showed two important points concerning these systems:

(a) The vapour pressures of pure ^{14}N and ^{15}N ammonias are equal at approximately 295 K (19);

(b) The transfer phenomenon is usually explained in terms of a "very rapid" reversible reaction,

$$^{15}NH_3(g) + {}^{14}NH_3(soln) \rightleftarrows {}^{14}NH_3(g) + {}^{15}NH_3(soln) \quad (3.1)$$

and the separation factor is taken as the equilibrium constant (greater than one) of this reaction.

The consideration of reversible reactions in gas-liquid mass transfer phenomena is relatively recent (75), and is only relevant when the reaction, taking place inside the liquid film, enhances the transfer process. If the present $^{15}NH_3$ transfer is gas-phase controlled as the literature seems to suggest (50,58), the use of a "reaction approach" is not only irrelevant but can also be misleading. Thus, a more fundamental explanation for the transfer process is proposed subsequently.

3.1.1 The separation factor

Two other points not specifically mentioned in chapter two need to be emphasized at this stage:

(a) The values of the separation factors experimentally determined for these systems can not be attributed to the ammonium ion that is always present in the

solution owing to the ionisation of dissolved ammonia. For water the ionisation equilibrium is

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (3.2)$$

and the ionisation constant is

$$K_i = (NH_4^+)\,(OH^-)/(NH_3) = 1.8 \times 10^{-5} \text{ mol } l^{-1} \qquad (3.3)$$

At 293 K and 10^5 N m^{-2} the solubility of ammonia in water is of the order of

$$S = (NH_3) + (NH_4^+) = 30 \text{ mol } l^{-1} \qquad (3.4)$$

and by manipulation

$$(NH_4^+) \,/\, (NH_3) = 7.7 \times 10^{-4} \qquad (3.5)$$

Therefore, although the separation factor for the $NH_3(g)/NH_4^+$ ^{15}N exchange is larger than for the $NH_3(g)/NH_3(soln)$ processes, the influence of NH_4^+ on the overall separation factor is pratically negligible.

(b) No theoretical confirmation of the experimental values of these separation factors is yet known. The equilibrium constants of a great number of exchange reactions were theoretically determined (5,22) in terms of ratios of partition functions estimated from spectroscopic data. Vapour pressure corrections were used for condensed phases and in general the agreement with experiment was remarkably good. But these calculations are not possible for the present systems because these involve association species which only exist in the liquid phase and in addition, the vapour pressures of the two isotopic ammonias are equal at the temperatures of interest.

A thermodynamically based interpretation of the separation factor, which also considers molecular scale evidence is now put forward. Consider a two-phase (gas and liquid) closed system, containing three components A,B and C in equilibrium, with A = $^{14}NH_3$, B = $^{15}NH_3$ and C = solvent. The separation factor of A versus B (α_{AB}) between the two phases is, by definition

$$\alpha_{AB} = (y_A/y_B) \; / \; (x_A/x_B) \qquad (3.6)$$

where x and y are liquid and gas mole fractions and the subscripts denote the appropriate component. Assuming an ideal gas phase, (3.6) becomes (82)

$$\alpha_{AB} = (\gamma_A \; p_A^o) \; / \; (\gamma_B \; p_B^o) \qquad (3.7)$$

where p_A^o and p_B^o are the vapour pressures of pure A and B (at the temperature of the system), and the activity coefficients γ_A and γ_B express deviation from Raoult's law, i.e., $\gamma_A \to 1$ when $x_A \to 1$, and $\gamma_B \to 1$ when $x_B \to 1$.

Now, since $p_A^o = p_B^o$ at room temperature (19) and $\alpha_{AB} > 1$ for the systems under consideration, it follows from (3.7) that

$$\gamma_A > \gamma_B \qquad (3.8)$$

Note that the solutions of ammonia in water and in several alcohols show negative deviation from Raoult's law, i.e., γ_A and γ_B are both smaller than one. Thus, equation (3.8) implies that the solutions of B in these solvents are more deviated from ideality then the solutions of A in the same solvents.

The non-ideality of solutions was recently correlated (76) in terms of hydrogen-bonded molecular associations. In general these associations can be of three types:

(a) between two solvent molecules;

(b) between two solute molecules;

(c) between solvent and solute molecules.

However, the first two types of hydrogen-bonded associations must be considered irrelevant to the present problem because:

(a) the interaction between solvent molecules is obviously unaffected by the ^{15}N isotopic substitution, and vice-versa;

(b) the association between two ammonia molecules can be expected to be statistically less significant than the ammonia-solvent interaction, and since the separation factors are experimentally found to depend on the solvent (different α for different solvent), the overall influence of the ammonia-ammonia association on the isotopic transfer can not be determining.

Thus, equation (3.8) suggests that the molecular association between B and the solvent is "stronger" than the association between A and the solvent.

Now, two types of hydrogen-bond associations between NH_3 and water are possible

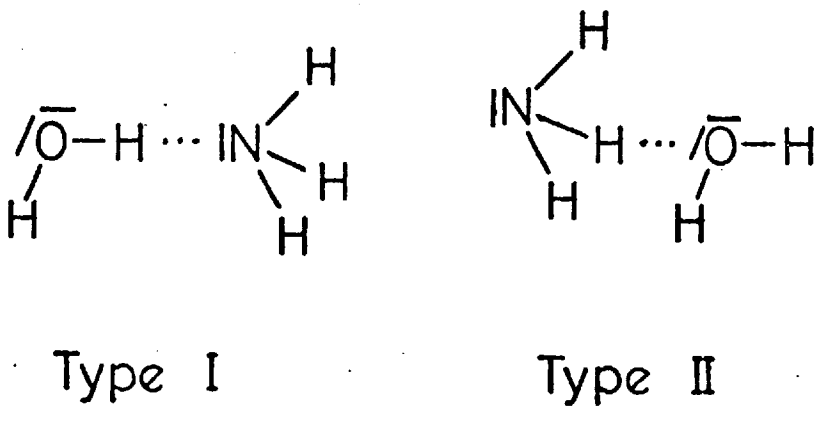


Figure 3.1 Ammonia-water H-bonds

These two types of H-bonds were detected (77) in the crystal structure of solid ammonia monohydrate (m.p. = 194 K), where no ionic bonds where found. The x-ray diffraction method showed that the distance between the O and N atoms is .278 nm for type I and .321 for type II bonds, i.e., type I bonds are stronger than type II. These measurements of the relative strength of type I and type II bonds are in good agreement with the fact that the group |O-H is a better proton donor than |N-H (electronegativity of O is greater than the electronegativity of N).

On the other hand, type I bonds can be expected to be more sensitive to the replacement of ^{14}N by ^{15}N than type II bonds, because in the later the isotopic substitution only produces a "secondary effect" (5).

Theoretical considerations (78,79) suggest that both the zero-energy level and the reduced mass effects contribute to the $^{15}N\cdots H\text{-}O$ bond to be stronger than $^{14}N\cdots H\text{-}O$, thus confirming the previous assessement based on equation (3.8).

In conclusion it is suggested that at room temperature:

(a) The ^{15}N ammonia concentrates in the liquid phase owing to a different non-ideality of the solutions of ^{14}N and ^{15}N ammonias in proton-donor solvents;

(b) This isotopic difference in non-ideality can be attributed primarily to type I H-bonds between the solvent and the solute;

(c) The separation factors for these systems are greater than one because the H-bond energy of $^{15}N\cdots H\text{-}O$ is greater than $^{14}N\cdots H\text{-}O$.

This explanation is consistent with two other experimental observations:

(a) No separation was detected (56) with the solvent acetone - $(CH_3)_2CO$ - where type I bonds can be expected to be much rarer than type II bonds, (ketones are extremely poor proton-donors since the electronegativity of C is still smaller than the electronegativity of N);

(b) The separation factors with alcohol solvents depend on the hydrocarbon chain (55) (see section 2.3.2), since this affects the acid character of the proton of the group |O-H of the alcohol (which is involved in the H-bond).

Finally note that at temperatures other than room temperature, this non-ideality effect is accompanied by the effect of the ratio of vapour pressures, according to (3.7).

3.1.2 Temperature dependence of the separation factor

Very little is known about the temperature dependence of the separation factors of the $NH_3(g)/NH_3(soln)$ systems. However, the available information (49,57) seems to indicate that the separation factor increases very slightly when the temperature decreases.

The approach outlined in the previous section could provide a better insight into the problem, because the temperature dependence of the activity coefficients can be expressed as

$$\left.\frac{\partial \log \gamma_A}{\partial (1/T)}\right|_{P,n_A,n_B,n_C} = -\frac{\Delta H_A}{2.303\ R} \qquad (3.9)$$

where T is the absolute temperature (K), n is the number of moles, R is the ideal gas constant (8.134 J mol^{-1} K^{-1}) and ΔH_A is the difference between the partial molar enthalpies of A in solution and in the pure state.

Since α_{AB} is given by (3.7) and the temperature dependence of p_A^o/p_B^o is known (see Table 2.2), it is found that

$$\frac{\partial \log \alpha_{AB}}{\partial (1/T)} = \frac{\Delta H_A - \Delta H_B}{2.303\ R} + 1.3655 \qquad (3.10)$$

where the condition P, n_A, n_B, n_C = constant was neglected because a small temperature interval was assumed.

Equation (3.10) could be used to estimate the temperature dependence of α_{AB} provided that a reasonably accurate estimate of $\Delta H_A - \Delta H_B$ could be made. As a first approximation and since the non-ideality was attributed to the ammonia-solvent association, the difference $\Delta H_A - \Delta H_B$ can be taken as $\Delta H_A^f - \Delta H_B^f$ where ΔH_A^f and ΔH_B^f are the enthalpy changes in the formation of the A-solvent and B-solvent type I associations. For the case of water

$$^{14}NH_3 + H_2O \rightleftarrows {}^{14}NH_3\text{-}H_2O \qquad \Delta H_A^f \qquad (3.11)$$

$$^{15}NH_3 + H_2O \rightleftarrows {}^{15}NH_3\text{-}H\ O \qquad \Delta H_B^f \qquad (3.12)$$

The difference in these enthalpy changes could be estimated from the total energies of the NH_3, H_2O and H-O-H···NH_3 species recently reported (78), provided that the difference of the pressure-volume terms is neglected. The total energies of the three species were theoretically computed for assumed geometric parameters using LCAO-SCF molecular orbitals, and an attempt was

made to estimate the ^{15}N isotope effect on these energies (assuming that the species H-O-H···NH_3 vibrates harmonically and using both zero-point energy and reduced mass corrections). The estimated value of $\Delta H_A^f - \Delta H_B^f$ was -75 J mol^{-1} (79) which would indicate from (3.10) that

$$\frac{\partial \log \alpha_{AB}}{\partial (1/T)} < 0 \qquad (3.13)$$

This is contrary to the available experimental evidence, but the assumptions throughout the derivation and the estimation of $\Delta H_A^f - \Delta H_B^f$ can introduce very large errors, particularly due to the vibrational anharmonicities which were not considered.

In conclusion, a new tentative approach to the estimation of the temperature dependence of α_{AB} did not prove conclusive, and until more experimental evidence is available α_{AB} has to be taken as approximately constant with temperature in the range 288-298 K.

3.1.3 The interphase mass transfer flux

It will be assumed that the equilibrium distribution is instantaneously established at the gas-liquid interface and in addition, the two-film model of interphase mass transfer will be used. Thus, the interphase mass transfer flux can be expressed by the product of an overall transfer coefficient and an overall driving force. K_{OG} will be used instead of K_{OL} (although this is irrelevant to the modelling problem) because the process is "a priori" believed to be gas-phase controlled. The literature qualitative conclusions (58) on the transfer process support this view and a similarity with the absorption of ammonia in water (where at least 85 % of the total transfer resistance lies in the gas film)

can also be argued for.

Nevertheless, the possibility of liquid-phase control was examined by assuming that the reversible reaction (3.1) was taking place in the liquid film (see Appendix A). Using Olander's model (75) for absorption with reversible chemical reaction, the enhancement factor was found to depend on the liquid phase concentration in ^{15}N but to be always larger than one (e.g., $E_f = K_L/K_L^o = 1.029$ for $x = .01$). Since K_L^o is assumed to be of the same order of magnitude as the liquid phase coefficient for the absorption of ammonia in water (i.e., $K_L^o >> K_G$), then this reversible reaction model seems to rule out the possibility of liquid phase control.

3.2 Dynamic model of the process system

In order to make the derivation more concrete, the present dynamic model was developed for the particular process under study. This does not affect however, the generality of most of the mathematical treatment and of the initial and boundary conditions in particular.

Three basic assumptions of the treatment, which seem perfectly justifiable for the present process, need to be kept in mind when applying this model to a different process:

(a) The gas-phase hold-up is neglected;

(b) The equilibrium relation is linearized assuming small enrichements;

(c) Thermal effects are not considered because any small difference in the heats of solution of the ^{14}N and ^{15}N ammonias is neglected.

3.2.1 Flow diagram

The proposed flow chart is shown in Figure 3.2, where F_m, G_m and W_m are the feed, gas and waste molar flow-rates, L_v and P_v are the liquid and product volumetric flow-rates and S is the NH_3 solubility in the particular solvent being used.

The product is withdrawn from the process system at the bottom of the column as liquid, since the desired isotope concentrates in this phase.

The feed is gaseous ammonia at the operating temperature and pressure, with a constant composition. This is the case in the installed pilot plant and will presumably be also the case in any industrial plant, which would ideally be located adjacent to an ammonia production plant.

Two alternative feed locations are shown in the diagram:

(a) At the top of the column, i.e. the waste and feed compositions only differ by one equilibrium stage;

(b) In the column.

The mathematical advantages of the first case are obvious because the differential mass balances are the same all over the column and a top boundary condition can be obtained without any particular assumptions concerning the feed location. In the second case however, the differential mass balances below and above feed location are different, and unless it is assumed that the concentration at feed height is always equal to the feed concentration (optimum feed location), it is not possible to derive an independent boundary condition at this height and thus, the two sets of differential equations (above and below feed point) are coupled.

Apart from this mathematical convenience, the economic

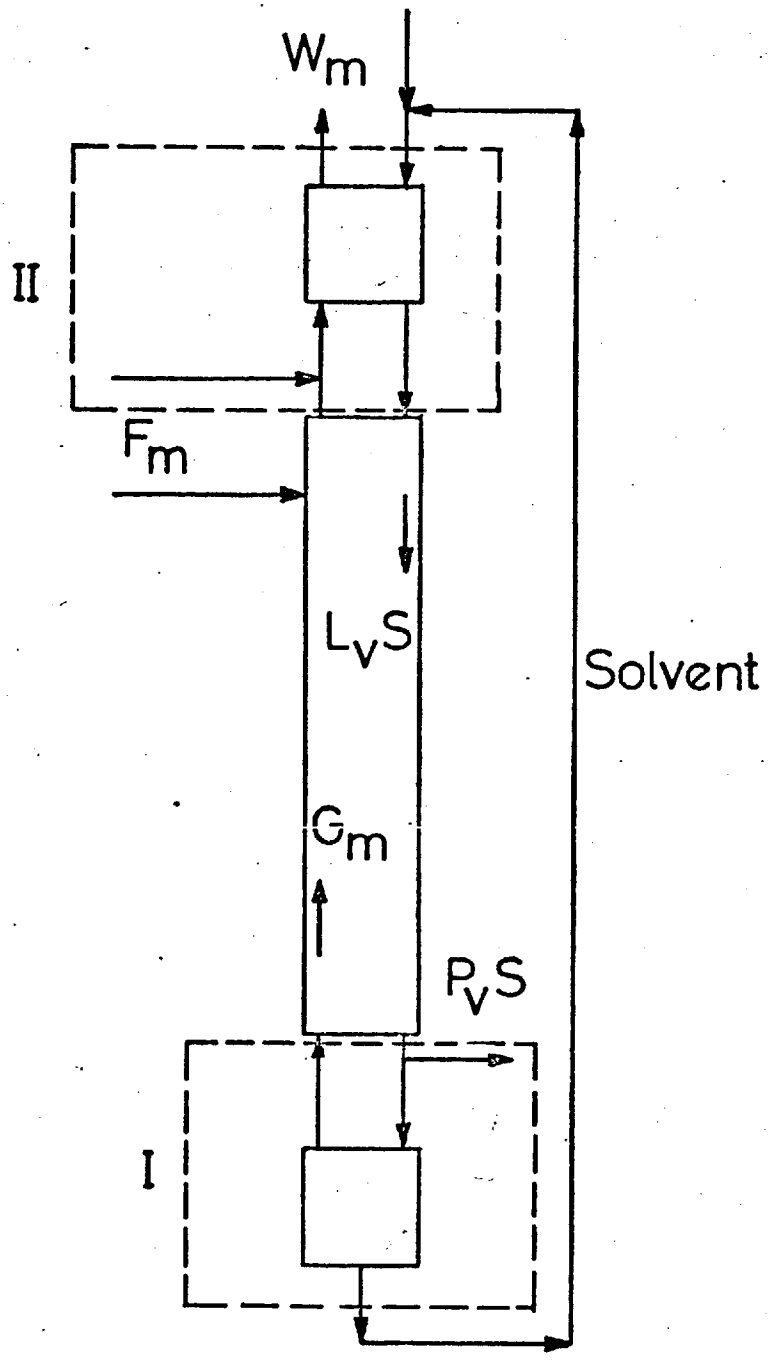


Fig. 3.2 Flow diagram

implications of the first case may not necessarily be disadvantageous, because if this ^{15}N separation plant is adjacent to an ammonia plant, large feed flow-rates are available at negligible costs. In addition, the total height of the plant (which can be a limiting factor) is used for enriching purposes since the stripping section is reduced to the top reservoir. This feed location will thus be adopted throughout the treatment, but a solution for the second case is nevertheless presented in Appendix B.

Before deriving the differential mass balances, it is appropriate to consider the "total ammonia" ($^{14}NH_3$ plus $^{15}NH_3$) balances. As mentioned earlier, the process can be assumed an equimolecular mass transfer between the two phases. Since the pressure drop for the type of packing used is usually small, the solubility of total ammonia in the inert solvent can be assumed height and time independent, and therefore the total ammonia flow rates are also independent of these two variables. That is, the unsteady state refers only to the $^{15}NH_3$-$^{14}NH_3$ separation.

Thus, from Figure 3.2, the total ammonia mass balances at the bottom and top sections are

$$L_v S - P_v S = G_m \tag{3.14}$$

$$G_m + F_m = W_m + L_v S \tag{3.15}$$

and the overall balance is

$$F_m = W_m + P_v S \tag{3.16}$$

It is also convenient at this stage to define two ratios of flow-rates as the "product ratio" (R) and the "feed ratio" (r)

$$R = P_v S/G_m \tag{3.17}$$

$$r = F_m/(L_v S) \tag{3.18}$$

It will later be shown that the different groups of flow-rates appearing in the differential equations and in the boundary conditions can be expressed in terms of these two parameters.

3.2.2 Differential mass balances

Consider a differential height dz in the packed bed.

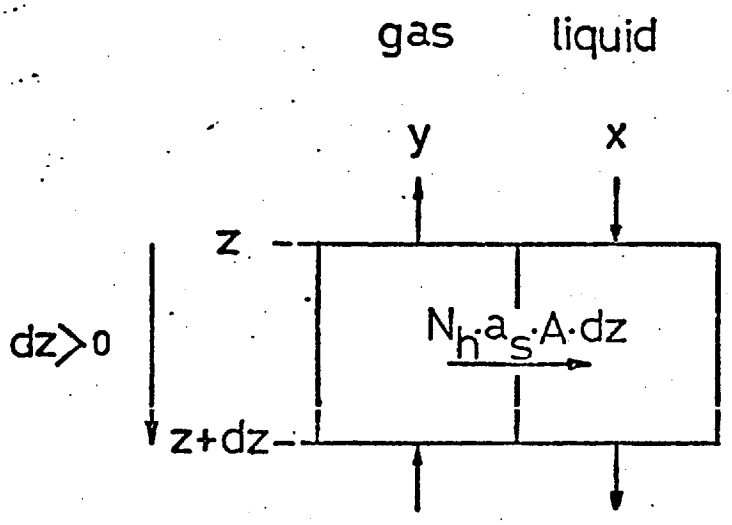


Figure 3.3 - Differential element of packing

Assuming "plug-flow", a mass balance of the "heavy" component for the liquid phase gives

$$L_v S\, x\Big|_z + N_h\, a_s\, A\, dz - L_v S\, x\Big|_{z+dz} = \frac{\partial}{\partial t}(AHS\, x\, dz) \tag{3.19}$$

where x is the liquid phase isotopic fraction of $^{15}NH_3$ (number of moles of $^{15}NH_3$ over the number of moles of $^{15}NH_3$ plus the number of moles of $^{14}NH_3$), A is the column cross-sectional area, a_s is interfacial area of packing per unit volume of bed, H is the volumetric liquid hold-up per unit volume of bed and N_h is the interfacial mass transfer flux of the heavy component.

Now, since

$$x\Big|_{z+dz} = x\Big|_{z} + \frac{\partial x}{\partial z}\Big|_{z} dz + \cdots \qquad (3.20)$$

equation (3.19) becomes

$$L_v S \frac{\partial x}{\partial z} + AHS \frac{\partial x}{\partial t} = N_h a_s A \qquad (3.21)$$

Neglecting the gas-phase hold-up, a similar balance for this phase gives

$$G_m y\Big|_{z+dz} - G_m y\Big|_{z} = N_h a_s A\, dz \qquad (3.22)$$

and as before

$$y\Big|_{z+dz} = y\Big|_{z} + \frac{\partial y}{\partial z}\Big|_{z} dz + \cdots \qquad (3.23)$$

Thus, equation (3.22) becomes

$$G_m \frac{\partial y}{\partial z} = N_h a_s A \qquad (3.24)$$

The interfacial mass transfer flux N_h can be expressed in terms of an overall driving force and an overall mass transfer coefficient

$$N_h = K_{OL} (\bar{x} - x) = K_{OG} (y - \bar{y}) \qquad (3.25)$$

where $\bar{x}$ and $\bar{y}$ are the liquid and gas concentrations in equilibrium with the actual gas and liquid concentrations.

The equilibrium-distribution relationship defines the separation factor α

$$\alpha = x\,(1-y) \,/\, \{y(1-x)\} \qquad (3.26)$$

Note that the separation factor so defined is greater than one, because x and y are isotopic fractions of the heavy component and this concentrates in the liquid phase.

For small ^{15}N enrichments (i.e., x and y less than , say, ~ 5%) equation (3.26) can be linearized by taking $x << 1$ and $y << 1$, to give

$$\alpha = x/y \tag{3.27}$$

This linear approximation will be used throught the derivation of the dynamic model, but a steady-state solution using equation (3.26) is derived in Appendix C.

With this linear approximation, equation (3.25) becomes

$$N_h = K_{OL}(\alpha y - x) = K_{OG}(y - x/\alpha) \tag{3.28}$$

and therefore the two differential equations (3.21) and (3.24) become

$$\frac{\partial x}{\partial z} + \frac{AH}{L_v}\frac{\partial x}{\partial t} = \frac{K_{OG}\, a_s\, A}{L_v S}\,(y - x/\alpha) \tag{3.29}$$

$$\frac{\partial y}{\partial z} = \frac{K_{OG}\, a_s\, A}{G_m}\,(y - x/\alpha) \tag{3.30}$$

By definition, the heights of overall transfer units based on the liquid and gas phase driving forces are

$$H_{OL} = L_v S/(K_{OL}\, a_s\, A) = h/N_{OL} \tag{3.31}$$

$$H_{OG} = G_m/(K_{OG}\, a_s\, A) = h/N_{OG} \tag{3.32}$$

where h is the bed height and N_{OL} and N_{OG} are the corresponding numbers of overall transfer units.

From equations (3.14), (3.17), (3.28), (3.31) and (3.32) the relationships between K_{OL} and K_{OG}, H_{OL} and H_{OG} and N_{OL} and N_{OG} are

$$K_{OG} = \alpha K_{OL} \tag{3.33}$$

$$H_{OG} = H_{OL} / \{\alpha(1+R)\} \tag{3.34}$$

$$N_{OG} = N_{OL} \alpha (1+R) \tag{3.35}$$

By analogy, a time of a transfer unit for the liquid phase can be defined (80) as

$$T_{OL} = \frac{AHS}{K_{OL} a_s A} = AHH_{OL}/L_v \tag{3.36}$$

this being equal to the liquid average residence time in each height of a transfer unit.

The parameters H_{OG} (or H_{OL}) and T_{OL} could be used as height and time references for the definition of dimensionless variables. However, it can be shown that H_{OG} (or H_{OL}) cannot be eliminated from the equations and boundary conditions by including it in the dimensionless variables (the same applies to α). Thus, the "best" choice of dimensionless variables is

$$x^* = \frac{x}{x_o} \quad ; \quad y^* = \frac{y}{x_o} \quad ; \quad z^* = \frac{z}{h} \quad ; \quad t^* = \frac{L_v t}{AHh} \tag{3.37}$$

where x_o is some reference concentration.

With these dimensionless coordinates the system of equations becomes

$$\frac{\partial x^*}{\partial z^*} + \frac{\partial x^*}{\partial t^*} = N_{OG}\,(y^* - x^*/\alpha)/(1+R) \qquad (3.38)$$

$$\frac{\partial y^*}{\partial z^*} = N_{OG}\,(y^* - x^*/\alpha) \qquad (3.39)$$

Equations (3.38) and (3.39) are two first-order simultaneous linear partial differential equations with constant coefficients. This equation-pair is hyperbolic, since the determinantal equation

$$\begin{vmatrix} 1-\zeta & 0 \\ 0 & -\zeta \end{vmatrix} = 0 \qquad (3.40)$$

has two real and distinct roots. The equation characteristics are

$$\zeta_1 = \frac{dt^*}{dz^*} = 0 \qquad (3.41)$$

$$\zeta_2 = \frac{dt^*}{dz^*} = 1 \qquad (3.42)$$

i.e., the two one-parameter families of integral curves are given by

$$t^* = \text{constant} \qquad (3.43)$$

$$t^* = z^* + \text{constant} \qquad (3.44)$$

and are shown in Figure 3.4. They are a direct consequence of the assumptions made and of the dimensionless coordinates used for the derivation of the equation-pair, because the gas-phase hold-up was neglected (and therefore the discontinuities in the boundary

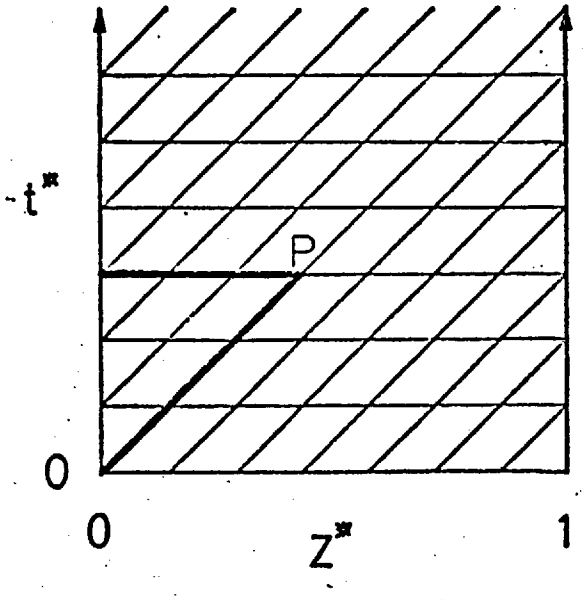


Figure 3.4 Characteristics of differential equation

conditions propagate instantaneously in this phase) and the liquid hold-up and flow-rate were included in the dimensionless time and thus the slope of the second characteristic is one.

3.2.3 Generalized initial condition

For most cases the initial concentration in the column will be constant with height, and the reference variable x_o can be taken as that initial concentration. The initial condition would then be

$$\text{at } t^* = 0, \quad x^*(z^*,0) = 1 \text{ for } 0 \leq z^* \leq 1 \tag{3.45}$$

However, a more general initial condition will be used

$$\text{at } t^* = 0, \quad x^*(z^*,0) = f(z^*) \text{ for } 0 \leq z^* \leq 1 \tag{3.46}$$

where the function $f(z^*)$ is still to be determined. The reason for this generalization lies in the possibility of using the model for the optimization of the column start-up procedure. Whatever the optimization criterion, the parameters r and R should be considered as functions of time and included in the set of variables to be

optimized. But to obtain a solution for this type of problem with time-dependent parameters presents obvious difficulties. However, if $r(t^*)$ and $R(t^*)$ could be assumed stepwise functions of time, then it would be possible to model the whole start-up period by shifting the time origin at each discontinuity in either $r(t^*)$ or $R(t^*)$. At such discontinuities, the concentration profile in the column would be fitted to a function $f(z^*)$, and this function could then be used as the initial condition for the next step.

It will be shown later that the steady-state concentration profiles in the column are given by a constant plus the product of a constant and an exponential of $N_{OG}\beta z^*$, where β is a constant (function of α and R). It seems therefore reasonable to assume that transient profiles can be fitted to

$$f(z^*) = A_1 \exp(A_2 z^*) + A_3 \qquad (3.47)$$

where A_1, A_2 and A_3 are constants to be numerically determined.

Experience has shown that in fact this function fits very well most transient profiles, with a standard deviation smaller than 1%, although two exponentials would give a still better fit for very short times.

Obviously equation (3.47) includes (3.45) either for $A_1 = 0$ and $A_3 = 1$, or $A_2 = 0$ and $A_1 + A_3 = 1$.

3.2.4 Boundary conditions

The boundary conditions at the top of the column ($z^*=0$) and at the bottom ($z^*=1$) were obtained from transient mass balances over the top and bottom reflux sections.

The dynamic behaviour of the reflux devices was taken into account, and two time-constants were considered at each

reflux section. The use of a time-lag in addition to the usual stirred-tank time-constant is believed to provide a more complete description of the reflux equipment, particularly for the separation processes under study, because:

(a) Both reflux sections include columns (absorption column at the top and ammonia-solvent separation column at the bottom);

(b) Since these processes use saturated solutions, it is usually necessary to provide the installed pumps with large static suction heads (in order to avoid cavitation) and this leads to relatively large hold-ups in pipes.

In order to make the derivation of the boundary conditions more concrete, the two time-constants at each reflux section were assigned (with no loss of generality) to separate equipment pieces:

(a) A reflux reservoir assumed to behave like a well-stirred tank;

(b) A transportation-lag in the pipe connecting the reservoir and the column.

Now, consider section I in Figure 3.2.A mass balance for the bottom stirred-tank gives

$$(L_V - P_V)S\,\underline{x} - G_m\,y\Big|_{z=h} = V_{BS}\,S\,\frac{\partial y}{\partial t}\Big|_{z=h} \qquad (3.48)$$

where V_{BS} is the volume of liquid in the bottom stirred-tank , and $\underline{x}$ is the composition in the liquid stream entering the tank (different from the composition of the liquid leaving the the column at the same instant of time).

The balance on the connecting pipe is

$$\underline{x}(t) = x(t - \tau_{BL}) \tag{3.49}$$

where

$$\tau_{BL} = V_{BL}/(L_v - P_v) \tag{3.50}$$

and V_{BL} is the liquid hold-up in the pipe. Introducing the dimensionless variables defined in (3.37) and the parameter R defined in (3.17), equations (3.48) and (3.49) become

$$\underline{x}^* - y^*\Big|_{z^*=1} = \tau^*_{BS} \left.\frac{\partial y^*}{\partial t^*}\right|_{z^*=1} \tag{3.51}$$

$$\underline{x}^*(t^*) = x^*(t^* - \tau^*_{BL}) \tag{3.52}$$

where the new time-constants are

$$\tau^*_{BS} = V_{BS}\,(1+R) \,/\, (AHh) \tag{3.53}$$

$$\tau^*_{BL} = V_{BL}\,(1+R) \,/\, (AHh) \tag{3.54}$$

Similar balances for section II in Figure 3.2 yield

$$G_m\, y\Big|_{z=0} + F_m\, x_o - L_v S\, \underline{\underline{x}} - W_m\, \underline{\underline{x}}/\alpha = V_{TS}\, S\, \frac{d\underline{\underline{x}}}{dt} \tag{3.55}$$

and

$$x(t) = \underline{\underline{x}}(t - \tau_{TL}) \tag{3.56}$$

where x_o is the feed composition, V_{TS} is the volume of liquid in

the top stirred-tank, $\underline{\underline{x}}$ is the liquid concentration in the stirred-tank (different from the concentration entering the top of the column at the same instant of time) and τ_{TL} is given by

$$\tau_{TL} = V_{TL}/L_v \tag{3.57}$$

where V_{TL} is the volume of liquid in the pipe. Introducing the parameters r and R and the dimensionless variables previously defined, equations (3.55) and (3.56) become

$$y^*\Big|_{z^*=0} + M - N\,\underline{\underline{x}}^* = \tau^*_{TS}\,\frac{d\underline{\underline{x}}^*}{dt^*} \tag{3.58}$$

$$x^*(t^*) = \underline{\underline{x}}^*(t^* - \tau^*_{TL}) \tag{3.59}$$

where the new time-constants are

$$\tau^*_{TS} = V_{TS}\,(1+R) \,/\, (AHh) \tag{3.60}$$

$$\tau^*_{TL} = V_{TL} \,/\, (AHh) \tag{3.61}$$

and the constants M and N are given by

$$M = r\,(1+R) \tag{3.62}$$

$$N = (1+R) + (M - R) \,/\, \alpha \tag{3.63}$$

3.2.5 A Laplace transform solution

The system of two first-order partial differential equations (3.38) and (3.39) can be rearranged into a single second order equation. From (3.38)

$$y^* = \left(\frac{\partial x^*}{\partial z^*} + \frac{\partial x^*}{\partial t^*} \right) (1+R) / N_{OG} + x^* / \alpha \qquad (3.64)$$

and with (3.39)

$$\frac{\partial^2 x^*}{\partial z^{*2}} + \frac{\partial^2 x^*}{\partial z^* \partial t^*} - N_{OG} \beta \frac{\partial x^*}{\partial z^*} - N_{OG} \frac{\partial x^*}{\partial t^*} = 0 \qquad (3.65)$$

where

$$\beta = \{\alpha(1+R) - 1\} / \{\alpha(1+R)\} \qquad (3.66)$$

Using the initial condition (3.46) the unilateral Laplace transform of (3.65) is

$$\frac{d^2\bar{X}^*}{dz^{*2}} + (s - N_{OG}\beta) \frac{d\bar{X}^*}{dz^*} - N_{OG}\, s\, \bar{X}^* = \frac{df(z^*)}{dz^*} - N_{OG}\, f(z^*) \qquad (3.67)$$

where $\bar{X}^*$ is the transform of x^* and s is the transform variable.

Similarly, the transforms of equations (3.51), (3.52), (3.58) and (3.59) are

$$\underline{\bar{X}}^* - \bar{Y}^*\Big|_{z^*=1} = \tau^*_{BS} \{s\, \bar{Y}^*\Big|_{z^*=1} - f(1)\} \qquad (3.68)$$

$$\underline{\bar{X}}^* = \bar{X}^*\Big|_{z^*=1} \exp(-s\tau^*_{BL}) + f(1) \{1 - \exp(-s\tau^*_{BL})\}/s \qquad (3.69)$$

$$\bar{Y}^*\Big|_{z^*=0} + M/s - N\underline{\bar{X}}^* = \tau^*_{TS} \{s\underline{\bar{X}}^* - f(0)\} \qquad (3.70)$$

$$\bar{X}^*\Big|_{z^*=0} = \underline{\bar{X}}^* \exp(-s\tau^*_{TL}) + f(0) \{1 - \exp(-s\tau^*_{TL})\}/s \qquad (3.71)$$

where $\bar{Y}^*$, $\underline{\bar{X}}^*$ and $\underline{\bar{\underline{X}}}^*$ are the transforms of y^*, $\underline{x}^*$ and $\underline{\underline{x}}^*$ and no

distinction is being made between the initial concentrations of the liquid and gas phases.

Eliminating the dummy variables $\underline{\bar{X}}^*$ and $\underline{\underline{\bar{X}}}^*$ from (3.68) and (3.69), and from (3.70) and (3.71) respectively

$$\bar{Y}^*\Big|_{z^*=1} = \bar{X}^*\Big|_{z^*=1} \Phi - f(1)\,(\Phi - 1)/s \tag{3.72}$$

$$\bar{Y}^*\Big|_{z^*=0} = \bar{X}^*\Big|_{z^*=0} \Psi - \{M + f(0)\,(\Psi - N)\}/s \tag{3.73}$$

where the transfer functions Φ and Ψ are

$$\Phi = \exp(-s\,\tau^*_{BL}) \,/\, (s\,\tau^*_{BS} + 1) \tag{3.74}$$

$$\Psi = (s\,\tau^*_{TS} + N) \,/\, \exp(-s\,\tau^*_{TL}) \tag{3.75}$$

To arrive at the boundary conditions in terms of $\bar{X}^*$ only, $\bar{Y}^*$ can be eliminated by considering the transform of (3.64) which is

$$\bar{Y}^* = \bar{X}^*/\alpha + \{\frac{dx^*}{dz^*} + s\,\bar{X}^* - f(z^*)\}\,(1+R)/N_{OG} \tag{3.76}$$

Finally upon substitution of (3.72) and (3.73) into (3.76), the boundary conditions become

$$\bar{X}^*\Big|_{z^*=1}\{\alpha\Phi - 1 - \frac{s}{N_{OG}(1-\beta)}\} = \frac{\frac{d\bar{X}^*}{dz^*}\Big|_{z^*=1} - f(1)}{N_{OG}(1-\beta)} + \alpha f(1)(\Phi-1)/s \tag{3.77}$$

$$\bar{X}^*\Big|_{z^*=0}\{\alpha\Psi - 1 - \frac{s}{N_{OG}(1-\beta)}\} = \frac{\frac{d\bar{X}^*}{dz^*}\Big|_{z^*=0} - f(0)}{N_{OG}(1-\beta)} + \alpha\{M+f(0)(\Psi-N)\}/s \tag{3.78}$$

Now, the general solution of equation (3.67) is

$$\bar{X}^* = A_3/s + A_1\exp(A_2 z^*)/(s-K) + C_1\exp(D_1 z^*) + C_2\exp(D_2 z^*) \quad (3.79)$$

where the first two terms are particular integrals and the other two terms are the solution of the homogeneous equation. The constants A_1, A_2 and A_3 were defined by (3.47) and the constant K is

$$K = A_2 (N_{OG}\beta - A_2) / (A_2 - N_{OG}) \quad (3.80)$$

D_1 and D_2 are the roots of the characteristic equation

$$D_1(s) = \lambda(s) + \theta(s)^{\frac{1}{2}} \quad (3.81)$$

$$D_2(s) = \lambda(s) - \theta(s)^{\frac{1}{2}} \quad (3.82)$$

with

$$\lambda(s) = (N_{OG}\beta - s)/2 \quad (3.83)$$

$$\theta(s) = \lambda(s)^2 + N_{OG}\, s \quad (3.84)$$

C_1 and C_2 are the integration constants. Using the boundary conditions (3.77) and (3.78) they are found to be given by

$$C_1 = - \frac{P_2\eta_2 - P_1\gamma_2\exp(D_2)}{s(s-K)\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}} \quad (3.85)$$

$$C_2 = \frac{P_2\eta_1 - P_1\gamma_1\exp(D_1)}{s(s-K)\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}} \quad (3.86)$$

where γ_1, γ_2, η_1, η_2, P_1 and P_2 are functions of s defined by

$$\gamma_1(s) = \alpha\,\Phi - 1 - (s+D_1)/\{N_{OG}(1-\beta)\} \tag{3.87}$$

$$\gamma_2(s) = \alpha\,\Phi - 1 - (s+D_2)/\{N_{OG}(1-\beta)\} \tag{3.88}$$

$$\eta_1(s) = \alpha\,\Psi - 1 - (s+D_1)/\{N_{OG}(1-\beta)\} \tag{3.89}$$

$$\eta_2(s) = \alpha\,\Psi - 1 - (s+D_2)/\{N_{OG}(1-\beta)\} \tag{3.90}$$

$$P_1(s) = sA_1\{\alpha\Psi-1-\frac{A_2+K}{N_{OG}(1-\beta)}\} + (s-K)A_3(\alpha N-1) - (s-K)\alpha\{M+A_1(\Psi-N)\} \tag{3.91}$$

$$P_2(s) = sA_1\{\alpha\Phi-1-\frac{A_2+K}{N_{OG}(1-\beta)}\}\exp(A_2) + (s-K)A_3(\alpha-1) -$$

$$- (s-K)\alpha\,A_1(\Phi-1)\exp(A_2) \tag{3.92}$$

Therefore the full transform solution is

$$\bar{X}^* = A_3/s + A_1\exp(A_2z^*)/(s-K) + F(s) \tag{3.93}$$

where

$$F(s)= \frac{\{P_2\eta_1-P_1\gamma_1\exp(D_1)\}\exp(D_2z^*)-\{P_2\eta_2-P_1\gamma_2\exp(D_2)\}\exp(D_1z^*)}{s(s-K)\,\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}} \tag{3.94}$$

Note that for K = 0 (i.e., either for $A_2 = 0$ or $A_2 = N_{OG}\beta$) , s = 0 is not a double root of F(s) because equation (3.93)

simplifies to

$$\bar{X}^* = \{A_1 \exp(A_2 z^*) + A_3\}/\, s + G(s) \qquad (3.95)$$

where

$$G(s) = \frac{\{Q_2\eta_1 - Q_1\gamma_1\exp(D_1 z^*)\}\exp(D_2 z^*) - \{Q_2\eta_2 - Q_1\gamma_2\exp(D_2 z^*)\}\exp(D_1 z^*)}{s\,\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}} \qquad (3.96)$$

and

$$Q_1(s) = A_1\{\alpha\Psi - 1 - \frac{A_2}{N_{OG}(1-\beta)}\} + A_3(\alpha N - 1) - \alpha\{M + A_1(\Psi - N)\} \qquad (3.97)$$

$$Q_2(s) = A_1\{\alpha\Phi - 1 - \frac{A_2}{N_{OG}(1-\beta)}\}\exp(A_2) + A_3(\alpha - 1) - \alpha A_1(\Phi - 1)\exp(A_2) \qquad (3.98)$$

3.2.6 Reverse transformation

The reverse transforms of the first two terms of (3.93) and the first term of (3.95) are immediate. G(s) has two types of singular points

$$s = 0 \qquad (3.99)$$

$$\eta_2\,\gamma_1\,\exp(D_1) = \eta_1\,\gamma_2\,\exp(D_2) \qquad (3.100)$$

and F(s) has a third singular point

$$s = K \qquad (3.101)$$

Using the "theorem of residues" the solutions for the cases $K = 0$ and $K \neq 0$ are

(a) $\underline{K = 0}$

$$x^*(z^*,t^*) = A_3 + A_1\exp(A_2 z^*) + \lim_{s\to 0}\{s\, G(s)\exp(st^*)\} +$$

$$+ \sum_{s_n} \lim_{s\to s_n}\{(s-s_n)\, G(s)\exp(st^*)\} \qquad (3.102)$$

where the s_n are the roots of (3.100);

(b) $\underline{K \neq 0}$

$$x^*(z^*,t^*) = A_3 + A_1\exp(A_2 z^*)\exp(Kt^*) + \lim_{s\to 0}\{s\, F(s)\exp(st^*)\} +$$

$$+ \lim_{s\to K}\{(s-K)\, F(s)\exp(st^*)\} + \sum_{s_n} \lim_{s\to s_n}\{(s-s_n)F(s)\exp(st^*)\} \qquad (3.103)$$

However, it can be shown (see Appendix D) that

$$\lim_{s\to K}\{(s-K)\, F(s)\exp(st^*)\} = -A_1\exp(A_2 z^*)\exp(Kt^*) \qquad (3.104)$$

and therefore equation (3.103) simplifies to

$$x^*(z^*,t^*) = A_3 + \lim_{s\to 0}\{sF(s)\exp(st^*)\} + \sum_{s_n} \lim_{s\to s_n}\{(s-s_n)F(s)\exp(st^*)\} \qquad (3.105)$$

The limits when $s \to 0$ lead to time-independent terms and the limits when $s \to s_n$ lead to transient terms.

3.2.6.1 The steady-state term

It can be shown (see Appendix E) that whether $K = 0$ or $K \neq 0$ the steady-state term $x^*(z^*,\infty)$ is always given by the same expression, that is

$$x^*(z^*,\infty) = A_3 + A_1\exp(A_2 z^*) + \lim_{s\to 0}\{s\, G(s)\exp(st^*)\} =$$

$$= A_3 + \lim_{s\to 0}\{s\, F(s)\exp(st^*)\} \qquad (3.106)$$

However, $x^*(z^*,\infty)$ is given by different equations depending on whether $r = R = 0$ or either $r \neq 0$ or $R \neq 0$.

(a) Either $r \neq 0$ or $R \neq 0$

In this case the limits $\lim_{s\to 0} \{s\, G(s) \exp(st^*)\}$ and $\lim_{s\to 0} \{s\, F(s) \exp(st^*)\}$ are obtained by direct substitution and the steady-state profile is given by (see Appendix E)

$$x^*(z^*,\infty) = \frac{\alpha\, r\, R + r\, \varepsilon \exp\{N_{OG}\beta(z^*-1)\}}{R\,(\varepsilon+r) + \varepsilon\,\{r - R/(1+R)\}\exp(-N_{OG}\beta) \,/\, \alpha} \qquad (3.107)$$

where

$$\varepsilon = \alpha - 1 \qquad (3.108)$$

Equation (3.107) suggests the following comments:

(i) It is indeterminate (0/0) for $r = R = 0$;

(ii) It can also be obtained by direct integration of (3.65) with $\partial / \partial t = 0$ (see Appendix C);

(iii) It is not a function of the constants A_1, A_2 and A_3 (the initial condition does not affect the steady-state);

(iv) It is only a function of four parameters α, r, R and N_{OG} (the feed point is specified);

(v) However, the ratio of the bottom and top concentrations (x_B^*/x_T^*) is only a function of two groups of three parameters, and is given by

$$x_B^*/x_T^* = \{1 + (\alpha R/\varepsilon)\} \,/\, \{(\alpha R/\varepsilon) + \exp(-N_{OG}\beta)\} \qquad (3.109)$$

The ratio x_B^*/x_T^* is plotted as a function of $N_{OG}\beta$ and with $\alpha R/\varepsilon$ as parameter in Figure 3.5.

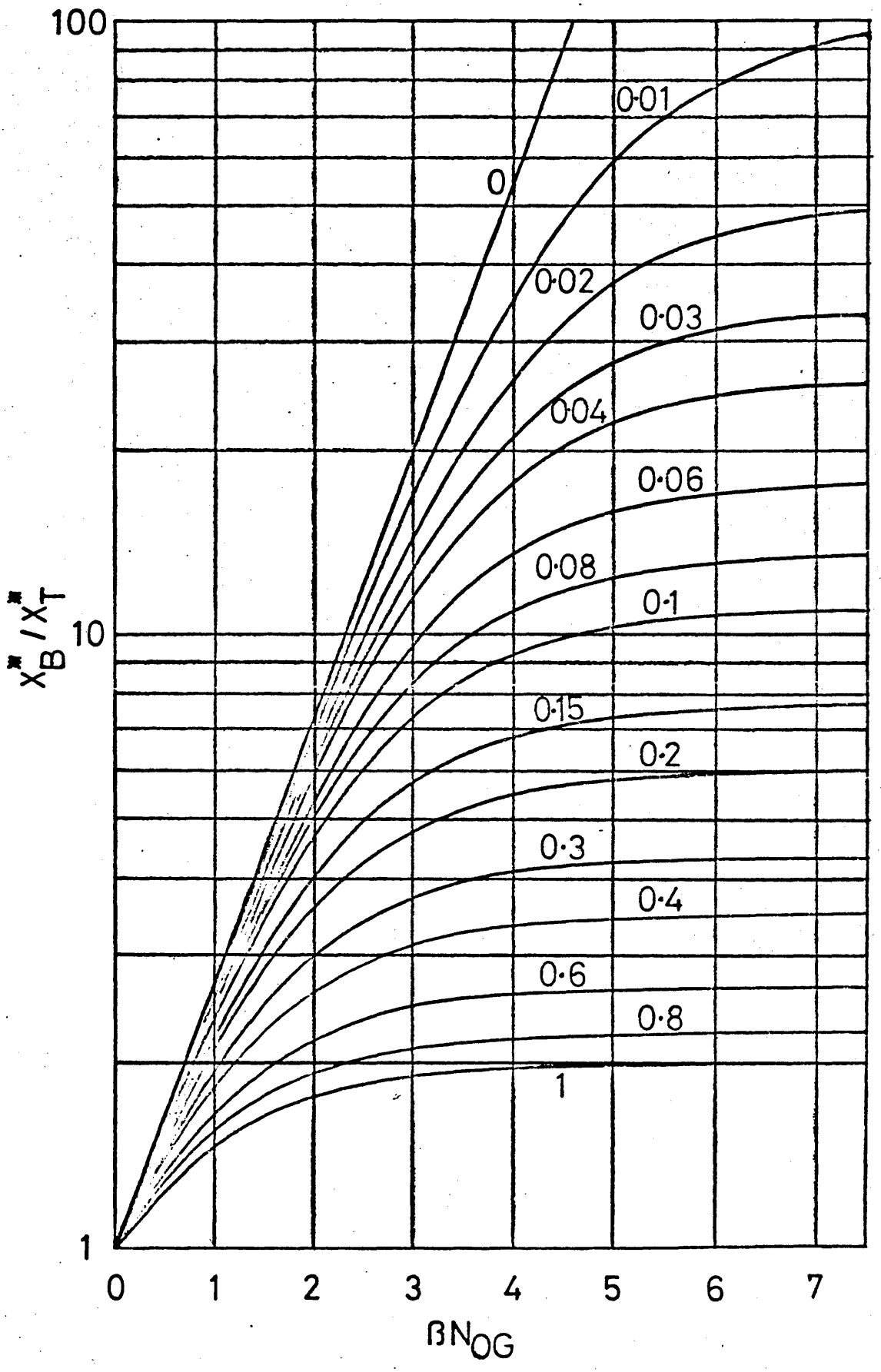


Figure 3.5 x_B^*/x_T^* as a function of $N_{OG}\beta$ with $\alpha R/\varepsilon$ as parameter

Note that from (3.109)

$$N_{OG} = - \ln \{(x_T^*/x_B^*)(1+\alpha R/\varepsilon) - \alpha R/\varepsilon\}/\beta \qquad (3.110)$$

and that this equation can also be obtained from the integral definition of N_{OG}

$$N_{OG} = \int_{y_T^*}^{y_B^*} dy^*/(y^* - x^*/\alpha) \qquad (3.111)$$

Using the operating line

$$y^* = (1+R)\, x^* - R\, x_B^* \qquad (3.112)$$

the calculation of the integral in (3.111) gives

$$N_{OG} = - \ln \{(y_T^*/y_B^*)(\alpha\beta/\varepsilon) - R/[\varepsilon(1+R)]\} / \beta \qquad (3.113)$$

and since from (3.112) the relation between y_T^*/y_B^* and x_T^*/x_B^* is

$$y_T^*/y_B^* = (1+R)\, x_T^*/x_B^* - R \qquad (3.114)$$

equation (3.110) is obtained.

(b) $\underline{r = R = 0}$

In this case, the limits $\lim_{s\to 0} \{s\, G(s) \exp(st^*)\}$ and $\lim_{s\to 0} \{s\, F(s) \exp(st^*)\}$ have to be evaluated using L'Hopital's rule and the steady-state profile is given by (see Appendix E)

$$x^*(z^*,\infty) = \frac{(1 + \tau_T^* + \tau_B^*) \exp(N_{OG}\, \beta\, z^*)}{\tau_T^* + \tau_B^* \exp(N_{OG}\beta) + \{\exp(N_{OG}\beta) - 1\}/(N_{OG}\beta)} \qquad (3.115)$$

where

$$\tau_B^* = \tau_{BL}^* + \tau_{BS}^* = (1+R)(V_{BS}+V_{BL})/(AHh) \qquad (3.116)$$

$$\tau_T^* = \tau_{TL}^* + \tau_{TS}^* = \{(1+R)\ V_{TS} + V_{TL}\}/(AHh) \qquad (3.117)$$

That is, the steady state is now a function of the total dimensionless hold-ups in both reflux sections.

3.2.6.2 The transient terms

The determination of the transient terms of the solution requires the knowledge of the roots of (3.100). This is an implicit equation in s which can be rearranged into

$$\eta_1\gamma_2/(\eta_2\gamma_1) = \exp(2\theta^{\frac{1}{2}}) \qquad (3.118)$$

In general the roots of (3.118) can only be obtained numerically and are found to be real and negative. The minimization routine used to determine these roots numerically is listed in Appendix G. However, for a special situation it is possible to obtain these roots in an explicit form and this case is discussed in section 3.2.7.

Note that $\theta^{\frac{1}{2}}$, η_1, η_2, γ_1 and γ_2 are complex variables in the interval between the roots of the quadratic $\theta(s) = 0$, and these roots are

$$s = -N_{OG}\{(2-\beta) \pm 2(1-\beta)^{\frac{1}{2}}\} \qquad (3.119)$$

Both roots are negative because by definition $\alpha > 1$ and $R \geq 0$, and therefore

$$0 < \beta < 1 \qquad (3.120)$$

and

$$(2 - \beta) - 2(1 - \beta)^{\frac{1}{2}} = \{(1 - \beta)^{\frac{1}{2}} - 1\}^2 > 0 \qquad (3.121)$$

The function $\theta(s)$ is schematically shown in Figure 3.6.

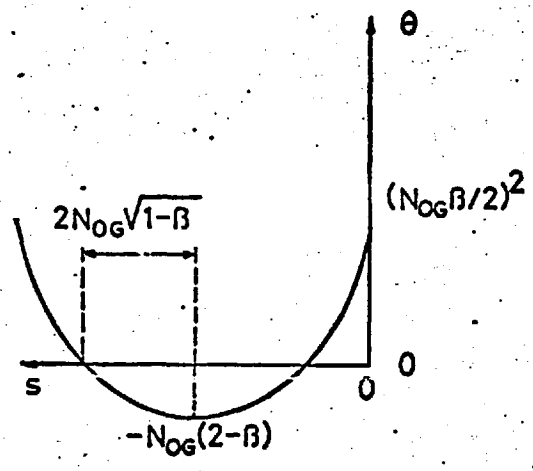


Figure 3.6 Function $\theta(s)$

Once the s_n are known the transient terms can be calculated because

$$\lim_{s\to s_n} \{(s-s_n)F(s)\exp(st^*)\} = \lim_{s\to s_n} \left\{\frac{(s-s_n)}{n_2\gamma_1\exp(D_1)-n_1\gamma_2\exp(D_2)}\right\} \cdot$$

$$\cdot \lim_{s\to s_n}\left(\frac{\{P_2n_1 - P_1\gamma_1\exp(D_1)\}\exp(D_2z^*)-\{P_2n_2-P_1\gamma_2\exp(D_2)\}\exp(D_1z^*)}{s\,(s-K)}\right)\cdot$$

$$\cdot \exp(s_nt^*) \qquad (3.122)$$

The first limit in (3.122) is evaluated using L'Hopital's rule

and the second by direct substitution.

Note that it is implicit in the derivation that $s = K$ is not a root of (3.118). Although no proof of this statement can be offered (because A_2 is obtained by a numerical fit), K was always found to be positive in contrast with the s_n which are negative. Also note that no distinction needs to be made from now on between the cases $K = 0$ and $K \neq 0$, because the second limit in (3.122) is equal to the equivalent limit for the case $K = 0$ (in terms of Q_1 and Q_2).

Finally the full solution can be expressed as

$$x^*(z^*,t^*) = x^*(z^*,\infty) + \sum_{s_n} C(z^*,s_n)\exp(s_n t^*) \qquad (3.123)$$

where $x^*(z^*,\infty)$ is either given by (3.107) or (3.115) depending on the values of r and R, and the coefficients $C(z^*,s_n)$ are given by

$$C(z^*,s_n) = \frac{\{\{P_2\eta_1 - P_1\gamma_1\exp(D_1)\}\exp(D_2 z^*) - \{P_2\eta_2 - P_1\gamma_2\exp(D_2)\}\exp(D_1 z^*)\}_{s=s_n}}{s_n\,(s_n - K)\left(\frac{d}{ds}\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}\right)_{s=s_n}} \qquad (3.124)$$

3.2.7 Explicit case

The roots of (3.118) can be made explicit if

$$\eta_1\gamma_2 = \eta_2\gamma_1 \qquad (3.125)$$

The non-trivial solution of this equation is

$$\Phi = \Psi \qquad (3.126)$$

which can only be satisfied for all s, if

$$\Phi = \Psi = 1 \tag{3.127}$$

i.e., if

$$r = R = \tau^*_{BL} = \tau^*_{BS} = \tau^*_{TL} = \tau^*_{TS} = 0 \tag{3.128}$$

That is, the roots of (3.118) can only be made explicit for the total reflux operation of a column whose reflux sections have negligible hold-ups. For this case equation (3.118) becomes

$$\exp(2\theta^{\frac{1}{2}}) = 1 = \exp(2\pi i n) \text{ with } n = 0,1,2,.. \tag{3.129}$$

Therefore

$$\theta_n = - \pi^2 n^2 \tag{3.130}$$

and using (3.66), (3.83), (3.84) and (3.128)

$$s_n = - N_{OG}(\alpha+1)/\alpha \pm 2 N_{OG}\{1/\alpha - (\pi n/N_{OG})^2\}^{\frac{1}{2}} \tag{3.131}$$

with n = 0,1,2,... The two roots for n = 0 are the roots of $\theta(s) = 0$ given by (3.119).

Note that due to the appearance of $\exp(s_n t^*)$ in the transient terms, the approach of the system to the steady state is ultimately controlled by the largest s_n (smallest in absolute value). This corresponds to the "plus" sign in (3.131), i.e.,

$$s_0 = - N_{OG}\{(\alpha+1) - 2\alpha^{\frac{1}{2}}\} / \alpha \tag{3.132}$$

Note that expanding $\alpha^{\frac{1}{2}}$ in a Taylor series

$$\alpha^{\frac{1}{2}} = (1+\epsilon)^{\frac{1}{2}} = 1 + \epsilon/2 - \epsilon^2/4 + \ldots \qquad (3.133)$$

and neglecting terms of order greater than two, it is found that

$$s_0 \simeq - N_{OG}\, \epsilon^2/(2\alpha) \qquad (3.134)$$

which shows the well-known (65,67) dependence on these two parameters of the rate of approach to the steady state.

Now, since the roots are explicitly given by (3.131), the coefficients of the transient terms can be calculated from (3.124) and, after considerable manipulation (see Appendix F), they are found to be

$$C(z^*,s_n) = \frac{- 2\pi n\beta \exp(\lambda_n z^*)\, \{1 - (-1)^n \exp(-\lambda_n)\}}{s_n^2\, \{s_n + N_{OG}\,(2-\beta)\}} \cdot$$

$$\cdot \{(s_n - N_{OG}\beta) \sin \pi n z^* - 2\pi n \cos \pi n z^*\} \qquad (3.135)$$

where λ_n is the value of λ for $s = s_n$. From (3.115), (3.128) and (3.135) the full solution at the bottom of the column ($z^*=1$) is

$$x^*(1,t^*) = \frac{N_{OG}\beta \exp(N_{OG}\beta)}{\exp(N_{OG}\beta)-1} - 4\pi^2\beta \sum_{n=1}^{\infty} \frac{n^2\{1-(-1)^n \exp(\lambda_n)\}}{s_n^2\{s_n+N_{OG}(2-\beta)\}} \exp(s_n t^*) \qquad (3.136)$$

and since it is a function of only two parameters (α and N_{OG}), if one is known the other can be measured by a single experimental determination of $x^*(1,t^*)$ at any particular t^*. Figure 3.7 was obtained using the first ten terms of (3.136) and allows

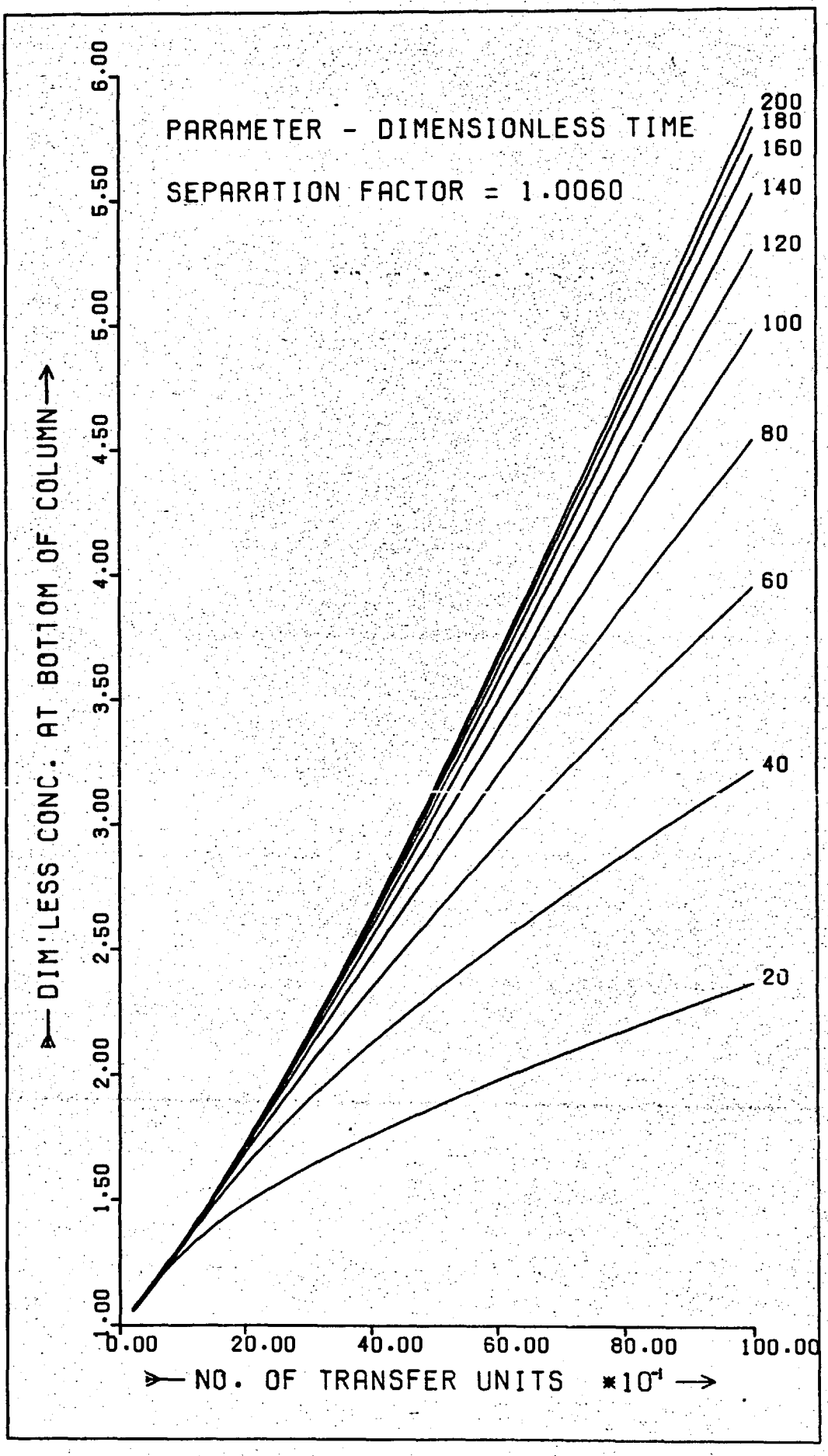


Figure 3.7 The estimation of N_{OG} from a single value of $x^*(1,t^*)$, when $r = R = \tau_B^* = \tau_T^* = 0$ and $\alpha = 1.006$.

the number of transfer units in any packed column to be determined for systems with $\alpha = 1.006$.

In conclusion, for this special and rather restrictive case it is possible to arrive at an explicit series of transient terms and to assess how the approach to steady state depends on α and N_{OG}. The influence of r, R and the reflux time-constants in a general situation can not, however, be determined in this way.

3.3 Applications of the model

Two particular application areas of this model will now be discussed. They are the experimental determination of the column separation performance using transient data and, the simulation of the column start-up when the feed and product flow-rates are not constant.

3.3.1 Parameter estimation

The slow dynamic behaviour of packed columns mentioned in section 2.4, has very undesirable implications from a research point of view. If only a steady-state model is available, the column separation performance can only be experimentally assessed after the attainment of a concentration steady state. This means that the equipment has to be operated continuously during long periods of time, thus incurring in large operating expenditure. In addition, the maintenance of steady-state flow conditions during such long periods requires additional control equipment, thus also affecting the capital costs. A method that allow the prediction of steady-state performance from start-up data is now proposed.

Numerical calculations have shown that the series in equation (3.123) converges very rapidly, because

$$|s_1| \ll |s_2| < |s_3| < \ldots \qquad (3.137)$$

and

$$|C(z^*,s_1)| >> |C(z^*,s_2)| > |C(z^*,s_3)| > \ldots \qquad (3.138)$$

particularly near both ends of the column (see example in Tables 3.4 and 3.5). Therefore, after an initial period of operation whose magnitude depends on the reflux time-constants, all but the first term can be neglected. Hence, for $z^* = 1$ the solution (3.123) can be approximated to

$$x^*(1,t^*) \simeq x^*(1,\infty) + C(1,s_1)\exp(s_1 t^*) \qquad (3.139)$$

or

$$\ln\{x^*(1,\infty) - x^*(1,t^*)\} \simeq s_1 t^* + \ln\{-C(1,s_1)\} \qquad (3.140)$$

Thus, given a set of experimental points $x^*(1,t^*)$ at different times t^* it is possible to optimize the steady-state concentration at the bottom of the column $x^*(1,\infty)$ that gives the "best" log-linear fit of the data. And since $x^*(1,\infty)$ is only a function of α, N_{OG} and other known parameters (either τ_B^* or τ_T^* for total reflux operation or r and R for production conditions), it is thus possible to estimate N_{OG} if α is known, and vice-versa, simply by following the approach to steady state at the bottom of the column.

The estimation of $x^*(1,\infty)$ was performed by a standard two-parameter minimization routine, which only requires function evaluations (no derivatives). The function to be minimized is arrived at by using the least-squares technique, and the necessary constraints are that $x^*(1,\infty)$ has to be greater than any of the $x^*(1,t^*)$ and of the same order of magnitude as the larger $x^*(1,t^*)$.

A computing programme (TRUNIT) implementing this method was written and a documented listing is presented in Appendix G.

This version was run on the I.C.C.C. CDC 6400 and Cyber 7314 computers under the Kronos 2.1 operating system. In general terms, the program optimizes the number of transfer units in a given column from transient start-up data, and then successively computes the steady-state concentration profile, a user-specified number of roots of equation (3.118), the same number of coefficients of the transient terms at several values of z*, the transient concentration profiles at a set of user-specified times and, the approach to steady state at both ends of the column. Moreover, it produces three microfilm plots of the log-linear fit used to estimate N_{OG}, the transient and steady-state concentration profiles, and the concentrations at both ends of the column as a function of time.

The total computing costs are very small. Storage requirements are under 20 K and execution times (including the microfilm plots) are of the order of ten seconds.

This method was first tested by simulation. The transient performance of the installed column (h = 510 cm and A = 5 cm^2) was computed for a given set of conditions, which included the value H_{OG} = 1.5 cm. Six calculated values of the concentration at the bottom of the column for six different times were then treated by TRUNIT and the results are shown in Figures 3.8 and 3.9. The estimated value of H_{OG} was 1.52 cm (relative error of 1.3%).The method was subsequently used in the treatment of the transient data (see section 5.3), and proved to be very satisfactory even for rather scattered data.

3.3.2 The column start-up

It was previously mentioned that in the case of isotope separation processes the dynamic behaviour of packed columns can be

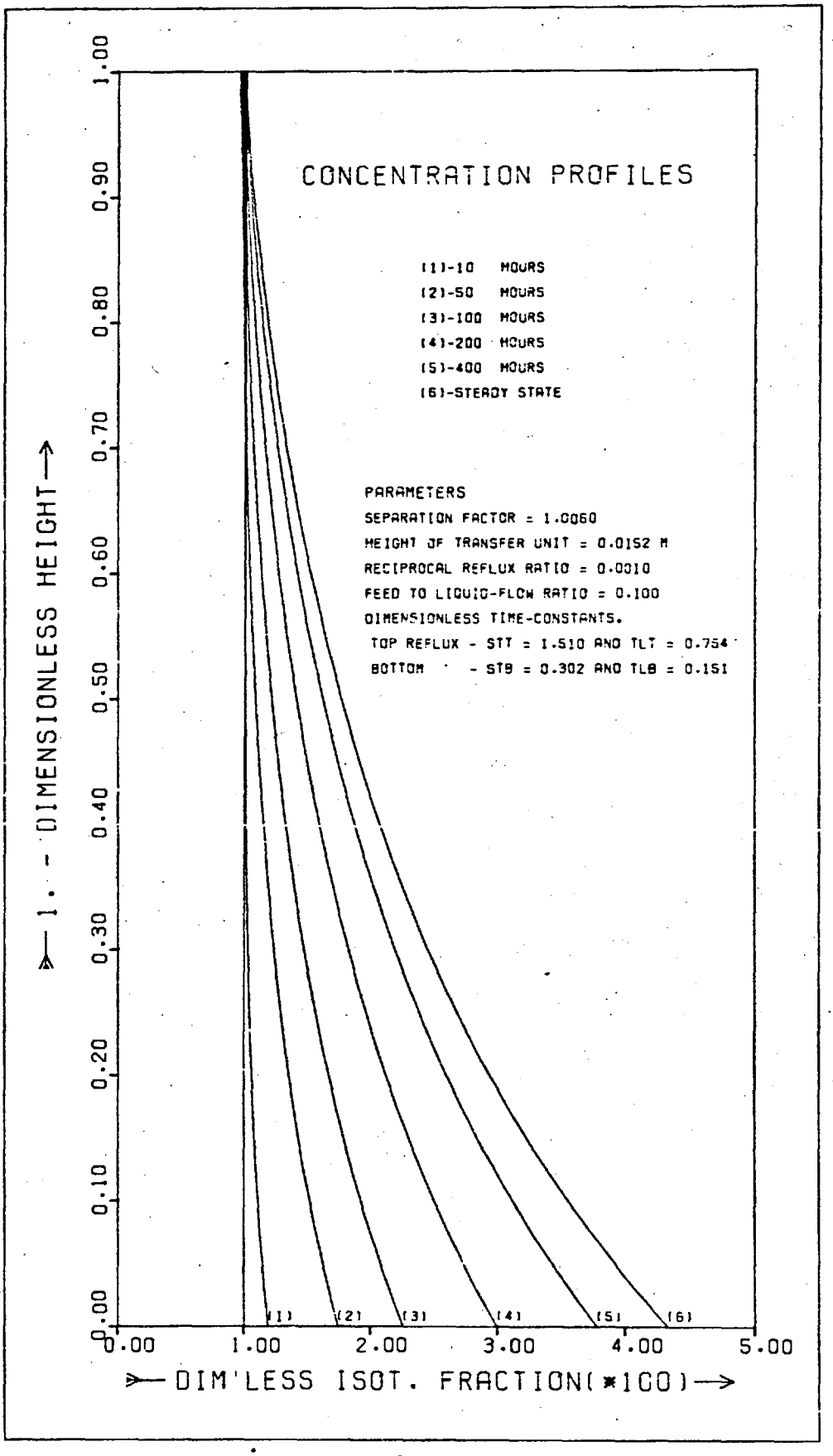
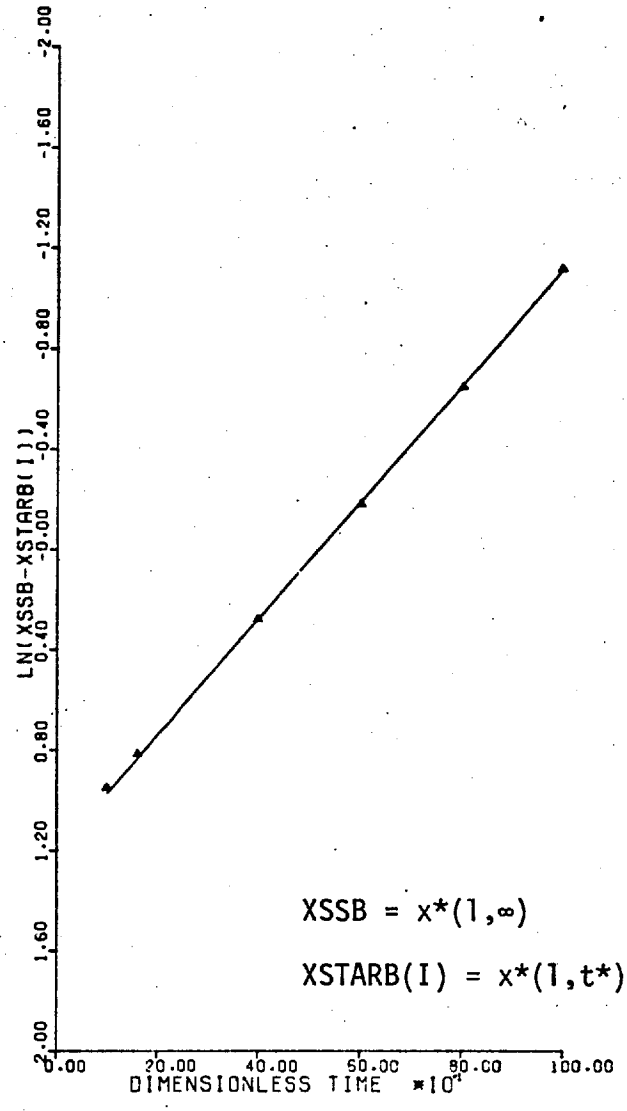
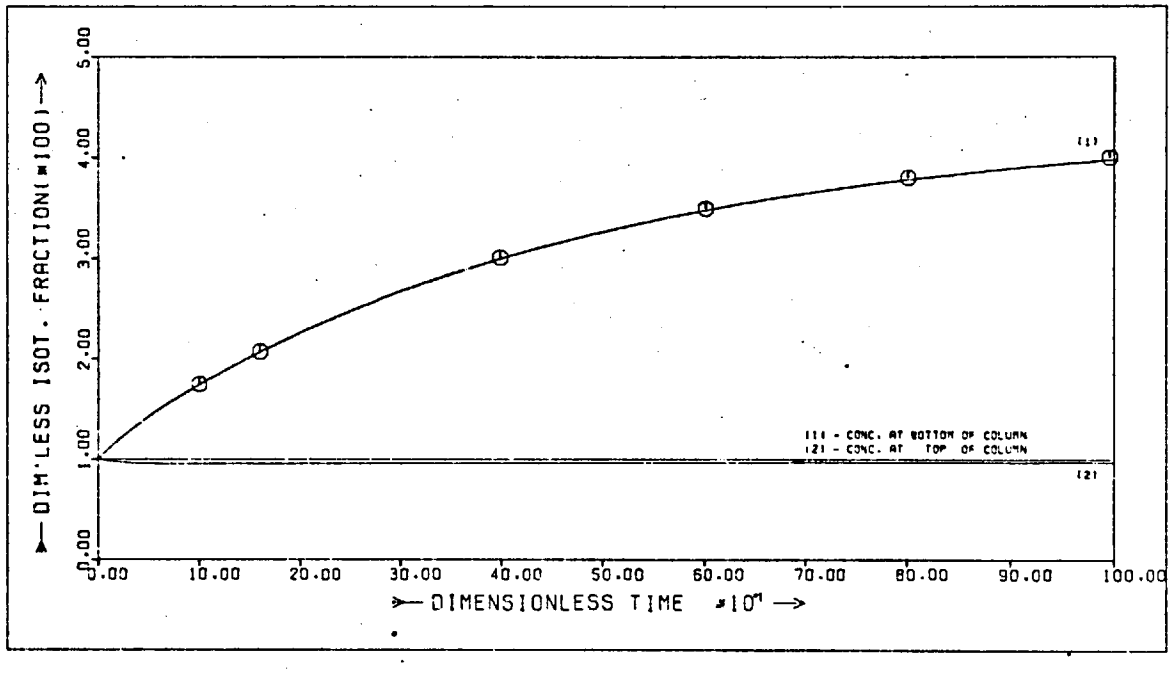


Figure 3.8 Five transient and the steady-state concentration profiles for the simulated example.



(a) The estimation of $x^*(1,\infty)$



(b) Time dependence of the concentration at both ends of the column.

Figure 3.9 Simulated example

extremely slow. Therefore, the optimization of the column start-up can be, in these cases, particularly rewarding.

The consideration of optimum control problems is outside the scope of the present work. However, the dynamic model derived in section 3.2 can be used to simulate the column start-up for a variety of conditions, provided that two input controls (the feed and product flow-rates) are assumed stepwise functions of time.

For exemplification purposes, consider the simplest possible case, i.e. only one discontinuity in $r(t^*)$ at the time t_r^* and another in $R(t^*)$ at t_R^*, according to Figure 3.10.

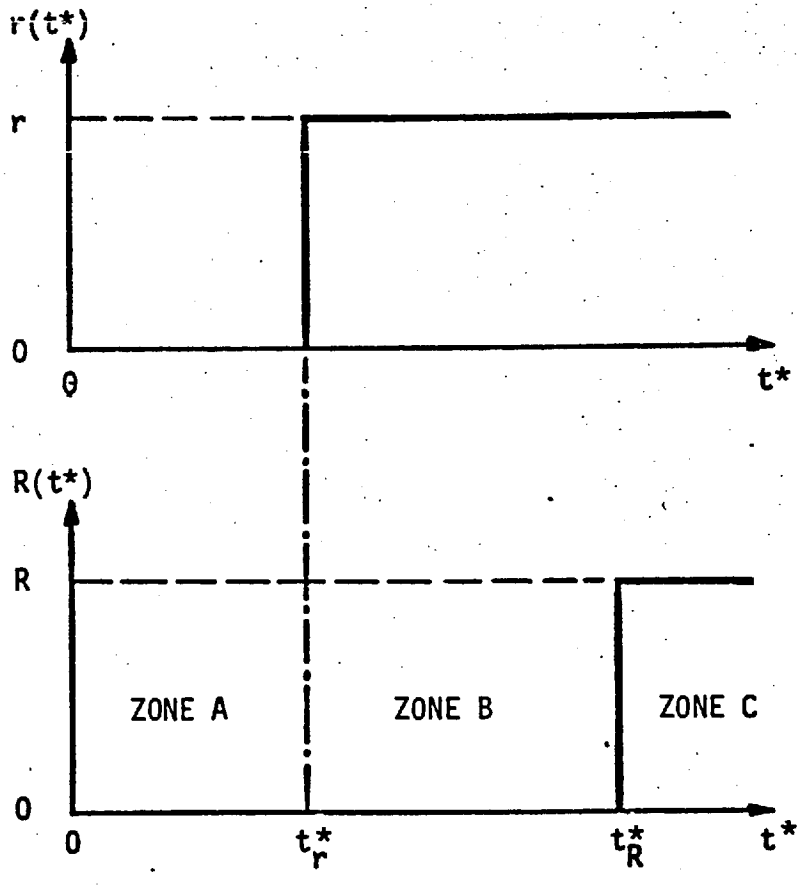


Figure 3.10 Unit-step functions

The start-up period can now be divided into three zones:

(a) A "total reflux" zone (A), where $r(t^*) = R(t^*) = 0$;

(b) A "build-up" zone (B), where $r(t^*) = r$ and $R(t^*) = 0$;

(c) A "production" zone (C), where $r(t^*) = r$ and $R(t^*) = R$.

That is, in each of these intervals both $r(t^*)$ and $R(t^*)$ are constant.

The first zone is covered by the model proposed in section 3.2, using a constant initial condition, i.e. with $f(z^*) = 1$ ($A_1 = 0$ and $A_3 = 1$ or $A_1 + A_3 = 1$ and $A_2 = 0$). The transient concentration profile thus computed for $t^* = t_r^*$ is numerically fitted to a new function $f(z^*)$, which is then used as the "initial" condition for zone B. Similarly, the concentration profile at t_R^* is again fitted to $f(z^*)$ and this is then used as the "initial" condition for zone C. Thus, the whole period can be modelled by simply shifting the time origin at each discontinuity in either $r(t^*)$ or $R(t^*)$.

A numerical example is shown in Table 3.1. The steady-state profiles indicated for the zones A and B are those that would eventually be attained if the feed and product flow-rates were not started. Details of the two fittings at $t_r = 40$ hours and $t_R = 400$ hours are shown in Table 3.2.

Table 3.2 The fittings of $f(z^*)$

TIME	A_1	A_2	A_3	STANDARD DEVIATION
t_r	.073	2.464	.774	.72 %
t_R	.531	2.133	.452	.09 %

A two-exponentials function $f(z^*)$ would result in a better fit, particularly when the discontinuities occur at very small times, but even the adopted function gives quite acceptable errors.

Table 3.1 Concentration profiles

ZONE	z* \ TIME (h)	0.	10	40	50	120	250	400	600	STEADY STATE
TOTAL REFLUX (A)	0.	1.	.952	.831						.412
	.1	1.	.968	.864						.505
	.2	1.	.980	.898						.619
	.3	1.	.989	.935						.759
	.4	1.	.996	.978						.931
	.5	1.	1.003	1.029						1.142
	.6	1.	1.013	1.094						1.400
	.7	1.	1.029	1.178						1.717
	.8	1.	1.059	1.290						2.106
	.9	1.	1.110	1.440						2.582
	1.	1.	1.197	1.642						3.167
BUILD-UP (B)	0.			.847	.909	.959	.971	.980		1.006
	.1			.867	.915	1.002	1.060	1.108		1.234
	.2			.895	.929	1.057	1.170	1.265		1.513
	.3			.927	.955	1.125	1.306	1.459		1.855
	.4			.969	.994	1.212	1.475	1.699		2.275
	.5			1.025	1.048	1.324	1.687	1.994		2.790
	.6			1.095	1.123	1.467	1.950	2.361		3.421
	.7			1.183	1.223	1.650	2.279	2.814		4.195
	.8			1.297	1.355	1.885	2.690	3.375		5.145
	.9			1.445	1.529	2.187	3.205	4.071		6.309
	1.			1.634	1.761	2.575	3.849	4.934		7.737
PRODUCTION (C)	0.							.982	.974	.972
	.1							1.109	1.075	1.065
	.2							1.265	1.203	1.183
	.3							1.458	1.365	1.332
	.4							1.698	1.571	1.522
	.5							1.994	1.832	1.763
	.6							2.360	2.162	2.068
	.7							2.814	2.580	2.456
	.8							3.377	3.109	2.948
	.9							4.071	3.780	3.572
	1.							4.934	4.629	4.364

Variables employed: $\alpha = 1.006$
$N_{OG} = 340$
$t_r = 40$ hours
$t_R = 400$ hours
$r = .1$
$R = .001$

$h = 510$ cm
$A = 5$ cm^2
$H = .13$
$L_v = 2 \times 10^2$ mm^{3}s^{-1}
$V_{TS} = 750$ cm^3
$V_{BS} = 150$ cm^3
$V_{BL} = V_{TL} = 0.$

Note that in this example, the concentration at the bottom of the column at t_R = 400 hours has already reached a level greater than the production steady state. That is, in zone C there is a continuous decrease in concentration towards the steady-state profile, in contrast with zones A and B in which there is a continuous build-up of enriched material.

This behaviour is more clearly shown in Figure 3.11 where the concentration at the bottom of the column is plotted against time for five different situations. The product withdrawal time t_R^* was kept constant and five different values of t_r^* were considered. All the other variables were as indicated in Table 3.1. This plot exemplifies the obvious conclusion that the quickest path to a production steady state is obtained by starting the feed stream at $t^* = 0$ and initiating production as soon as the concentration at the bottom of the column reaches the design level.

A Fortran IV computing program (STARTUP) that implements this calculation technique was written, and is listed in Appendix H. Storage requirements are under 21 K and the total compilation and execution time for the example shown in Table 3.1 was less than thirteen seconds.

More realistic start-up situations in which the feed and product flow-rates are gradually increased, can also be treated by this method, by considering a larger number of zones. The present version of STARTUP shows that for most applications this extension should not prove prohibitive in terms of computing time.

3.4 An approximate solution

In the present notation, the similarity conditions (2.27) and (2.28) can be expressed as

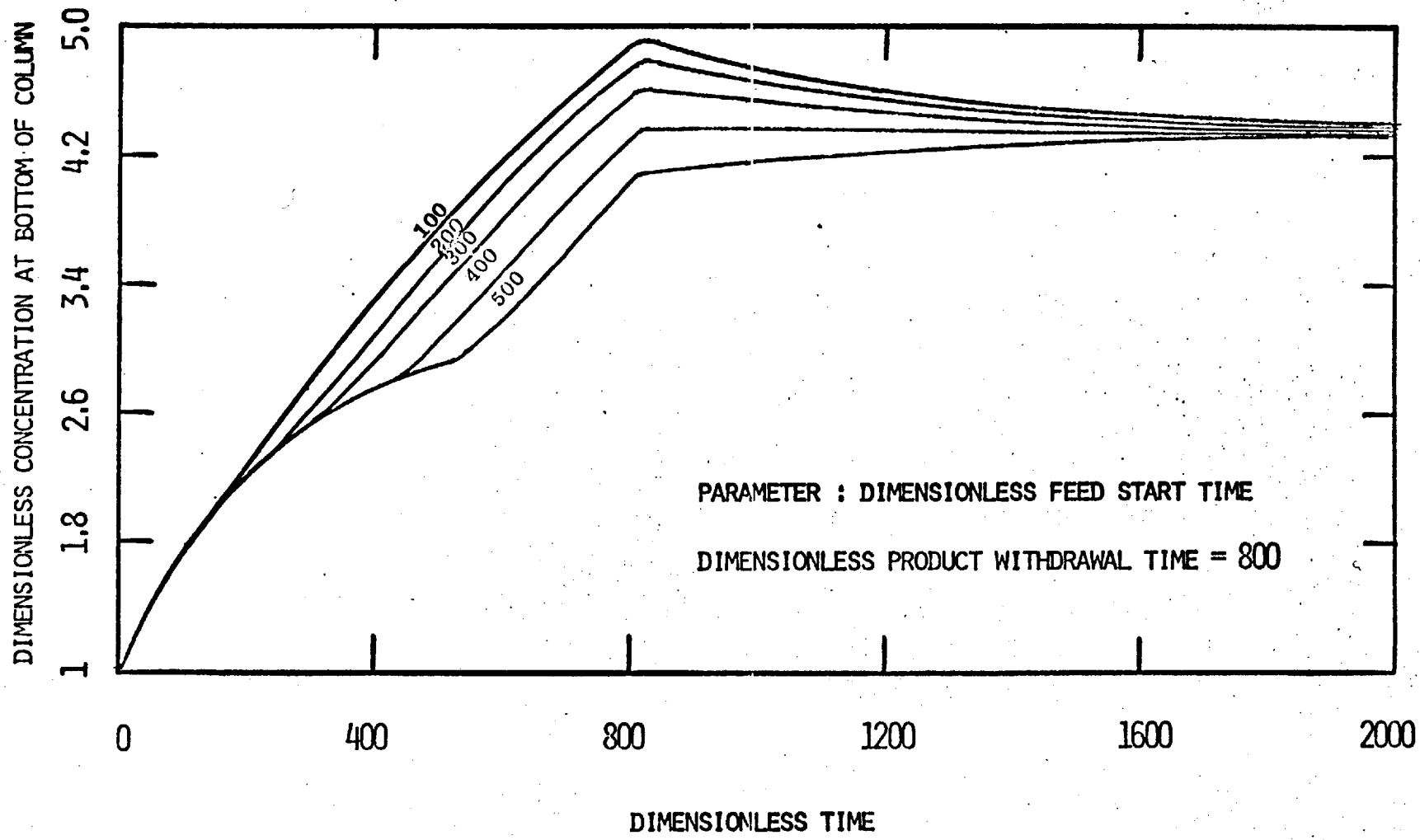


Figure 3.11 Time dependence of the concentration at the bottom of the column, for $t_R^* = 800$ and for five different values of t_r^* (other variables as in Table 3.1)

$$\frac{x^*(z^*,t^*) - 1}{x^*(z^*, \infty) - 1} = f(t^*) \qquad (3.141)$$

and

$$\frac{x^*(z^*,t^*) - 1}{x^*(1,t^*) - 1} = g(z^*) \qquad (3.142)$$

Since there is a height z_0^* defined by

$$x^*(z_0^*,\infty) = 1 \qquad (3.143)$$

and equation (3.142) is supposed to be satisfied at any height z^* as close to z_0^* as required, condition (3.142) implies that all the transient profiles contain z_0^*. This suggests that approximate solutions for the zones above and below z_0^* can be obtained (using the same method as in section 3.2) with the boundary condition

$$x^*(z_0^*,t^*) = 1 \quad \text{for all } 0 \leq t^* \leq \infty \qquad (3.144)$$

Two examples of the concentration profiles produced by these solutions are shown in Figures 3.12 and 3.13. In Figure 3.12 the total hold-ups of the two reflux sections are zero. It is clear that the transient profiles above z_0^* and for small times are not similar. This means that equation (3.144) is not sufficient for the condition (3.142) to be satisfied. In the second case (Figure 3.13) the hold-ups in the reflux sections are V_{TS} = 484 cm^3 and V_{BS} = = 250 cm^3 (the relation between V_{TS} and V_{BS} was chosen so that z_0^* is the same in both cases). All the other variables are as in the first case. The hold-ups in the reflux sections are now responsible for a much slower approach to the same steady-state. This can be detected by comparing the times of the transient profiles in the two cases, and is more clearly shown in Figure 3.14, where the

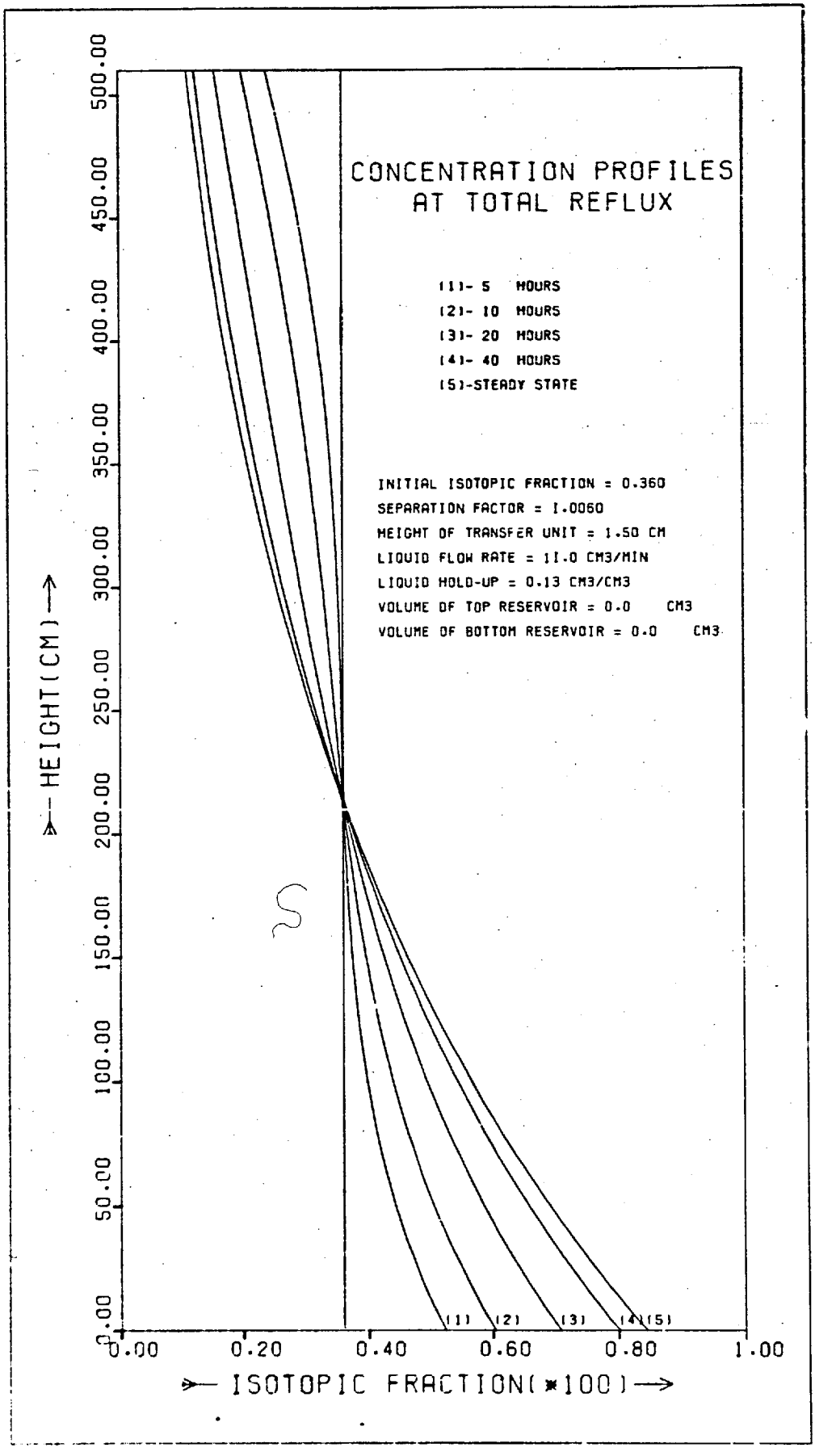


Figure 3.12 Approximate solution (no hold-ups in the reflux sections).

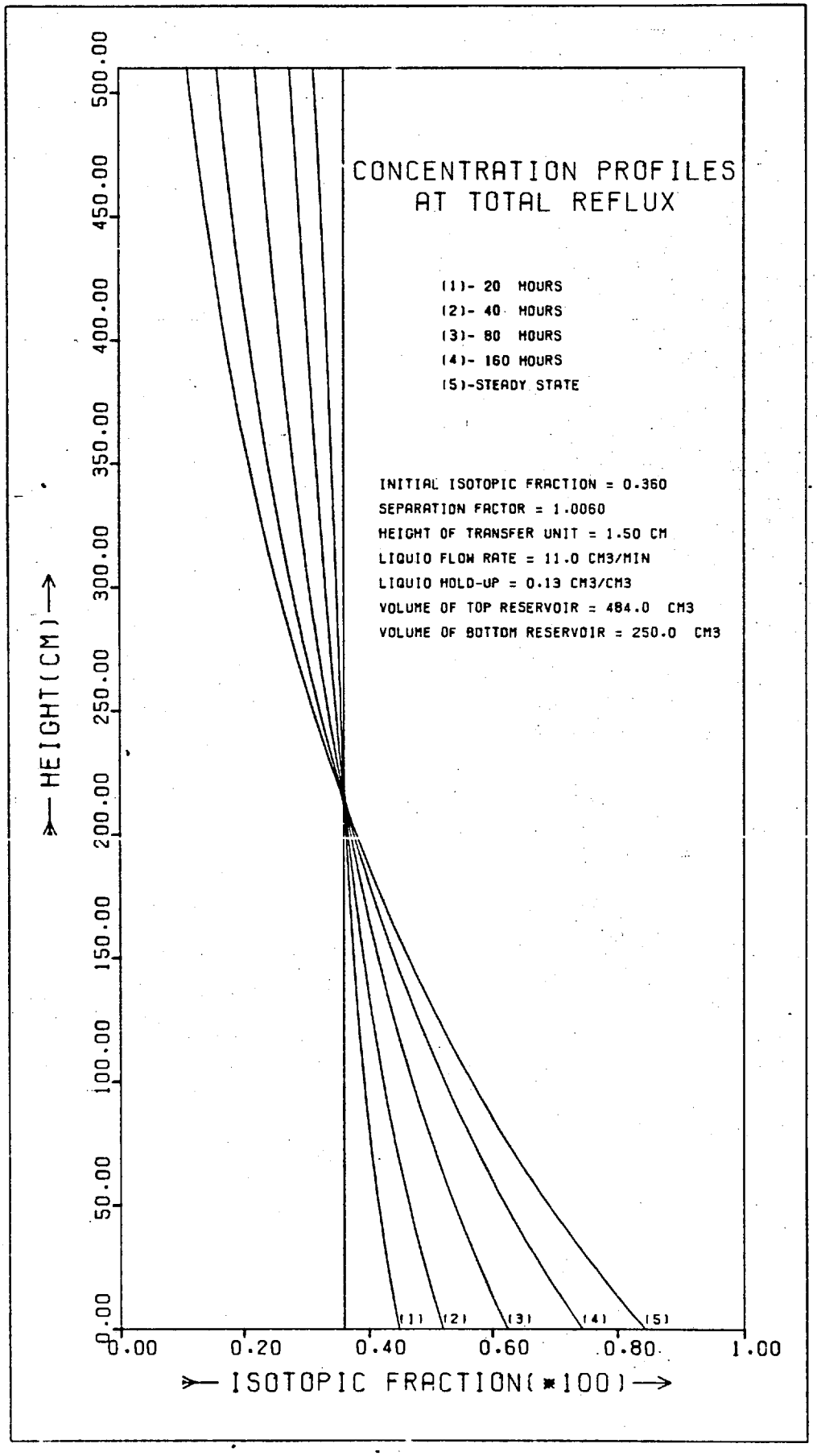
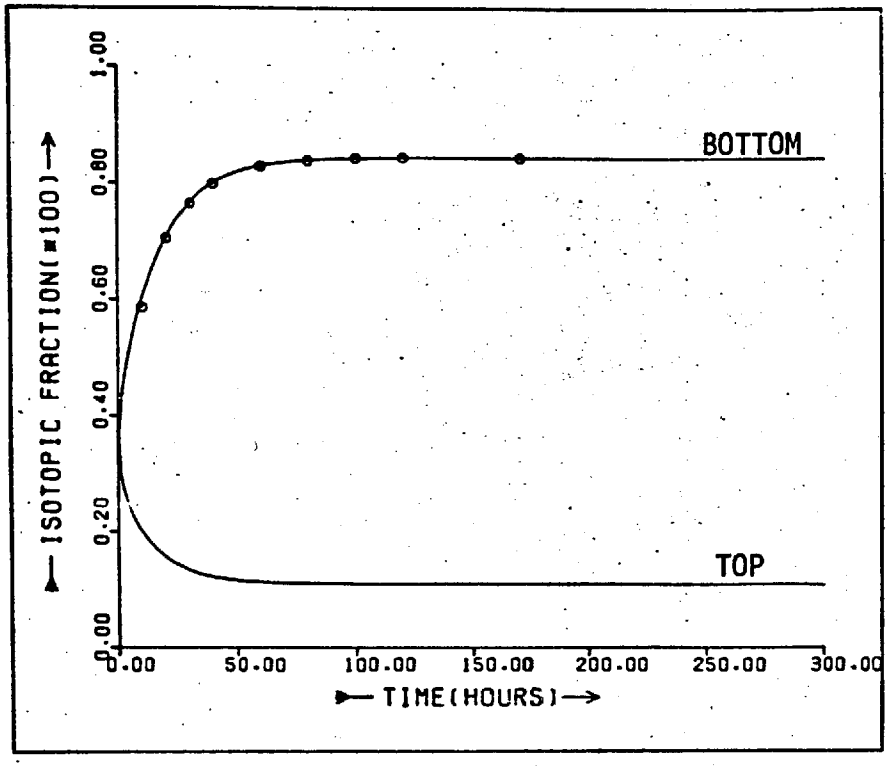
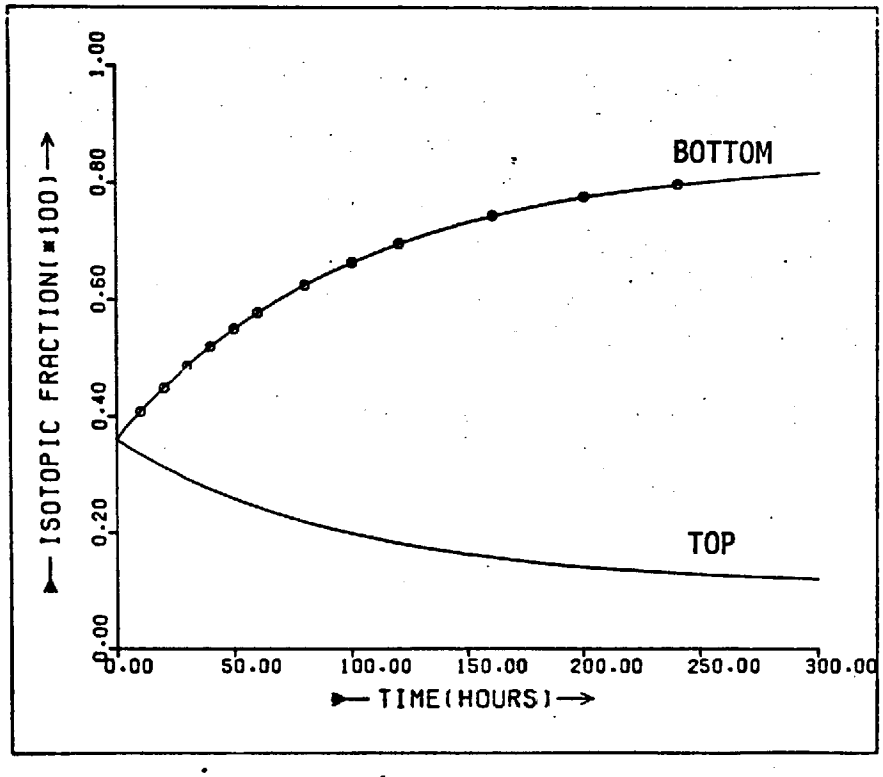


Figure 3.13 Approximate solution (with hold-ups in the reflux sections but with z_0^* as in Figure 3.12)



(a) Case shown in Figure 3.12



(b) Case shown in Figure 3.13

Figure 3.14 Time dependence of the concentration at both ends of the column.

evolution with time of the concentrations at the bottom and top of the column, for the two examples, are plotted.

Note that the similarity conditions (3.141) and (3.142) are not exact solutions of equation (3.65). A separation of variables solution of the problem involves not only leaving-out the cross--derivative term in (3.65), but also the use of less general boundary conditions. However, this analysis confirms the asymptotic character (near steady state) of the similarity solutions. This was mentioned in greater detail in section 2.4, where the available experimental evidence was also quoted. The present approximate solution based on the constancy of z_o^* supports those views.

Similar conclusions can also be drawn from Table 3.3 and Figure 3.15. These show the profiles obtained by the exact solution (section 2.3) for the same conditions as in Figure 3.13. Although, strictly speaking, the transient profiles for very short times do not contain z_o^*, it seems that the condition (3.144) is reasonably accurate . For reference purposes, the values of s_n and $C(z^*,s_n)$ computed for this example are shown in Tables 3.4 and 3.5, respectively.

All these considerations about the validity of approximate solutions may also be used to support the parameter estimation method proposed in section 3.3.1. Note that from (3.139)

$$\frac{x^*(1,\infty) - x^*(1,t^*)}{x^*(z^*,\infty) - x^*(z^*,t^*)} = \frac{C(1,s_1)}{C(z^*,s_1)} = g(z^*) \qquad (3.145)$$

that is, the use of only the first of the transient terms implies a similarity condition which is analogous to (3.142).

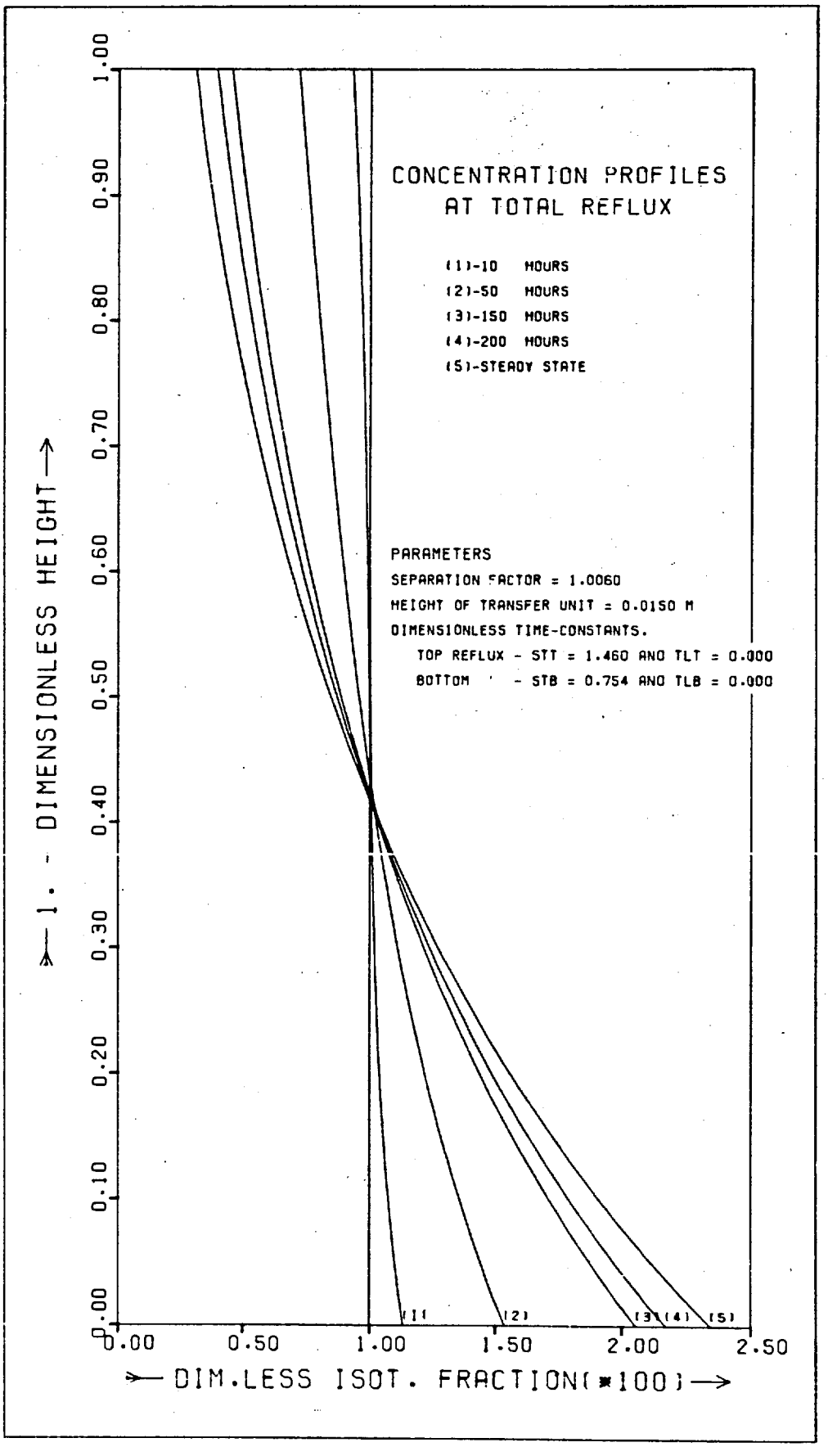


Figure 3.15 Exact solution for the example of Figure 3.13

Table 3.3 Transient and steady-state concentration profiles (exact solution) for the example with V_{TS} = = 484 cm^3 and V_{BS} = 250 cm^3.

t(hours) / z* \ t*	10	50	150	200	STEADY STATE
0.	.9292	.7184	.4541	.3949	.3065
.1	.9520	.7595	.5132	.4580	.3756
.2	.9694	.8024	.5830	.5337	.4603
.3	.9819	.8483	.6661	.6251	.5641
.4	.9911	.8990	.7659	.7360	.6913
.5	.9987	.9572	.8868	.8709	.8472
.6	1.0070	1.0263	1.0341	1.0358	1.0382
.7	1.0191	1.1112	1.2147	1.2378	1.2723
.8	1.0396	1.2184	1.4372	1.4861	1.5591
.9	1.0748	1.3563	1.7121	1.7918	1.9107
1.	1.1336	1.5360	2.0528	2.1686	2.3415

Table 3.4 Values of the first eight roots of (3.118) for the example shown in Table 3.3.

s_1	-.005155
s_2	-.041496
s_3	-.129550
s_4	-.274336
s_5	-.476677
s_6	-.736787
s_7	-1.054781
s_8	-1.430760

Table 3.5 Values of the coefficients $C(z^*,s_n)$ for the example shown in Table 3.3.

z^*	$C(s_1)$	$C(s_2)$	$C(s_3)$	$C(s_4)$	$C(s_5)$	$C(s_6)$	$C(s_7)$	$C(s_8)$
0.	.687996	.003759	.001462	.000113	.000096	.000024	.000008	.000004
.1	.641414	-.004102	-.008311	-.001386	-.001904	-.000626	-.000494	-.000260
.2	.571816	-.013139	-.016494	-.001926	-.001409	-.000020	.000340	.000353
.3	.475351	-.022217	-.018815	-.000733	.001497	.000827	.000423	-.000128
.4	.347824	-.029937	.012756	.001483	.002821	.000011	-.000773	-.000320
.5	.184692	-.034785	.000827	.002831	.000020	-.001091	-.000010	.000629
.6	-.018919	-.035347	.017298	.001776	-.003639	.000006	.001060	-.000431
.7	-.268201	-.030547	.029525	-.001281	-.002430	.001439	-.000762	-.000286
.8	-.568626	-.019894	.030675	-.003885	.003038	-.000035	-.000886	.001010
.9	-.925913	-.003693	.017526	-.003387	.005173	-.001898	.001687	-.001013
1.	-1.345963	.016816	-.007126	.000534	-.000413	.000080	-.000029	-.000007

CHAPTER FOUR

EXPERIMENTAL

4.1 Pilot plant

In order to measure the steady-state and transient performances of a packed column operating on the present type of ^{15}N separation processes, a pilot plant was designed and constructed. Details of the plant are subsequently reported.

4.1.1 General description

A schematic flow diagram of the complete plant is shown in Figure 4.1 and the principal pieces of equipment are identified in Table 4.1.

Table 4.1 Plant equipment

CODE	DESCRIPTION
T1	^{15}N separation column
T2	Ammonia-solvent stripping column
E1	Reboiler
E2	Partial condenser
E3	Ammonia absorption column
D1	Solvent storage tank
D2	Ammonia waste disposal tank
LC	Level controller

The plant was designed to operate at atmospheric pressure and room temperature and is composed of three main sections:

(a) The ^{15}N separation column T1 where the gas-liquid transfer of $^{15}NH_3$ takes place. The liquid phase is a saturated solution of ammonia and the gas phase is essentially ammonia containing the amount of solvent corresponding to its vapour tension

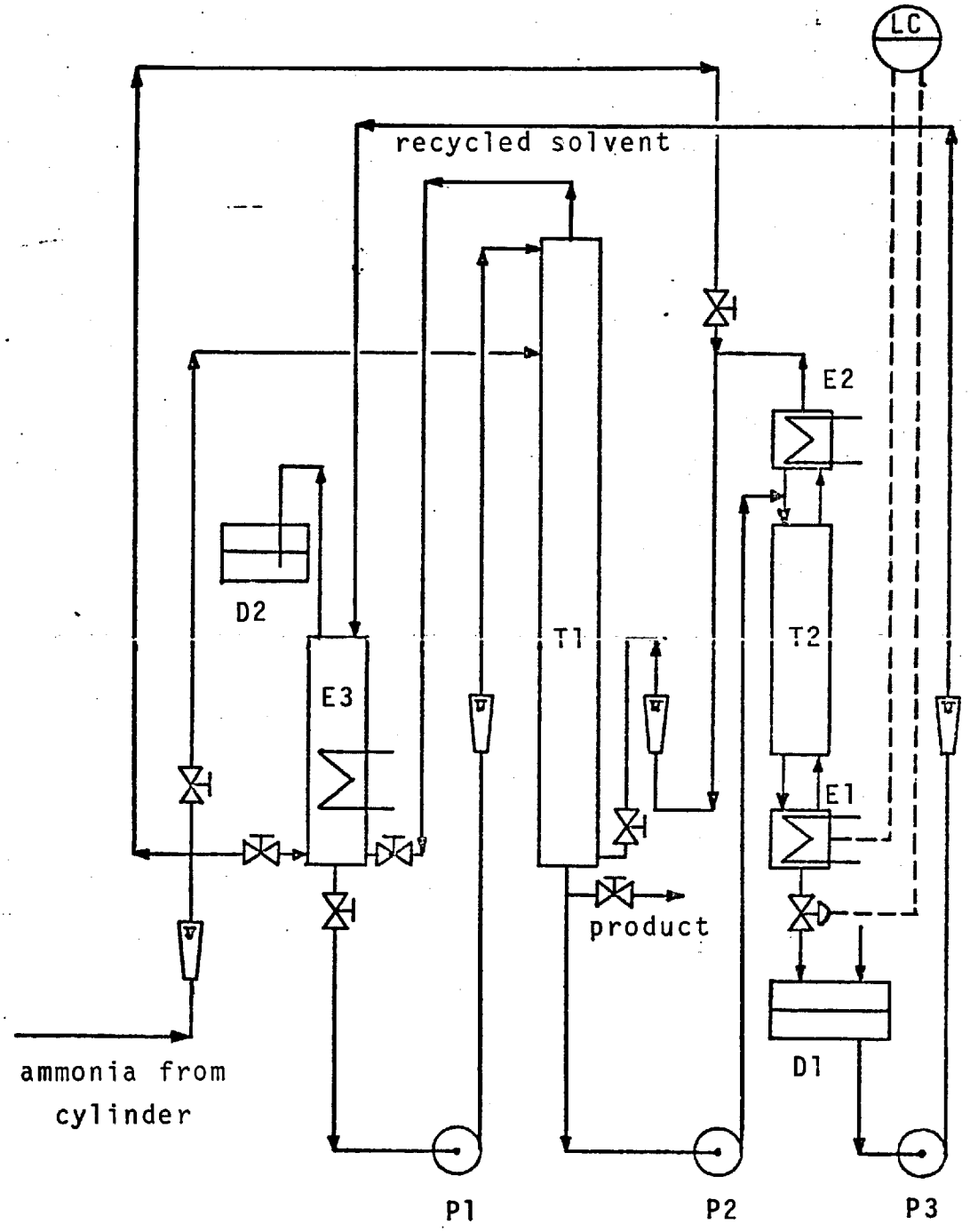


Figure 4.1. Pilot plant flow-sheet

at the operating conditions;

(b) A top reflux section E3 where the gas stream is absorbed in the recycled solvent in order to produce the liquid solution;

(c) A bottom reflux section T2, E1 and E2 where the liquid phase is stripped of ammonia by solvent vapour.

These three sections could be installed one on top of the other, in which case the total liquid hold-up would be much smaller and only one pump would be required. However, in the present plant they were mounted side by side, because the total available room height was used for the separation column.

4.1.2 Equipment

Both the columns and heat exchangers were in QVF glass (J.A. Jobling & Co. Ltd.), with the dimensions shown in Tables 4.2 and 4.3.

Table 4.2 Columns characteristics

EQUIPMENT	DIMENSIONS		PACKING	
	Height(cm)	Diameter(cm)	Type	Size(mm)
T1	510	2.5	Raschig	2
T2	100	7.5	Dixon	3

Table 4.3 Heat transfer equipment

EQUIPMENT	HEAT TRANSFER AREA (dm^2)
E1	6.3
E2	20.
E3	20.

Owing to the corrosive properties of ammonia and its solutions, P.T.F.E. gaskets were used throughout.

Micrometering pumps (type 2/30 D by Metering Pumps Ltd.) with mechanically actuated diaphragms were used, the maximum pumping capacity being of the order of .5 cm^3 s^{-1}. The pump heads were in 18/8/3 stainless steel and the nitrile rubber diaphragms were P.T.F.E. faced. A peristaltic flow inducer (type MHRE/200 by Watson-Marlow Ltd.) was also ocasionally employed. In order to eliminate pump cavitation, large static suction heads were installed and entry lines were fitted with water jacketed coolers.

Flow rates were measured with previously calibrated rotameters (by Glass Precision Instruments Ltd.), fitted with stainless steel floats and coupled to pulsation dampers. Gas flow rates were also checked with bubble meters.

Gas pipings were in 1.25 cm i.d. semi-rigid polyethylene and liquid lines were in silicone rubber of .8 mm i.d. for delivery and 8 mm i.d. for suction. Non-controlling valves were of the ball type in polyethylene. The ammonia cylinder was fitted with a two--stage pressure regulator (Air Products Ltd.) containing a stainless steel needle valve.

The reboiler E1 was externally heated by a heating tape manually controlled by a "Variac" rheostat. The maximum power output was 1.5 Kw. The liquid level in the reboiler was automatically controlled by a pressure-difference driven control element, which operated a P.T.F.E. faced on/off solenoid valve (Alexander Controls Ltd.). This specially designed controller achieved reasonable operation stability, which was virtually unaffected by the operating conditions (pressure drop, etc.) of column T1. A schematic diagram of the controller is shown in Figure 4.2.

The cooling water for the heat exchangers E2 and E3 was not recycled, but the inlet temperature was controlled via thermostatic

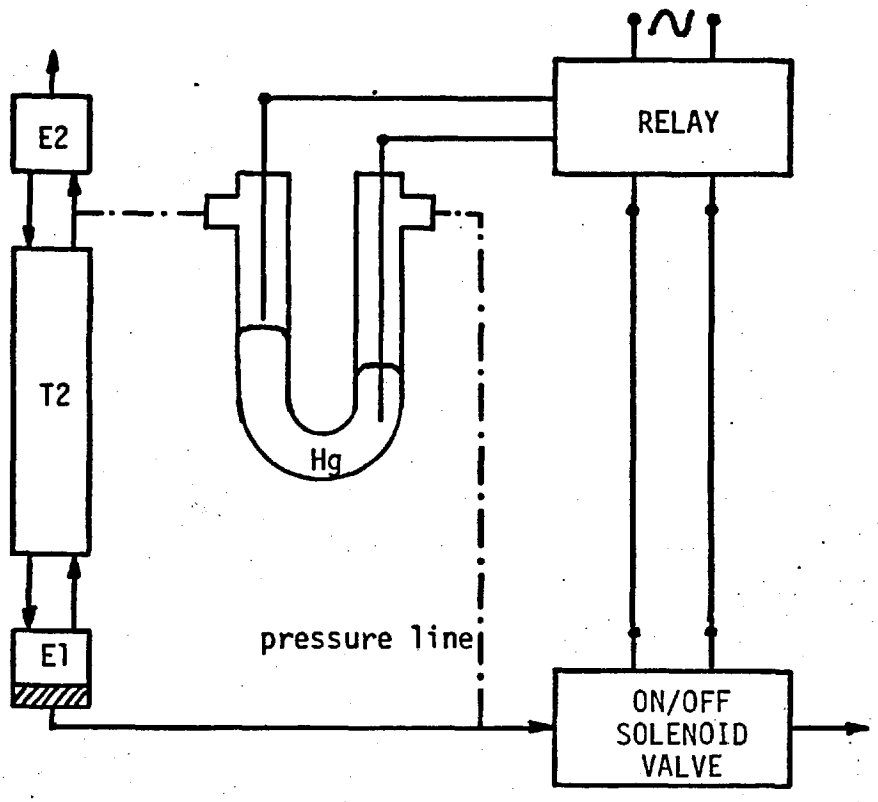


Figure 4.2 Level controller

baths. E3 was fitted with a one-way air inlet, to prevent admission of solution from the ammonia waste disposal tank D2, in case of a sudden pressure drop in the system. Continuous operation of this tank was not envisaged because all runs were at total reflux.

Columns T1 and T2 were packed with stainless steel wire gauze rings of the type and size indicated in Table 4.2. Additional data for similar rings are shown in Table 4.4.

Table 4.4 Packing characteristics

TYPE	SIZE(mm)	MESH/cm	no./dm^3	WEIGHT(g dm^{-3})	FREE GAS SPACE(%)
Dixon	3.2	32	1.8×10^4	418	95
"	1.6	40	8.1×10^4	611	93

Both packings were chemically pre-treated in order to remove grease films and to increase surface roughness. This treatment consisted of prolonged boiling in a 10w% NaOH solution, followed by etching in a .2M $Fe_2(SO_4)_3$ solution containing 4 v% of HF. The etching solution was heated until a gas-producing reaction started and, the reaction was allowed to proceed for five minutes. The packing was then rinsed in cold water and dried with propanol.

4.2 Analytical method

Liquid samples collected during plant operation were analysed for ^{15}N content by mass-spectrometry. Details of the sample preparation and analysis are now described.

4.2.1 Sample preparation

It is not possible to determine directly the ^{15}N atomic abundance of ammonia aqueous solutions, because both $^{15}NH_3$ and water give the same 18-mass signal and are thus undistinguishable. It is therefore necessary to oxidize the ammonia into nitrogen and then determine the ^{15}N content of the nitrogen samples via the peaks of masses 28 and 29. The oxidation can be done in two ways:

(a) Liquid-phase oxidation by a sodium hypobromite solution (43);

(b) Gas-phase catalytic oxidation over cupric oxide at 773K (55).

The first method was adopted. The oxidation was performed in a two--compartment glass cell, connected to the inlet system of the mass spectrometer. The sample (.1-.3 cm^3) and an excess of hypobromite solution were introduced in separate compartments in the cell, which was then imersed in liquid nitrogen and evacuated. The oxidizing solution was subsequently defrozen and added to the sample. The nitrogen thus produced was finally admitted into the mass spectrometer.

This method proved satisfactory and the only relative disadvantage is the handling of the hypobromite solution (prepared by adding equal volumes of a 8 w/v % solution of potassium bromide and a 31 w/v % solution of Na_2O). The excess of hypobromite solution prevents selective oxidation of the sample, thus avoiding separation of the two N isotopes during the oxidation.

4.2.2 Mass spectrometer

All the analysis were performed in an ATLAS M-86 mass spectrometer using a double collector measurement technique. The high voltage supply is adjusted in such a way that peaks 28 and 29 fall into two different collectors. Alternate admission of the sample and of a standard allows direct determination of the $^{15}N/^{14}N$ isotopic ratio, with a claimed precision of the order of .01%. The standard used was air, since analysis of several air samples at different times showed a negligible difference between them.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Pressure drop and liquid hold-up

Some measurements of pressure drop and dynamic liquid hold-up, in the installed column and for the system air-water, were initially undertaken. At the start of the experiments the column was preflooded and operating flow-rates were then imposed. Readings were taken after the attainment of steady flow conditions.

Pressure drops were measured with an open water manometer connected to the bottom of the column. Saturated air was blown up the column, which was open to the atmosphere at the top. The measured pressure drops for the dry packing and for three different liquid flow rates are shown in Table 5.1 and are plotted in Figure 5.1.

Table 5.1 Pressure drops in cm H_2O m^{-1}

		G x 10^3 (g cm^{-2} s^{-1})										
		4.4	8.8	13.2	14.1	19.8	35.2	41.0	44.0	48.4	52.8	56.0
L_v x 10^2 (cm^3 cm^{-2} s^{-1})	DRY	.23	-	1.45	-	2.38	5.93	-	8.90	-	11.78	12.20
	1.3	.49	-	-	2.43	3.60	8.35	11.05	12.70	15.40	-	-
	3.7	.57	1.47	-	2.80	4.35	9.59	13.30	15.50	-	-	-
	6.7	.64	-	-	3.38	5.11	13.25	16.00	-	-	-	-

Dynamic liquid hold-ups were measured by stopping the operation and collecting the drained liquid at the bottom of the column for 24 hours. The results are shown in Table 5.2 and are plotted in Figure 5.2.

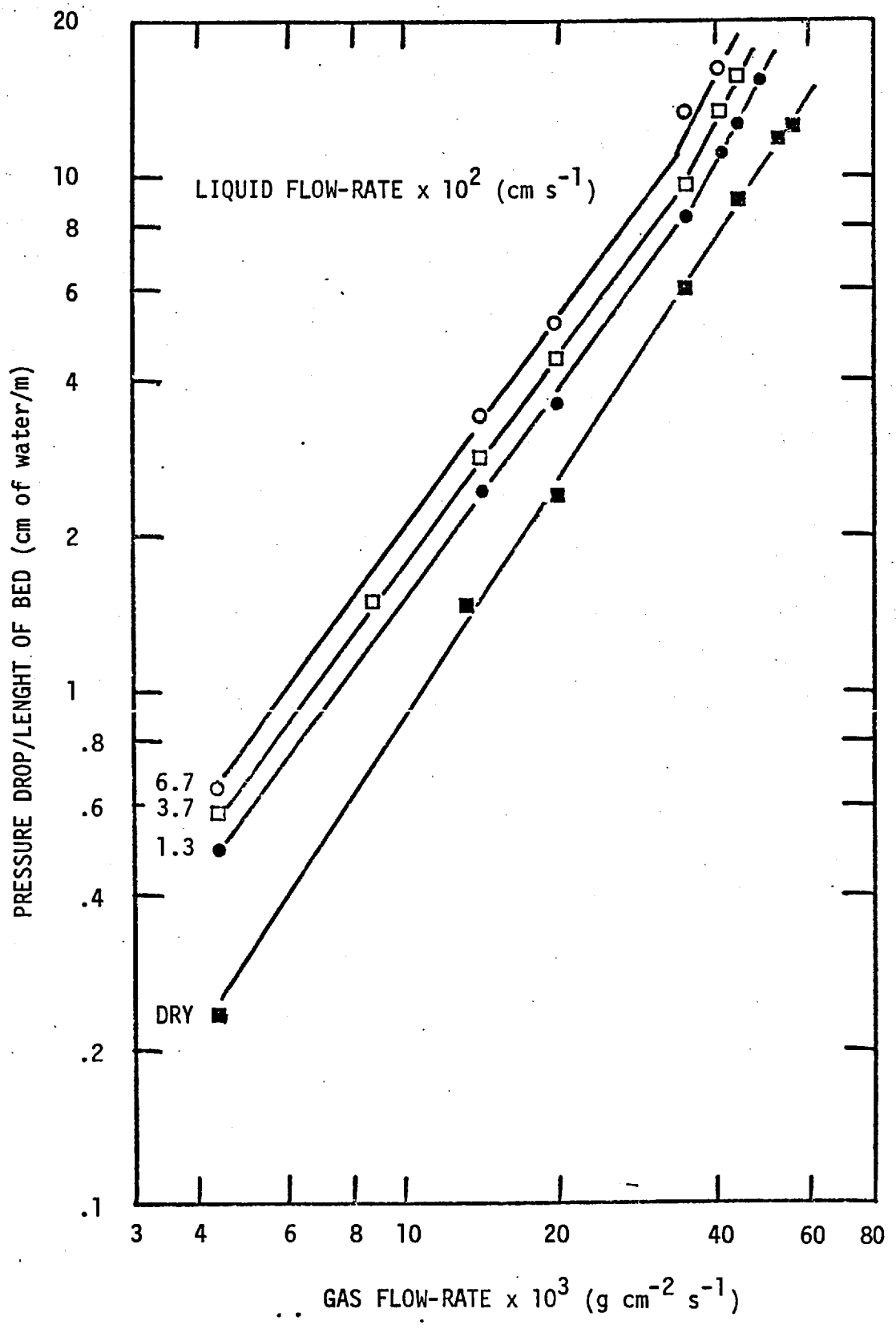


Figure 5.1 Pressure drop for 2 mm s.s. wire gauze Raschig rings (system air-water)

Table 5.2 Liquid hold-up/volume of bed

		G x 10^3 (g cm^{-2} s^{-1})						
		4.4	8.8	14.1	19.8	30.8	44.0	48.4
L_v x 10^2 ($cm^3 cm^{-2} s^{-1}$)	1.3	.088	-	.090	.097	-	-	.104
	3.7	.124	.132	.126	.134	-	.136	-
	6.7	.165	-	.173	.172	.184	-	-

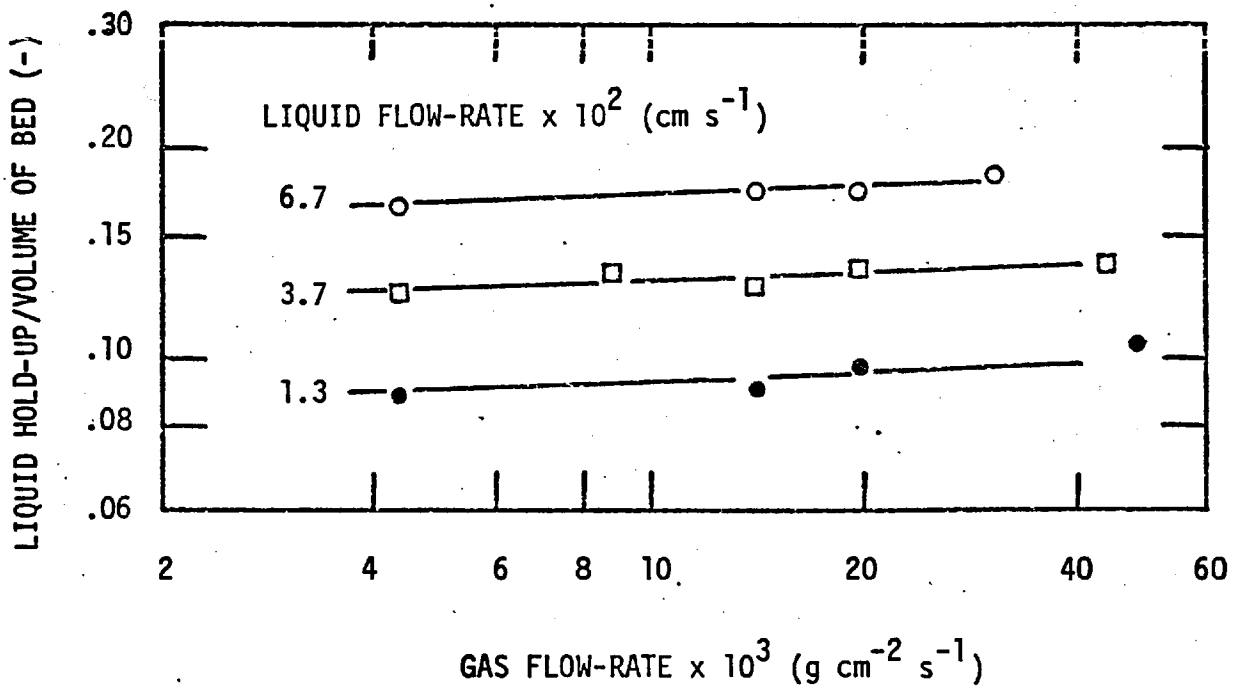


Figure 5.2 Liquid hold-up for 2 mm s.s. wire gauze Raschig rings (system air-water)

5.2 Column separation performance

The installed column was used to separate $^{15}NH_3$ from its natural abundance, with the system ammonia-water. All the runs were at total reflux and the column was always preflooded.

Liquid samples were periodically collected at the bottom of the column and were then analysed for ^{15}N content by the method described in section 4.2. The operating conditions and the measured concentrations are shown in Table 5.3.

Table 5.3 Experimental data for the system ammonia-water, at total reflux and room temperature

RUN	1		2		3	
L_v ($mm^3 s^{-1}$)	83.3		166.6		249.9	
H	.09		.13		.18	
V_{BS} (cm^3)	100		100		100	
V_{BL} (cm^3)	50		50		50	
V_{TS} (cm^3)	1000		300		1000	
V_{TL} (cm^3)	100		100		100	
	t(hours)	x(1,t)%	t(hours)	x(1,t)%	t(hours)	x(1,t)%
	5.5	.377	5.5	.433	10.0	.451
	20.0	.477	18.0	.496	22.5	.534
	34.0	.512	30.5	.577	43.0	.628
	41.0	.558	60.0	.663	68.0	.707
	60.0	.570	76.0	.673	114.0	.766
	85.0	.661	100.0	.715	195.0	.834
	130.0	.751				
	250.0	.876				
	452.0	.978				

Other variables: A=5 cm^2; h=510 cm ; α=1.006 ; x_o=.365%

Other published data obtained on similar packings are shown in Table 5.4. Five runs with three different solvents and covering a wide-range of flow rates were considered.

Table 5.4 Experimental data of Kuznetsov and Panchenkov

RUN	I		II		III		IV		V	
SOLVENT	water		1-propanol		1-propanol		1-propanol		2-propanol	
α	1.006		1.0055		1.0055		1.0055		1.0055	
$L_{v_{(mm^3s^{-1})}}$	11.7		16.7		30.		83.3		8.3	
H	.08		.10		.15		.20		.05	
x_o	.751		.746		.737		1.		1.	
REFERENCE	(56)		(54-Run4)		(54-Run2)		(57-Fig1)		(57-Fig4)	
	t (hrs)	x(1,t) (%)	t (hrs)	x(1,t) (%)	t (hrs)	x(1,t) (%)	t (hrs)	x(1,t) (%)	t (hrs)	x(1,t) (%)
	2.	.772	10.	.839	11.	.825	5.8	1.043	12.7	1.196
	5.	.828	44.	1.032	18.	.887	17.4	1.120	50.3	1.455
	7.75	.845	82.	1.085	30.5	.922	29.0	1.172	138.3	1.512
	19.	.930	131.5	1.103	55.	.986	81.2	1.257	194.3	1.534
	32.	1.005	183.	1.106	79.	1.026	243.6	1.386	240.	1.556
	60.	1.060								
	99.	1.114								
	120.	1.115								
	191.	1.135								

Other variables: A = 2 cm^2 ; h = 140 cm (except in Run I where it was h = 135 cm) ; hold-ups in the reflux sections were estimated from the description of apparatus : V_{BS} = 5 cm^3 ; V_{BL} = 5 cm^3 ; V_{TS} = 5000 cm^3 and V_{TL} = 10 cm^3.

5.3 Analysis of results

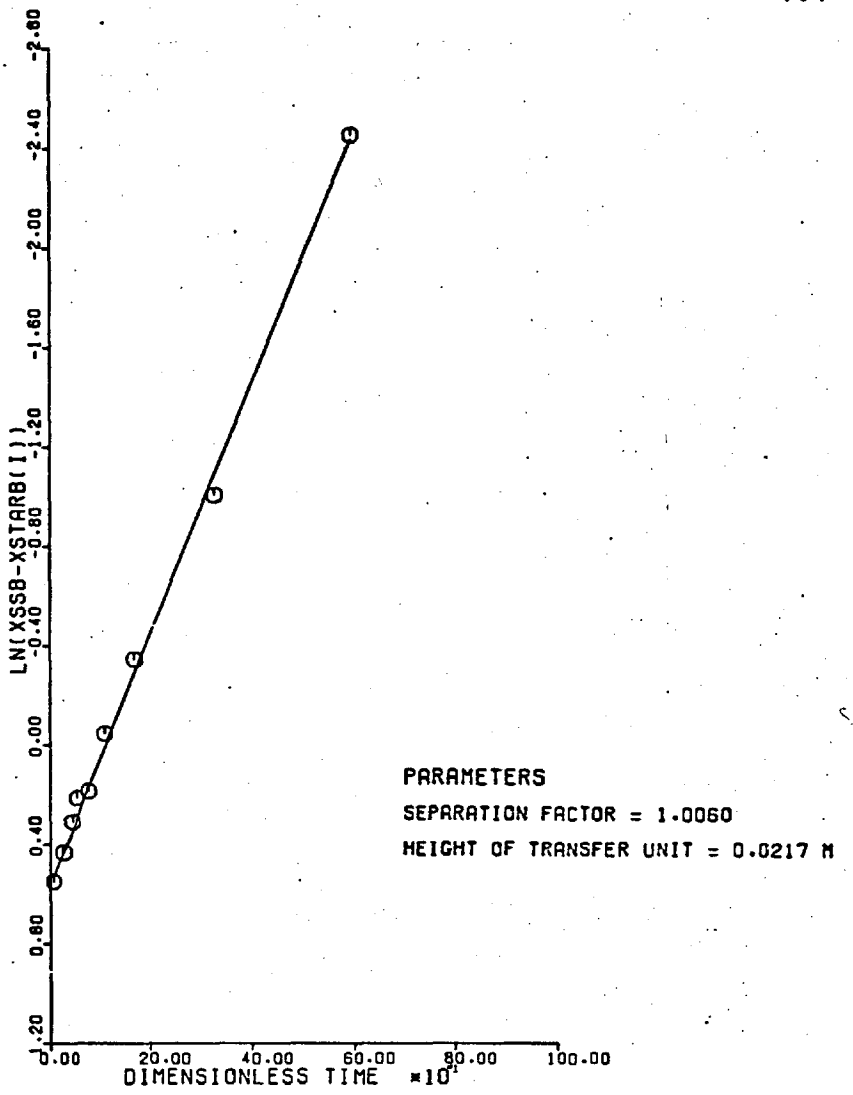
The eight runs described in the previous section were treated by the model developed in Chapter Three. The separation performance was estimated by the method described in section 3.3.1. The log-linear fit used to determine H_{OG} and the time dependence of the concentration at both ends of the column are shown, for the eight runs, in Figures 5.3 to 5.10. The results are summarized in Table 5.5.

Table 5.5 Data analysis

RUN	SOLVENT	L_v ($mm^3 cm^{-2} s^{-1}$)	S(82,84) ($mmol\ mm^{-3}$)	G_m ($mmol\ cm^{-2} s^{-1}$)	H_{OG} (cm)	$K_{OG} \cdot a_s$ ($mmol\ cm^{-3} s^{-1}$)
1	water	16.7	.031	.52	2.17	.235
2	"	33.3	"	1.03	2.23	.462
3	"	50.0	"	1.55	2.49	.619
I	"	5.9	"	.18	1.94	.093
II	1-propanol	8.4	.018	.15	1.87	.080
III	"	15.0	"	.27	2.10	.129
IV	"	41.7	"	.75	2.26	.332
V	2-propanol	4.2	"	.08	1.71	.046

A simple empirical relation for the overall mass transfer coefficient was derived. This was obtained by a least-squares fitting of an expression of the type $\log(K_{OG}a_s)=f(\log G_m)$ to the data. The linear regression analysis showed that the data were well correlated by

$$K_{OG}\, a_s = .43\, G_m^{.88} \qquad (5.1)$$



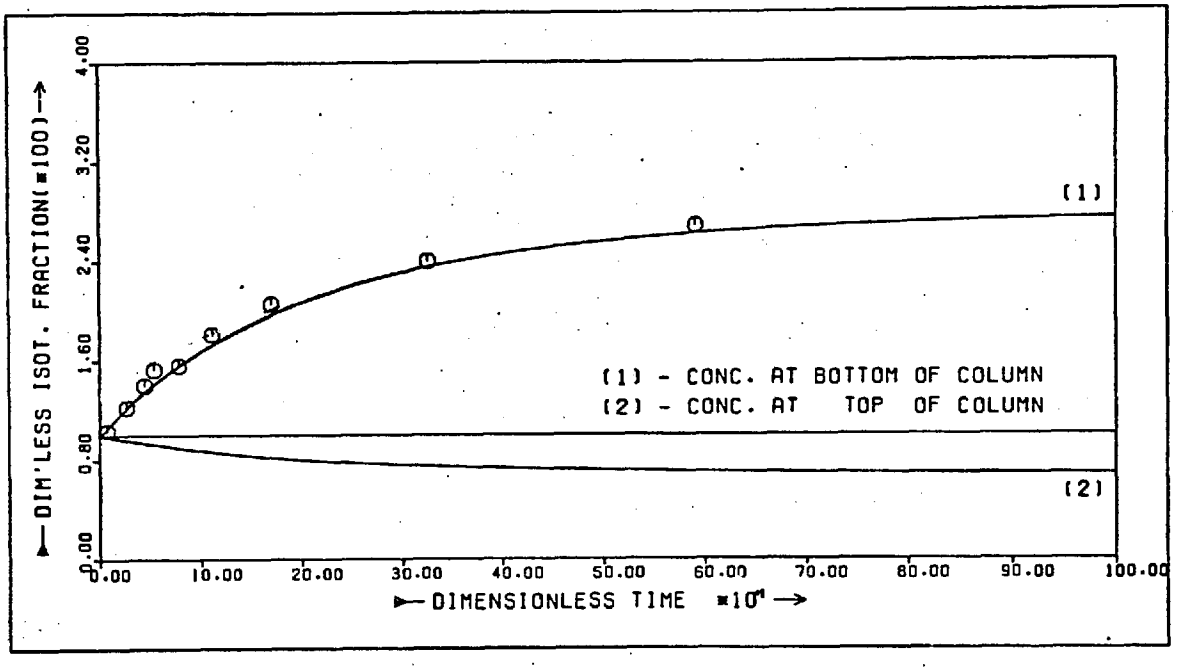
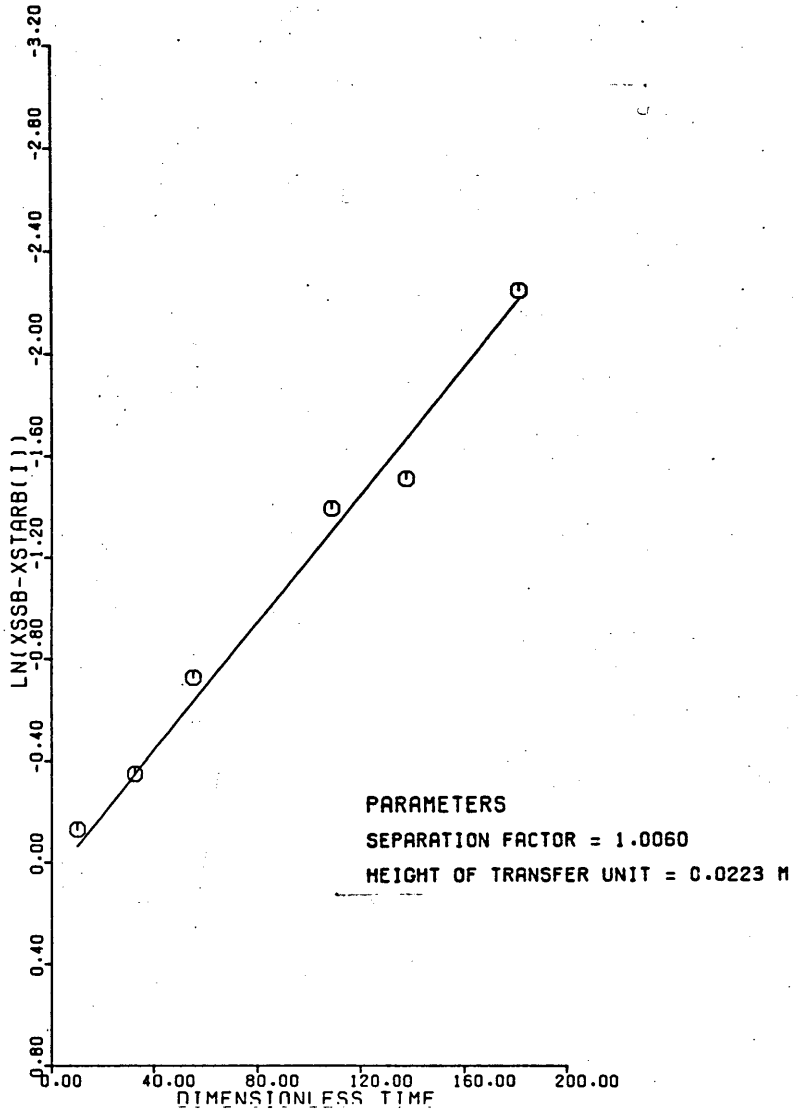


Figure 5.3 Run 1

● Experimental

— Model



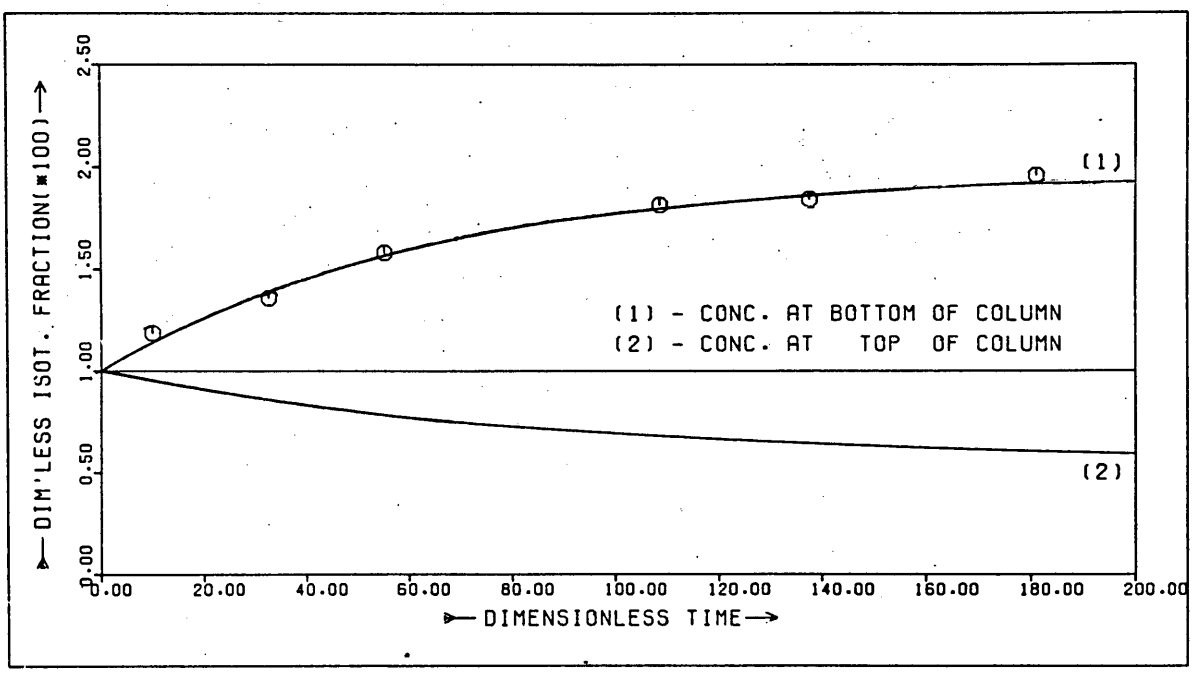
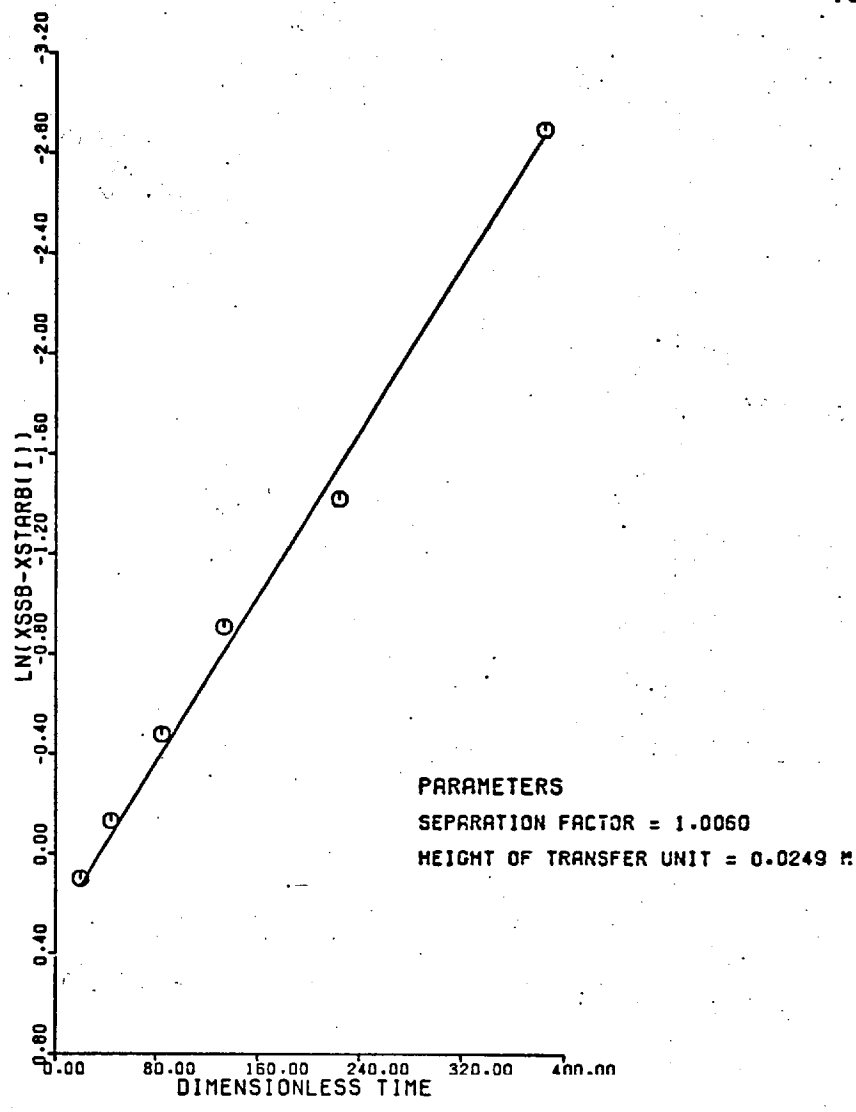


Figure 5.4 Run 2

⊙ Experimental
— Model



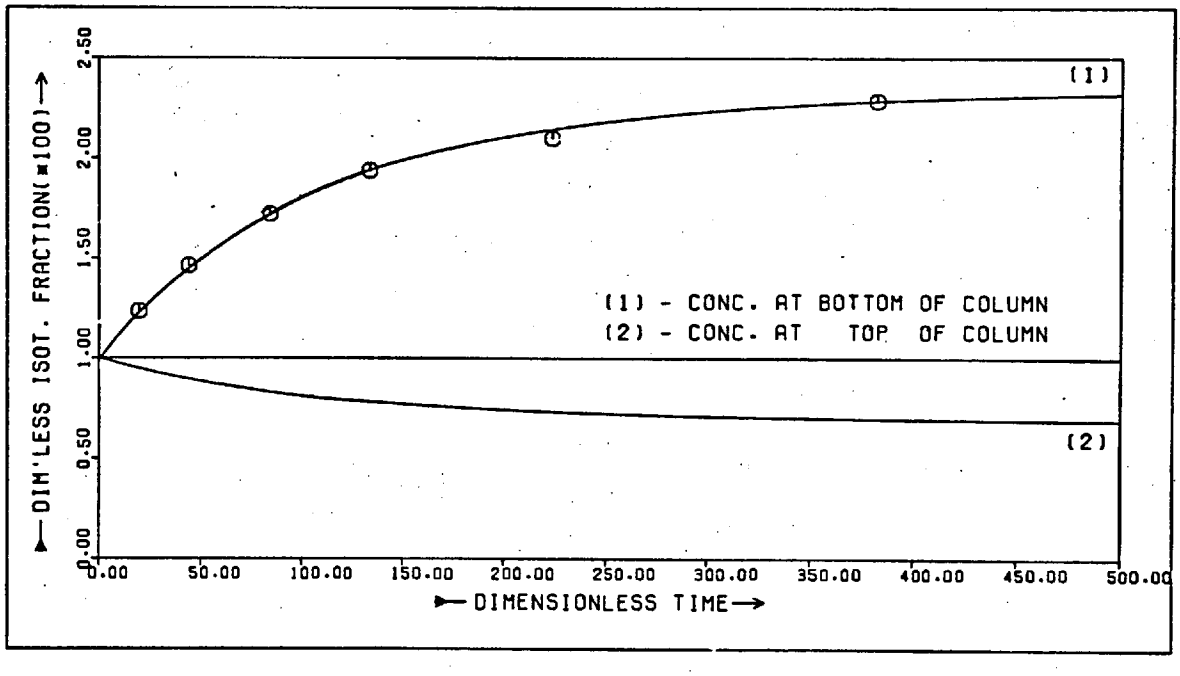
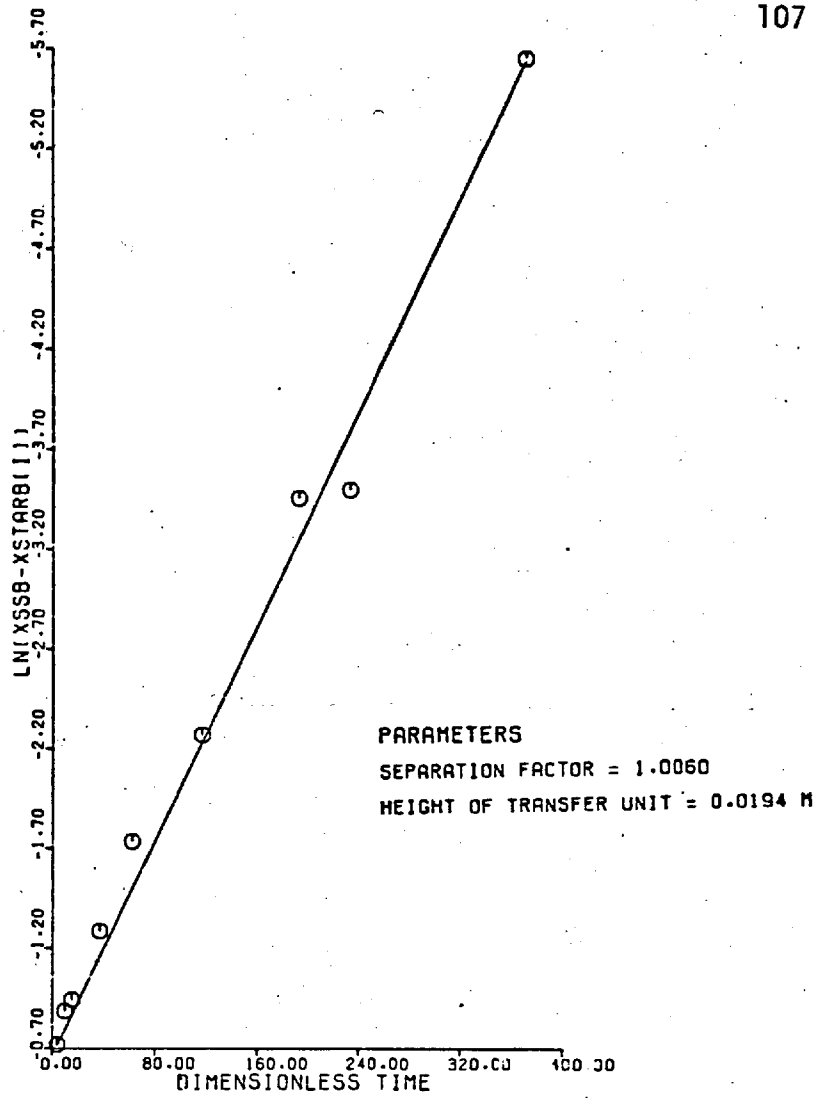


Figure 5.5 Run 3

o Experimental
— Model



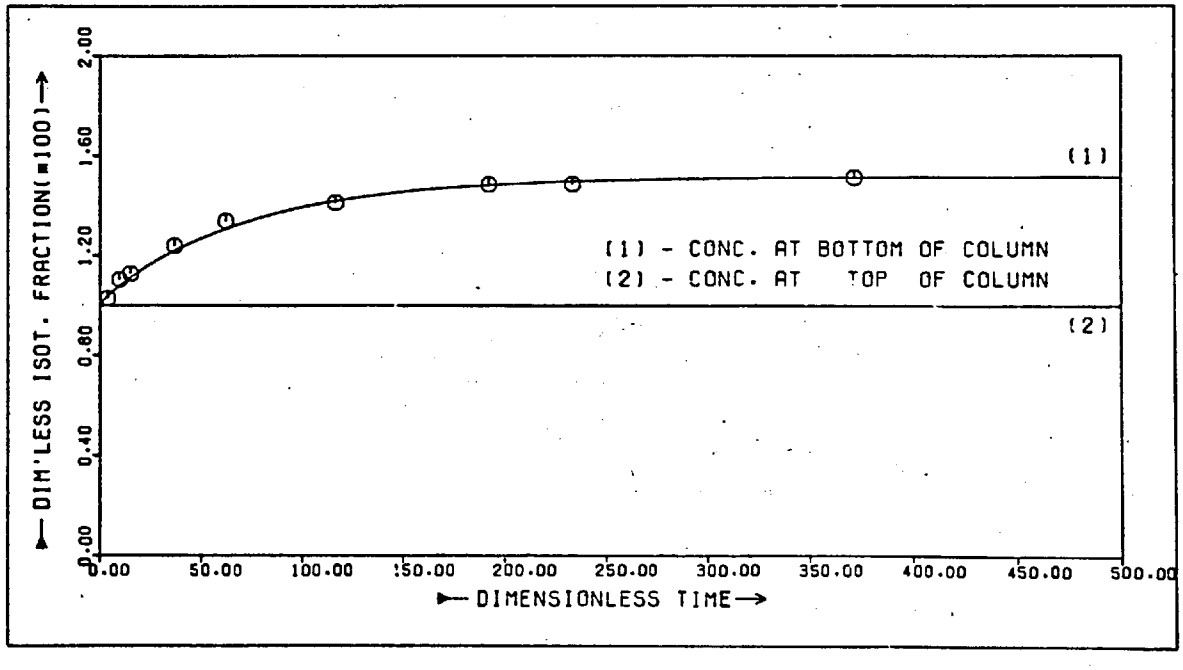
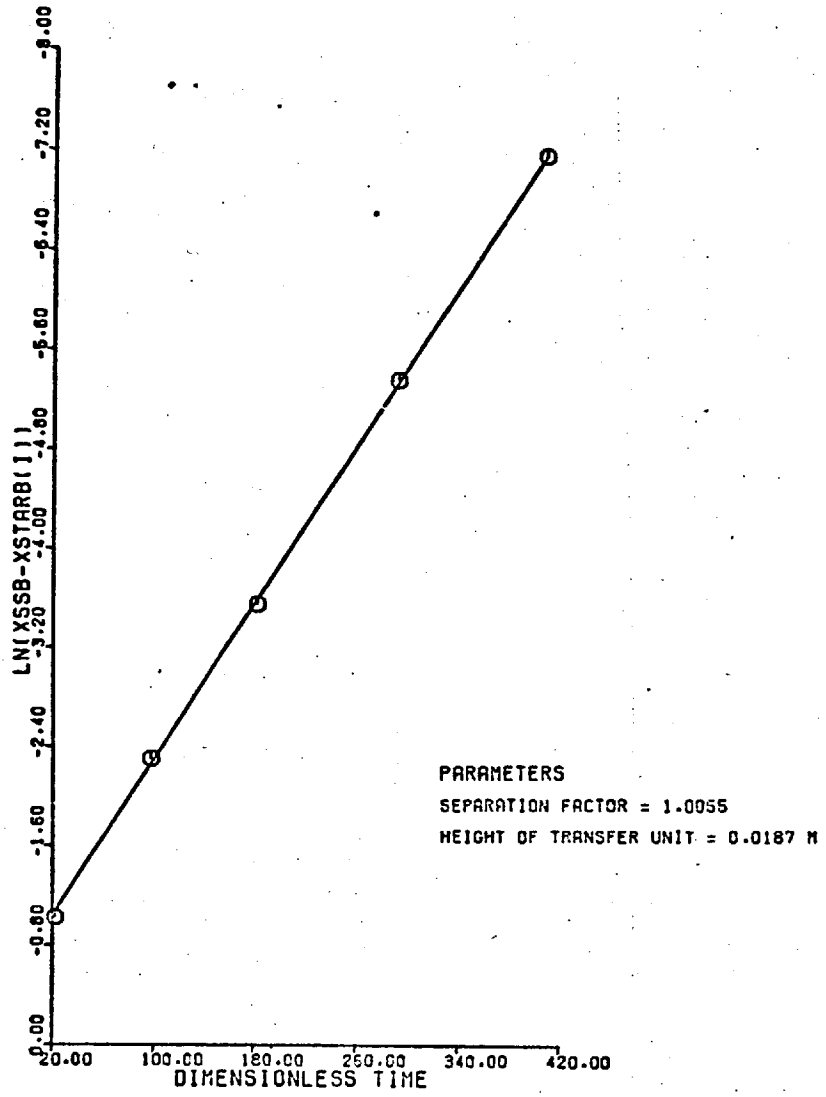


Figure 5.6 Run I

● Experimental
— Model



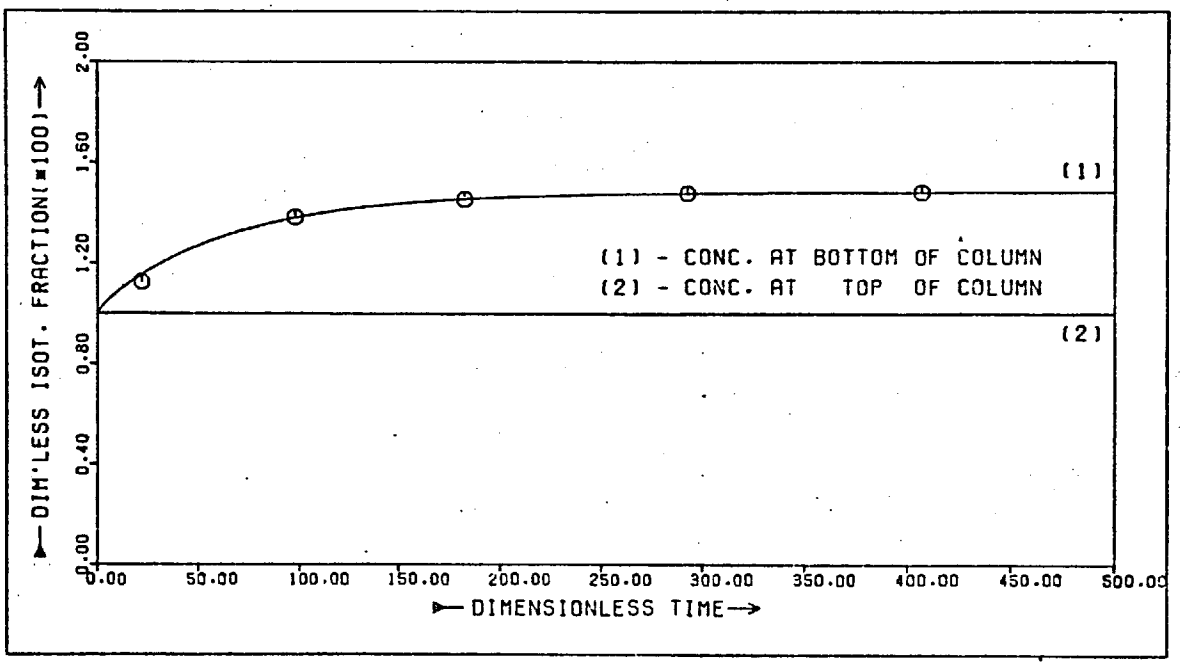
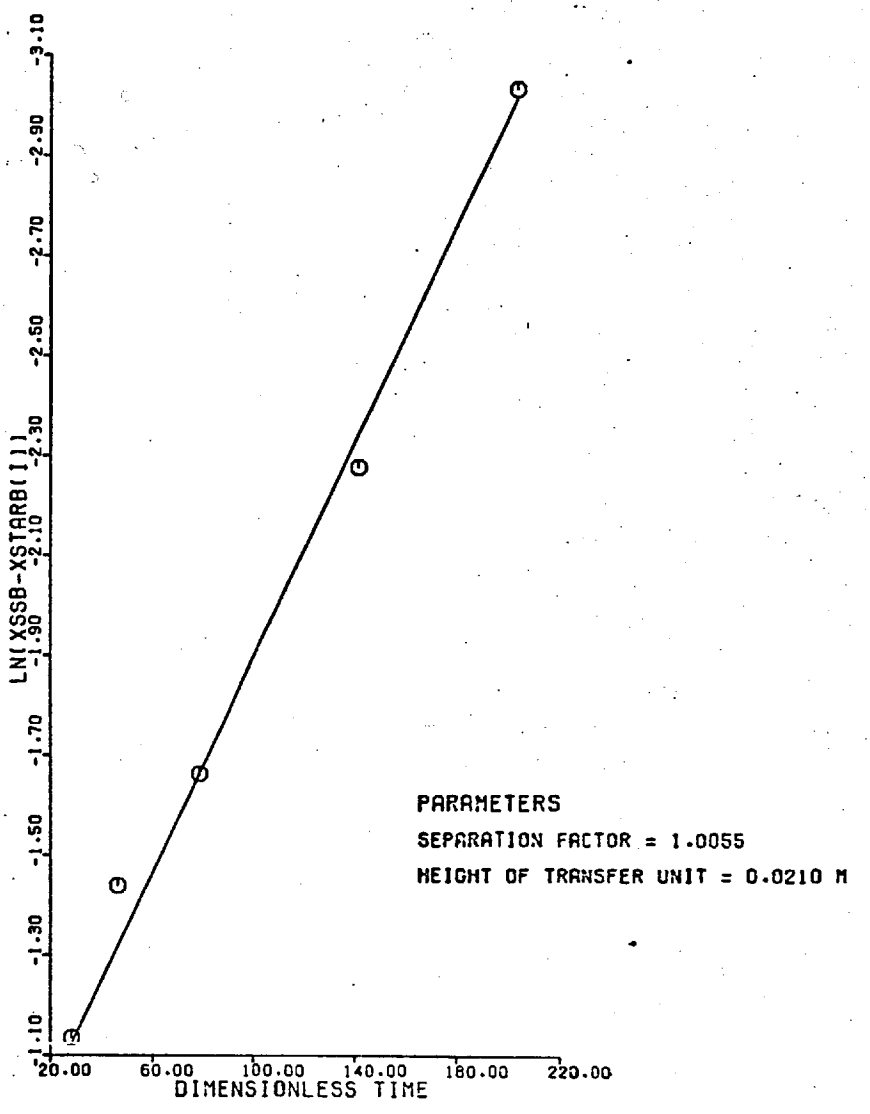


Figure 5.7 Run II

o Experimental
— Model



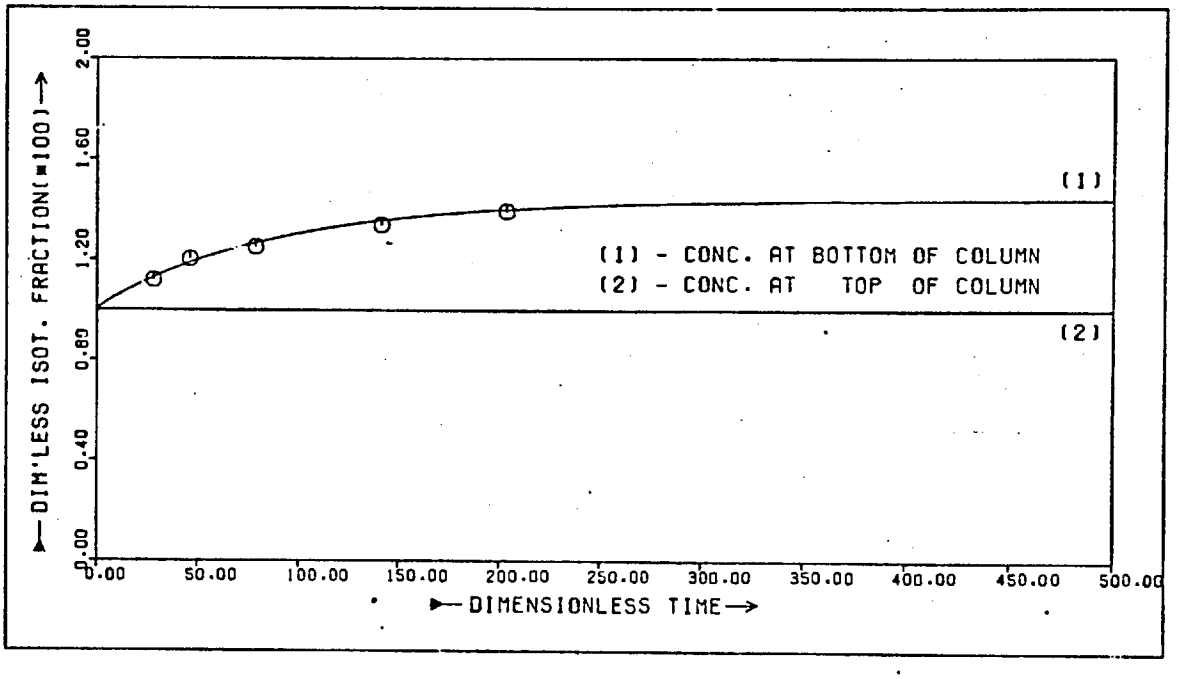
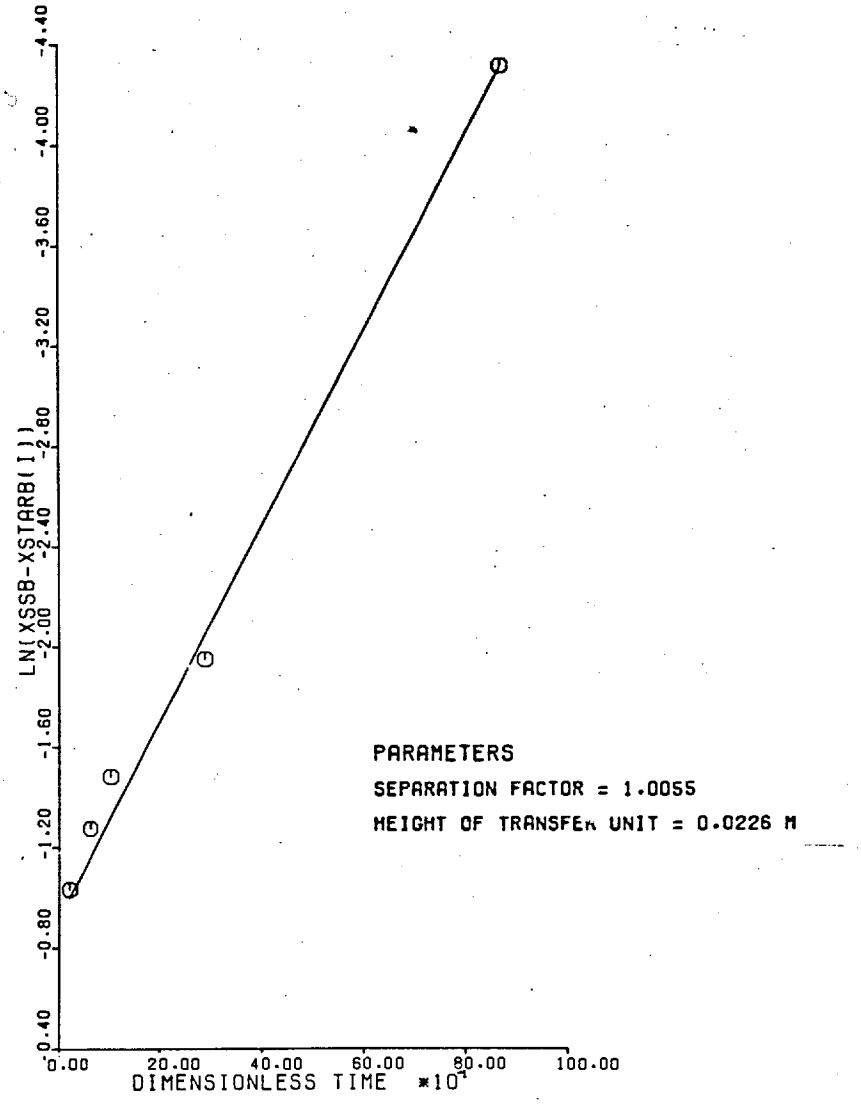


Figure 5.8 Run III

o Experimental
— Model



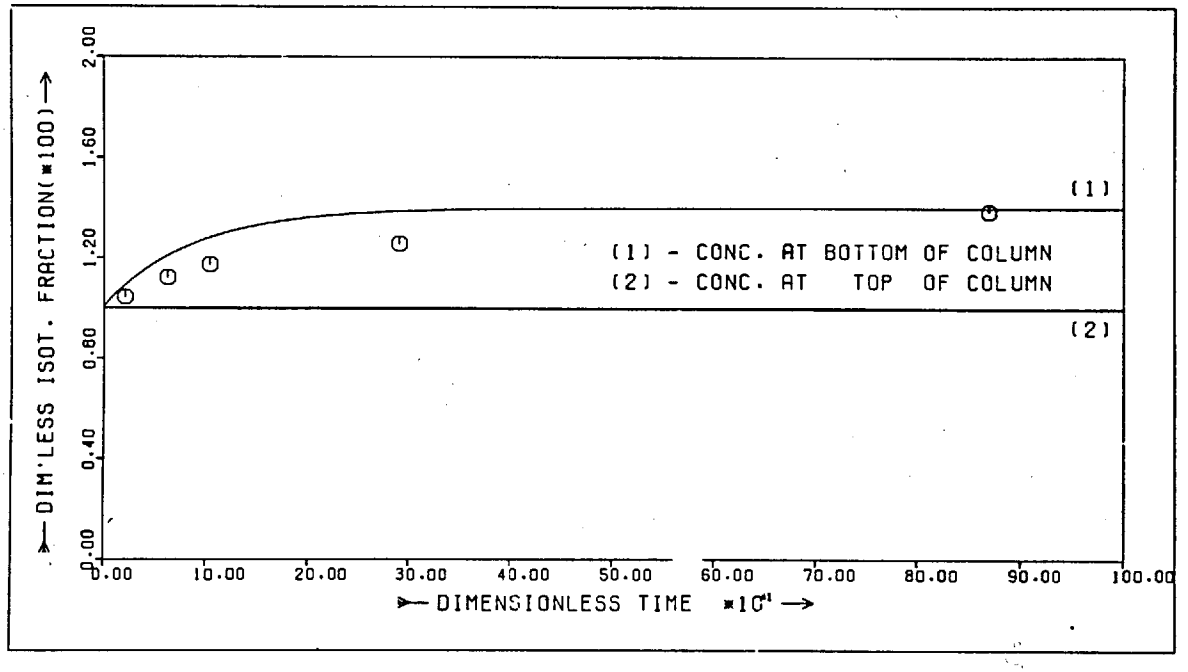
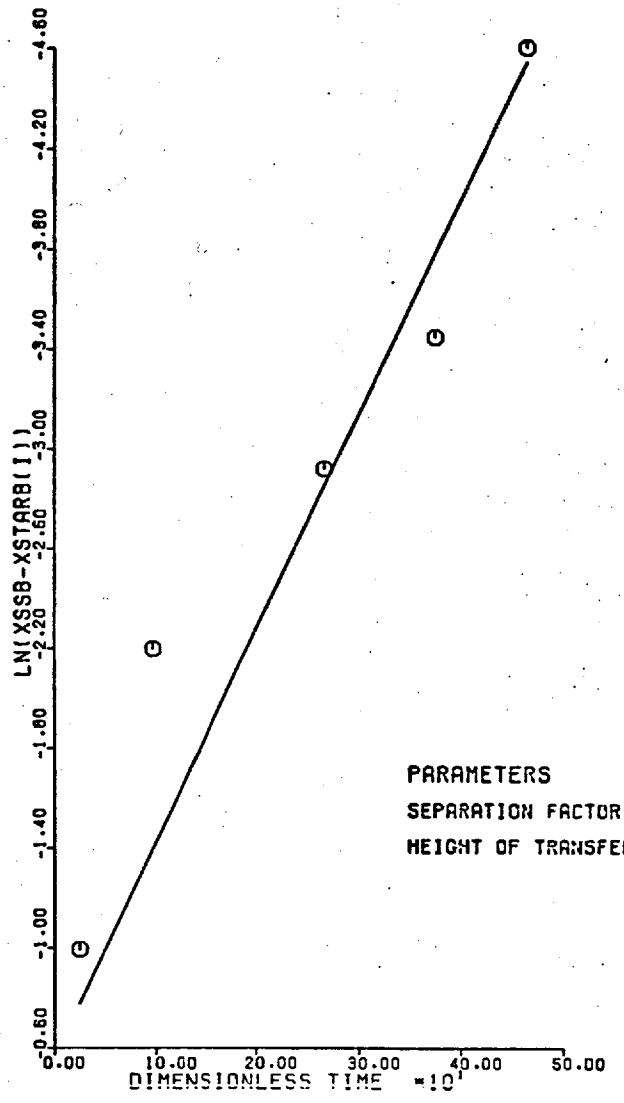


Figure 5.9 Run IV ⊙ Experimental — Model



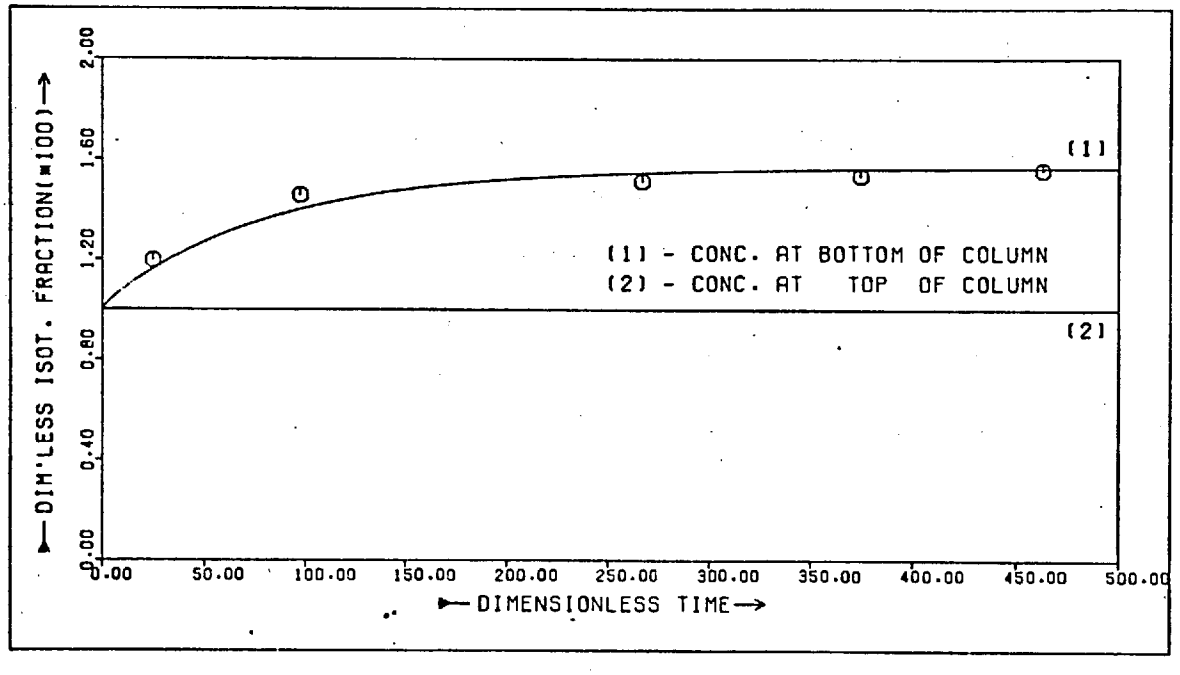


Figure 5.10 Run V

o Experimental
— Model

where $K_{OG}a_s$ and G_m are expressed in mmol cm^{-3} s^{-1} and mmol cm^{-2} s^{-1}, respectively. The sum of the squares of the residuals was 8.4×10^{-4}. From (3.32) and (5.1)

$$H_{OG} = 2.33\ G_m^{.12} \tag{5.2}$$

where H_{OG} and G_m are expressed in cm and mmol cm^{-2} s^{-1}, respectively. The experimental points and equations (5.1) and (5.2) are plotted in Figures 5.11 and 5.12.

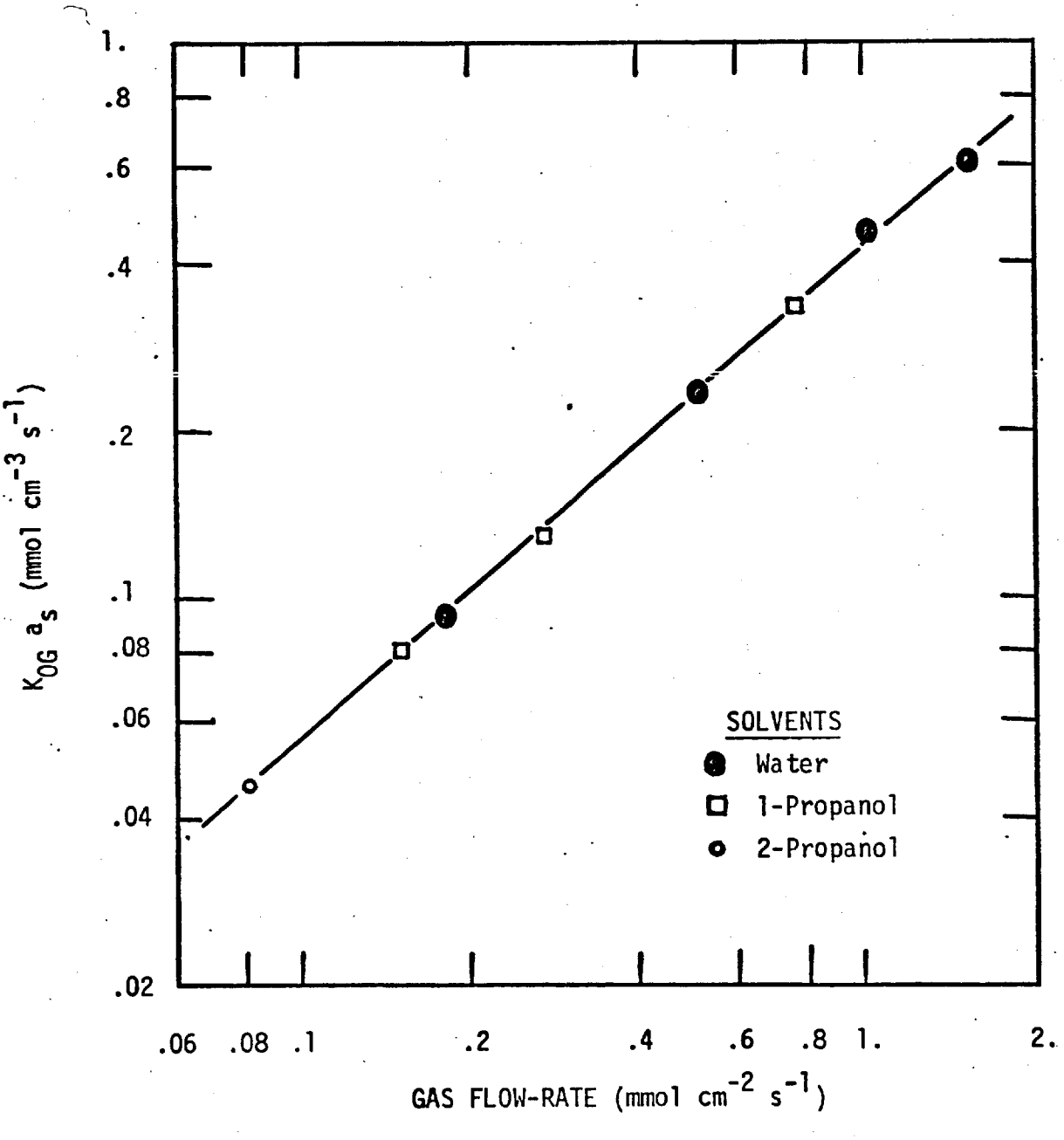


Figure 5.11 The overall mass transfer coefficient as a function of the gas flow rate.

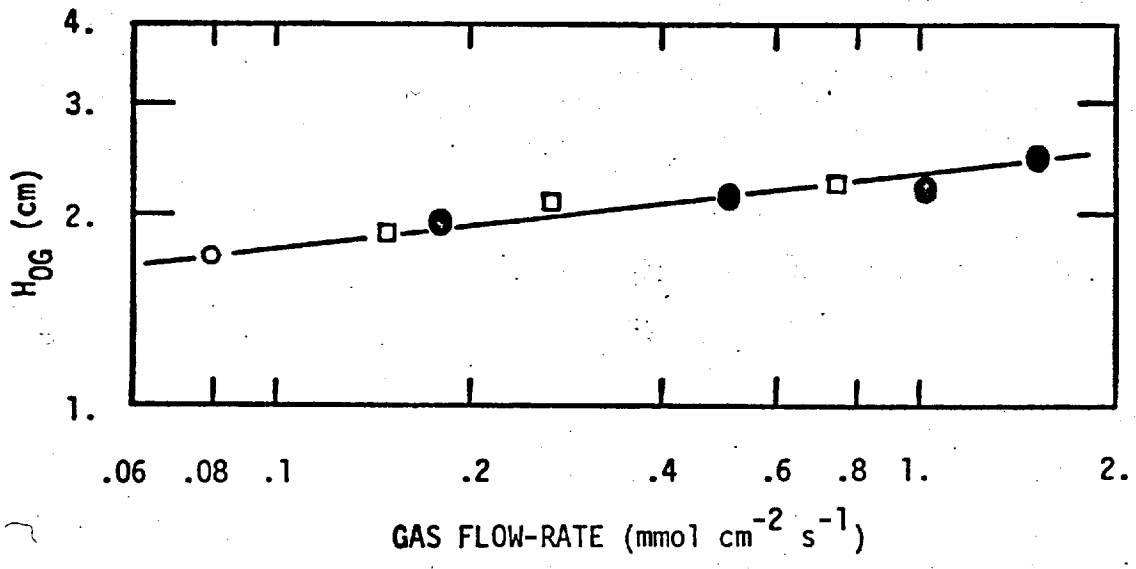


Figure 5.12 The height of the overall transfer unit as a function of the gas flow rate.

Equation (5.1) suggests that the transfer process is gas-phase controlled, and this confirms published qualitative evidence (50,58). The fact that a reasonable correlation is obtained without correction for physical properties, is due to the small concentrations of solvent vapour in the gas phase. In addition, any small differences in the gas density and viscosity between the eight runs, have an even smaller effect on the gas-phase Sherwood number. In fact, most empirical correlations for the gas transfer coefficient are of the form

$$Sh = a\ Re^{b}\ Sc^{c}$$

(where b and c are positive constants, smaller than one). Therefore the overall effect of ρ and μ on Sh is only $(\rho/\mu)^{b-c}$.

CHAPTER SIX

CONCLUSIONS

The conclusions of the present work can be summarized as follows:

1. A method to separate ^{15}N using a gas-liquid contact between ammonia and ammonia solutions was investigated. The fact that $^{15}NH_3$ concentrates in the liquid phase even at room temperature (when the saturation vapour pressures of pure ^{14}N and ^{15}N ammonias are equal), was attributed to the isotopic selectivity of certain H-bonded molecular associations between the solute and the solvent. The solvent dependence of the single stage separation factor was thus explained, and ionic effects were shown to be negligible.

2. The interphase mass transfer process was modelled as an equimolecular counterdiffusion of ^{14}N and ^{15}N ammonias, through an inert solvent. Differences in the solubilities and heats of solution of ^{14}N and ^{15}N ammonias were neglected.

3. Experimental results on the separation performance of a packed column suggest that the transfer process is gas-phase controlled. A simple correlation for the overall mass transfer coefficient was obtained, and since the concentration of solvent vapour in the gas phase was always small no correction for gas physical properties was needed.

4. A mathematical model for the transient operation of a packed column was developed, and the agreement with experimental data was good. The solution of the model allowed the estimation of H_{OG} from column start-up data. It was also possible to predict the column start-up with varying feed and product flow rates, using a mixed analytical-numerical method which is based on the

inclusion in the model of a height-dependent initial condition.

Suggestions for future work

1. A preliminary cost estimate on these processes should now be made, using the equilibrium data available in the literature and the present correlation for the overall mass transfer coefficient.

2. Additional experiments with other solvents (methanol, ethanol, etc.) should be carried out.

3. An attempt should be made to improve the accuracy of the experimental determinations of single-stage separation factors, and to measure their temperature dependence.

4. Other ^{15}N separation processes (such as the distillation of liquid NO and the low-temperature sorption of liquid nitrogen in CaA zeolites) deserve further exploration at pilot plant scale.

APPENDIX A

A TENTATIVE INTERPHASE TRANSFER MODEL IN TERMS OF A LIQUID-PHASE REVERSIBLE REACTION

(a) Assumptions

i) Apart from the solvent there are four distinguishable species A,B,E and F in the solution, with A = $^{15}NH_3$, B = $^{14}NH_3$-solvent, E = $^{14}NH_3$ and F = $^{15}NH_3$-solvent.

ii) Instantaneous equilibrium between these four species is attained inside the liquid film and the mass action law is maintained throughout the diffusion path (75), i.e.,

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} E + F \qquad (A.1)$$

$$K_1 = \frac{(E).(F)}{(A).(B)} = k_1/k_2 = \alpha \qquad (A.2)$$

iii) The flow of these four species is unidirectional and under zero-nett flux conditions.

iv) Species B and F are non-volatile, i.e., the mass transfer flux of these species across the interface is zero.

v) The transfer of the other two species across the interface is equimolecular, because the solution is assumed saturated and differences in the solubilities of A and E are neglected.

(b) Material balances

The unsteady-state mass balances for the four species in a slab of lenght dz across the diffusion path give:

$$\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial z^2} - k_1 A B + k_2 E F \qquad (A.3)$$

$$\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial z^2} - k_1 A B + k_2 E F \qquad (A.4)$$

$$\frac{\partial E}{\partial t} = D_E \frac{\partial^2 E}{\partial z^2} - k_2 E F + k_1 A B \qquad (A.5)$$

$$\frac{\partial F}{\partial t} = D_F \frac{\partial^2 F}{\partial z^2} - k_2 E F + k_1 A B \qquad (A.6)$$

where D are binary effective diffusivities, t is time, z is the diffusion path (0 at the interface) and k_1 and k_2 are the forward and reverse rate constants, respectively.

At steady state and eliminating k_1 and k_2 these four equations become

$$D_A \frac{d^2 A}{dz^2} + D_E \frac{d^2 E}{dz^2} = 0 \qquad (A.7)$$

$$D_A \frac{d^2 A}{dz^2} + D_F \frac{d^2 F}{dz^2} = 0 \qquad (A.8)$$

$$D_B \frac{d^2 B}{dz^2} + D_E \frac{d^2 E}{dz^2} = 0 \qquad (A.9)$$

$$D_B \frac{d^2 B}{dz^2} + D_F \frac{d^2 F}{dz^2} = 0 \qquad (A.10)$$

Only three of these four equations are independent. Discarding (A.8) and integrating

$$D_A A + D_E E = C_1 z + C_2 \qquad (A.11)$$

$$D_B B + D_E E = C_3 z + C_4 \qquad (A.12)$$

$$D_B B + D_F F = C_5 z + C_6 \tag{A.13}$$

where C_1, C_2, C_3, C_4, C_5 and C_6 are integration constants to be determined by the boundary conditions.

From assumption (iv)

$$N_B\Big|_{z=0} = N_F\Big|_{z=0} = 0 \tag{A.14}$$

that is,

$$D_B \frac{dB}{dz}\Big|_{z=0} = D_F \frac{dF}{dz}\Big|_{z=0} = 0 \tag{A.15}$$

Thus, from (A.15) and the derivative of (A.13)

$$C_5 = 0 \tag{A.16}$$

Similarly, from assumption (v)

$$N_A\Big|_{z=0} = - N_E\Big|_{z=0} \tag{A.17}$$

$$D_A \frac{dA}{dz}\Big|_{z=0} + D_E \frac{dE}{dz}\Big|_{z=0} = 0 \tag{A.18}$$

and from (A.18) and the derivative of (A.11)

$$C_1 = 0 \tag{A.19}$$

Thus, equations (A.11), (A.12) and (A.13) become

$$D_A A + D_E E = C_2 \tag{A.20}$$

$$D_B B + D_E E = C_3 z + C_4 \tag{A.21}$$

$$D_B B + D_F F = C_6 \tag{A.22}$$

(c) Boundary conditions

(i) At the interface (z=0)

$$D_A A_i + D_E E_i = C_2 \qquad (A.23)$$

$$D_B B_i + D_E E_i = C_4 \qquad (A.24)$$

$$D_B B_i + D_F F_i = C_6 \qquad (A.25)$$

(ii) At the liquid bulk ($z=\delta$)

$$D_A A_b + D_E E_b = C_2 \qquad (A.26)$$

$$D_B B_b + D_E E_b = C_3 \delta + C_4 \qquad (A.27)$$

$$D_B B_b + D_F F_b = C_6 \qquad (A.28)$$

where the subscripts i and b denote interface and bulk, respectively, and δ is the liquid film width.

These six equations determine the four remaining integration constants and, in addition, lead to

$$D_A (A_i - A_b) = D_E (E_b - E_i) \qquad (A.29)$$

$$D_B (B_i - B_b) = D_F (F_b - F_i) \qquad (A.30)$$

(d) The transfer rate of A

The transfer flux of A across the interphase is equal to the "total" A (A+F) flux inside the liquid film, i.e.,

$$N_A = - D_A \frac{dA}{dz} - D_F \frac{dF}{dz} = - C_1 + C_3 - C_5 \qquad (A.31)$$

and since C_1 and C_5 are both zero

$$N_A = C_3 \qquad (A.32)$$

Then, from (A.24) and (A.27)

$$C_3 \delta = D_B (B_b - B_i) + D_E (E_b - E_i) \qquad (A.33)$$

or in terms of A and F (using (A.29) and (A.30))

$$C_3 \delta = D_A (A_i - A_b) + D_F (F_i - F_b) \qquad (A.34)$$

Therefore from (A.32) and (A.34)

$$N_A = D_A (A_i - A_b) \{ 1 + (D_F/D_A) (F_i - F_b)/(A_i - A_b) \} / \delta \qquad (A.35)$$

Defining the liquid phase mass transfer coefficients with and without reaction by

$$K_L = N_A / (A_i - A_b) \qquad (A.36)$$

$$K_L^o = D_A / \delta \qquad (A.37)$$

equation (A.35) becomes

$$E_f = K_L/K_L^o = 1 + (D_F/D_A)(F_i - F_b)/(A_i - A_b) \qquad (A.38)$$

(e) Measurable variables

In the previous section the enhancement factor was expressed in terms of the interphase and bulk concentrations of the "bonded" and "free" ^{15}N species. The ratio between the "bonded" and "free" species can be expressed in terms of the "H-bonding factor" (σ) as defined by Hayduk and Laudie (76).

All together, four variables can be measured in the solution:

(i) The ammonia solubility (S)

$$S = A_b + B_b + E_b + F_b \ (\text{mol } l^{-1}) \qquad (A.39)$$

(ii) The ^{15}N isotopic fraction (x)

$$x = (A_b + F_b) / S \qquad (A.40)$$

(iii) The separation factor (α)

$$\alpha = E_b F_b / (A_b B_b) \qquad (A.41)$$

(iv) The H-bonding factor (σ)

$$\sigma = 1 + (1 - SV_m) E_b / B_b \qquad (A.42)$$

where V_m is the molar volume of the saturated solution (SV_m is the solubility in mole fraction).

By manipulation

$$A_b = S \times (\sigma-1) / \{\alpha(1-SV_m) + (\sigma-1)\} \qquad (A.43)$$

$$B_b = S (1-x) (1-SV_m) / (\sigma-SV_m) \qquad (A.44)$$

$$E_b = S (1-x) (\sigma-1) / (\sigma-SV_m) \qquad (A.45)$$

$$F_b = S \alpha x (1-SV_m) / \{ \alpha (1-SV_m) + (\sigma-1) \} \qquad (A.46)$$

The concentration of A at the interface can be expressed in terms of the gas phase partial pressure

$$A_i = p_A / H \qquad (A.47)$$

where H is Henry's constant.

In addition and according to assumption (ii)

$$\alpha = E_i F_i / (A_i B_i) \qquad (A.48)$$

Therefore, the four interphase concentrations can be expressed in terms of p_A, α and bulk concentrations using (A.29), (A.30) (A.47) and (A.48).

(f) A numerical example

Assume that the solvent is water and the operating conditions are 10^5 N m^{-2} and 293 K. Then S = 31 mol l^{-1} (82), SV_m = .35 (82), H = .033 x 10^5 N mol m^{-2} l^{-1}(82), α = 1.006 (60) and σ = 2.46 (76).

The four binary diffusivities were estimated as follows. D_E was taken as the diffusivity of ammonia in a dilute aqueous solution D_E = 6.9 x 10^{-5} ft^2 h^{-1} = 1.73 x 10^{-5} cm^2 s^{-1}. (83). D_B was estimated from the diffusivity of a saturated solution, assuming that

$$D_{sat} (E + B) = D_E E + D_B B \qquad (A.49)$$

where D_{sat} = 4.9 x 10^{-5} ft^2 h^{-1} = 1.23 x 10^{-5} cm^2 s^{-1}(83). Using (A.42) it is found that E/B = 2.25 and D_B = 1.05x10^{-6} cm^2 s^{-1}. The diffusivities of the ^{15}N species (A and F) were estimated using a molecular weight correction

$$D_E/D_A = \left(\frac{1/18 + 1/17}{1/18 + 1/18}\right)^{\frac{1}{2}} = 1.015 \qquad (A.50)$$

$$D_B/D_F = \left(\frac{1/18 + 1/35}{1/18 + 1/36}\right)^{\frac{1}{2}} = 1.005 \qquad (A.51)$$

Then, for a 1% enrichement (x = .01 and $p_A = (x/\alpha).10^5$ N m^{-2}) it is found that E_f = 1.029.

The consideration of the presence of the equilibrium reaction (A.1) would thus enhance the transfer process. Since K_L^o can be expected to be of the order of magnitude of the liquid phase coefficient for the absorption of ammonia in water ($K_L^o >> K_G$), it seems that this reaction approach tends to rule out the possibility of liquid phase control in the present case.

APPENDIX B

FEED POINT BETWEEN $z^*=0$ AND $z^*=1$

As discussed in the text, an explicit solution for this case can only be obtained for optimum feed location. Since the differential mass balances above and below feed point are different, two solutions are needed, one for each zone. Only the lower section of the column will be treated here, but the differential equation and the boundary conditions for the upper zone will also be presented.

A new boundary condition at feed height is required for both zones. Assume that the feed is introduced in the column at a given height z_F, or in dimensionless coordinates $z_F^* = z_F/h$. Then, assuming optimum feed location, the concentration at this height is always equal to the feed concentration, i.e.,

$$y^*(z_F^*,t^*) = 1 \text{ for } t^* \geq 0 \qquad (B.1)$$

or from (3.64)

$$x^* = \alpha - \xi \left(\frac{\partial x^*}{\partial z^*} + \frac{\partial x^*}{\partial t^*} \right) \qquad (B.2)$$

with

$$\xi = \alpha (1+R)/N_{OG} \qquad (B.3)$$

Using the initial condition (3.45), the Laplace transform of (B.2) is

$$\bar{X}^*\Big|_{z^*=z_F^*} (1+\xi s) + \xi \left.\frac{d\bar{X}^*}{dz^*}\right|_{z^*=z_F^*} - \alpha/s - \xi = 0 \qquad (B.4)$$

and this is the new boundary condition at $z^*=z_F^*$. With the same initial condition, the Laplace transform of (3.65) is

$$\frac{d^2\bar{X}^*}{dz^{*2}} + (s - \beta N_{OG}) \frac{d\bar{X}^*}{dz^*} - N_{OG}(s\bar{X}^* - 1) = 0 \quad (B.5)$$

and the boundary condition at the bottom of the column is, from (3.77) with $f(1) = 1$,

$$\bar{X}^*\Big|_{z^*=1} (\alpha\Phi - 1 - \xi s) = \xi\left(\frac{d\bar{X}^*}{dz^*}\Big|_{z^*=1} - 1\right) + \alpha(\Phi - 1)/s \quad (B.6)$$

The solution of equation (B.5) subject to boundary conditions (B.4) and (B.6) is

$$\bar{X}^* = 1/s + \frac{\varepsilon}{s} \cdot \frac{\{\eta_1 - \gamma_1 e^{D_1(1-z_F^*)}\} e^{D_2(z^*-z_F^*)} - \{\eta_2 - \gamma_2 e^{D_2(1-z_F^*)}\} e^{D_1(z^*-z_F^*)}}{\eta_2\gamma_1 \exp\{D_1(1-z_F^*)\} - \eta_1\gamma_2 \exp\{D_2(1-z_F^*)\}} \quad (B.7)$$

where D_1, D_2, γ_1 and γ_2 are the functions of s defined in (3.81), (3.82), (3.87) and (3.88), and η_1 and η_2 are now given by

$$\eta_1(s) = -1 - \xi (s + D_1) \quad (B.8)$$

$$\eta_2(s) = -1 - \xi (s + D_2) \quad (B.9)$$

Obtaining the reverse transform as in the case discussed in the text, the solution is

$$x^*(z^*,t^*) = x^*(z^*,\infty) + \varepsilon \sum_{s_n} C(z^*,s_n) \exp(s_n t^*) \quad (B.10)$$

where

$$x^*(z^*,\infty) = \frac{\alpha R + \varepsilon \exp\{\beta N_{OG}(z^*-1)\}}{R + \varepsilon(1+R) \exp\{\beta N_{OG}(z_F^*-1)\}} \quad (B.11)$$

$$C(z^*,s_n)=\frac{\{(n_1-\gamma_1 e^{D_1(1-z_F^*)})e^{D_2(z^*-z_F^*)}-(n_2-\gamma_2 e^{D_2(1-z_F^*)})e^{D_1(z^*-z_F^*)}\}s=s_n}{s_n\{\frac{d}{ds}(n_2\gamma_1 e^{D_1(1-z_F^*)}-n_1\gamma_2 e^{D_2(1-z_F^*)})\}\ s=s_n} \tag{B.12}$$

and the s_n's are the roots of

$$n_1\gamma_2/(n_2\gamma_1) = \exp\{2\theta^{\frac{1}{2}}(1-z_F^*)\} \tag{B.13}$$

For the zone above z_F^* the differential equation is

$$\frac{\partial^2 x^*}{\partial z^{*2}} + \frac{\partial^2 x^*}{\partial z^*\partial t^*} - \frac{N_{OG}K}{(1+M)}\frac{\partial x^*}{\partial z^*} - \frac{N_{OG}}{(1+M)}\frac{\partial x^*}{\partial t^*} = 0 \tag{B.14}$$

where

$$K = \beta - r/\alpha \tag{B.15}$$

and M is given by (3.62). The boundary condition at $z^*=0$ is now (instead of (5.58)),

$$y^*\Big|_{z^*=1} - N\,\underline{x}^*/(1+M) = \frac{\tau_{TS}^*}{(1+M)}\frac{d\underline{x}^*}{dt^*} \tag{B.16}$$

APPENDIX C

STEADY-STATE SOLUTIONS FOR THE NON-LINEAR AND LINEAR EQUATIONS

Using the non-linear equilibrium relation

$$\alpha = x(1 - y)/\{y(1 - x)\} \tag{C.1}$$

the mass transfer flux of the heavy component is, from (3.25)

$$N_h = K_{OG}\{y - x/(\alpha - \epsilon x)\} = K_{OL}\{\alpha y/(1 + \epsilon y) - x\} \tag{C.2}$$

Using the dimensionless variables z* and t* defined in (3.37), equations (3.23) and (3.24) become

$$\frac{\partial x}{\partial z^*} + \frac{\partial x}{\partial t^*} = \frac{N_{OG}}{(1+R)}\left(y - \frac{x}{\alpha - \epsilon x}\right) \tag{C.3}$$

$$\frac{\partial y}{\partial z^*} = N_{OG}\left(y - \frac{x}{\alpha - \epsilon x}\right) \tag{C.4}$$

and the equivalent second-order equation is

$$\frac{\partial^2 x}{\partial z^{*2}} + \frac{\partial^2 x}{\partial z^* \partial t^*} - N_{OG}\left\{1 - \frac{\alpha}{(1+R)(\alpha - \epsilon x)^2}\right\}\frac{\partial x}{\partial z^*} - N_{OG}\frac{\partial x}{\partial t^*} = 0 \tag{C.5}$$

At steady state, (C.5) becomes

$$\frac{d^2 x}{dz^{*2}} - N_{OG}\left\{1 - \frac{\alpha}{(1+R)(\alpha - \epsilon x)^2}\right\}\frac{dx}{dz^*} = 0 \tag{C.6}$$

(a) The linear approximation

The linear approximation used throughout the text is

$$\alpha - \varepsilon x \simeq \alpha \tag{C.7}$$

in which case equation (C.6) becomes

$$\frac{d^2x}{dz^{*2}} - N_{OG}\,\beta\,\frac{dx}{dz^*} = 0 \tag{C.8}$$

where β is the constant defined in (3.66). Apart from the use of x instead of x*, this is equation (3.65) for steady-state conditions.

The solution (3.107) can also be obtained by direct integration of (C.8). Introducing x* (to use the same notation) the general solution of (C.8) is

$$x^* = C_1 \exp(N_{OG}\beta z^*)/(N_{OG}\beta) + C_2 \tag{C.9}$$

From (3.51) and (3.58) the boundary conditions are

$$\text{at } z^* = 1, \quad x^* = y^* ; \tag{C.10}$$

$$\text{at } z^* = 0, \quad y^* + M = Nx^* \tag{C.11}$$

From (3.64)

$$y^* = \frac{(1+R)}{N_{OG}}\,\frac{dx^*}{dz^*} + x^*/\alpha \tag{C.12}$$

From (C.10), (C.11) and (C.12) the integration constants are

$$C_1 = \frac{\varepsilon\,\beta\,M\,N_{OG}}{\varepsilon(M-R)/\alpha + R(\alpha N-1)\,\exp(N_{OG}\beta)} \tag{C.13}$$

$$C_2 = \frac{\alpha\,M\,R\,\exp(N_{OG}\beta)}{\varepsilon(M-R)/\alpha + R(\alpha N-1)\,\exp(N_{OG}\beta)} \tag{C.14}$$

and using the definitions of β, M and N, equation (3.107) is obtained.

(b) A non-linear approximation

Equation (C.6) can be integrated and the solution is

$$\frac{-z^*}{\varepsilon(1+R)} = \frac{2\alpha+\varepsilon B/A}{D^{\frac{1}{2}}} \tanh^{-1}\left(\frac{2Ax+B}{D^{\frac{1}{2}}}\right) + (\varepsilon/2A)\ln|Ax^2+Bx+C| + C_2 \quad (C.15)$$

where the constants A, B, C and D are

$$A = - N_{OG}\, \varepsilon^2\, (1+R) \quad (C.16)$$

$$B = \varepsilon(1+R)\, (N_{OG} - \varepsilon C_1) \quad (C.17)$$

$$C = - \alpha\, \{N_{OG} - \varepsilon\, C_1\, (1+R)\} \quad (C.18)$$

$$D = B^2 - 4\, A\, C \quad (C.19)$$

and C_1 and C_2 are the integration constants.

An explicit solution of (C.6) can be obtained if the coefficient of dx/dz^* is expanded in series

$$1 - \frac{\alpha}{(1+R)(\alpha-\varepsilon x)^2} = \beta - 2\varepsilon(1-\beta)x/\alpha - 3(\varepsilon/\alpha)^2(1-\beta)x^2 + \ldots \quad (C.20)$$

and terms of order greater than x are neglected. Then (C.6) becomes

$$\frac{d^2x}{dz^{*2}} - N_{OG}\, \{\beta - 2\varepsilon(1-\beta)x/\alpha\}\, \frac{dx}{dz^*} = 0 \quad (C.21)$$

and the solution of (C.21) is

$$x = \frac{\alpha\beta}{2\varepsilon(1-\beta)} - \frac{\alpha D^{\frac{1}{2}}}{2N_{OG}\varepsilon(1-\beta)} \tanh\{(C_2 - z^*)\, D^{\frac{1}{2}} / 2\} \qquad (C.22)$$

where

$$D = (N_{OG}\beta)^2 + 4N_{OG}\varepsilon(1-\beta)C_1/\alpha \qquad (C.23)$$

and C_1 and C_2 are the integration constants.

The boundary conditions are now

$$\text{at } z^*=1 , \qquad y = x \qquad (C.24)$$

$$\text{at } z^*=0 , \; y + Mx_o - (1+R)x - (M-R)x/(\alpha-\varepsilon x)=0 \qquad (C.25)$$

where x_o is the feed composition and y is, from (C.3)

$$y = \frac{x}{\alpha - \varepsilon x} + \frac{(1+R)}{N_{OG}} \frac{dx}{dz^*} \qquad (C.26)$$

The constants C_1 and C_2 were determined numerically from (C.24) and (C.25), and a listing of the computer program written for this purpose is included at the end of the appendix.

(c) A numerical example

In order to compare the concentration profiles given by the linear and non-linear approximations (i.e., equations (3.107) and (C.22)), two numerical examples were computed and the results are shown in Table C.1. A large value of N_{OG} was chosen in order to emphasize that the linear approximation can give concentrations greater than 100%. The results for case 1 are also plotted in Figure C.1.

TABLE C.1 CONCENTRATION PROFILES AT STEADY-STATE

z*	$x(z^*,\infty)$(%)			
	CASE 1 (R=0)		CASE 2 ($R=5\times10^{-4}$)	
	LINEAR EQN.	NON-LINEAR EQ.	LINEAR EQN.	NON-LINEAR EQ.
0	.367	.362	.347	.347
0.1	.667	.588	.353	.353
0.2	1.210	.994	.365	.364
0.3	2.198	1.722	.387	.385
0.4	3.990	3.017	.429	.425
0.5	7.244	5.280	.509	.501
0.6	13.153	9.128	.661	.647
0.7	23.881	15.368	.948	.925
0.8	43.358	24.751	1.490	1.456
0.9	78.722	37.372	2.505	2.469
1.0	142.928	52.024	4.401	4.382

Parameters used:

$x_o = .365$ (%)

$\alpha = 1.006$

$r = .1$

$N_{OG} = 1000$

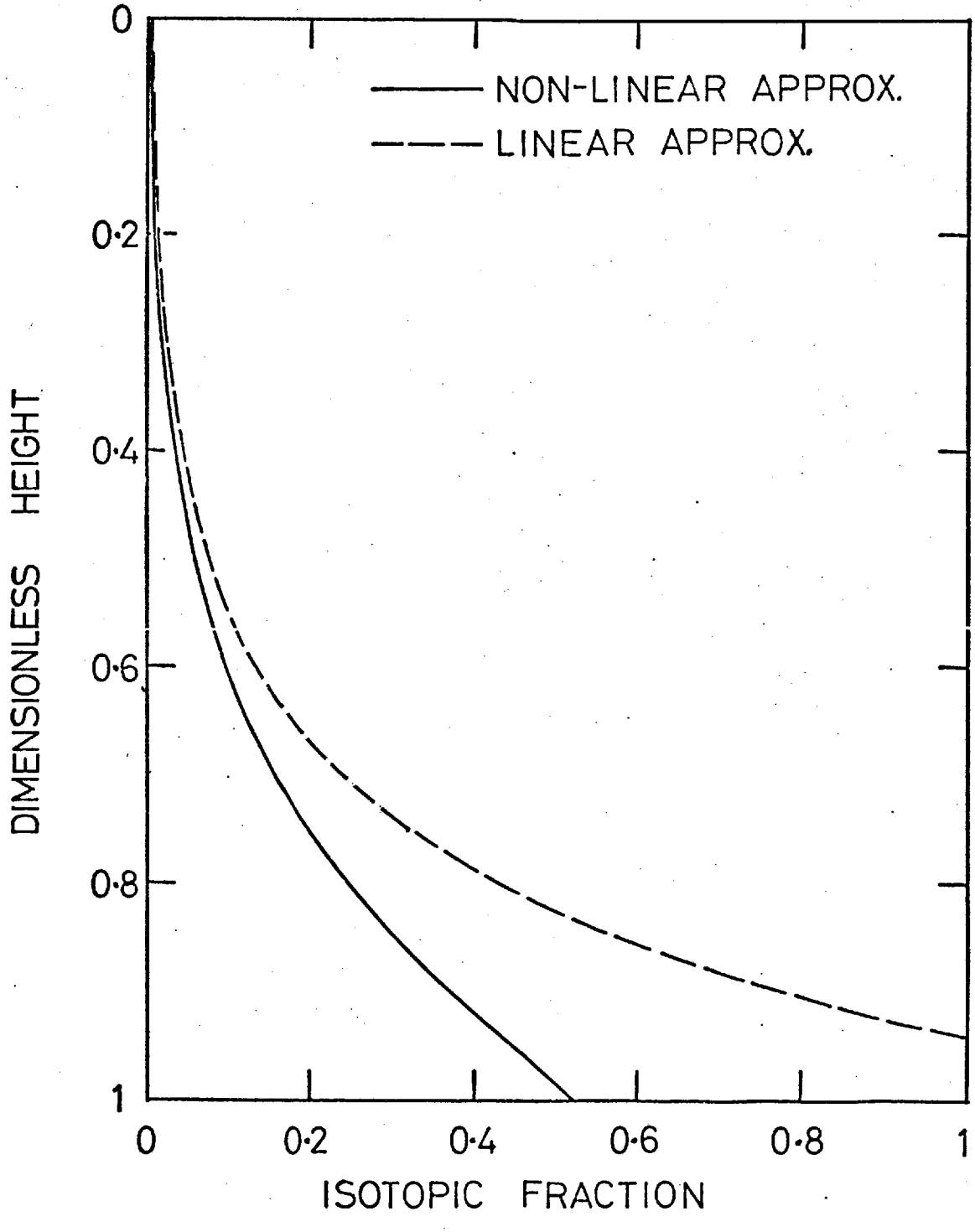


Figure C.1. Steady-state concentration profiles given by the linear and non-linear approximations for the case of R=0.

```
JOB(UMECP25,J1)
PASSWOP(AMMONIA)
FORTRAN(C=.,O,R=2,R=BIN)
MAP(P)
BIN.
      PROGRAM NONLIN (OUTPUT,TAPE6=OUTPUT)
      COMPLEX SD,F1,F3,F5,G1,G2,F4
      DIMENSION XSTAR(21),X(21)
      COMMON   ALFA,ANOG,AM,AN,BETA,C1,C2,EPSILO,R,RR,XX0,A,B,BB
      ALFA=1.000
      ANOG=100.
      XX0=.00365
      R=.1
      RR=0.
      EPSILO=ALFA-1.
      BETA=(ALFA*(1.+RR)-1.)/(ALFA*(1.+RR))
      BB=1.-BETA
      A1=ALFA*R*RR
      A2=EPSILO*R
      A3=EXP(ANOG*BETA)
      A4=RR*(EPSILO+R)
      A5=EPSILO*(R-RR/(1.+RR))/ALFA
      A6=A1*A3
      A7=(A4*A3+A5)/XX0
      AB=A6/A7
      A9=A2/A7
      AM=R*(1.+RR)
      AN=1.+RR+(AM-RR)/ALFA
      CALL CONST
      D=(ANOG*BETA)**2+4.*EPSILO*ANOG*C1/ALFA*BB
      IF(D.GT.0.) GO TO 10
      AD=ABS(D)
      SRD=SQRT(AD)
      SD=CMPLX(0.,SRD)
      GO TO 20
   10 SRD=SQRT(D)
      SD=CMPLX(SRD, 0.)
   20 F1=-ALFA*SD/(2.*ANOG*EPSILO*BB)
      F2=ALFA*BETA/(2.*EPSILO*BB)
      F3=SD/2.
      WRITE(6,1010) D,F1,F2,F3
      WRITE(6,1020)
        DO 100 I=1,21
      AI=I
      ZSTAR=(AI-1.)*.05
      ZZ=ZSTAR-C2
      F5=-F3*ZZ
      RE=REAL(F5)
      RAI=AIMAG(F5)
      IF(RE.GT.145.) RE=145.
      IF (RE.LT.-145.) RE=-145.
      F5=CMPLX(RE,RAI)
      G1=CEXP(F5)
      G2=1./G1
      F4=(G1-G2)/(G1+G2)
      X(I)=F1*F4+F2
      XSTAR(I)=AB+A9*EXP(ANOG*BETA*ZSTAR)
      WRITE(6,1030) ZSTAR,X(I),XSTAR(I),F4
  100 CONTINUE
 1000 FORMAT(1X,3(F8.5,5X),5X,2(F9.5,5X))
 1010 FORMAT(12X,2HD=,F9.4,5X,3HF1=,2(F9.5,5X),3HF2=,F9.5,5X,3HF3=,
     12(F9.5,5X))
 1020 FORMAT(12X,5HZSTAR,10X,4HX(I),5X,6HXSTAR(I),10X,4HTANH)
      STOP
      END
```

```
      SUBROUTINE CONST
      EXTERNAL CALCFX
      DIMENSION X(2),E(2),W(1)
      COMMON   ALFA,ANOG,AM,AN,BETA,C1,C2,EPSILO,R,RR,XX,A,B,BB
      DATA E/1.E-6,1.E-9/
      DATA X/-1.,1./
      N=2
      IPRINT=2
      ESCALE=5.E+6
      ICON=2
      N3N=N*(N+3)
      MAXFUN=1**4*N
      MAXIT=1**N**3
      CALL VA04A(X,E,N,F,ESCALE,IPRINT,ICON,MAXIT,CALCFX,W,N3N,MAXFUN)
      C1=X(1)
      C2=X(2)
      WRITE(6,110) C1,C2,F
  110 FORMAT(1X,3HC1=,F9.5,5X,3HC2=,F9.5,5X,2HF=,E10.3)
      RETURN
      END
      SUBROUTINE CALCFX(N,X,F)
      DIMENSION X(2),E(2),W(1)
      COMPLEX SD,F1,F3,AA0,AAA0,AAB0,A0,AA1,AAA1,AAB1,A1,SA0,SA1,DX0,
     1DX1,X0,X1,S1,S
      COMMON   ALFA,ANOG,AM,AN,BETA,C1,C2,EPSILO,R,RR,XX,A,B,BB
      D=(ANOG*BETA)**2+4.*EPSILO*ANOG*X(1)/ALFA*BB
      IF(D.GT.0.) GO TO 1
      AD=ABS(D)
      SRD=SQRT(AD)
      SD=CMPLX(0.,SRD)
      GO TO 2
    1 SRD=SQRT(D)
      SD=CMPLX(SRD, 0.)
    2 F1=-ALFA*SD/(2.*ANOG*EPSILO*BB)
      F2=ALFA*BETA/(2.*EPSILO*BB)
      F3=SD/2.
      AA0=X(2)*F3
      R0=REAL(AA0)
      AI0=AIMAG(AA0)
      IF(R0.GT.145.)  R0=145.
      IF(R0.LT.-145.)R0=-145.
      AA0=CMPLX(R0,AI0)
      AAA0=CEXP(AA0)
      AAB0=1./AAA0
      A0=(AAA0-AAB0)/(AAA0+AAB0)
      AA1=(X(2)-1.)*F3
      R1=REAL(AA1)
      AI1=AIMAG(AA1)
      IF(R1.GT.145.) R1=145.
      IF(R1.LT.-145.) R1=-145.
      AA1=CMPLX(R1,AI1)
      AAA1=CEXP(AA1)
      AAB1=1./AAA1
      A1=(AAA1-AAB1)/(AAA1+AAB1)
      SA0=A0**2
      SA1=A1**2
      DD=ALFA*D/(4.*ANOG*EPSILO*BB)
      DX0=DD*(1.-SA0)
      DX1=DD*(1.-SA1)
      X0=F1*A0+F2
      X1=F1*A1+F2
      E1=DX1+ANOG*EPSILO*X1*(X1-1.)/((1.+RR)*(ALFA-EPSILO*X1))
      E0=DX0*(1.+RR)/ANOG+A0*XX*(1.+RR)*X0+X0*(1.-AM+RR)/(ALFA-EPSILO*
     1X0)
      F=CABS(E0)+CABS(E1)
      F=F**4
      RETURN
      END
```

APPENDIX D

THE RESIDUE AT s = K

To prove that equation (3.104) is satisfied, recall that K was defined by

$$K = A_2 (N_{OG}\beta - A_2) / (A_2 - N_{OG}) \tag{D.1}$$

Therefore A_2 is, in terms of K,

$$A_2 = - (K - N_{OG}\beta)/2 \pm \{(K - N_{OG}\beta)^2 + 4KN_{OG}\}^{\frac{1}{2}}/2 \tag{D.2}$$

From the definitions of $\lambda(s)$ and $\theta(s)$ (equations (3.83) and (3.84)), it follows that

$$A_2 = \lambda(K) \pm \theta(K)^{\frac{1}{2}} \tag{D.3}$$

where $\lambda(K)$ and $\theta(K)$ are the values of $\lambda(s)$ and $\theta(s)$ for s=K . From (D.3), (3.81) and (3.82) it follows that either $A_2=D_1(K)$ or $A_2=D_2(K)$. It will be shown subsequently that (3.104) is valid in both these cases.

(a) $A_2 = D_1(K)$

From (3.91) and (3.92)

$$P_1(K) = K A_1 \{\alpha\Psi - 1 - \frac{A_2+K}{N_{OG}(1-\beta)}\} \tag{D.4}$$

$$P_2(K) = K A_1 \{\alpha\Phi - 1 - \frac{A_2+K}{N_{OG}(1-\beta)}\} \exp(A_2) \tag{D.5}$$

and from (3.87) and (3.89)

$$P_1(K) = K A_1 \eta_1(K) \tag{D.6}$$

$$P_2(K) = K A_1 \gamma_1(K) \exp(A_2) \tag{D.7}$$

Therefore

$$\lim_{s\to K} \{(s-K) F(s) \exp(st^*)\} = \exp(Kt^*) .$$

$$\frac{KA_1\{\gamma_1\eta_1\exp(A_2)-\eta_1\gamma_1\exp(D_1)\}\exp(D_2z^*)-KA_1\{\gamma_1\eta_2\exp(A_2)-\eta_1\gamma_2\exp(D_2)\}\exp(D_1z^*)}{K\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}} \tag{D.8}$$

But since $A_2 = D_1$,

$$\lim_{s\to K} \{(s-K) F(s) \exp(st^*)\} = - A_1 \exp(A_2 z^*) \exp(Kt^*) \tag{D.9}$$

(b) $A_2 = D_2(K)$

From (D.4), (D.5), (3.88) and (3.90)

$$P_1(K) = K A_1 \eta_2(K) \tag{D.10}$$

$$P_2(K) = K A_1 \gamma_2(K) \exp(A_2) \tag{D.11}$$

and the limit is again given by (D.9).

APPENDIX E

THE RESIDUE AT s = 0

(a) $r \neq 0$ or $R \neq 0$

It was stated in the text (section 3.2.6.1) that in this case the steady state is, for K = 0

$$x^*(z^*,\infty)=A_1\exp(A_2 z^*) + A_3 + \lim_{s\to 0} \{sG(s)\exp(st^*)\} \tag{E.1}$$

and for $K \neq 0$

$$x^*(z^*,\infty) = A_3 + \lim_{s\to 0} \{s\, F(s)\, \exp(st^*)\} \tag{E.2}$$

These two limits will now be calculated in order to prove (3.107).

(i) $K \neq 0$

From (3.91) and (3.92)

$$P_1(0) = - K A_3 (\alpha N - 1) + K \alpha \{M + A_1(\Psi - N)\} \tag{E.3}$$

$$P_2(0) = - K \varepsilon A_3 + K \alpha A_1 (\Phi - 1) \exp(A_2) \tag{E.4}$$

But

$$\Phi(0) = 1 \tag{E.5}$$

$$\Psi(0) = N \tag{E.6}$$

$$\lambda(0) = \theta(0)^{\frac{1}{2}} = N_{0G}\beta/2 \tag{E.7}$$

$$D_1(0) = N_{0G}\beta \tag{E.8}$$

$$D_2(0) = 0 \tag{E.9}$$

$$\gamma_1(0) = -\alpha R \tag{E.10}$$

$$\gamma_2(0) = \varepsilon \tag{E.11}$$

$$\eta_1(0) = \alpha\{N - (1+R)\} \tag{E.12}$$

$$\eta_2(0) = \alpha N - 1 \tag{E.13}$$

Thus

$$P_1(0) = -K\{A_3(\alpha N - 1) - \alpha M\} \tag{E.14}$$

$$P_2(0) = -K\varepsilon A_3 \tag{E.15}$$

and by direct substitution it is found that

$$\lim_{s\to 0}\{sF(s)\exp(st^*)\} = -A_3 + \frac{\alpha r R + r\varepsilon \exp\{N_{OG}\beta(z^*-1)\}}{R(\varepsilon+r)+\varepsilon\{r-R/(1+R)\}\exp(-N_{OG}\beta)/\alpha} \tag{E.16}$$

thus proving (3.107).

(ii) $\underline{K = 0}$

From the definition of K (equation (3.80)),this can arise in two cases, either $A_2=0$ or $A_2=N_{OG}\beta$. For $A_2=0$,

$$Q_1(0) = (A_1 + A_3)(\alpha N - 1) - \alpha M \tag{E.17}$$

$$Q_2(0) = (A_1 + A_3)\varepsilon \tag{E.18}$$

and by manipulation

$$\lim_{s\to 0} \{sG(s)\exp(st^*)\} = -(A_1+A_3) + \frac{\alpha\, r\, R + r\, \varepsilon \exp N_{0G}\beta(z^*-1)}{R(\varepsilon+r)+\varepsilon\{r-R/(1+R)\}\exp(-N_{0G}\beta)/\alpha} \tag{E.19}$$

again leading to (3.107).

For $A_2 = N_{0G}\beta$,

$$Q_1(0) = A_1\ \{\alpha N - 1 - \beta/(1-\beta)\} + A_3(\alpha N - 1) - \alpha M \tag{E.20}$$

$$Q_2(0) = A_1\ \exp(N_{0G}\beta)\ \{\varepsilon - \beta/(1-\beta)\} + \varepsilon A_3 \tag{E.21}$$

but since

$$\varepsilon - \beta/(1-\beta) = -\ \alpha R \tag{E.22}$$

$$\alpha N - 1 - \beta/(1-\beta) = \alpha\{N - (1+R)\} \tag{E.23}$$

it is found that

$$\lim_{s\to 0} \{s\ G(s)\ \exp(st^*)\} = -\{A_3 + A_1\ \exp(N_{0G}\beta z^*)\} + \frac{\alpha\, r\, R + r\, \varepsilon\ \exp\{N_{0G}\beta(z^*-1)\}}{R(\varepsilon+r) + \varepsilon\{r-R/(1+R)\}\exp(-N_{0G}\beta)/\alpha} \tag{E.24}$$

again proving (3.107)

(b) $\underline{r = R = 0}$

For simplicity, the discussion will now be restricted to a constant initial condition. Take for instance $A_1 = 0$ and

$A_3 = 1$ which do not affect K. Then,

$$M = \gamma_1(0) = \eta_1(0) = D_2(0) = 0 \tag{E.25}$$

$$N = \Phi(0) = \Psi(0) = 1 \tag{E.26}$$

$$\lambda(0) = \theta(0)^{\frac{1}{2}} = N_{0G}\beta/2 \tag{E.27}$$

$$\beta = \varepsilon/\alpha \tag{E.28}$$

$$D_1(0) = N_{0G}\beta \tag{E.29}$$

$$\gamma_2(0) = \eta_2(0) = P_1(0) = P_2(0) = \varepsilon \tag{E.30}$$

As mentioned in the text (section 3.2.6.1(b)), the limit $\lim_{s\to 0} \{s\, F(s) \exp(st^*)\}$ has to be evaluated using L'Hopital's rule. Thus,

$$\lim_{s\to 0} \{s\, F(s) \exp(st^*)\} =$$

$$\frac{\frac{d}{ds}\left(\{P_2\eta_1 - P_1\gamma_1\exp(D_1)\}\exp(D_2z^*) - \{P_2\eta_2 - P_1\gamma_2\exp(D_2)\}\exp(D_1z^*)\right)_{s=0}}{\frac{d}{ds}\left((s-K)\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}\right)_{s=0}} \tag{E.31}$$

The derivative in the denominator of (E.31) is

$$\left.\frac{dDen}{ds}\right|_{s=0} = -K\left(\frac{d}{ds}\{\eta_2\gamma_1\exp(D_1) - \eta_1\gamma_2\exp(D_2)\}\right)_{s=0}$$

$$= -K\varepsilon\left\{\left.\frac{d\gamma_1}{ds}\right|_{s=0}\exp(N_{0G}\beta) - \left.\frac{d\eta_1}{ds}\right|_{s=0}\right\} \tag{E.32}$$

But from (3.87), (3.89), (3.74) and (3.75)

$$\left.\frac{d\gamma_1}{ds}\right|_{s=0} = \left.\frac{d\Phi}{ds}\right|_{s=0} - (1 + \left.\frac{dD_1}{ds}\right|_{s=0})/\{N_{OG}(1-\beta)\} \tag{E.33}$$

$$\left.\frac{d\eta_1}{ds}\right|_{s=0} = \left.\frac{d\Psi}{ds}\right|_{s=0} - (1 + \left.\frac{dD_1}{ds}\right|_{s=0})/\{N_{OG}(1-\beta)\} \tag{E.34}$$

$$\left.\frac{d\Phi}{ds}\right|_{s=0} = -(\tau^*_{BL} + \tau^*_{BS}) = -\tau^*_B \tag{E.35}$$

$$\left.\frac{d\Psi}{ds}\right|_{s=0} = \tau^*_{TL} + \tau^*_{TS} = \tau^*_T \tag{E.36}$$

Also

$$\left.\frac{dD_1}{ds}\right|_{s=0} = \left.\frac{d\lambda}{ds}\right|_{s=0} + (\left.\frac{d\theta}{ds}\right|_{s=0})/\{2\theta(0)^{\frac{1}{2}}\} = 1/\varepsilon \tag{E.37}$$

because

$$\left.\frac{d\lambda}{ds}\right|_{s=0} = -1/2 \tag{E.38}$$

$$\left.\frac{d\theta}{ds}\right|_{s=0} = N_{OG}\,(1 - \beta/2) \tag{E.39}$$

Therefore equation (E.32) becomes

$$\left.\frac{dDen}{ds}\right|_{s=0} = K\alpha\varepsilon\left[\tau^*_T + \tau^*_B \exp(N_{OG}\beta) + \{\exp(N_{OG}\beta)-1\}/(N_{OG}\beta)\right] \tag{E.40}$$

Similarly, the derivative in the numerator of (E.31) is,

$$\left.\frac{dNum}{ds}\right|_{s=0} = - K\varepsilon \left\{\left.\frac{d\eta_1}{ds}\right|_{s=0} - \exp(N_{OG}\beta) \left.\frac{d\gamma_1}{ds}\right|_{s=0}\right\} -$$

$$- \exp(N_{OG}\beta z^*) \left(\frac{d}{ds}\{P_2\eta_2 - P_1\gamma_2\exp(D_2)\}\right)_{s=0} \qquad (E.41)$$

But since

$$\left.\frac{dP_1}{ds}\right|_{s=0} = \left.\frac{dP_2}{ds}\right|_{s=0} = - K\varepsilon \qquad (E.42)$$

the derivative in the second term of (E.41) is

$$\left(\frac{d}{ds}\{P_2\eta_2 - P_1\gamma_2\exp(D_2)\}\right)_{s=0} = -K\varepsilon\left(\left.\frac{d\eta_2}{ds}\right|_{s=0} - \left.\frac{d\gamma_2}{ds}\right|_{s=0} - \varepsilon\left.\frac{dD_2}{ds}\right|_{s=0}\right) \qquad (E.43)$$

Also,

$$\left.\frac{d\eta_2}{ds}\right|_{s=0} = \alpha\,\tau_T^* + 1/(N_{OG}\beta) \qquad (E.44)$$

$$\left.\frac{d\gamma_2}{ds}\right|_{s=0} = - \alpha\,\tau_B^* + 1/(N_{OG}\beta) \qquad (E.45)$$

$$\left.\frac{dD_2}{ds}\right|_{s=0} = - 1/\beta \qquad (E.46)$$

Thus,

$$\left.\frac{dNum}{ds}\right|_{s=0} = K\ \alpha\,\varepsilon \exp(N_{OG}\beta z^*)\ (1 + \tau_T^* + \tau_B^*) -$$

$$- K\,\alpha\,\varepsilon\left(\tau_T^* + \tau_B^* \exp(N_{OG}\beta) - \{1 - \exp(N_{OG}\beta)\}/(N_{OG}\beta)\right) \qquad (E.47)$$

Finally from (E.31), (E.40) and (E.47)

$$\frac{\left.\frac{dNum}{ds}\right|_{s=0}}{\left.\frac{dDen}{ds}\right|_{s=0}} = -1 + \frac{(1 + \tau_T^* + \tau_B^*)\exp(N_{OG}\,\beta z^*)}{\tau_T^* + \tau_B^*\exp(N_{OG}\beta) + \{\exp(N_{OG}\beta)-1\}/(N_{OG}\beta)} \qquad \text{(E.48)}$$

and since the term -1 cancels out with $A_3=1$ in (3.105), equation (3.115) is obtained.

APPENDIX F

THE RESIDUES AT $s = s_n$ FOR $\Phi = \Psi = 1$

Recall that the special case (section 3.2.7) implies

$$r = R = \tau_T^* = \tau_B^* = M = 0 \tag{F.1}$$

$$\eta_1 = \gamma_1 \tag{F.2}$$

$$\eta_2 = \gamma_2 \tag{F.3}$$

$$N = 1 \tag{F.4}$$

Since this is a total reflux situation, a height-independent initial condition will be used. Take for instance, $A_1=0$ and $A_3=1$. Then

$$P_1(s_n) = P_2(s_n) = \varepsilon\ (s_n - K) \tag{F.5}$$

and the numerator of (3.124) becomes

$$\text{Num} = (s_n-K) \lim_{s\to s_n} \left(\eta_1\{1-\exp(D_1)\}\exp(D_2 z^*) - \eta_2\{1-\exp(D_2)\}\exp(D_1 z^*)\right) \tag{F.6}$$

From (F.2) and (F.3) it follows that

$$\exp(D_1) = \exp(D_2) \tag{F.7}$$

and therefore, the derivative in the denominator of (3.124) is

$$\left(\frac{d}{ds}\{\eta_2\gamma_1\exp(D_1)-\eta_1\gamma_2\exp(D_2)\}\right)_{s=s_n}=\eta_1\eta_2\left(\frac{d}{ds}\{\exp(D_1)-\exp(D_2)\}\right)_{s=s_n}$$

(F.8)

Therefore, equation (3.124) becomes

$$C(z^*,s_n)=\frac{\lim_{s\to s_n}\left(\eta_1\{1-\exp(D_1)\}\exp(D_2z^*)-\eta_2\{1-\exp(D_2)\}\exp(D_1z^*)\right)_{s=s_n}}{s_n\cdot\eta_1(s_n)\cdot\eta_2(s_n)\left(\frac{d}{ds}\{\exp(D_1)-\exp(D_2)\}\right)_{s=s_n}}$$

(F.9)

From (3.89) and (3.90)

$$\eta_1(s_n)\cdot\eta_2(s_n) = -\alpha^2 s_n/N_{OG} \qquad \text{(F.10)}$$

Also

$$\left(\frac{d}{ds}\{\exp(D_1)-\exp(D_2)\}\right)_{s=s_n}=\exp(\lambda_n)\left\{\left.\frac{dD_1}{ds}\right|_{s=s_n}\exp(\theta_n^{\frac{1}{2}})-\left.\frac{dD_2}{ds}\right|_{s=s_n}\exp(-\theta_n^{\frac{1}{2}})\right\} \qquad \text{(F.11)}$$

where λ_n and θ_n are the values of $\lambda(s)$ and $\theta(s)$ for $s=s_n$.

Now,

$$\left.\frac{dD_1}{ds}\right|_{s=s_n}=\left.\frac{d\lambda}{ds}\right|_{s=s_n}+\left(\left.\frac{d\theta}{ds}\right|_{s=s_n}\right)/(2\theta^{\frac{1}{2}}) \qquad \text{(F.12)}$$

$$\left.\frac{dD_2}{ds}\right|_{s=s_n}=\left.\frac{d\lambda}{ds}\right|_{s=s_n}-\left(\left.\frac{d\theta}{ds}\right|_{s=s_n}\right)/(2\theta^{\frac{1}{2}}) \qquad \text{(F.13)}$$

$$\frac{d\lambda}{ds} = -1/2 \qquad \text{(F.14)}$$

$$\left.\frac{d\theta}{ds}\right|_{s=s_n} = \{s_n + N_{OG}(2-\beta)\}/2 \qquad (F.15)$$

Therefore,

$$\left(\frac{d}{ds}\{\exp(D_1)-\exp(D_2)\}\right)_{s=s_n} = \exp(\lambda_n)\{\frac{s_n + N_{OG}(2-\beta)}{2\theta_n^{\frac{1}{2}}}.\cosh(\theta_n^{\frac{1}{2}}) - \sinh(\theta_n^{\frac{1}{2}})\} \qquad (F.16)$$

Now from (3.130)

$$\cosh(\theta_n^{\frac{1}{2}}) = \cosh \pi n i = \cos \pi n = (-1)^n \qquad (F.17)$$

$$\sinh(\theta_n^{\frac{1}{2}}) = \sinh \pi n i = i \sin \pi n = 0 \qquad (F.18)$$

and therefore (F.16) becomes

$$\left(\frac{d}{ds}\{\exp(D_1)-\exp(D_2)\}\right)_{s=s_n} = \frac{(-1)^n \exp(\lambda_n)\{s_n+N_{OG}(2-\beta)\}}{2\ \theta_n^{\frac{1}{2}}} \qquad (F.19)$$

On the other hand, the limit in the numerator of (F.9) is obtained by direct substitution

$$Num = \{\alpha\ \varepsilon\ \exp(\lambda_n z^*)/N_{OG}\}\left((s_n - N_{OG}\beta)\sinh(\theta_n^{\frac{1}{2}}z^*) - 2\ \theta_n^{\frac{1}{2}}\cosh(\theta_n^{\frac{1}{2}}z^*) - (s_n - N_{OG}\beta)\exp(\lambda_n)\sinh\{\theta_n^{\frac{1}{2}}(z^*-1)\} + 2\ \theta_n^{\frac{1}{2}}\exp(\lambda_n)\cosh\{\theta_n^{\frac{1}{2}}(z^*-1)\}\right) \qquad (F.20)$$

But,

$$\sinh\{\theta_n^{\frac{1}{2}}(z^*-1)\} = \sinh(\theta_n^{\frac{1}{2}}z^*).\cosh(\theta_n^{\frac{1}{2}}) - \cosh(\theta_n^{\frac{1}{2}}z^*).\sinh(\theta_n^{\frac{1}{2}}) \qquad (F.21)$$

$$\cosh\{\theta_n^{\frac{1}{2}}(z^*-1)\} = \cosh(\theta_n^{\frac{1}{2}}z^*).\cosh(\theta_n^{\frac{1}{2}}) - \sinh(\theta_n^{\frac{1}{2}}z^*).\sinh(\theta_n^{\frac{1}{2}}) \tag{F.22}$$

and using (F.17) and (F.18), equation (F.20) becomes

$$\text{Num} = \varepsilon\ \alpha\ \exp(\lambda_n z^*)\ \{1 - (-1)^n \exp(\lambda_n)\}/N_{OG}\ .$$

$$.\{(s_n - N_{OG}\beta).\sinh(\theta_n^{\frac{1}{2}}z^*) - 2\ \theta_n^{\frac{1}{2}}.\cosh(\theta_n^{\frac{1}{2}}z^*)\} \tag{F.23}$$

Thus, from (F.10), (F.19) and (F.23), the coefficients of the transient terms are

$$C(z^*,s_n) = \frac{2\ \beta\ \theta_n^{\frac{1}{2}}\ \exp(\lambda_n z^*)\ \{1 - (-1)^n \exp(-\lambda_n)\}}{s_n^2\ \{s_n + N_{OG}(2-\beta)\}}\ .$$

$$.\{(s_n - N_{OG}\beta).\sinh(\theta_n^{\frac{1}{2}}z^*) - 2\ \theta_n^{\frac{1}{2}}.\cosh(\theta_n^{\frac{1}{2}}z^*)\} \tag{F.24}$$

Finally since

$$\theta_n^{\frac{1}{2}}\ \sinh(\theta_n^{\frac{1}{2}}z^*) = -\ \pi\ n\ \sin(\pi n z^*) \tag{F.25}$$

$$\theta_n\ \cosh(\theta_n^{\frac{1}{2}}z^*) = -\ \pi^2\ n^2\ \cos(\pi n z^*) \tag{F.26}$$

equation (F.24) becomes

$$C(z^*,s_n) = \frac{-\ 2\ \pi\ n\ \beta\ \exp(\lambda_n z^*)\{1 - (-1)^n \exp(-\lambda_n)\}}{s_n^2\ \{s_n + N_{OG}(2-\beta)\}}\ .$$

$$.\{(s_n - N_{OG}\beta).\sin\ (\pi n z^*) - 2\ \pi\ n\ \cos(\pi n z^*)\} \tag{F.27}$$

At the bottom of the column ($z^* = 1$)

$$\sin\ \pi\ n = 0 \tag{F.28}$$

$$\cos \pi n = (-1)^n \tag{F.29}$$

and therefore equation (F.27) becomes

$$C(1,s_n) = \frac{-4 \pi^2 \beta n^2 \{1 - (-1)^n \exp(\lambda_n)\}}{s_n^2 \{s_n + N_{OG}(2-\beta)\}} \tag{F.30}$$

APPENDIX G

PROGRAM TRUNIT

```
JOB(UMECR25,J1)
PASSWOR(AMMONIA)
ATTACH(ICLIB/UN=LIBRARY)
MNF(D,E=2,B=BIN)
LIBRARY(ICLIB)
GET(MICMNF/UN=CMAAE09)
CALL,MICMNF(L=BIN)
,
      PROGRAM TRUNIT(OUTPUT,TAPE6=OUTPUT,TAPE62)
C
C          TRUNIT - A PROGRAM TO COMPUTE THE NUMBER OF OVERALL TRANSFER
C                   UNITS IN A PACKED COLUMN, USING DATA FROM
C                   UNSTEADY-STATE OPERATION.
C                   VERSION 3 - 74/02/28 - J.J. ROMAO DE SOUSA
C
C
CCC        THEORETICAL BASIS
C          ----------------
C
C              THIS PROGRAM IS BASED ON A LINEAR MODEL, DEVELOPED FOR
C          ISOTOPE SEPARATION CHEMICAL EXCHANGE SYSTEMS, WITH THE ASSUMPTIONS
C
C              1)- A LINEAR GAS-LIQUID EQUILIBRIUM LINE.
C              2)- ISOTHERMAL AND EQUIMOLECULAR INTERPHASE MASS-TRANSFER.
C              3)- NEGLIGIBLE  GAS-PHASE HOLD-UP
C
C              THE MODEL  INCLUDES TWO TIME-CONSTANTS AT EACH REFLUX
C          SECTION, IN ORDER TO FULLY ACCOUNT FOR THEIR DYNAMIC BEHAVIOUR.
C
C              THE MASS BALANCE IN A DIFFERENTIAL HEIGHT IN THE COLUMN
C          PRODUCES AN HYPERBOLIC PARTIAL DIFFERENTIAL EQUATION. A LAPLACE
C          TRANSFORM SOLUTION OF THE PROBLEM IS GIVEN BY A STEADY-STATE
C          TERM AND A SERIES OF TRANSIENT TERMS (THE SUMMATION BEEING
C          EXTENDED IN GENERAL TO THE ROOTS OF A TRANSCENDENTAL EQN.).
C
C              FOR FURTHER DETAILS SEE THE DOCUMENTATION IN EACH ROUTINE.
C
C
CCC        USING THE PROGRAM
C          -----------------
C
C              THE USER MUST SPECIFY (IN DATA STATEMENTS) THE FOLLOWING
C          VARIABLES AND ARRAYS,
C
C              1)- CHEMICAL SYSTEM DATA
C                  --------------------
C              ALFA - SEPARATION FACTOR
C
C              2)- COLUMN SPECIFICATIONS
C                  ---------------------
C              AHEIG - HEIGHT OF PACKING (METERS)
C              AREA - CROSS-SECTIONAL AREA (SQUARE METERS)
C
C              3)- OPERATING CONDITIONS
C                  --------------------
C              FLOW - VOLUMETRIC LIQUID FLOW RATE (CUBIC METERS/HOUR)
C              OLDUP - VOLUMETRIC LIQUID PHASE HOLD-UP PER VOLUME OF PACKING
C              STVT - STIRRED-TANK VOLUME FOR TOP REFLUX SECTION (M3)
C              STVB -    '     '     '     ' BOTTOM  '     '     '
```

```
C               TLVT - TRANSPORTATION LAG VOL. FOR TOP REFLUX SECTION (M3)
C               TLVB -          '          '   '    ' BOTTOM  '       '      '
C               R - RATIO OF FEED TO LIQUID-PHASE FLOW-RATES
C               RR - RECIPROCAL REFLUX RATIO
C               X0 - INITIAL CONCENTRATION
C
C               4)- EXPERIMENTAL POINTS
C                   ------------------
C               NDP - NO. OF DATA POINTS (UP TO 50)
C               BOTCON(NDP) - CONCENTRATION AT BOTTOM OF COLUMN AT T=TIME
C               TIME(NDP) - TIME (HOURS)
C
C               5)- USER'S REQUIREMENTS
C                   ------------------
C               NROOTS - NO. OF TRANSIENT TERMS REQUIRED IN SERIES(UP TO 10)
C               NPROF - '   '      '    PROFILES    '    (UP TO 10)
C               TPROF(NPROF) - TIMES OF TRANSIENT PROFILES (IN HOURS), OR INSTEAD
C               TIMES(NPROF) -    '    '       '          '  (DIMENSIONLESS)
C               NPRINT - CONTROLS PRINTING
C                        - IF NPRINT=0 THERE WILL BE NO PRINTING
C                        - IF NPRINT=1 THERE WILL BE PRINTING FROM
C                              - PROGRAM TRUNIT
C                              - ROUTINE OPTIM
C                              - ROUTINE ENDTIM
C                        - IF NPRINT=-1 THERE WILL BE PRINTING FROM ALL ROUTINES
C                              (APPROX. 200 LINES)
C               ITIM - CONTROLS TIMES OF TRANS. PROFILES INPUT,
C                        - IF TIMES(NPROF) IS SPECIFIED THEN SET ITIM=0
C                        - INSTEAD, IF TPROF(NPROF) IS SPECIFIED, SET ITIM=1
C               IFILM - CONTROLS CALLING OF SUBROUTINE FILM
C                        - IF IFILM=0 THE SUB. WILL NOT BE CALLED
C                        - IF IFILM EQUALS ANY INTEGER(+ OR -) SUB. WILL BE CALLED
C               XLEN - LENGHT IN INCHES OF X-AXIS (FOR MICROFILM PLOTS )
C               YLEN - LENGHT IN INCHES OF Y-AXIS (FOR MICROFILM PLOTS )
C
C
CCC         LIMITATIONS
C           -----------
C
C               1)- THOSE ARISING FROM THE THEORETICAL BASIS
C               2)- THE DIMENSIONAL LIMITS
C
C
CC          PROGRAM CALLS
C           -------------
C
C           SUBROUTINE SETPAR
C           SUBROUTINE OPTIM
C           SUBROUTINE STEADY
C           SUBROUTINE ROOTS
C           SUBROUTINE COEF
C           SUBROUTINE PROFIL
C           SUBROUTINE ENDTIM
C           SUBROUTINE FILM (OPTIONAL)
C
C
CCC         MACHINE DEPENDENCE
C           ------------------
C
```

```
C            PROGRAM HEADER CARD - THE PROGRAM WAS WRITTEN ON A
C          CDC 6400 COMPUTER WHICH USED THE KRONOS OPERATING SYSTEM
C          (VER 2) AND A PROGRAM CARD WAS NEEDED. ITS PURPOSE IS
C          TO ASSIGN INPUT/OUTPUT DEVICES.
C
C
CC         ALGORITHM
C          ---------
C
C
      COMMON/SIZES/XLEN,YLEN
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),X0,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON/PRINT/NPRINT
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
      DATA XLEN,YLEN/5.,10./
      DATA AHEIG,ALFA,AREA/5.1,1.006,.0005/
      DATA FLOW,OLDUP,X0/.00066,.13,.36/
      DATA TIME/50.,80.,200.,301.5,402.01,500./
      DATA BOTCON/.6274,.7445,1.082,1.257,1.3686,1.4393/
      DATA R,RR/.1,.001/
      DATA STVT,TLVT,STVB,TLVB/.0005,.00025,.0001,.00005/
      DATA ITIM,NPRINT,IFILM/1,-1,1/
      DATA NDP/6/
      DATA NPROF,NROOTS/5,10/
      DATA TPROF/10.,50.,100.,200.,400./
      CALL SETPAR
      CALL OPTIM
      CALL STEADY
      CALL ROOTS
      CALL COEF
      CALL PROFIL
      CALL ENDTIM
      IF (IFILM) 10,20,10
   10 CALL FILM
   20 STOP
      END
```

```
      SUBROUTINE SETPAR
C
C          SETPAR - REARRANGES THE USER'S DATA INTO DIMENSIONLESS FORM
C                   AND WRITES IT OUT.
C
C
CC         SUBROUTINE CALLED BY
C          --------------------
C
C          PROGRAM TRUNIT
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          NO ROUTINE
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON PRINT
C
C
CC         VARIABLES ASSOCIATED WITH THIS ROUTINE
C          --------------------------------------
C
C          ADDITIONS -
C
C              TNOT - REFERENCE TIME
C              TSTAR - DIMENSIONLESS TIME
C              XSTARB - DIMENSIONLESS CONCENTRATION AT BOTTOM OF COLUMN(EXP.)
C              STT - DIMENSLESS TIME CONSTANT (STIRRED-TANK AT TOP )
C              STB - DIMENSLESS TIME CONSTANT (STIRRED-TANK AT BOTTOM )
C              TLT - DIMENSLESS TIME CONSTANT ( TRANSP. LAG AT TOP )
C              TLB - DIMENSLESS TIME CONSTANT ( TRANSP. LAG AT BOTTOM )
C
C
CC         ALGORITHM
C          ---------
C
C
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),XO,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON A,AMIN(11),B,C(10,10),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
C
C               COMPUTE DIMENSIONLESS TIME(TSTAR) AND BOTTOM CONC.(XSTARB)
C
      EPSILO=ALFA-1.
      FA=AREA*AHEIG*OLDUP
      STT=STVT*(1.+RR)/FA
      STB=STVB*(1.+RR)/FA
      TLT=TLVT/FA
```

```
      TLB=TLVB*(1.+RR)/FA
      TNOT=AREA*AHEIG*OLDUP/FLOW
        DO 100 I=1,NDP
      TSTAR(I)=TIME(I)/TNOT
      XSTARB(I)=BOTCON(I)/X0
  100 CONTINUE
C
C             COMPUTE EITHER TPROF(NPROF) OR TIMES(NPROF), ACCORDING TO ITIM
C
      IF (ITIM) 20,10,20
   10   DO 200 I=1,NPROF
      TPROF(I)=TIMES(I)*TNOT
  200 CONTINUE
      GO TO 30
   20   DO 300 I=1,NPROF
      TIMES(I)=TPROF(I)/TNOT
  300 CONTINUE
   30 TB=STB+TLB
      TT=STT+TLT
      IF (NPRINT) 40,50,40
C
C             WRITE OUT DATA
C
   40 WRITE(6,1000)
      WRITE(6,1010)
      WRITE(6,1020) ALFA
      WRITE(6,1030) AHEIG
      WRITE(6,1040) AREA
      WRITE(6,1050) FLOW
      WRITE(6,1060) OLDUP
      WRITE(6,1070) R
      WRITE(6,1080) RR
      WRITE(6,1090) STVT,STT
      WRITE(6,1100) TLVT,TLT
      WRITE(6,1110) STVB,STB
      WRITE(6,1120) TLVB,TLB
      WRITE(6,1130)
      WRITE(6,1140)
        DO 400 I=1,NDP
      WRITE(6,1150) TIME(I),TSTAR(I),BOTCON(I),XSTARB(I)
  400 CONTINUE
 1000 FORMAT(1H1,9X,17H***USER'S DATA***)
 1010 FORMAT(10X,17H================)
 1020 FORMAT(1H0,20X,27HSYSTEM SEPARATION FACTOR = ,F7.4)
 1030 FORMAT(1H0,20X,16HCOLUMN HEIGHT = ,F5.3,7H METERS)
 1040 FORMAT(1H0,20X,26HCOLUMN CROSS-SECT. AREA = ,F7.5,11H SQ. METERS)
 1050 FORMAT(1H0,20X,19HLIQUID FLOW-RATE = ,F8.6,18H CUBIC METERS/HOUR)
 1060 FORMAT(1H0,20X,17HLIQUID HOLD-UP = ,F5.3)
 1070 FORMAT(1H0,20X,31HDIMENSIONLESS FEED FLOW-RATE = ,F5.3)
 1080 FORMAT(1H0,20X,26HRECIPROCAL REFLUX RATIO = ,F7.5)
 1090 FORMAT(1H0,7HSTVT = ,F9.6,12HCUBIC METERS,2X,8H( STT = ,F7.3,2H ))
 1100 FORMAT(1H0,7HTLVT = ,F9.6,12H      ',      ,2X,8H( TLT = ,F7.3,2H ))
 1110 FORMAT(1H0,7HSTVB = ,F9.6,12H      ',      ,2X,8H( STB = ,F7.3,2H ))
 1120 FORMAT(1H0,7HTLVB = ,F9.6,12H      ',      ,2X,8H( TLB = ,F7.3,2H ))
 1130 FORMAT(1H0,20X,11HTIME(HOURS),9X,5HTSTAR,13X,6HBOTCON,12X,6HXSTARB
     1)
 1140 FORMAT(21X,11H==========,9X,5H=====,13X,6H======,12X,6H======)
 1150 FORMAT(1H0,10X,4(9X,F9.4))
   50 RETURN
      END
```

```
      SUBROUTINE OPTIM
C
C          OPTIM - DETERMINES THE STEADY-STATE CONC. AT THE BOTTOM OF
C                  COLUMN. BY MINIMIZING THE SUM OF SQUARES OF DEVIATIONS
C                  BETWEEN EXPERIMENTAL POINTS AND THE LOG-LINEAR DEPENDENC
C                  OF XSSB-XSTARB(I) AND TSTAR(I) GIVEN BY THE MODEL .
C
C
CC         SUBROUTINE CALLED BY
C          --------------------
C
C          PROGRAM TRUNIT
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          ROUTINE VA04A
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON POINTS
C          COMMON PRINT
C
C
CC         VARIABLES ASSOCIATED WITH THIS ROUTINE
C          --------------------------------------
C
C          ADDITIONS -
C
C              XSSB - STEADY-STATE CONC. AT BOTTOM OF COLUMN
C              TU - NO. OF OVERALL TRANSFER UNITS
C              HTU - HEIGHT OF OVERALL TRANSFER UNIT
C
C
CC         ALGORITHM
C          ---------
C
C
      EXTERNAL CALCFX
      DIMENSION X(2),E(2),W(10)
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),X0,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/POINTS/CALC(50),DEV(50),EXPT(50)
      COMMON/PRINT/NPRINT
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
      DATA X/50.,-.00001/
      DATA E/.001,10.E-8/
      N=2
      ESCALE=10.E+3
      ICON=2
      N3N=N*(N+3)
      MAXFUN=10**4*N
```

```
      MAXIT=100*N
      IF (NPRINT) 10,20,20
   10 IPRINT=2
      WRITE(6,1000)
      WRITE(6,1010)
      GO TO 30
   20 IPRINT=0
   30 CALL VA04A(X,E,N,F,ESCALE,IPRINT,ICON,MAXIT,CALCFX,W,N3N,MAXFUN)
      TU=X(1)
      HTU=AHEIG/TU
      IF (NPRINT) 40,50,40
   40 WRITE(6,1020)
      WRITE(6,1010)
      WRITE(6,1030)
      WRITE(6,1040)
        DO 100 I=1,NDP
      WRITE(6,1050) EXPT(I),CALC(I),DEV(I)
  100 CONTINUE
      WRITE(6,1060) XSSB
      WRITE(6,1070) HTU
 1000 FORMAT(1H1,9X,26H***SUB. VA04A PRINT-OUT***)
 1010 FORMAT(10X,26H==========================)
 1020 FORMAT(1H1,9X,26H***SUB. OPTIM PRINT-OUT***)
 1030 FORMAT(1H0,29X,4HEXPT,10X,4HCALC,10X,3HDEV)
 1040 FORMAT(30X,4H====,10X,4H====,10X,3H===)
 1050 FORMAT(1H0,20X,3(F14.6))
 1060 FORMAT(1H0,20X,36HBOTTOM STEADY-STATE CONCENTRATION = ,F7.4)
 1070 FORMAT(1H0,20X,34HHEIGHT OF OVERALL TRANSFER UNIT = ,F7.4,8H  METE
     1RS)
   50 RETURN
      END
```

```
      SUBROUTINE STEADY
C
C          STEADY - COMPUTES 101 POINTS OF THE STEADY-STATE PROFILE,
C                   ( WITH AN INCREMENT OF ZSTAR = .01 )
C
C
CC         SUBROUTINE CALLED BY
C          --------------------
C
C          PROGRAM TRUNIT
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          NO ROUTINE
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON PRINT
C
C
CC         VARIABLES ASSOCIATED WITH THIS ROUTINE
C          --------------------------------------
C
C          ADDITIONS -
C
C              XSTAR - STEADY-STATE DIMENSIONLESS CONCENTRATION
C
C
CC         ALGORITHM
C          ---------
C
C
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),XO,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/PRINT/NPRINT
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
      FACT=TU*(ALFA*(1.+RR)-1.)
      EFACT=EXP(FACT)
      Y=10.E-10
      IF (R.LT.Y.AND.RR.LT.Y ) GO TO 10
      GO TO 20
   10 T=TT+TB+1.
      DENOM=TT+TB*EFACT+(EFACT-1.)/FACT
        DO 100 I=1,101
      AI=I-1
      ZSTAR(I)=AI*.01
      XSTAR(I)=T*EXP(FACT*ZSTAR(I))/DENOM
  100 CONTINUE
      GO TO 50
   20 DENOM=RR*(R+EPSILO)*EFACT+EPSILO*(R-RR/(1.+RR))/ALFA
      AUX=ALFA*R*RR*EFACT
```

```
      BUX=EPSILO*R
        DO 200 I=1,101
      AI=I-1
      ZSTAR(I)=AI*.01
      XSTAR(I)=(AUX+BUX*EXP(FACT*ZSTAR(I)))/DENOM
  200 CONTINUE
   30 IF (NPRINT) 40,50,50
C
C           PRINT 21 POINTS ON LINE-PRINTER
C
   40 WRITE(6,1010)
      WRITE(6,1020)
      WRITE(6,1030)
      WRITE(6,1040)
        DO 300 I=1,101,5
      WRITE(6,1050) I, ZSTAR(I), XSTAR(I)
  300 CONTINUE
 1010 FORMAT(1H1,9X,27H***SUB. STEADY PRINT-OUT***)
 1020 FORMAT(10X,27H===========================)
 1030 FORMAT(1H0,20X,1HI,11X,5HZSTAR,11X,5HXSTAR)
 1040 FORMAT(21X,1H=,11X,5H=====,11X,5H=====)
 1050 FORMAT(1H0,18X,I3,2(9X,F7.4))
   50 RETURN
      END
```

```
      SUBROUTINE ROOTS
C
C          ROOTS - FINDS THE FIRST NROOTS ROOTS OF THE TRANSCENDENTAL EQN.
C
C
CC         SUBROUTINE CALLED BY
C          --------------------
C
C          PROGRAM TRUNIT
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          ROUTINE VD01A
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON PRINT
C          COMMON SPECIF
C
C
CC         VARIABLES ASSOCIATED WITH THIS ROUTINE
C          --------------------------------------
C
C          ADDITIONS -
C
C              F - FUNCTION WHOSE ROOTS ARE TO BE DETERMINED
C              AMIN - MINIMUMS OF F
C              FUN - VALUES OF F AT MINIMUMS
C              AMAX - MAXIMUMS OF F
C
CC         ALGORITHM
C          ---------
C
C
      COMPLEX SRTETA,DONE,DTWO,D1,D2,AONE,ATWO,BONE,BTWO,FC
      DIMENSION FUN(11),AMAX(11)
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),XO,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
      S=-10.E-09
      ITEST=2
      RELACC=10.E-15
      ABSACC=10.E-10
      MAXFUN=4000
      SSTEP=10.E-05
      A=((1.+RR)*(R+EPSILO)+1.)/ALFA
      B=R*(1.+RR)
      IF (NPRINT) 10,12,12
   10 WRITE(6,1010)
```

```
      WRITE(6,1020)
   12   DO 100 I=1,NROOTS
C
C              FIND MINIMUM
C
   14 CALL VD01A(ITEST,S,F,MAXFUN,ABSACC,RELACC,SSTEP)
      GO TO (20,16,16,16) , ITEST
   16 IF (NPRINT) 18,40,40
   18 GO TO (20,34,36,38) , ITEST
   20 IF (S. GE. 0.0 ) GO TO 32
      IF (I. NE. 1) GO TO 22
      GO TO 24
   22 II=I-1
      IF (S. GE. AMAX(II)) GO TO 32
      GO TO 26
   24 IF ( S. GT. -10.E-09. AND . S. LT . 0.0 ) GO TO 32
   26 TAMBDA=(FACT-S)/2.
      TETA=TAMBDA**2+TU*ALFA*S*(1.+RR)
      IF ( TETA . GT . 0.) GO TO 28
      ATETA=ABS(TETA)
      RTETA=SQRT(ATETA)
      SRTETA=CMPLX(0.,RTETA)
      GO TO 30
   28 RTETA=SQRT(TETA)
      SRTETA=CMPLX(RTETA,0.)
   30 DONE=TAMBDA+SRTETA
      DTWO=TAMBDA-SRTETA
      AM=EXP(-S*TLB)/(S*STB+1.)
      AN=EXP(S*TLT)*(S*STT+A)
      AA=ALFA*AN-1.-S/TU
      BB=ALFA*AM-1.-S/TU
      D1=DONE/TU
      D2=DTWO/TU
      AONE=AA-D1
      ATWO=AA-D2
      BONE=BB-D1
      BTWO=BB-D2
      FC=CEXP(2.*SRTETA)-AONE*BTWO/(ATWO*BONE)
      F=CABS(FC)
      GO TO 14
   32 F=1.E+10*(S+10.)
      GO TO 14
   34 WRITE(6,1030) I,S,F
      GO TO 40
   36 WRITE(6,1040) I
      GO TO 40
   38 WRITE(6,1050) I
   40 AMIN(I)=S
      FUN(I)=F
      ITEST=2
C
C              FIND MAXIMUM
C
   42 CALL VD01A(ITEST,S,F,MAXFUN,ABSACC,RELACC,SSTEP)
      GO TO (48,44,44,44) , ITEST
   44 IF (NPRINT) 46,64,64
   46 GO TO (48,56,58,60) , ITEST
   48 IF ( S. GE . AMIN(I)-10.E-07) GO TO 54
      TAMBDA=(FACT-S)/2.
```

```
      TETA=TAMBDA**2+TU*ALFA*S*(1.+RR)
      IF ( TETA . GT . 0.) GO TO 50
      ATETA=ABS(TETA)
      RTETA=SQRT(ATETA)
      SRTETA=CMPLX(0.,RTETA)
      GO TO 52
   50 RTETA=SQRT(TETA)
      SRTETA=CMPLX(RTETA,0.)
   52 DONE=TAMBDA+SRTETA
      DTWO=TAMBDA-SRTETA
      AM=EXP(-S*TLB)/(S*STB+1.)
      AN=EXP(S*TLT)*(S*STT+A)
      AA=ALFA*AN-1.-S/TU
      BB=ALFA*AM-1.-S/TU
      D1=DONE/TU
      D2=DTWO/TU
      AONE=AA-D1
      ATWO=AA-D2
      BONE=BB-D1
      BTWO=BB-D2
      FC=CEXP(2.*SRTETA)-AONE*BTWO/(ATWO*BONE)
      F=1./CABS(FC)
      IF (F . LT. 10.E-05) GO TO 62
      GO TO 42
   54 F=1.E+05*(S+10.)
      GO TO 42
   56 WRITE(6,1060) I,S,F
      GO TO 64
   58 WRITE(6,1070) I
      GO TO 64
   60 WRITE(6,1080) I
      GO TO 64
   62 S=S-10.E-07
      GO TO 58
   64 AMAX(I)=S
      ITEST=2
  100 CONTINUE
      KOUNT=0
        DO 200 I=1,NROOTS
      IF( FUN(I) . GT . 1.E-05) GO TO 68
   66 IDUM=I-KOUNT
      AMIN(IDUM)=AMIN(I)
      FUN(IDUM)=FUN(I)
      AMAX(IDUM)=AMAX(I)
      GO TO 200
   68 KOUNT=KOUNT+1
      IF (I+KOUNT . GT . NROOTS ) GO TO 70
  200 CONTINUE
   70 IF (KOUNT .LT. 1) GO TO 72
      NROOTS=NROOTS-KOUNT
      WRITE(6,1090) NROOTS
   72 IF (NPRINT) 74,78,78
   74 WRITE(6,1100)
      WRITE(6,1110)
   76   DO 300 I=1,NROOTS
      WRITE(6,1120) I,AMIN(I),FUN(I),AMAX(I)
  300 CONTINUE
 1010 FORMAT(1H1,9X,26H***SUB. ROOTS PRINT-OUT***)
 1020 FORMAT(10X,26H==========================)
 1030 FORMAT(30X,4HMIN(,I2,7H) FOUND,50X,4HS = ,F9.6,5X,4HF = ,F9.6)
 1040 FORMAT(30X,23HROUNDING ERRORS AT MIN(,I2,1H))
 1050 FORMAT(30X,26HMAXFUN EVALUATIONS AT MIN(,I2,1H))
 1060 FORMAT(60X,4HMAX(,I2,7H) FOUND,20X,4HS = ,F9.6,5X,4HF = ,F9.6)
 1070 FORMAT(60X,23HROUNDING ERRORS AT MAX(,I2,1H))
 1080 FORMAT(60X,26HMAXFUN EVALUATIONS AT MAX(,I2,1H))
 1090 FORMAT(10X,29HNOTE - NROOTS WAS REDUCED TO ,I2,2X,67HIF MORE TRANS
     1IENT TERMS ARE REQUIRED, INCREASE ITS SPECIFIED VALUE))
 1100 FORMAT(1H0,21X,1HI,10X,3HMIN,11X,5HFUNCT,11X,3HMAX)
 1110 FORMAT(22X,1H=,10X,3H===,11X,5H=====,11X,3H===)
 1120 FORMAT(1H0,20X,I2,3(5X,F10.6))
   78 RETURN
      END
```

```
      SUBROUTINE COEF
C
C          COEF - COMPUTES THE COEFFICIENTS OF THE TRANSIENT TERMS (WHICH
C                 ARE A FUNCTION OF HEIGHT ONLY), AND STORES THEM IN
C                 C(NROOTS,ZSTAR)
C
C
CC         SUBROUTINE CALLED BY
C          ---------------------
C
C          PROGRAM TRUNIT
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          NO ROUTINE
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON PRINT
C          COMMON SPECIF
C
C
CC         VARIABLES ASSOCIATED WITH THIS ROUTINE
C          --------------------------------------
C
C          ADDITIONS -
C
C              C - COEFFICIENTS OF TRANSIENT TERMS
C
C
CC         ALGORITHM
C          ---------
C
C
      COMPLEX SRTETA,DONE,DTWO,D1,D2,AONE,ATWO,BONE,BTWO,DSRTET,DDONE,
     1DDTWO,DD1,DD2,DAONE,DBONE,DBTWO,FLIMIT,SLIMIT,V1,V2
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),XO,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
      SIGMA=(ALFA*(A-B)-1.)/EPSILO
        DO 100 M=1,NROOTS
      S=AMIN(M)
      U=TLB*S
      UU=TLT*S
      UUU=STB*S+1.
      UUUU=STT*S+A
      TAMBDA=(FACT-S)/2.
      TETA=TAMBDA**2+TU*ALFA*S*(1.+RR)
      IF ( TETA . GT . 0.) GO TO 10
```

```
      ATETA=ABS(TETA)
      RTETA=SQRT(ATETA)
      SQTETA=CMPLX(0.,RTETA)
      GO TO 20
   10 RTETA=SQRT(TETA)
      SQTETA=CMPLX(RTETA,0.)
   20 DONE=TAMBDA+SRTETA
      DTWO=TAMBDA-SRTETA
      AM=EXP(-U)/UUU
      AN=EXP(UU)*UUUU
      DM=-AM*(TLB+STB/UUU)
      DN=EXP(UU)*(STT+TLT*UUUU)
      AA=ALFA*AN-1.-S/TU
      BB=ALFA*AM-1.-S/TU
      D1=DONE/TU
      D2=DTWO/TU
      AONE=AA-D1
      ATWO=AA-D2
      BONE=BB-D1
      BTWO=BB-D2
      DTAMBD=-.5
      DTETA=2.*TAMBDA*DTAMBD+ALFA*TU*(1.+RR)
      DSRTET=DTETA/(2.*SRTETA)
      DDONE=DTAMBD+DSRTET
      DDTWO=DTAMBD-DSRTET
      DAA=ALFA*DN-1./TU
      DBB=ALFA*DM-1./TU
      DD1=DDONE/TU
      DD2=DDTWO/TU
      DAONE=DAA-DD1
      DATWO=DAA-DD2
      DBONE=DBB-DD1
      DBTWO=DBB-DD2
      V1=AONE-BONE*CEXP(DONE)*SIGMA
      V2=ATWO-BTWO*CEXP(DTWO)*SIGMA
      SLIMIT=CEXP(DONE)*(DATWO*BONE+ATWO*DBONE+ATWO*BONE*DDONE)-CEXP(
     1DTWO)*(DAONE*BTWO+AONE*DBTWO+AONE*BTWO*DDTWO)
        DO 200 I=1,101
      FLIMIT=(V1*CEXP(DTWO*ZSTAR(I))-V2*CEXP(DONE*ZSTAR(I)))/S
      C(M,I)=EPSILO*FLIMIT/SLIMIT
  200 CONTINUE
  100 CONTINUE
      IF (NPRINT) 30,40,40
   30 WRITE(6,1030)
      WRITE(6,1040)
      WRITE(6,1000)
      WRITE(6,1010)
        DO 300 I=1,101,5
      WRITE(6,1020)  ZSTAR(I),(C(M,I),M=1,NROOTS)
  300 CONTINUE
 1000 FORMAT(1X,5HZSTAR,3X,9H1ST COEF.,3X,9H2ND COEF.,3X,9H3RD COEF.,3X,
     19H4TH COEF.,3X,9H5TH COEF.,3X,9H6TH COEF.,3X,9H7TH COEF.,3X,9H8TH
     2COEF.,3X,9H9TH COEF.,3X,10H10TH COEF.)
 1010 FORMAT(1X,5H=====,3X,9H=========,3X,9H=========,3X,9H=========,3X,
     19H=========,3X,9H=========,3X,9H=========,3X,9H=========,3X,9H====
     2=====,3X,9H==========,3X,10H==========)
 1020 FORMAT(1H0,F5.3,10(3X,F9.6))
 1030 FORMAT(1H1,9X,25H***SUB. COEF PRINT-OUT***)
 1040 FORMAT(10X,25H=========================)
   40 RETURN
      END
```

```
      SUBROUTINE PROFIL
C
C         PROFIL - COMPUTES NPROF TRANSIENT PROFILES STORING THE CONC.
C                  IN TXSTAR(NPROF,ZSTAR)
C
C
CC        SUBROUTINE CALLED BY
C         --------------------
C
C         PROGRAM TRUNIT
C
C
CC        SUBROUTINE CALLS
C         ----------------
C
C         NO ROUTINE
C
C
CC        COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C         ------------------------------------------
C
C         BLANK COMMON
C         COMMON PRINT
C         COMMON SPECIF
C
C
CC        VARIABLES ASSOCIATED WITH THIS ROUTINE
C         --------------------------------------
C
C         ADDITIONS -
C
C             TXSTAR - TRANSIENT CONCENTRATIONS
C
C
CC        ALGORITHM
C         ---------
C
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
        DO 100 I=1,101
        DO 200  N=1,NPROF
      SUM=0.
        DO 300 M=1,NROOTS
      SUM=SUM+C(M,I)*EXP(AMIN(M)*TIMES(N))
  300 CONTINUE
      TXSTAR(N,I)=SUM+XSTAR(I)
  200 CONTINUE
  100 CONTINUE
      IF (NPRINT) 10,20,20
   10 WRITE(6,1000)
      WRITE(6,1010)
      WRITE(6,1020) (TPROF(I),I=1,NPROF)
      WRITE(6,1030) (TIMES(I),I=1,NPROF)
      WRITE(6,1040)
        DO 400 I=1,101,5
      WRITE(6,1050) ZSTAR(I),(TXSTAR(N,I),N=1,NPROF)
  400 CONTINUE
 1000 FORMAT(1H1,9X,27H***SUB. PROFIL PRINT-OUT***)
 1010 FORMAT(10X,27H=========================)
 1020 FORMAT(1H0,9X,14HTPROF(HOURS) =,10(4X,F6.2))
 1030 FORMAT(1H0,9X,14HTIMES        =,1X,10(1X,1H(,F7.2,1H)))
 1040 FORMAT(2X,5HZSTAR,3X,116H==========================================
     1=========================================================
     2=========)
 1050 FORMAT(1H0,1X,F5.3,17X,10(4X,F6.4))
   20 RETURN
      END
```

```
      SUBROUTINE ENDTIM
C
C          ENDTIM - COMPUTES THE TIME DEPENDENCE OF THE CONCENTRATION
C                   AT THE TOP AND BOTTOM OF COLUMN.
C
C
CC        SUBROUTINE CALLED BY
C         --------------------
C
C         PROGRAM TRUNIT
C
C
CC        SUBROUTINE CALLS
C         ----------------
C
C         NO ROUTINE
C
C
CC        COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C         ------------------------------------------
C
C         BLANK COMMON
C         COMMON ENDS
C         COMMON PRINT
C         COMMON SPECIF
C
C
CC        VARIABLES ASSOCIATED WITH THIS ROUTINE
C         --------------------------------------
C
C         ADDITIONS -
C
C              BSST - STEADY-STATE CONC. AT BOTTOM
C              TSST - STEADY-STATE CONC. AT TOP
C              TTSTAR - DIMENSIONLESS TIME
C              XBOT - TRANSIENT CONC. AT BOTTOM USING NROOTS
C              XBOTOM - TRANSIENT CONC. AT BOTTOM USING FIRST ROOT ONLY
C              XTOP - TRANSIENT CONC. AT TOP USING NROOTS
C
C
CC        ALGORITHM
C         ---------
C
C
      COMMON/ENDS/ TTSTAR(501),XBOT(501),XBOTON(501),XTOP(501)
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON/PRINT/NPRINT
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
      TSST=XSTAR(1)
      BSST=XSTAR(101)
        DO 100 I=1,501
      N=I+I-2
      TTSTAR(I)=N
      SUMB=0.
      SUMT=0.
        DO 200 M=1,NROOTS
      V=EXP(AMIN(M)*TTSTAR(I))
```

```
      SUMT=SUMT+C(M,1)*V
      SUMB=SUMB+C(M,101)*V
  200 CONTINUE
      XBOT(I)=BSST+SUMB
      XTOP(I)=TSST+SUMT
      XBOTON(I)=C(I,101)*EXP(AMIN(I)*TTSTAR(I))+BSST
  100 CONTINUE
      IF (NPRINT) 10,20,10
   10 WRITE(6,1000)
      WRITE(6,1010)
      WRITE(6,1020)
      WRITE(6,1030)
      WRITE(6,1040)
        DO 300 I=1,501,10
      WRITE(6,1050) TTSTAR(I),XBOT(I),XBOTON(I),XTOP(I)
  300 CONTINUE
 1000 FORMAT(1H1,9X,27H***SUB. ENDTIM PRINT-OUT***)
 1010 FORMAT(10X,27H==========================)
 1020 FORMAT(1H0,20X,18HDIMENSIONLESS TIME,30X,12HBOTTOM CONC.,30X,9HTOP
     1 CONC.)
 1030 FORMAT(21X,18H==========,30X,12H==========,30X,9H=======
     1=)
 1040 FORMAT(54X,21H(NROOTS TRANS. TERMS),2X,17H(ONE TRANS. TERM))
 1050 FORMAT(1H0,25X,F7.1,27X,F7.4,15X,F7.4,22X,F7.4)
   20 RETURN
      END
```

```
      SUBROUTINE CALCFX(N,X,F)
C
C          CALCFX(N,X,F) - EVALUATES F, GIVEN X(I).
C
CC         SUBROUTINE CALLED BY
C          --------------------
C
C          ROUTINE VA04A
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          NO ROUTINE
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON POINTS
C
C
CC         ALGORITHM
C          ---------
C
C
      DIMENSION X(2),E(2),W(10)
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),X0,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/POINTS/CALC(50),DEV(50),EXPT(50)
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
C
C               AN OBVIOUS CONSTRAINT IS THAT TU MUST BE GREATER THAN ONE
C
      IF(X(1).LT.1.) GO TO 30
      FACT=X(1)*(ALFA*(1.+RR)-1.)
      EFACT=EXP(FACT)
      Y=10.E-10
      IF (R.LT.Y.AND.RR.LT.Y ) GO TO 10
      XSSB=R*(ALFA*RR+EPSILO)/(RR*(R+EPSILO)+EPSILO*(R-RR/(1.+RR))/
     1(EFACT*ALFA))
      GO TO 20
   10 T=TT+TB+1.
      XSSB=T*EFACT*FACT/(TT+TB*EFACT+EFACT-1.)
   20   DO 100 I=1,NDP
      DIF=XSSB-XSTARB(I)
C
C               AND XSSB MUST BE GREATER THAN EACH XSTARB(I)
C
      IF(DIF.LT.0.) GO TO 40
  100 CONTINUE
      SUM=0.
        DO 200 I=1,NDP
      EXPT(I)=ALOG(XSSB-XSTARB(I))
      CALC(I)=ALOG(XSSB-1.)+X(2)*TSTAR(I)
      DEV(I)=CALC(I)-EXPT(I)
      SUM=SUM+DEV(I)**2
  200 CONTINUE
      ANDP=NDP
      AN=N
C
C               THE USE  OF XSSB**2 IN F IS TO PREVENT THE OPTIMIZATION TO
C               PROCEED TO A MINIMUM CORRESPONDING TO A VERY LARGE XSSB.
C               (IN WHICH CASE THE DIFFERENCES XSSB-XSTARB(I) WOULD BE SMALL
C               AND THE LINEAR FIT WOULD BE ARTIFICIALLY FAVOURED
C
      F=SQRT(SUM/(ANDP-AN))*XSSB**5
      RETURN
   30 F=10.E+10*(1.1-X(1))
      RETURN
   40 F=10.E+10/X(1)
      RETURN
      END
```

```
      SUBROUTINE FILM
C
C          FILM - PRODUCES 3 MICROFILM PLOTS.
C                 1)- A ZSTAR V. XSTAR GRAPH. SHOWING THE STEADY-STATE
C                     AND NPROF TRANSIENT PROFILES (WHOSE TIMES ARE
C                     TIMES(NPROF)). GIVEN BY THE MODEL.
C                 2)- A XSTAR V. TTSTAR GRAPH. SHOWING THE EVOLUTION WITH
C                     TIME OF THE CONC. AT TOP AND BOTTOM OF COLUMN (ALSO
C                     PLOTTING EXPERIMENTAL POINTS).
C                 3)- A LN(XSSB-XSTARB) V. TTSTAR GRAPH. SHOWING THE
C                     LOG-LINEAR FITTING EXECUTED BY SUB. OPTIM (ALSO
C                     PLOTTING EXP. POINTS).
C
C
CC         SUBROUTINE CALLED BY
C          --------------------
C
C          PROGRAM TRUNIT
C
C
CC         SUBROUTINE CALLS
C          ----------------
C
C          SUBROUTINE AXIS
C          SUBROUTINE ENPLOT
C          SUBROUTINE GRAF
C          SUBROUTINE LINE
C          SUBROUTINE NEWPAGE
C          SUBROUTINE NUMBER
C          SUBROUTINE PLOT
C          SUBROUTINE SCALE
C          SUBROUTINE START
C          SUBROUTINE SYMBOL
C
C
CC         COMMON BLOCKS ASSOCIATED WITH THIS ROUTINE
C          ------------------------------------------
C
C          BLANK COMMON
C          COMMON DATA
C          COMMON ENDS
C          COMMON POINTS
C          COMMON SIZES
C          COMMON SPECIF
C
C
CC         VARIABLES ASSOCIATED WITH THIS ROUTINE
C          --------------------------------------
C
C
CC         ALGORITHM
C          ---------
C
      DIMENSION XAX(1120),YAX(1120),NUM(14),BA(11),BB(11)
      COMMON/DATA/AHEIG,ALFA,AREA,BOTCON(50),FLOW,NDP,OLDUP,TIME(50),X0,
     1R,RR,STVB,STVT,TLVB,TLVT
      COMMON/ENDS/ TTSTAR(501),XBOT(501),XBOTON(501),XTOP(501)
      COMMON/POINTS/CALC(50),DEV(50),EXPT(50)
      COMMON/SIZES/XLEN,YLEN
```

```
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON A,AMIN(11),B,C(10,101),DENOM,EFACT,EPSILO,FACT,HTU,STB,STT,
     1T,TB,TLB,TLT,TSTAR(50),TT,TU,TXSTAR(10,101),XSSB,XSTAR(101),
     2XSTARB(50),ZSTAR(101)
C
      CALL START(1)
C
C           FIRST PLOT  -  CONCENTRATION PROFILES
C
        DO 100 I=1,101
      XAX(I)=XSTAR(I)
      YAX(I)=1.-ZSTAR(I)
        DO 150 N=1,NPROF
      J=101*N+I
      XAX(J)=TXSTAR(N,I)
      YAX(J)=1.-ZSTAR(I)
  150 CONTINUE
  100 CONTINUE
      N=NPROF+1
        DO 200 I=1,N
      NUM(I)=101
  200 CONTINUE
        DO 250 I=1,3
      NN=N+1
      NUM(NN)=2
  250 CONTINUE
      WRITE(6,1010) J
 1010 FORMAT(10X,4HJ = ,I4)
      J=J+1
      XAX(J)=0.
      YAX(J)=1.
      CALL SCALE(XAX,XLEN,J,1)
      N=J+1
      XAX(J)=XAX(N)
      M=N+1
      XAX(N)=XAX(M)
      FIRSTV=XAX(J)
      DELTA=XAX(N)
      J=J-1
      GREATV=FIRSTV+DELTA*XLEN
      WRITE(6,1000) FIRSTV,GREATV
 1000 FORMAT(10X,9HFIRSTV = ,F7.3,10X,9HGREATV = ,F7.3)
        DO 300 I=1,NPROF
      II=101*(I+1)
      BA(I)=XAX(II)*XLEN/(GREATV-FIRSTV)+.9
  300 CONTINUE
      N=NPROF+1
      BA(N)=XAX(101)*XLEN/(GREATV-FIRSTV)+.9
        DO 350 I=1,N
      BB(I)=BA(I)+.07
  350 CONTINUE
      BJ=J+1
        DO 400 I=1,2
      N=J+1
      AN=N
      AI=I
      YAX(N)=1.
      XAX(N)=(AN-BJ)*GREATV
      JJ=N+2
```

```
      XAX(JJ)=GREATV
      YAX(JJ)=2.-AI
      JK=JJ+2
      XAX(JK)=1.
      YAX(JK)=2.-AI
  400 CONTINUE
      ITOT=NPROF+4
      CALL PLOT(3.,3.,-3)
      CALL GRAF(XAX,YAX,NUM,ITOT,0,29HDIM,LESS ISOT. FRACTION(*100),29,2
     15HI. - DIMENSIONLESS HEIGHT,25,XLEN,YLEN)
      DO 450 I=1,JK
      XAX(I)=0.
      YAX(I)=0.
  450 CONTINUE
      YLEN1=YLEN+1.4
      CALL PLOT(0.,-YLEN1,-3)
      ONE=XLEN/(GREATV-FIRSTV)
      ADD1=(XLEN-ONE-3.08)/2.
      XLEN1=ONE+ADD1+.9
      XLEN2=XLEN1+.93
      CALL SYMBOL(XLEN1,YLEN,.14,22HCONCENTRATION PROFILES,0.,22)
      YLEN1=YLEN-2.5
      XLEN1=XLEN1+.5
      CALL SYMBOL(XLEN1,YLEN1,.08,10HPARAMETERS,0.,10)
      YLEN1=YLEN1-.2
      CALL SYMBOL(XLEN1,YLEN1,.07,20HSEPARATION FACTOR = ,0.,20)
      ON=XLEN1+1.4
      CALL NUMBER(ON,YLEN1,.07,ALFA,0.,4)
      YLEN1=YLEN1-.2
      CALL SYMBOL(XLEN1,YLEN1,.07,34HHEIGHT OF TRANSFER UNIT =          M,
     10.,34)
      ON=XLEN1+1.82
      CALL NUMBER(ON,YLEN1,.07,HTU,0.,4)
      YLEN1=YLEN1-.2
      CALL SYMBOL(XLEN1,YLEN1,.07,26HRECIPROCAL REFLUX RATIO = ,0.,26)
      ON=XLEN1+1.82
      CALL NUMBER(ON,YLEN1,.07,RR,0.,4)
      YLEN1=YLEN1-.2
      CALL SYMBOL(XLEN1,YLEN1,.07,28HFEED TO LIQUID-FLOW RATIO = ,0.,28)
      ON=XLEN1+1.96
      CALL NUMBER(ON,YLEN1,.07,R,0.,3)
      YLEN1=YLEN1-.2
      CALL SYMBOL(XLEN1,YLEN1,.07,29HDIMENSIONLESS TIME-CONSTANTS,,0.,
     129)
      ON=XLEN1+.05
      YLEN1=YLEN1-.2
      CALL SYMBOL(ON,YLEN1,.07,40HTOP REFLUX - STT =        AND TLT =
     1   ,0.,40)
      YLEN1=YLEN1-.2
      CALL SYMBOL(ON,YLEN1,.07,40HBOTTOM   '   - STB =        AND TLB =
     1    ,0.,40)
      ON=XLEN1+1.38
      CALL NUMBER(ON,YLEN1,.07,STB,0.,3)
      YLEN1=YLEN1+.2
      CALL NUMBER(ON,YLEN1,.07,STT,0.,3)
      ON=XLEN1+2.5
      CALL NUMBER(ON,YLEN1,.07,TLT,0.,3)
      YLEN1=YLEN1-.2
      CALL NUMBER(ON,YLEN1,.07,TLB,0.,3)
```

```
      AN=XLEN2+.28
        DO 500 I=1,NPROF
      AI=I
      ON=9.5-AI*.2
      IF (ITIM) 10,20,10
   10 CALL SYMBOL(XLEN2,ON,.07,14H( )-      HOURS,0.,14)
      CALL NUMBER(AN,ON,.07,TPROF(I),0.,-1)
      GO TO 500
   20 CALL SYMBOL(XLEN2,ON,.07,4H( )-,0.,4)
      CALL NUMBER(AN,ON,.07,TIMES(I),0.,2)
  500 CONTINUE
      ON=ON-.2
      CALL SYMBOL(XLEN2,ON,.07,16H( )-STEADY STATE,0.,16)
      ON2=XLEN2+.07
      N=NPROF+1
        DO 550 I=1,N
      AI=I
      ON=9.5-AI*.2
      CALL SYMBOL(BA(I),.95,.07,3H( ),0.,3)
      CALL NUMBER(ON2,ON,.07,AI,0.,-1)
      CALL NUMBER(BB(I),.95,.07,AI,0.,-1)
  550 CONTINUE
C
C           SECOND PLOT  -  COLUMN ENDS RELAXATION TIME
C
      CALL NEWPAGE
      CALL PLOT(3.,3.,-3)
        DO 600 I=1,501
      XAX(I)=TTSTAR(I)
      YAX(I)=XBOT(I)
      J=501+I
      XAX(J)=TTSTAR(I)
      YAX(J)=XTOP(I)
  600 CONTINUE
      BJ=J+1
        DO 650 I=1,2
      NUM(I)=501
      N=J+1
      AN=N
      AI=I
      XAX(N)=(AN-BJ)*1000.
      YAX(N)=GREATV
      JJ=N+2
      XAX(JJ)=1000.
      YAX(JJ)=(AN-BJ)*GREATV
      JK=JJ+2
      XAX(JK)=(AN-BJ)*1000.
      YAX(JK)=1.
  650 CONTINUE
        DO 700 I=1,3
      II=I+2
      NUM(II)=2
  700 CONTINUE
      CALL GRAF(XAX,YAX,NUM,5,0,18HDIMENSIONLESS TIME,18,29HDIM,LESS ISO
     1T. FRACTION(*100),29,YLEN,XLEN)
        DO 750 I=1,JK
      XAX(I)=0.
      YAX(I)=0.
  750 CONTINUE
```

```
      XLEN1=XLEN+.5
      CALL PLOT(.9,-XLEN1,-3)
        DO 800 I=1,NDP
      TSTAR(I)=TSTAR(I)*YLEN/1000.
      XSTARB(I)=XSTARB(I)*XLEN/(GREATV-FIRSTV)
      CALL SYMBOL(TSTAR(I),XSTARB(I),.14,1,0.,-1)
  800 CONTINUE
      CON=XLEN/(GREATV-FIRSTV)
      YL=TTSTAR(501)*YLEN/1000.-.35
      BA(1)=XBOT(501)*CON+.15
      BA(2)=XTOP(501)*CON-.15
      DO 820 I=1,2
      AI=I
      CALL SYMBOL(YL,BA(I),.07,3H( ),0.,3)
      YL=YL+.07
      CALL NUMBER(YL,BA(I),.07,AI,0.,-1)
      YL=YL-.07
  820 CONTINUE
      YL=YLEN-3.
      CON=CON+.21
      CALL SYMBOL(YL,CON,.07,31H(1) - CONC. AT BOTTOM OF COLUMN,0.,31)
      CON=CON-.14
      CALL SYMBOL(YL,CON,.07,31H(2) - CONC. AT   TOP  OF COLUMN,0.,31)
C
C          THIRD PLOT  -  LINEAR FIT TO OPTIMIZE NOL
C
      CALL NEWPAGE
        DO 850 I=1,NDP
      TSTAR(I)=TSTAR(I)*1000./YLEN
      YAX(I)=CALC(I)
      J=I+NDP
      YAX(J)=EXPT(I)
  850 CONTINUE
      DO 950 I=1,J
      WRITE (6,1020) YAX(I)
 1020 FORMAT(20X,F10.6)
  950 CONTINUE
      CALL SCALE(YAX,YLEN,J,-1)
      J=J+1
      FIRSTY=YAX(J)
      J=J+1
      DELTAY=YAX(J)
      GRTVY=FIRSTY+YLEN*DELTAY
      WRITE (6,1100) FIRSTY,DELTAY,GRTVY
 1100 FORMAT(10X,9HFIRSTY = ,F9.5,10X,9HDELTAY = ,F9.5,10X,8HGRTVY = ,
     1F9.5)
      J=NDP+1
      YAX(J)=FIRSTY
      J=J+1
      YAX(J)=DELTAY
      CALL SCALE(TSTAR,XLEN,NDP,1)
      J=NDP+1
      FIRSTX=TSTAR(J)
      J=J+1
      DELTAX=TSTAR(J)
      GRTVX=FIRSTX+XLEN*DELTAX
      WRITE (6,1110) FIRSTX,DELTAX,GRTVX
 1110 FORMAT(10X,9HFIRSTX = ,F9.5,10X,9HDELTAX = ,F9.5,10X,8HGRTVX = ,
     1F9.5)
```

```
      CALL PLOT(3.,5.,-3)
      CALL AXIS(0.0,0.0,18HDIMENSIONLESS TIME,-18,XLEN,0.,FIRSTX,DELTAX)
      CALL AXIS(0.0,0.0,18HLN(XSSB-XSTARB(I)),18,YLEN,90.,FIRSTY,DELTAY)
      J=NDP+1
      YAX(J)=FIRSTY
      J=J+1
      YAX(J)=DELTAY
      CALL LINE(TSTAR,YAX,NDP,1,0,0)
        DO 900 I=1,NDP
      YAX(I)=EXPT(I)
  900 CONTINUE
      J=NDP+1
      YAX(J)=FIRSTY
      J=J+1
      YAX(J)=DELTAY
      CALL LINE(TSTAR,YAX,NDP,1,-1,2)
      CALL ENPLOT
      RETURN
      END
```

APPENDIX H

PROGRAM STARTUP

```
JOB(UMECR25,J1)
PASSWOR(AMMONIA)
COPYCF(INPUT,AB)
SUBMIT,AB,D=CF200.
'
JOB(UMECR25,J7,CM29000,T24)
PASSWOR(AMMONIA)
SETOT(B)
ATTACH(ICLIB/UN=LIBRARY)
FORTRAN(O,E=2,R=2,C=0,B=BIN)
LIBRARY(ICLIB)
GET(MICMNF/UN=CMAAE24)
CALL,MICMNF(L=BIN)
'
      PROGRAM STARTUP (OUTPUT,TAPE6=OUTPUT,TAPE62)
      NOLIST
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON/DATA/AHEIG,ALFA,AREA,FLOW,OLDUP,R,RR,STVB,STVT,TLVT,TLVB,
     1TR,TRR,X0
      COMMON/PRINT/NPRINT
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSIL0,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      DATA AHEIG,ALFA,AREA/5.1,1.006,.0005/
      DATA FLOW,OLDUP,X0/.00066,.13,.365/
      DATA STVT,STVB,TLVB,TLVT/.00075,.00015,0.,0./
      DATA ITIM,NPRINT,IFILM/1,0,1/
      DATA NPROF,NROOTS/5,12/
      DATA TPROF/10.,50.,120.,240.,600./
      R=.1
      RR=.001
      FF=AREA*OLDUP*AHEIG/FLOW
      TRR=800.*FF
      TU=340.
      DO 100 NN=1,5
      AI=NN
      TR=AI*100.*FF
      NROOTS=12
      CALL SET
      CALL STEAD
      CALL ROOT
      CALL COEF
      CALL ENDT(NN)
  100 CONTINUE
      CALL FILM
      STOP
      END
```

```
      SUBROUTINE SET
      COMMON/DATA/AHEIG,ALFA,AREA,FLOW,OLDUP,R,RR,STVB,STVT,TLVT,TLVB,
     1TP,TRR,X0
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      EPSILO=ALFA-1.
      FB=AREA*AHEIG*OLDUP
      TLT=TLVT/FB
      TNOT=FB/FLOW
      DTR=TR/TNOT
      DTRR=TRR/TNOT
      IF(DTR.LT.1.) KZ=2
      KZ=1
C
C             COMPUTE EITHER TPROF(NPROF) OR TIMES(NPROF), ACCORDING TO ITIM
C
      IF (ITIM) 20,10,20
   10   DO 200 I=1,NPROF
      TPROF(I)=TIMES(I)*TNOT
  200 CONTINUE
      GO TO 30
   20   DO 300 I=1,NPROF
      TIMES(I)=TPROF(I)/TNOT
  300 CONTINUE
   30 IF (NPRINT) 40,50,40
C
C             WRITE OUT DATA
C
   40 WRITE(6,1000)
      WRITE(6,1010)
      WRITE(6,1020) ALFA
      WRITE(6,1030) AHEIG
      WRITE(6,1040) AREA
      WRITE(6,1050) FLOW
      WRITE(6,1060) OLDUP
      WRITE(6,1070) R
      WRITE(6,1080) RR
      WRITE(6,1130) TR
      WRITE(6,1140) TRR
      WRITE(6,1090) STVT
      WRITE(6,1110) STVB
 1000 FORMAT(1H1,9X,17H***USER'S DATA***)
 1010 FORMAT(10X,17H==============)
 1020 FORMAT(1H0,20X,27HSYSTEM SEPARATION FACTOR = ,F7.4)
 1030 FORMAT(1H0,20X,16HCOLUMN HEIGHT = ,F6.3,7H METERS)
 1040 FORMAT(1H0,20X,26HCOLUMN CROSS-SECT. AREA = ,F7.5,11H SQ. METERS)
 1050 FORMAT(1H0,20X,19HLIQUID FLOW-RATE = ,F8.6,18H CUBIC METERS/HOUR)
 1060 FORMAT(1H0,20X,17HLIQUID HOLD-UP = ,F5.3)
 1070 FORMAT(1H0,20X,31HDIMENSIONLESS FEED FLOW-RATE = ,F5.3)
 1080 FORMAT(1H0,20X,26HRECIPROCAL REFLUX RATIO = ,F7.5)
 1090 FORMAT(1H0,20X,7HSTVT = ,F9.6,12HCUBIC METERS)
 1110 FORMAT(1H0,20X,7HSTVB = ,F9.6,12H       )
 1130 FORMAT(1H0,20X,21HFEED STARTING TIME = ,F7.2,6H HOURS)
 1140 FORMAT(1H0,20X,24HPRODUCT STARTING TIME = ,F7.2,6H HOURS)
   50 RETURN
      END
```

```
      SUBROUTINE STEAD
      COMMON/DATA/AHEIG,ALFA,AREA,FLOW,OLDUP,R,RR,STVB,STVT,TLVT,TLVB,
     1TR,TRR,X0
      COMMON/PRINT/NPRINT
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
        DO 300 J=KZ,3
      U=R
      UU=RR
      GO TO (10,20,30),J
   10 U=0.
      UU=0.
      GO TO 30
   20 UU=0.
   30 FACT=TU*(ALFA*(1.+UU)-1.)
      EFACT=EXP(FACT)
      IF (J.EQ.1) GO TO 40
      GO TO 50
   40 STB=STVB*(1.+UU)/FB
      STT=STVT*(1.+UU)/FB
      TLB=TLVB*(1.+UU)/FB
      T=STT+STB+TLT+TLB+1.
      DENOM=STT+STB*EFACT+(EFACT-1.)/FACT
        DO 100 I=1,21
      AI=I-1
      ZSTAR(I)=AI*.05
      XSTAR(I,J)=T*EXP(FACT*ZSTAR(I))/DENOM
  100 CONTINUE
      GO TO 300
   50 DENOM=UU*(U+EPSILO)*EFACT+EPSILO*(U-UU/(1.+UU))/ALFA
      AUX=ALFA*U*UU*EFACT
      BUX=EPSILO*U
        DO 200 I=1,21
      AI=I-1
      ZSTAR(I)=AI*.05
      XSTAR(I,J)=(AUX+BUX*EXP(FACT*ZSTAR(I)))/DENOM
  200 CONTINUE
  300 CONTINUE
      IF (NPRINT) 60,70,70
C
C          PRINT 21 POINTS ON LINE-PRINTER
C
   60 WRITE(6,1010)
      WRITE(6,1020)
      WRITE(6,1030)
      WRITE(6,1040)
        DO 400 I=1,21
      WRITE(6,1050) I, ZSTAR(I),(XSTAR(I,J),J=1,3)
  400 CONTINUE
 1010 FORMAT(1H1,9X,26H***SUB. STEAD PRINT-OUT***)
 1020 FORMAT(10X,26H==========================)
 1030 FORMAT(1H0,20X,1HI,11X,5HZSTAR,11X,5HXSTAR)
 1040 FORMAT(21X,1H=,11X,5H=====,11X,5H=====)
 1050 FORMAT(1H0,18X,I3,4(9X,F7.4))
   70 RETURN
      END
```

```
      SUBROUTINE ROOT
      COMPLEX D1,D2,DONE,DTWO,ETA1,ETA2,GAMA1,GAMA2,FC,SRTETA
      DIMENSION FUN(15,3),AMAX(15,3)
      COMMON/DATA/AHEIG,ALFA,AREA,FLOW,OLDUP,R,RR,STVB,STVT,TLVT,TLVB,
     1TR,TRR,X0
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      ITEST=2
      RELACC=10.E-15
      ABSACC=10.E-10
      MAXFUN=4000
      SSTEP=10.E-05
      IF (NPRINT) 4,6,6
    4 WRITE(6,1010)
      WRITE(6,1020)
    6   DO 400 J=KZ,3
      WRITE(6,1130) J
      S=-10.E-09
      U=R
      UU=RR
      GO TO (8,10,12),J
    8 U=0.
      UU=0.
      GO TO 12
   10 UU=0.
   12 FACT=TU*(ALFA*(1.+UU)-1.)
      STT=STVT*(1.+UU)/FB
      STB=STVB*(1.+UU)/FB
      TLB=TLVB*(1.+UU)/FB
      AN=((1.+UU)*(U+EPSILO)+1.)/ALFA
      AM=U*(1.+UU)
        DO 100 I=1,NROOTS
C
C             FIND MINIMUM
C
   14 CALL VD01A(ITEST,S,F,MAXFUN,ABSACC,RELACC,SSTEP)
      GO TO (20,16,16,16) , ITEST
   16 IF (NPRINT) 18,40,40
   18 GO TO (20,34,36,38) , ITEST
   20 IF (S. GE. 0.0 ) GO TO 32
      IF (I. NE. 1) GO TO 22
      GO TO 24
   22 II=I-1
      IF (S. GE. AMAX(II,J)) GO TO 32
      GO TO 26
   24 IF ( S. GT. -10.E-09. AND . S. LT . 0.0 ) GO TO 32
   26 TAMBDA=(FACT-S)/2.
      TETA=TAMBDA**2+TU*ALFA*S*(1.+UU)
      IF ( TETA . GT . 0.) GO TO 28
      ATETA=ABS(TETA)
      RTETA=SQRT(ATETA)
      SRTETA=CMPLX(0.,RTETA)
      GO TO 30
   28 RTETA=SQRT(TETA)
      SRTETA=CMPLX(RTETA,0.)
   30 DONE=TAMBDA+SRTETA
      DTWO=TAMBDA-SRTETA
      FI=EXP(-S*TLB)/(S*STB+1.)
      PSI=EXP(S*TLT)*(S*STT+AN)
      AA=ALFA*PSI-1.-S/TU
      BB=ALFA*FI-1.-S/TU
      D1=DONE/TU
      D2=DTWO/TU
      ETA1=AA-D1
      ETA2=AA-D2
      GAMA1=BB-D1
      GAMA2=BB-D2
      FC=CEXP(2.*SRTETA)-ETA1*GAMA2/(ETA2*GAMA1)
      F=CABS(FC)
      GO TO 14
   32 F=1.E+10*(S+10.)
      GO TO 14
```

```
   34 WRITE(6,1030) I,S,F
      GO TO 40
   36 WRITE(6,1040) I
      GO TO 40
   38 WRITE(6,1050) I
   40 AMIN(I,J)=S
      FUN(I,J)=F
      ITEST=2
C
C              FIND MAXIMUM
C
   42 CALL VD01A(ITEST,S,F,MAXFUN,ABSACC,RELACC,SSTEP)
      GO TO (48,44,44,44) , ITEST
   44 IF (NPRINT) 46,64,64
   46 GO TO (48,56,58,60) , ITEST
   48 IF ( S. GE . AMIN(I,J)-10.E-07) GO TO 54
      TAMBDA=(FACT-S)/2.
      TETA=TAMBDA**2+TU*ALFA*S*(1.+UU)
      IF ( TETA . GT . 0.) GO TO 50
      ATETA=ABS(TETA)
      RTETA=SQRT(ATETA)
      SRTETA=CMPLX(0.,RTETA)
      GO TO 52
   50 RTETA=SQRT(TETA)
      SRTETA=CMPLX(RTETA,0.)
   52 DONE=TAMBDA+SRTETA
      DTWO=TAMBDA-SRTETA
      FI=EXP(-S*TLB)/(S*STB+1.)
      PSI=EXP(S*TLT)*(S*STT+AN)
      AA=ALFA*PSI-1.-S/TU
      BB=ALFA*FI-1.-S/TU
      D1=DONE/TU
      D2=DTWO/TU
      ETA1=AA-D1
      ETA2=AA-D2
      GAMA1=BB-D1
      GAMA2=BB-D2
      FC=CEXP(2.*SRTETA)-ETA1*GAMA2/(ETA2*GAMA1)
      F=1./CABS(FC)
      IF (F . LT. 10.E-05) GO TO 62
      GO TO 42
   54 F=1.E+05*(S+10.)
      GO TO 42
   56 WRITE(6,1060) I,S,F
      GO TO 64
   58 WRITE(6,1070) I
      GO TO 64
   60 WRITE(6,1080) I
      GO TO 64
   62 S=S-10.E-07
      GO TO 58
   64 AMAX(I,J)=S
      ITEST=2
  100 CONTINUE
      KOUNT=0
        DO 200 I=1,NROOTS
      IF( FUN(I,J) . GT . 1.E-05) GO TO 68
   66 IDUM=1-KOUNT
      AMIN(IDUM,J)=AMIN(I,J)
```

```
      FUN(IDUM,J)=FUN(I,J)
      AMAX(IDUM,J)=AMAX(I,J)
      GO TO 200
   68 KOUNT=KOUNT+1
      IF (I+KOUNT .GT. NROOTS ) GO TO 70
  200 CONTINUE
   70 IF (KOUNT .LT. 1) GO TO 72
      NROOTS=NROOTS-KOUNT
      WRITE(6,1090) NROOTS
   72 IF (NPRINT) 74,400,400
   74 WRITE(6,1100)
      WRITE(6,1110)
   76   DO 300 I=1,NROOTS
      WRITE(6,1120) I,AMIN(I,J),FUN(I,J),AMAX(I,J)
  300 CONTINUE
  400 CONTINUE
 1010 FORMAT(1H1,9X,25H***SUB. ROOT PRINT-OUT***)
 1020 FORMAT(10X,25H=========================)
 1030 FORMAT(30X,4HMIN(,I2,7H) FOUND,50X,4HS = ,F9.6,5X,4HF = ,F9.6)
 1040 FORMAT(30X,23HROUNDING ERRORS AT MIN(,I2,1H))
 1050 FORMAT(30X,26HMAXFUN EVALUATIONS AT MIN(,I2,1H))
 1060 FORMAT(60X,4HMAX(,I2,7H) FOUND,20X,4HS = ,F9.6,5X,4HF = ,F9.6)
 1070 FORMAT(60X,23HROUNDING ERRORS AT MAX(,I2,1H))
 1080 FORMAT(60X,26HMAXFUN EVALUATIONS AT MAX(,I2,1H))
 1090 FORMAT(10X,29HNOTE - NROOTS WAS REDUCED TO ,I2,2X,67HIF MORE TRANS
     1IENT TERMS ARE REQUIRED, INCREASE ITS SPECIFIED VALUE))
 1100 FORMAT(1H0,21X,1HI,10X,3HMIN,11X,5HFUNCT,11X,3HMAX)
 1110 FORMAT(22X,1H=,10X,3H===,11X,5H=====,11X,3H===)
 1120 FORMAT(1H0,20X,I2,3(5X,F10.6))
 1130 FORMAT(1X,4HJ = ,I2)
   78 RETURN
      END
```

```
      SUBROUTINE COEF
      COMPLEX D1,D2,DDONE,DDTWO,DD1,DD2,DETA1,DETA2,DGAMA1,DGAMA2,DONE,
     1DSRTET,DTWO,ETA1,ETA2,GAMA1,GAMA2,SLIMIT,SRTETA,V1,V2
      COMMON/DATA/AHEIG,ALFA,AREA,FLOW,OLDUP,R,RR,STVB,STVT,TLVT,TLVB,
     1TR,TRR,X0
      COMMON/PRINT/NPRINT
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      DT=DTRR-DTR
        DO 400 J=KZ,3
      U=R
      UU=RR
      GO TO (10,12,14),J
   10 U=0.
      UU=0.
      GO TO 16
   12 UU=0.
      CALL FIT(DTR,1,UU)
      GO TO 16
   14 CALL FIT(DT,2,UU)
   16 FACT=TU*(ALFA*(1.+UU)-1.)
      STB=STVB*(1.+UU)/FB
      STT=STVT*(1.+UU)/FB
      TLB=TLVB*(1.+UU)/FB
      AN=((1.+UU)*(U+EPSILO)+1.)/ALFA
      AM=U*(1.+UU)
        DO 200 M=1,NROOTS
      S=AMIN(M,J)
      TAMBDA=(FACT-S)/2.
      TETA=TAMBDA**2+TU*ALFA*S*(1.+UU)
      IF ( TETA . GT . 0.) GO TO 18
      ATETA=ABS(TETA)
      RTETA=SQRT(ATETA)
      SRTETA=CMPLX(0.,RTETA)
      GO TO 20
   18 RTETA=SQRT(TETA)
      SRTETA=CMPLX(RTETA,0.)
   20 DONE=TAMBDA+SRTETA
      DTWO=TAMBDA-SRTETA
      F1=EXP(-S*TLB)/(S*STB+1.)
      PSI=EXP(S*TLT)*(S*STT+AN)
      DFI=-FI*(TLB+STB/(STB*S+1.))
      DPSI=EXP(S*TLT)*(STT+TLT*(STT*S+AN))
      AA=ALFA*PSI-1.-S/TU
      BB=ALFA*FI-1.-S/TU
      D1=DONE/TU
      D2=DTWO/TU
      ETA1=AA-D1
      ETA2=AA-D2
      GAMA1=BB-D1
      GAMA2=BB-D2
      DTAMBD=-.5
      DTETA=2.*TAMBDA*DTAMBD+ALFA*TU*(1.+UU)
      DSRTET=DTETA/(2.*SRTETA)
      DDONE=DTAMBD+DSRTET
      DDTWO=DTAMBD-DSRTET
      DAA=ALFA*DPSI-1./TU
      DBB=ALFA*DFI-1./TU
      DD1=DDONE/TU
      DD2=DDTWO/TU
      DETA1=DAA-DD1
      DETA2=DAA-DD2
      DGAMA1=DBB-DD1
      DGAMA2=DBB-DD2
```

```
      SLIMIT=CEXP(DONE)*(DETA2*GAMA1+ETA2*DGAMA1+ETA2*GAMA1*DDONE)-
     1CEXP(DTWO)*(DETA1*GAMA2+ETA1*DGAMA2+ETA1*GAMA2*DDTWO)
      GO TO (22,26,26),J
   22 P1=ALFA*(AN-AM)-1.
      P2=EPSILO
   24 V1=P2*ETA1-P1*GAMA1*CEXP(DONE)
      V2=P2*ETA2-P1*GAMA2*CEXP(DTWO)
        DO 100 I=1,21
      C(M,I,J)=(V1*CEXP(DTWO*ZSTAR(I))-V2*CEXP(DONE*ZSTAR(I)))/(S*SLIMIT
     1)
  100 CONTINUE
      GO TO 200
   26 JJ=J-1
      AJ=AP(JJ)
      BJ=BP(JJ)
      CC=CP(JJ)
      CD=CO(JJ)
      XT=S+BJ*(1.+TU/CC)
      XZ=1.-BJ/CC
      P1=-ALFA*(AM+AJ*(PSI-AN))-S*AJ*(XZ-ALFA*PSI)/XT+CD*(ALFA*AN-1.)
      P2=-AJ*EXP(BJ)*(S*(XZ-ALFA*F1)/XT+ALFA*(F1-1.))+CD*EPSILO
      GO TO 24
  200 CONTINUE
      IF (NPRINT) 28,400,400
   28 WRITE(6,1030)
      WRITE(6,1040)
      WRITE(6,1050) J
      WRITE(6,1000)
      WRITE(6,1010)
        DO 300 I=1,21
      WRITE(6,1020)  ZSTAR(I),(C(M,I,J),M=1,NROOTS)
  300 CONTINUE
  400 CONTINUE
 1000 FORMAT(1X,5HZSTAR,3X,9H1ST COEF.,3X,9H2ND COEF.,3X,9H3RD COEF.,3X,
     19H4TH COEF.,3X,9H5TH COEF.,3X,9H6TH COEF.,3X,9H7TH COEF.,3X,9H8TH
     2COEF.,3X,9H9TH COEF.,3X,10H10TH COEF.)
 1010 FORMAT(1X,5H=====,3X,9H=========,3X,9H=========,3X,9H=========,3X,
     19H=========,3X,9H=========,3X,9H=========,3X,9H=========,3X,9H====
     2=====,3X,9H=========,3X,10H==========)
 1020 FORMAT(1H0,F5.3,10(3X,F9.5))
 1030 FORMAT(1H1,9X,25H***SUB. COEF PRINT-OUT***)
 1040 FORMAT(10X,25H=========================)
 1050 FORMAT(1X,4HJ = ,I1)
   30 RETURN
      END
```

```
      SUBROUTINE ENDT(NN)
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON/PRINT/NPRINT
      COMMON/PLOT/TS(405),XB(405,5)
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      DIMENSION XBOT(405,3)
      K=1
        DO 100 I=1,401
      AI=(I+1-2)*2.5
      P=AI-DTR
      IF(P) 10,12,16
   10 TS(I)=AI
      GO TO 100
   12 TS(I)=DTR
   14 K=K+1
      GO TO 100
   16 IF(K.GT.1) GO TO 18
      TS(I+1) =AI
      GO TO 12
   18 Q=AI-DTRR
      IF (Q) 20,22,24
   20 TS(I+1)=AI
      GO TO 100
   22 TS(I+1)=DTRR
      GO TO 14
   24 IF (K.GT.2) GO TO 26
      TS(I+2)=AI
      GO TO 22
   26 TS(I+2)=AI
  100 CONTINUE
        DO 400 J=KZ,3
      IF (J.LT.2) GO TO 28
      JJ=J-1
      AJ=AP(JJ)
      BJ=BP(JJ)
      CC=CP(JJ)
   28 BSST=XSTAR(21,J)
        DO 300 I=1,403
      IF (J.EQ.3.AND.TS(I).LT.DTRR) GO TO 300
      IF (J.EQ.1.AND.TS(I).GT.DTR) GO TO 400
      IF (J.EQ.2.AND.TS(I).LT.DTR) GO TO 300
      IF (J.EQ.2.AND.TS(I).GT.DTRR) GO TO 400
      SUMB=0.
        DO 200 M=1,NROOTS
      GO TO (30,32,34),J
   30 TI=0.
      GO TO 36
   32 TI=DTR
      GO TO 36
   34 TI=DTRR
   36 V=AMIN(M,J)*(TS(I)-TI)
      IF(V.GT.100..OR.V.LT.-100.) GO TO 37
      VV=EXP(V)
      GO TO 38
   37 VV=1.
   38 SUMB=SUMB+C(M,21,J)*VV
```

```
  200 CONTINUE
      XBOT(I,J)=BSST+SUMB
  300 CONTINUE
  400 CONTINUE
      DO 600 I=1,403
      IF(TS(I).LT.DTR)  XB(I,NN)=XBOT(I,1)
      IF(TS(I).GE.DTR.AND.TS(I).LE.DTRR) XB(I,NN)=XBOT(I,2)
      IF (TS(I).GT.DTRR)  XB(I,NN)=XBOT(I,3)
  600 CONTINUE
      IF (NPRINT) 40,42,40
   40 WRITE(6,1000)
      WRITE(6,1010)
        DO 500 I=1,103
      WRITE(6,1050) TS(I),(XBOT(I,J),J=1,3)
  500 CONTINUE
 1000 FORMAT(1H1,9X,25H***SUB. ENDT PRINT-OUT***)
 1010 FORMAT(10X,25H=========================)
 1050 FORMAT(1H0,5X,F7.2,15X,3(5X,F8.3))
   42 RETURN
      END
```

```
      SUBROUTINE FILM
      COMMON/PLOT/TS(405),XB(405,5)
      DIMENSION Y(2025),NUM(5),X(2025)
      DO 200 NN=1,5
      NUM(NN)=403
      DO 100 I=1,403
      NA=403*(NN-1)+I
      Y(NA)=XB(I,NN)
      X(NA)=TS(I)
  100 CONTINUE
  200 CONTINUE
      CALL START(2)
      CALL INTENSE(24)
      CALL PLOT(5.3,5.175,-3)
      CALL GRAF(X,Y,NUM,5,0.18HDIMENSIONLESS TIME,18,21HBOTTOM DIM'LESS
     1CONC.,21,10.,5.)
      CALL PLOT (-5.5,.9,-3)
      CALL SYMBOL(4.5,2.,.1,41HPARAMETER - DIMENSIONLESS FEED START TIME
     1,0.,41)
      CALL SYMBOL (4.5,1.75,.1,35HDIM'LESS PRODUCT WITHDRAWAL TIME = ,0.
     1,35)
      CALL NUMBER(8.,1.75,.1,800.,0.,-1)
      CALL NUMBER(1.85,2.75,.1,100.,50.,-1)
      CALL NUMBER(2.15,2.75,.1,200.,50.,-1)
      CALL NUMBER(2.45,2.75,.1,300.,50.,-1)
      CALL NUMBER(2.70,2.75,.1,400.,50.,-1)
      CALL NUMBER(3.10,2.75,.1,500.,50.,-1)
      CALL ENPLOT
      RETURN
      END
```

```
      SUBROUTINE FIT(TIM,JA,UU)
      EXTERNAL FTN
      DIMENSION X(3),E(3),W(20)
      COMMON/DATA/AHEIG,ALFA,AREA,FLOW,OLDUP,R,RR,STVB,STVT,TLVT,TLVB,
     1TR,TRR,XO
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON/PROFI/TXT(21)
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      DATA X/.9,2.,1./
      DATA E/.00002,.00001,.00001/
      WRITE(6,1000)
      WRITE(6,1010)
         DO 100 I=1,21
      SUM=0.
         DO 200 M=1,NROOTS
      SUM=SUM+C(M,I,JA)*EXP(AMIN(M,JA)*TIM)
  200 CONTINUE
      TXT(I)=SUM+XSTAR(I,JA)
  100 CONTINUE
      CALL VA04A(X,E,3,F,100,.0,1,200,FTN,W,20,2000)
      AP(JA)=X(1)
      BP(JA)=X(2)
      CO(JA)=X(3)
      CP(JA)=BP(JA)-TU*ALFA*(1.+UU)
      F=SQRT(F/20.)*100.
      WRITE(6,1020) JA,F
      WRITE(6,1030) JA,AP(JA),JA,BP(JA),JA,CO(JA)
 1000 FORMAT(1H0,9X,24H***SUB. FIT PRINT-OUT***)
 1010 FORMAT(10X,24H==========================)
 1020 FORMAT(1H0,9X,8HFITTING ,I1,10X,21HSTANDARD DEVIATION = ,F5.2,2X,
     18HPER CENT)
 1030 FORMAT(1H0,9X,3HAP(,I1,4H) = ,F7.4,10X,3HBP(,I1,4H) = ,F7.4,10X,3H
     1CO(,I1,4H) = ,F7.4)
      RETURN
      END
```

```
      SUBROUTINE FTN(N,X,F)
      DIMENSION X(3),E(3),W(20)
      COMMON/PROFI/TXT(21)
      COMMON/SPECIF/ITIM,NPROF,NROOTS,TPROF(10),TIMES(10),IFILM
      COMMON AMIN(15,3),AP(10),BP(10),C(10,21,3),CO(10),CP(10),DTR,DTRR,
     1EFACT,EPSILO,FACT,FB,HTU,KZ,TLT,TU,XSTAR(21,3),ZSTAR(21)
      F=0.
      DO 100 I=1,21
      CAL=X(1)*EXP(X(2)*ZSTAR(I))+X(3)
      F=F+(TXT(I)-CAL)**2
  100 CONTINUE
      RETURN
      END
```

NOMENCLATURE

A	cross-sectional area of column
	constant defined by eqn. (2.1)
	" " " " (C.16) (Appendix C)
	concentration defined by eqn. (2.9)
	" (Appendix A)
A_1, A_2, A_3	constants defined by eqn. (3.47)
a_s	interfacial area per unit volume of packing
B	constant defined by eqn. (2.1)
	" " " " (C.17) (Appendix C)
	concentration defined by eqn. (2.9)
	" (Appendix A)
C	constant defined by eqn. (C.18) (Appendix C)
	concentration defined by eqn. (2.9)
$C(z^*,s_n)$	coefficients of the transient terms of the solution
C_1 to C_6	integration constants
c	constant in eqn. (2.29)
D	constant defined by eqn. (C.19) (Appendix C)
	concentration defined by eqn. (2.9)
	binary effective diffusivity (Appendix A)
D_1,D_2	functions of s defined by eqns. (3.81) and (3.82)
E	concentration defined by eqn. (2.9)
	" (Appendix A)
E_f	enhancement factor
F	concentration defined by eqn. (2.9)
	" (Appendix A)
F_m	molar feed flow-rate
$F(s)$	function of s defined by eqn. (3.94)
$f(t)$,$f(t^*)$	functions of time defined by eqns. (2.27) and (3.141)
$f(z^*)$	initial condition (3.47)
G_m	molar gas flow-rate
G	concentration defined by eqn. (2.20)

$G(s)$	function of s defined by eqn. (3.96)
$g(z), g(z^*)$	functions of height defined by eqns. (2.28) and (3.142)
H	concentration defined by eqn. (2.21) volumetric liquid hold-up per unit volume of bed
ΔH	enthalpy difference
H	Henry's Law constant
H_{OG}	height of overall gas transfer unit
H_{OL}	" " " liquid " "
h	height of column
K	constant defined by eqn. (3.80) " " " " (B.15) (Appendix B)
K_1, K_2, K_3	equilibrium constants
K_i	ionisation constant
K_G	gas-phase mass transfer coefficient
K_L	liquid-phase mass transfer coefficient, with chemical reaction
K_L^o	liquid-phase mass transfer coefficient for physical absorption
K_{OG}	overall gas mass transfer coefficient
K_{OL}	" liquid " " "
k_1, k_2	rate constants
L_v	volumetric liquid flow-rate
M	constant defined by eqn. (3.62) molar fraction defined by eqn. (2.11)
M_1, M_2, M_3	molar fractions defined by eqns. (2.23),(2.24) and (2.25)
N	constant defined by eqn. (3.63)
N_h	interfacial mass transfer flux of the heavy component
N_{OG}	number of overall gas transfer units
N_{OL}	" " " liquid " "
N_p	" " theoretical plates

n	number of moles (section 3.1) indice in series (section 3.2)
P	total pressure
P_1, P_2	functions of s defined by eqns. (3.91) and (3.92)
P_v	volumetric product flow-rate
p	partial pressure
p^o	vapour pressure
Q_1, Q_2	functions of s defined by eqns. (3.97) and (3.98)
R	product ratio ideal gas constant
r	feed ratio
S	ammonia solubility
S_t	ratio of the concentrations at both ends of the column, at time t
S_∞	idem, at steady state
s	Laplace transform variable
T	absolute temperature
T_{OL}	liquid average residence time in each transfer unit
t	time variable
t_r	feed start time
t_R	product withdrawal time
V	volume of liquid
V_m	molar volume
W_m	molar waste flow-rate
$\bar{X}$	Laplace transform of x
$\underline{\bar{X}}$	" " " $\underline{x}$
$\underline{\underline{\bar{X}}}$	" " " $\underline{\underline{x}}$
x	isotopic fraction of the heavy component in the liquid phase, in the column
$\underline{x}$	idem, entering the bottom stirred tank

$\underline{\underline{x}}$	idem, in top stirred tank
$\bar{x}$	idem, in equilibrium with the actual gas isotopic fraction
$\bar{Y}$	Laplace transform of y
y	isotopic fraction of the heavy component in the gas phase, in the column
$\bar{y}$	idem, in equilibrium with the actual liquid isotopic fraction
z	height variable axis normal to gas-liquid interface (Appendix A)
z_0^*	dimensionless height defined by eqn. (3.143)

Greek letters

α	separation factor
β	parameter defined by eqn. (3.66)
δ	liquid film thickness
ε	$\alpha - 1$
γ_1, γ_2	functions of s defined by eqns. (3.87) and (3.88)
η_1, η_2	" " " " " " (3.89) " (3.90)
ζ_1, ζ_2	characteristics of hyperbolic equation
γ	activity coefficient
λ	function of s defined by eqn. (3.83)
θ	" " " " " " (3.84)
σ	H-bonding factor
τ	time constant
Φ	transfer function defined by eqn. (3.74)
Ψ	" " " " " (3.75)

Superscripts

*	dimensionless variable
f	formation

Subscripts

A,B,E,F	component
i	interface
b	bulk
l	light component
h	heavy "
B	bottom of the column
T	top " " "
F	feed height
L	transportation lag
S	stirred tank
n	value of function of s for $s = s_n$
o	reference value

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