

SOLVENT RECOVERY BY
ADSORPTION

Ph.D. Thesis, May 1973

Graham Jones, B.Sc.

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217

This thesis is submitted in part fulfillment of the requirements for the degree of Doctor of Philosophy at the Victoria University of Manchester. Unless otherwise stated the work is that of the author and has not been previously submitted in whole or in part at this, or any other University.

May, 1972.

The author graduated with B.Sc. (Hons) in Chemical Engineering from the University of Manchester Institute of Science and Technology in July, 1968. Between October 1968 and December, 1969 the author was engaged in full-time research in the Department of Chemical Engineering. From January 1970 to May 1972 the author was engaged in part-time research in the Department of Chemical Engineering whilst holding the position of Assistant Lecturer (later retitled Lecturer) in Chemical Engineering. The author carried out the research described in this thesis under the direction of Dr. H.J. Abrams and Professor T.K. Ross.

The author would like to thank the occupants past and present of the post-graduate school of the Chemical Engineering Department, the multitude of Undergraduates who have come under my teaching influence; and my extra-mural associates, male and female, for the relief of boredom and the prevention of academic isolation.

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My apologies must be presented to my academic colleague Mr. R. Krishna who has had to suffer my company for most of the past three years. To my other academic colleagues, I must wish them the best of luck with the central heating system.

I conclude with thanks and appreciation for the guidance and supervision of Dr. H. J. Abrams.

To Sue and the Future.

"Whenever the stakes are precious, words must no fail us any more. The same scientific method by which we have made our means of destruction so utterly effective must be used to make our communications, and so our social organisation, correspondingly efficient. In releasing the long-pent-up fury of the atom, we have created for ourselves, the necessity of quickly becoming what we might have been, of designing and establishing a scientific education that will wipe out our semantic blockades which make impossible the sanity and co-operation that are now simply essential for remaining alive. We can no longer afford serious conflict, aggression, contempt and hate. We can no longer tolerate studied confusion, cultivated distrust and verbal irresponsibility. It is a practical down-to-earth question of survival. Uranium hangs heavy over our heads so long as we cherish and strive to preserve beliefs, loyalties and institutions that disunite us - so long as we cherish the old superstitions, prides and prejudices with which we have muddled through to the crumbling edge of blind disintegration".

Wendell Johnson, "People in Quandries".

This thesis considers how the available analytical solutions that predict the interaction between adsorbate and adsorbent can be developed to represent the industrial adsorption operation. Possible operating objectives are established for a specific industrial unit; and an optimum operating policy proposed for this constrained system. The theories proposed are backed up by appropriate numerical calculations, experimental results and an appropriate worked example.

INDEX

1 INTRODUCTION

CHAPTER I

- 12 1.1 Material Balances
- 13 1.2 Transfer Mechanisms
- 14 1.2.1 Diffusion across a stagnant fluid film surrounding the particle
- 1.2.2 Diffusion within the pores of the particle
- 15 1.2.3 Adsorption of the adsorbate on the particle surface
- 16 1.3 Analytical solutions
- 18 1.3.1 CASE/1
- 19 1.3.2 CASE/2
- 21 1.3.3 CASE/3
- 1.3.4 CASE/4
- 22 1.3.5 CASE/5
- 23 1.3.6 CASE/6
- 1.3.7 CASE/7
- 24 1.3.8 CASE/8
- 26 1.3.9 CASE/9
- 1.3.10 CASE/10
- 27 1.3.11 CASE/11
- 1.3.12 CASE/12

CHAPTER II

- 32 2.1 The programming of Cases 1 to 7
- 35 2.1.1 Case 1
- 2.1.2 Case 2
- 36 2.1.3 Case 3
- 2.1.4 Case 4
- 37 2.1.5 Case 5
- 2.1.6 Case 6
- 38 2.1.7 Case 7
- 39 2.2 The programming of Cases 8 to 12

40 2.3 Comparison of Case 8 with Cases 1 to 7

CHAPTER III

45 3.1 A description of the general system

50 3.2 The absence of the intraparticle effects

52 3.3 Solution by numerical methods

55 3.4 Programming the solution

3.4.1 General form of the adsorption equilibria

58 3.4.2 Determination of $\rho_c(\theta)$

59 3.5 Results of computation

CHAPTER IV

66 4.1 Isothermal case

70 4.2 General heat and mass transfer operations

72 4.3 General heat and mass transfer plus regenerative fluid

79 4.4 Programming the solutions

4.4.1 Determination of c_r

81 4.4.2 Determination of $\rho_c(\theta)$

4.4.3 Determination of $\text{chos}(\theta)$ and $\text{chs}(\theta)$

4.4.4 Linearisation of adsorption equilibria

83 4.5 Programming the Isothermal models (Cases 1 to 7)

84 4.5.1 Model for Case 1

85 4.5.2 Model for Case 2

4.5.3 Model for Case 3

4.5.4 Model for Case 4

4.5.5 Model for Case 5

86 4.5.6 Model for Case 6

4.5.7 Model for Case 7

4.5.8 Conclusions on comparison between MOD and CASE results

88 4.6 Programming of general heat and mass transfer operations

90 4.6.1 The programme GENHAM

95 4.6.2 The programme WETBED

CHAPTER V

101 5.1 Regeneration - General considerations

104	5.2	Regeneration by a heated non-condensable inert
105	5.3	Regeneration by a heated condensable inert
108	5.3.1	Two or three cycle operations
111	5.4	The regeneration effects on cyclic operations

CHAPTER VI

117	6.1	Basic adsorption data
	6.1.1	Adsorption isotherms
118	6.1.2	The adsorbent
	6.1.3	The adsorption system
120	6.2	Elucidating the adsorption mechanism
121	6.3	Adsorption theory in practice

CHAPTER VII

127	7.1	The Industrial unit
130	7.1.1	Measurements taken on the Industrial unit
136	7.2	The package unit
139	7.2.1	Measurements taken on the package unit
141	7.3	The experimental unit
143	7.3.1	Measurements taken on the experimental unit

CHAPTER VIII

148	8.1	The system variables
151	8.2	Economic assessment (cycles independant)
155	8.2.1	Effects of changes in the input variables
159	8.3	Economic assessment (cycles interacting)
165	8.3.1	The overall economic objective

CHAPTER IX

168	9.1	The available data
170	9.2	Operating limitations
173	9.3	A better optimum policy for the Industrial unit ?

182	APPENDICIES
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NOMENCLATURE

REFERENCES

TABLES AND FIGURES

INTRODUCTION

An operation which occurs in many branches of chemical engineering is that in which a fluid - gas or liquid - is passed through a bed of granular solids for the purpose of removing something from, or adding something to, the fluid. In the oil and sugar industries, oils or syrups are passed through beds of solids to remove impurities causing colour and other undesired effects. In the recovery of volatile solvents, air charged with solvent vapour is passed over solid adsorbents which retain the solvents and allow the air to discharge safely. More recent developments have enabled the large scale separation of multi-component fluids in beds of suitably active material. The individual physical processes occurring may be grouped together under the titles of Adsorption, Dialysis and Ion-Exchange. The similarities of these three processes have been compared by Monet (1).

In this thesis it is proposed to deal with one such physical process, and one specific application of this process, namely the application of adsorption to the recovery of organic vapours (solvents) from air. This introduction gives a review of the major aspects of the system by considering each briefly in turn, starting with adsorption itself. Various commercial adsorbents are described, followed by a general consideration of the principles involved in their application to large scale processes. The industrial operation of recovery by adsorption is introduced prior to more extensive discussion later in the text as a means of identifying the areas into which past work in this field has been directed; and hence to outline the contribution to future work to be made by this thesis.

Adsorption.

Adsorption is a process involving concentration of molecules from a fluid phase at a boundary surface. As in any spontaneous process, it

is accompanied by a lowering of the free energy of the system. The extent of this change is a measure of the strength with which the adsorbed molecules are bound to the interface. The adsorbent surface may be an interface between gas and liquid, liquid and liquid, gas and solid or liquid and solid. Solid - solid systems are also possible but have received little study owing to the slowness of diffusion through solids. The energy with which an adsorbed molecule is bound to an interface varies with the nature of the bond formed.

The term physical adsorption is applied when this bond consists of Van der Waals' energy, dipole - dipole interaction, or electrostatic energy as in the case of hydrogen bonding. The heat of physical adsorption is usually in the range of 2 - 15 k cal./mole, the larger values occurring in hydrogen bonding or in cases representing more than one point of contact between an adsorbate molecule and the adsorbent surface.

The term chemisorption is applied when this bond may be considered a chemical bond, with a heat of adsorption usually in the range of 30-100 k cal./mole. Chemisorption differs from ordinary chemical reaction only in that the reacting atoms of solid surface retain their identity within the original solid lattice. Any further adsorption on top of these chemisorbed molecules can only occur by the process of physical adsorption.

Processes in which physical adsorption represents the final equilibrium state (rather than a transient prelude to chemisorption) can be well explained in terms of equilibrium measurements. An analytical expression representing such equilibrium data is called an adsorption isotherm (see 1.2.3 and footnote). For the purposes of all work carried

Authors Note : Where reference is made to other parts of this thesis the notation "a. b. c" is used, in which "a" refers to the chapter number. "b" refers to the section of that chapter; and "c" the sub-section of that section (if any). References to the Appendices and diagrams are given in full in the text).

out in this thesis it will be assumed that physical adsorption is solely responsible for the attachment of the adsorbate molecules to the adsorbent surface.

Commercial Adsorbents.

Almost all known solids have some ability to adsorb, but relatively few are commercially important. Some of the qualities which make a solid a commercially important adsorbent are :-

- a) Available in large quantity.
- b) High capacity for the adsorbates to be adsorbed.
- c) High selectivity of adsorbate.
- d) Ability to reduce the concentration of adsorbate in the fluid to a low value.
- e) Ability to be regenerated and so re-used.
- f) Physical strength.
- g) Chemical inertness.

Adsorbents vary in the extent to which they possess each of these quantities, just as adsorbents vary in the uses to which they may be put. Some adsorbents are more suited to the adsorption of polar molecules (water, alcohols, etc.); some more suited to adsorption of hydrocarbon material. The most important adsorbents used in adsorption systems are :-

- a) Activated carbon.
- b) Activated alumina.
- c) Molecular sieves.
- d) Silica gel.

Activated carbon can be produced from a wide range of materials including many kinds of wood, bone, blood, nut shells, coals and tars. Many manufacturing processes are possible, which in general, require

carbonization of the raw material followed by a process of activation that removes inerts, enlarges the porous structure and promotes the formation of regions of high activity (active sites).

Activated alumina is made by thermal processing to produce a highly porous amorphous aluminium oxide from a starting material of bauxite (alumina trihydrate).

Molecular sieves are synthetic sodium or calcium alumino-silicate zeolite adsorbents. They differ from other commercial adsorbents since they are crystalline rather than amorphous and have pore openings of fixed and uniform dimensions. Adsorption occurs inside cavities to which the pore openings lead. Several types and particle sizes are available so that it is possible to choose a molecular sieve to selectively remove a single adsorbate from a mixed adsorbate fluid.

Silica gel is manufactured from silicic acid. The term 'gel' is misleading since the material when ready for use is hard and glass-like. During one of the manufacturing stages it is precipitated from a colloidal solution of silicic acid, hence its name (2).

Various arrangements have been proposed to enable effective contact with the solid adsorbent and the fluid stream. Early large-scale systems were confined to multiple fixed bed adsorbers operating in a cyclic manner to permit continuous adsorption and continuous or semi-continuous regeneration. Recent operating processes have employed fluidised bed systems with continual addition of regenerated adsorbent to the fluidised bed. Fluidised systems, whilst offering economics in usage of regenerative agent (usually steam) and greater mean adsorbate loading on the adsorbent, do require mechanical handling of the adsorbent. The porous nature of many adsorbents make them unsuitable for fluidisation as continual handling and agitation tends to cause attrition

and degradation of the particles. So that fluidised systems can have higher adsorbent replacement costs, as well as incurring extra operating costs for the conveyance of the adsorbent within the system, over a comparable fixed bed arrangement.

As well as the single large fixed bed arrangement within a unit, it is also possible to have a multiplicity of smaller fixed beds with suitable valving so that the adsorbate can be passed through a particular number of beds, whilst another number of beds are being regenerated. The inclusion of a heat accumulator between each bed enables the retention of the excess heat used in the regeneration. This heat can then be used to dry the bed prior to a further adsorption period.

It is also possible to operate with adsorption and regeneration carried out on the stationary adsorbent, but to transfer mechanically the adsorbent between these two stages as required. So that during the conveying the saturated adsorbent can be preheated; and the regenerated adsorbent can be dried and cooled.

In batch adsorption processes the adsorbate and adsorbent can be highly mixed either by agitation in liquid systems or by turbulence in a gaseous system. The good contact and the generally fine adsorbent particles used are then separated by filtration prior to being regenerated.

This thesis is restricted to considerations of multiple large fixed beds of adsorbent operated continuously on a cyclic basis, and described in more detail later in the text.

Activated carbon is commonly used as the adsorbent for the large scale adsorption of organic and other non-polar adsorbates. It is usual for its method of activation to avoid the use of inorganic agents which may leave residual amounts within the adsorbent, even after repeated washings. Heating in the presence of steam for prolonged periods

suitably activates the carbon, and in removing those impurities that will react with water produces an adsorbent that has little adsorption affinity for water or other polar molecules.

Once activated it is not unusual for the adsorbent to exhibit a decrease in capacity during continual usage, particularly in rapid cyclic operations. This may be an initial rapid loss followed by a prolonged period of more or less constant activity, a general slow decline in capacity over a prolonged period or a relatively high and rapid loss in capacity during operations. Whether its causes are due to blinding of the active sites or blocking of the flow channels in the interparticle and intraparticle spaces it will eventually require reactivation (3). The economic aspects of this deactivation and subsequent replacement have been discussed later in the text. However, for the work proposed in this thesis, unless otherwise specifically stated, it will be assumed that the adsorbent used is activated carbon and that its capacity (or activity) has reached a constant value.

Representation of the System.

A general picture of what occurs within a commercial adsorbent can easily be described. A small section of the surface is considered as adsorbate molecules are admitted at some fixed concentration. A typical molecule will reside on the surface for some finite time before it acquires sufficient energy to leave. Given sufficient time an equilibrium state will be reached. The number of molecules arriving will then just equal the number of molecules leaving the surface. The number of molecules on the surface will in general depend upon the following factors:-

- a) The nature of the adsorbent (see above and (2), (4), (5).

In general, it can be said that the nature of the solids' chemical composition, and its surface configuration affect

the kinds of molecules it will selectively adsorb.

(b) The nature of the molecule being adsorbed. Such properties as boiling point, molecular weight, configuration, degree of polarity or polarisability and degree of unsaturation (if a carbon compound) help to determine whether a molecule will adsorb on a solid.

(c) The temperature of the system. In general, a higher temperature means less material adsorbed or a shorter residence time on the surface.

(d) The concentration of the adsorbate. A higher concentration of adsorbate above the adsorbent surface means more molecules will be adsorbed.

(e) The relative amounts of adsorbate(s) and other components already adsorbed. The presence of multiple adsorbates on the solid can lead to one adsorbate being adsorbed preferentially to another.

(f) The flow properties of the fluid stream through the arrangement of the adsorbent solid. If mal-distribution or channeling occurs all the adsorbent will not be accessible.

It is usual to assume that the first three factors are held constant; and that there exists a uniform distribution of adsorbent material within the system. The first two assumptions are perfectly valid, as there is little evidence of mixed adsorbents being used in the same system. Although processes do exist where the fluid passes through a section of one adsorbent before passing through a section of a second adsorbate. This can easily be considered as two separate but inter-related systems. It is also unusual on large scale applications to vary the nature of the adsorbate, most systems being operated on a fixed small

number of adsorbates. However, it is of interest to note that early applications of the adsorption process in gas-masks were specifically for multi-component fluids. The third assumption of isothermality is not a good one for industrial systems, especially where rapid cyclic operations produce continual variations in the adsorbent temperature. All but recent mathematical analysis of adsorption systems is based on this assumption. It is a simplifying assumption in that it enables solution of the otherwise intractable partial differential equations. Much small scale experimental work attempts to achieve isothermal conditions by use of small bed lengths, low adsorbate flow rates or high inert fluid flows and arrangements to maintain a constant temperature environment. The heat of adsorption is thus removed rapidly and is generated in limited amounts.

It is proposed in the later analytical work of this thesis to remove this isothermal restriction yet show that the procedure used does accurately represent work carried out under isothermal conditions. Furthermore, experimental work is presented for large scale beds and a small scale experimental bed system to illustrate the applications of the analytical methods developed in this thesis.

If, however, these usual assumptions are made it is possible to represent the results of the processes occurring within the adsorbent bed in a simple manner (6). A typical distribution curve showing the concentration of adsorbate in the fluid above various points in the bed of adsorbent is shown by Fig. (1a) for a given point in time. The term adsorption wave is generally applied to this profile as it moves through the bed with increasing time. The region in which this variable concentration exists is also called the mass transfer zone or MTZ, and is part of a more recent approach to the system. A typical effluent curve

illustrating the variation with time of the concentration of adsorbate in the fluid leaving the bed at a point just outside the bed is shown by Fig. (1b). The term breakthrough curve is generally applied to this profile during the continuous passage of adsorbate laden fluid through the bed. It is necessary to stipulate the continuous passage of fluid, as any discontinuities in time allow the slower diffusional processes to have an effect.

Most interest has been focused on the shape of the breakthrough curve and the value of the breakthrough time τ . It is not possible to continually increase the depth of the adsorbent bed so that the value of τ is made continually larger, as problems involving the mechanical strengths of the system must be considered together with economic operation at a suitable pressure drop across the bed. Choice therefore has to be made as to the values of the other factors mentioned above. Ideally the requirement is for some objective function to be set-up and the values of the relevant parameters chosen to optimise this objective function. For the simple case considered so far this is an easy matter. However, problems arise when actual operating systems are considered. These problems are explained and dealt with in the text of this thesis.

Although the general case is of more interest in practical systems, it is of course more complex analytically. It is possible, however, to consider a number of simple yet interesting cases by way of introduction. Figs. (2a) and (2b) illustrate a number of those cases where precise assumptions can be made as to the nature of the processes taking place within the adsorption system.

CASE A : If the interaction with the adsorbent is instantaneous and if the adsorbent is infinitely fine grained, none of the adsorbate would penetrate the bed until some time

γ , at which the adsorbent would be saturated; and then the adsorbate would penetrate at full influent concentration.

CASE B : This is the general case. Only in specific instances is the curve symmetrical.

CASE C : If the adsorbent material acts as a catalyst for a reaction involving the adsorbate, the effluent concentration curve may rise very slowly; and if the adsorbent remains at least partially unpoisoned, the transmission of adsorbate may never reach the influent value.

CASE D : It is also conceivable that as in CASE C above, the rate of catalysis may be very high compared to the rate of supply of the adsorbate. In such circumstances the effluent curve would be the time axis. Hence, none of the adsorbate as such would penetrate the bed.

The work in this thesis will pursue CASE B as fully as possible. It should therefore be stressed that CASES C and D which both involve catalytic properties of the adsorbent will not be considered further. This is valid for the physical adsorption by activated carbon of most organic compounds from air, although there are organic compounds which can react with the adsorbent producing hazardous conditions within the bed (the degeneration of methyl ethyl ketone and its resultant fire risk being such a case).

The information on the shape and occurrence of the breakthrough has been used as the basis for the design of industrial adsorption units, often coupled with pilot scale studies. It is the view of this author that, while previous design calculations may in certain limiting circumstances (see later text) be suitable, the present state fails to take into

account the dynamic nature of any cyclically operating system. Thus the residual effects of incomplete regeneration and any economic assessment of the overall operating system are not fully taken into account, nor is it usual to operate at effluent values approaching the influent value. The case for these views is put in the text, together with the proposals of this author for a new approach to the system. However, it is necessary to first review the available methods of previous authors to show that this work is consistent with their work. Suitable improved procedures will then be developed.

The text begins by considering the available analytical expressions for the breakthrough curves (as described in Chapter I); and then proceeds to illustrate these solutions for various parameter values, as determined by digital computational methods (and described in Chapter II). Further limitations of the analytical approach are described in Chapter III, which summarises the work done and conclusions reached by other authors on the analytical approach. The derivation and testing of a "stirred-tank" approach to the analytical models is described in Chapter IV; and compared to the results obtained from Chapter III. The analytical work is completed by Chapter IV which describes the necessary modifications to the model to represent the real operating adsorption/regeneration system which is discussed further in Chapter V.

The remaining Chapters describe the experimental work carried out by this author with small-scale, pilot-scale and industrial adsorption systems. The qualitative and quantitative aspects of this work are discussed in the light of present knowledge, and recommendations by this author for optimisation studies are proposed.

C H A P T E R I

Mass balances on the adsorbate over a section of the bed and over an adsorbent particle are established as a prelude to discussing the various possible physical mechanisms affecting the transfer of adsorbate from the fluid to the solid. The available analytical solutions are presented for twelve particular cases where one or more physical processes are assumed to be rate-controlling and where lumped parameter models have been proposed to describe the transfer mechanism.

1.1 Material Balances

It is possible to set up material balances for the adsorbate across an infinitesimal section of the adsorption bed perpendicular to the bulk flow direction, and across a spherical shell of infinitesimal thickness within an adsorbent particle itself. The derivation of these material balances is in no way dependant upon the assumptions as to the mechanism or mechanisms controlling the removal of the adsorbate from the fluid stream (7).

It is assumed that any variations in velocity or concentration over a given cross-section of the bed can be neglected (8). That is radial diffusion is neglected. If moreover the effect of possible longitudinal diffusion is also neglected (8, 9) simplifications result. These assumptions are generally acceptable for operating adsorption systems, but not for ion-exchange or chromatographic studies where these diffusion effects must be considered (10). Hence for the adsorption system the concentrations of adsorbate in the fluid and on the adsorbent depend solely upon the space variable z and the time variable t so that $c = c(z, t)$ and $n = n(z, t)$. It is then a simple exercise to show that the material balance over the bed element gives (11) :

$$V \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + (1/\alpha) \frac{\partial n}{\partial t} = 0 \quad \text{-----I}$$

If intraparticle effects are not considered then I is sufficient to describe the system once a suitable formulation for $\partial n / \partial t$ (the local rate of change of the adsorbate concentration on the adsorbent) is available. When considering intraparticle effects some authors (12) prefer to use I in a less ambiguous form.

$$U \frac{\partial c}{\partial z} + \alpha \frac{\partial c}{\partial t} + k_c = 0 \quad \text{-----Ia}$$

Suitable expressions for k_c (the local rate of removal of adsorbate from the fluid) are then defined separately, and not necessarily in terms of n only.

It is assumed that the adsorbent is in the form of uniform porous spheres, and that flow into and out of the spherical shell is by diffusion only. It can then again be easily shown that a material balance on the adsorbate produces (7) :

$$D_i \left(\frac{\partial^2 \bar{c}}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{c}}{\partial r} \right) = \gamma \frac{\partial \bar{c}}{\partial t} + \rho_p \frac{\partial \bar{q}}{\partial t} \quad \text{-----II}$$

Various forms of II have been presented by other authors (13,14) but are analogous to the form of II used in this text.

1.2. Transfer Mechanisms

Before dealing with the use of I and II to produce analytical solutions for the concentration of adsorbate in the fluid stream leaving the bed as a function of time, it is necessary to consider those mechanisms which contribute to the transfer of adsorbate from the fluid stream

Authors Note: A consistent notation has been used in this thesis to ensure that the work of the various authors quoted in the text are correctly represented. In most cases the original notation of the authors can be simply transformed to the notation of this thesis.

to its adsorbed state on the particle surface.

It is possible to describe three mechanisms which have a physical basis. These are illustrated in Fig. (3).

1.2.1 Diffusion across a stagnant fluid film surrounding the particle.

A film of stagnant fluid surrounds each adsorbent particle within the bed. The turbulent motion of the bulk gas phase in the inter-particle space maintains an adsorbate concentration equal to that of the bulk fluid at the exterior surface of the film. Adsorbate must diffuse across this film from a concentration c to a concentration at the gross surface of the particle of $\bar{c}_{r=R}$. The rate at which this film diffusion occurs is then taken as proportional to the concentration change across the film $c - \bar{c}_{r=R}$. It is possible that variations in the flow pattern around the particle will produce a film of fluid that may not surround the particle uniformly. However, it is usual to choose the proportionality constant or fluid film mass transfer coefficient k_o so that $k_o \cdot (c - \bar{c}_{r=R})$ gives the average rate of flow across the surface film surrounding a particle per unit gross surface area. It is clear that this requires small particles so that the change in concentration in the fluid stream over a distance equal to the particle diameter can be neglected, that is $2R \cdot (\partial c / \partial z) \ll c$.

1.2.2 Diffusion within the pores of the particle.

The transport of an adsorbate through a porous solid is known to occur by several different mechanisms. For a gas the ratio of the mean free path in the gas phase to the width of the pores or cavities in the solid determines the type of flow (15). Several types of flow have been identified and their characteristics defined (16). These are :

molecular streaming (Knudsen flow); streamline (or Poiseuille) flow; turbulent flow; and orifice flow. Furthermore, if the gas is adsorbed appreciably onto the solid, an additional transport due to the surface migration of the adsorbate on the porous solid can be considered. For porous materials any non-uniformity of pore diameters, length, pore-to-pore connections means that the transport process within the solid is seldom unique. Transport is further complicated by mixing in the pore labyrinth and the presence of blank or dead end pores, which offer an infinite resistance to diffusion (17). It is thus usual to define an effective diffusion coefficient to smooth out point variations and produce expressions for the average rate of transport within the particle.

1.2.3 Adsorption of the adsorbate on the particle surface.

The general term adsorption isotherm is given to the representation of the equilibrium relationship between the concentration of adsorbate in the fluid immediately in contact with the adsorbent, and the concentration of adsorbate held by the adsorbent on its surface for a specified constant temperature. Due to the inhomogeneous nature of the interior surface of the adsorbent, active sites for the adsorption of the adsorbate tend to show a wide range of activation energies. So that adsorption frequently occurs non-uniformly on the surface. It is thus possible to have single molecules of adsorbate at specific points or a single layer (monolayer) of adsorbate molecules held at several points on the surface, or multilayers of adsorbate molecules attached to the adsorbent surface. The amount actually adsorbed at equilibrium is thus dependant upon the nature of the adsorbent and adsorbate and the system temperature. Graphical plots of adsorption isotherms take a wide variety of shapes, which have been qualitatively classified as shown in Fig.(4).

Type 1 represents adsorption of a single monolayer on identical sites with no interaction between adsorbed molecules, commonly called Langmuir adsorption. Type 2 begins like type 1, but the last part of the isotherm is modified by multilayer adsorption and possibly by capillary condensation. Type 3 isotherms are rare. They occur when the initial adsorption favours a very few strong sites and interaction between adsorbed molecules is so strong that the sites adjacent to occupied sites are much stronger than any other vacant sites. Under these conditions the number of effective sites actually increases with coverage of the adsorbate on the adsorbent. Types 4 and 5 are similar to 2 and 3 respectively, except that they show saturation or filling of pore spaces at high coverage. Type 6 resembles type 3 for the first monolayer, but continues with deposition of a multilayer film (18).

These graphical representations of Fig. (4) show the equilibrium situation. It is necessary to consider the possibility that adsorption at the adsorbent surface is not in equilibrium, as the rate of adsorption is not equal to the rate of desorption. Hence, it is usual to define the overall surface rate as being the difference between the rate of adsorption $k_a \bar{c}$, and the rate of desorption $k_d \bar{q}$.

1.3 Analytical Solutions.

The mathematical solution for the adsorption of an adsorbate from a fluid in beds is complicated to the extent that the possible mechanisms which can be imagined have some basis in physical fact as described in 1.2. Thus the adsorption system can be described by a three-step mechanism: diffusion from the bulk fluid to the external surface of the particle, diffusion into the particle and adsorption on the interior surface. In the general case all three steps can contribute to the overall rate measured in

terms of the concentration in the bulk fluid. There is then the possibility of considering each of the three dual step cases contributing, and each of the three single step cases contributing as the overall rate-controlling mechanism. There have also been proposed several lumped parameter models to represent the overall removal rate. In total some twelve cases can be identified as described below.

The basic procedure is to solve the relevant form of the mass balance equation with a suitable expression for the rate-controlling step; and subject to the simplifications introduced in formulating the problem for an analytical solution. The mathematical complications have their origins in the non-linear partial differential equations which arise. Certain problems have been solved completely, while others have been solved only partially either by linearising approximations or numerical methods. The solutions to some of the cases shown below have been produced in more than one form. The solutions presented below are believed by this author to be those most suitable for efficient application of digital computational methods as shown in Chapter II. Reference is made to the authors of the original formulation and solution of the particular cases considered where a suitable solution is presented. Work carried out by this author, where the available solutions are incomplete or unsuitable, is shown in the Appendices referenced in the text.

The first seven cases describe the rate of change of the concentration of the adsorbate on the adsorbent in terms of n and c only. Variations within the particle are not considered. Thus the individual rate equations from CASE/1 to CASE/7 are solved in conjunction with the mass balance equation I. The remaining five cases consider variations within the particle, so that the individual rate equations from CASE/8

to CASE/12 are solved in conjunction with the mass balance equations Ia and II.

1.3.1 CASE/1 Diffusion across the fluid film.

In the particular case where the concentration of adsorbate at the gross exterior surface of the particle is zero, the concentration gradient across the stagnant fluid film is thus 0. Hence intraparticle diffusion and surface adsorption occur very rapidly, and it is assumed that the adsorbate on the solid has negligible back pressure. The adsorbate must of course cease to be removed from the fluid stream as the adsorbate concentration on the adsorbent reaches the saturation value N_{os} . The rate of removal from the fluid is then :

$$(1/\alpha) \partial n / \partial t = k_f (a \rho_s / \alpha \rho_c) c \text{ ————— III}$$

An equivalent form of III is described by Klotz (11) with a mass transfer coefficient defined in terms of the mass of adsorbate plus fluid per unit particle surface area per unit time, and a modified particle specific surface defined as the gross surface area of particle per unit volume of packed bed. Klotz also reports the solution as :

$$c = C_0 \exp \left\{ - k_f (a \rho_s / \alpha \rho_c) z/V \right\}, \quad t \leq t_0 \text{ ————— IV}$$

It is noted that the profile is independent of time for all times up to t_0 when $n = N_{os}$ at the entrance face of the bed. For times greater than t_0 the solution for the adsorbate concentration in the fluid is :

$$c = C_0 \exp \left\{ - k_f (a \rho_s / \alpha \rho_c) z/V + t/t_0 - 1.0 \right\}, \quad t \geq t_0 \text{ — V}$$

It can easily be shown that V is equivalent to the form presented by Klotz (see Appendix I).

1.3.2 CASE/2 a) Diffusion across the fluid film.

In the case where the concentration of adsorbate at the gross surface of the particle is non-zero, the gradient across the stagnant film is $c - \bar{c}_{r=R}$. This assumes that intraparticle diffusion and surface adsorption occur very rapidly; but that the material adsorbed on the particle exerts a back pressure. So that the adsorbate is adsorbed reversibly. As in this case there are no concentration gradients of adsorbate within the particle it is assumed that the particle contains an adsorbate concentration of n ; and for the simplest case of a linear adsorption isotherm then $\bar{c}_{r=R} = bn$. Hence as reported by Klotz (11) the rate expression is :

$$(1/\alpha) \partial n / \partial t = k_f (a \rho_b / \alpha \rho_c) (c - bn) \text{ ----- VI}$$

b) Surface Adsorption.

Here it is assumed that there is negligible resistance in the fluid film, and that intraparticle diffusion occurs rapidly; but there is a finite overall rate of removal by adsorption on the interior particle surface. The formulation presented by Masamune and Smith (12) will be used in the form :

$$(1/\alpha) \partial n / \partial t = k_a (\rho_b / \alpha) (c - n / \rho_p k_e) \text{ ----- VII}$$

The adsorbate concentration in the intraparticle void volume is that of the bulk fluid and there is no variation in the adsorbate concentration on the particle.

It is noted that VI and VII can be considered together despite the basic differences in the rate - controlling mechanism. The general form for the rate expression in both cases becomes :

$$(1/\alpha) \partial n / \partial t = k_1 c - k_2 n \text{ ----- VIII}$$

Where the definitions of k_1 and k_2 are dependant upon the mechanism used to represent the system. Thus $k_1 = k_f a \rho_B / \alpha \rho_c$, $k_2 = k_f a \rho_B b / \alpha \rho_c$ for fluid film rate-controlling or $k_1 = \rho_B k_a / \alpha$, $k_2 = \rho_B k_a / \alpha \rho_p k_e$ for surface adsorption rate -controlling. Although Masamune and Smith (12) have presented a solution to this case, the solution developed by Amundson (19) will be produced below in preference as it involves a finite upper limit of integration; and includes a term for the initial distribution of adsorbate on the adsorbent. Assuming that C_0 and n_0 are constant then :

$$\begin{aligned} -c \left(\exp(k_1 x + k_2 y) \right) &= g'(y) - \\ & k_2 \int_0^x f'(\xi) \cdot I_0(2\sqrt{k_1 k_2 y (x - \xi)}) \cdot d\xi + \\ & \int_0^x f'(\xi) \cdot \sqrt{k_1 k_2 (x - \xi)/y} \cdot I_1(2\sqrt{k_1 k_2 y (x - \xi)}) \cdot d\xi - \\ & k_2 \int_0^y g'(\eta) \cdot I_0(2\sqrt{k_1 k_2 x (y - \eta)}) \cdot d\eta + \\ & \int_0^y g'(\eta) \cdot \sqrt{k_1 k_2 x/(y - \eta)} \cdot I_1(2\sqrt{k_1 k_2 x (y - \eta)}) \cdot d\eta \text{ --- IX} \end{aligned}$$

where:

$$f'(x) = n_0 (1 + k_1 x) \exp(k_1 x) \text{ ----- X}$$

$$g'(y) = -C_0 (1 + k_2 y) \exp(k_2 y) \text{ ----- XI}$$

$$y = \alpha(t - z/V)$$

$$x = z/V$$

$I_0(p)$ = Bessel function of the zero order with imaginary argument

$I_1(p)$ = Bessel function of the first order with imaginary argument.

This solution is thus capable of covering both the cases where there is mass transfer resistance, and also where adsorption itself may be rate-controlling.

1.3.3 CASE/3 Lumped parameter.

The earliest analysis of the adsorption rate made by Bohart and Adams (20) for the removal of chlorine by charcoal assumed a combined driving force model as represented below. It was assumed that the rate of removal of adsorbate from the fluid is proportional to the unused adsorption capacity of the adsorbent, and to the concentration of adsorbate in the bulk fluid. The mechanism was later developed by other authors (21). The rate expression will be used in the form :

$$(1/\alpha) \partial n / \partial t = k_1 c (N_{os} - n) \text{-----XII}$$

Amundson (30) has presented the solution for the problem in a general form. For the assumption of C_o and n_o constant the general solution reduces to :

$$c = \frac{C_o \exp(k_1 \alpha C_o (t - z/V))}{(\exp(k_1 (N_{os} - n_o) z/V) + \exp(k_1 \alpha C_o (t - z/V)) - 1.0)} \text{-----XIII}$$

1.3.4 CASE/4 Lumped parameter.

This case has the same basis as 1.3.3; but it is assumed that the adsorption is reversible, and the adsorbate exerts a back pressure. Hence the rate expression becomes :

$$(1/\alpha) \partial n / \partial t = k_1 c (N_{os} - n) - k_2 n \text{-----XIV}$$

The general solution has been presented by Amundson (19). For the assumption of C_o and n_o constant the general solution reduces to :

$$\alpha = \frac{1}{k_1} \frac{\partial \phi}{\partial y} \frac{1}{\phi} = \frac{k_1}{k_2} \text{-----XV}$$

- where :

$$\phi = I_0(2\sqrt{k_1 k_2} \text{ Nos } x y) + \int_0^y G'(\eta) \cdot I_0(2\sqrt{k_1 k_2} \text{ Nos } x (y - \eta)) \cdot d\eta$$

$$+ \int_0^x F'(\xi) \cdot I_0(2\sqrt{k_1 k_2} \text{ Nos } y (x - \xi)) \cdot d\xi \text{-----XVI}$$

$$\partial \phi / \partial y = G'(y) + \sqrt{k_1 k_2} \text{ Nos } x / y \cdot I_1(2\sqrt{k_1 k_2} \text{ Nos } x y)$$

$$+ \int_0^x F'(\xi) \cdot \sqrt{k_1 k_2} \text{ Nos } (x - \xi) / y \cdot I_1(2\sqrt{k_1 k_2} \text{ Nos } y (x - \xi)) \cdot d\xi$$

$$+ \int_0^y G'(\eta) \cdot \sqrt{k_1 k_2} \text{ Nos } x / (y - \eta) \cdot I_1(2\sqrt{k_1 k_2} \text{ Nos } x (y - \eta)) \cdot d\eta \text{-----XVII}$$

$$F'(x) = k_1 (\text{Nos} - n_o) \exp(k_1 x (\text{Nos} - n_o)) \text{-----XVIII}$$

$$G'(y) = (k_1 C_o + k_2) \exp(y (k_1 C_o + k_2)) \text{-----XIX}$$

(x, y, I₀, I₁, are defined in 1.3.2)

1.3.5 CASE/5 Lumped parameter

This case has been titled by Kostecki, Manning and Canjar (22) as simultaneous external mass transfer and reversible second order surface reaction. They presented the rate equation in a form analagous to the one given below. It was originally formulated by Glueckauf and Coates (23) for chromatographic theory. The rate expression can be represented as :

$$(1/\alpha) \partial n / \partial t = k_1 (N_{os} - n) \text{-----XX}$$

The analytical solution for this case is presented in Appendix II as :

$$c = C_o - k_1 \frac{z}{V} (N_{os} - n_o) \exp(-k_1 \alpha (t - z/V)) \text{-----XXI}$$

1.3.6 CASE/6 Lumped parameter.

This case has been described by Vermeulen (24) who assumed a quadratic driving force. It was offered as a good general approximation, somewhat more accurate than Glueckauf and Coates's relation for a linear driving force (see 1.3.5). The rate expression can be represented as :

$$(1/\alpha) \partial n / \partial t = k_o ((N_{os}^2 - n^2) / 2n) \text{-----XXII}$$

The analytical solution for this case is presented in Appendix III as :

$$c = C_o - \frac{0.5 k_o x (N_{os}^2 - n_o^2) \exp(-k_o y)}{[N_{os}^2 - (N_{os}^2 - n_o^2) \exp(-k_o y)]^{1/2}} \text{-----XXIII}$$

(x, y are defined in 1.3.2)

1.3.7 CASE/7 Lumped parameter.

This empirical relationship has been proposed (25, 26) to take into account the equilibrium characteristics of the system. It was first introduced by Thomas (27) who applied it to ion-exchange phenomena. The rate expression can be represented as :

$$(1/\alpha) \partial n / \partial t = k_1 c (N_{os} - n) - k_2 n (C_o - c) \text{-----XXIV}$$

By suitable change of variable the solution proceeds similar to that shown by Amundson (19) and is described in Appendix IV.

This gives :

$$c = - \frac{k_2 C_o}{(k_1 - k_2)} + \frac{1}{(k_1 - k_2)} \cdot \frac{\partial \phi}{\partial y} \cdot \frac{1}{\phi}$$

...where :

$$\begin{aligned} \phi = & I_0 (2 \sqrt{k_1 k_2 \text{ Nos Co } x y}) \\ & + \int_0^y G'(\eta) \cdot I_0 (2 \sqrt{k_1 k_2 \text{ Nos Co } x (y - \eta)}) \cdot d\eta \\ & + \int_0^x F'(\xi) \cdot I_0 (2 \sqrt{k_1 k_2 \text{ Nos Co } y (x - \xi)}) \cdot d\xi \quad \text{---XXVI} \end{aligned}$$

$$\begin{aligned} \partial \phi / \partial y = & \sqrt{k_1 k_2 \text{ Nos Co } x / (y - \eta)} \cdot I_1 (2 \sqrt{k_1 k_2 \text{ Nos Co } x y}) + G'(y) \\ & + \int_0^y G'(\eta) \cdot \sqrt{k_1 k_2 \text{ Nos Co } x / (y - \eta)} \cdot I_1 (2 \sqrt{k_1 k_2 \text{ Nos Co } x (y - \eta)}) \cdot d\eta \\ & + \int_0^x F'(\xi) \cdot \sqrt{k_1 k_2 \text{ Nos Co } (x - \xi) / y} \cdot I_1 (2 \sqrt{k_1 k_2 \text{ Nos Co } y (x - \xi)}) \cdot d\xi \quad \text{---XXVII} \end{aligned}$$

$$G'(Y) = k_1 C_o \exp(k_1 C_o y) \quad \text{---XXVIII}$$

$$F'(x) = [k_1 \text{ Nos} - (k_1 - k_2) n_o] \cdot \exp [x (k_1 \text{ Nos} - (k_1 - k_2) n_o)] \quad \text{---XXIX}$$

(x, y, I₀, I₁ are defined in 1.3.2).

1.3.8 CASE/8 Intraparticle diffusion and film diffusion

Here it is considered that the rate-controlling factor is the process of combined diffusion into the particle itself, and diffusion of adsorbate through the fluid film surrounding the particle. Surface

adsorption is considered instantaneous so that $k_c c = q$. Then diffusion across the surface film can be represented by :

$$k_c = 3 \frac{\rho_B k_f}{\rho_P R} \left(c - \frac{1}{k_c} \bar{q} \right) \text{---XXX}$$

The solution to this problem has been presented by Masamune and Smith (12), and in a similar form by Rosen (8,28). The solution can be represented by :

$$c / C_0 = 0.5 + \frac{2}{\pi} \int_0^{\infty} \exp(\alpha_1) \cdot \sin(\alpha_2) \cdot \frac{d\lambda}{\lambda} \text{---XXXI}$$

-- where :

$$\alpha_1 = (-3 k_4 / k_3) \Omega_1 \text{---XXXII}$$

$$\alpha_2 = (2 k_6 k_4 / k_3) \lambda^2 - (3 k_4 / k_3) \Omega_2 \text{---XXXIII}$$

$$\Omega_1 = (\psi_1 + k_7 (\psi_1^2 + \psi_2^2)) / [(1 + k_7 \psi_1)^2 + (k_7 \psi_2)^2] \text{---XXXIV}$$

$$\Omega_2 = \psi_1 / [(1 + k_7 \psi_1)^2 + (k_7 \psi_2)^2] \text{---XXXV}$$

$$\psi_1 = [\phi_1 \sin 2\phi_1 + \phi_2 \sinh 2\phi_2] / (\cosh 2\phi_2 - \cos 2\phi_1) - 1.0 \text{---XXXVI}$$

$$\psi_2 = [\phi_2 \sin 2\phi_1 - \phi_1 \sinh 2\phi_2] / (\cosh 2\phi_2 - \cos 2\phi_1) \text{---XXXVII}$$

$$\phi_1 = -\lambda \text{---XXXVIII}$$

$$\phi_2 = \lambda \text{---XXXIX}$$

$$k_3 = R^2 k_a \rho_P / D_i$$

$$k_4 = \rho_B k_a h / \alpha V$$

$$k_6 = V \alpha (t - z/V) / \rho_B k_e h \quad k_7 = D_i / k_e R$$

1.3.9 CASE/9 Intraparticle diffusion.

This case where intraparticle diffusion only is rate controlling has been considered as a special form of 1.3.8 (8), when the value of the external film mass transfer coefficient becomes infinite; and hence the adsorbate concentration in the fluid at the gross particle surface is equal to the bulk value. The solution for 1.3.8 can thus be reduced by letting k_7 equal zero, so that XXXIV and XXXV are replaced by:

$$\Omega_1 = \psi_1 \text{-----} \text{XXXX}$$

$$\Omega_2 = \psi_2 \text{-----} \text{XXXI}$$

1.3.10 CASE/10 Intraparticle diffusion and surface adsorption.

Here there is no resistance in the external surface film so that $c = \bar{c}$, with:

$$k_c = 4 \pi R^2 \bar{n} D_i (\partial c / \partial r)_{r=R} \text{-----} \text{XXXII}$$

$$\partial \bar{q} / \partial t = k_a \left(\bar{c} - \frac{1}{k_e} \bar{q} \right) \text{-----} \text{XXXIII}$$

The solution is given by equation XXXI with XXXII, XXX, XXXXI, XXXVI, XXXVII and:

$$\alpha_2 = k_4 k_6 \lambda^2 - (3 k_4 / k_3) \Omega_2 \text{-----} \text{XXXIV}$$

$$\phi_1 = - (k_3)^{1/2} \lambda \cdot [1 / \{ 2 \cdot (\lambda^4 + 1) \cdot (\sqrt{\lambda^4 + 1} + \lambda^2) \}]^{1/2} \text{-----} \text{XXXV}$$

$$\phi_2 = (k_3)^{1/2} \lambda \cdot [1 / \{ 2 \cdot (\lambda^4 + 1) \cdot (\sqrt{\lambda^4 + 1} - \lambda^2) \}]^{1/2} \text{-----} \text{XXXVI}$$

1.3.11 CASE/11 External film diffusion and surface adsorption.

Here there are no intraparticle diffusion resistances so that

$$\delta \bar{c} / \delta r = 0, \text{ with } \underline{\text{XXXX11.1}} \text{ and :}$$

$$k_c = (3 \rho_B / R \rho_P) k_f (c - \bar{c}) \text{----- XXXXVII}$$

The solution is given (12) by equation XXXI with XXX,

XXXX1 and :

$$\alpha_1 = - k_A k_q \Omega_1 \text{----- XXXXVIII}$$

$$\alpha_2 = k_B k_A \lambda^2 - k_A k_q \Omega_2 \text{----- XXXXIX}$$

$$\psi_1 = \phi_1 \text{----- L}$$

$$\psi_2 = \phi_2 \text{----- LI}$$

$$\phi_1 = \lambda^4 / (1 + \lambda^4) \text{----- LII}$$

$$\phi_2 = \lambda^2 / (1 + \lambda^4) \text{----- LIII}$$

$$k_q = k_g / (k_a + k_g) \qquad k_g = 3 k_f / R \rho_P$$

1.3.12 CASE/12 External film diffusion, intraparticle diffusion and surface adsorption.

In this case where all three mechanisms contribute to the overall rate, the relevant equations are XXXI1, XXX111 and

$$k_f (c - \bar{c}_{r=R}) = D_i \left(\partial \bar{c} / \partial r \right)_{r=R} \text{-----LIV}$$

The solution proposed by Masamune and Smith (29) is given by XXXI with XXXII, XXXIII, XXXIV, XXXV, XXXVI, XXXVII, XXXVIII and XXXIX.

This completes the available analytical solutions that have been programmed in Chapter II to illustrate the various shapes of the profiles of the concentration of adsorbate in the fluid leaving the bed for suitable parameter values.

C H A P T E R II.

In Chapter I twelve cases were proposed to account for the mechanisms contributing to the mass transfer of adsorbate from a flowing fluid stream to a stationary adsorbent. Two assumptions were made so that analytical solutions could be produced, namely those of a linear adsorption isotherm and isothermal operations. Examination of the characteristic shapes of the major types of adsorption isotherms (see Fig. (4)) indicates that for low adsorbate concentrations a linear approximation of the lower region of the isotherm is possible. An approach to isothermal operation is possible by considering certain characteristics of the system as described in Chapter III. For present purposes it can be seen that dilute adsorbate/carrier fluids favour isothermal operation and a linear approximation of the adsorption isotherm. Considerable interest has, therefore, been shown in the past concerning the use of these analytical solutions for the prediction of the performance of adsorption units.

The analytical solutions of the partial differential equations were presented in terms of certain constants ($k_i; i = 1, 2 \dots 9$). It was possible in some instances to define these constants in terms of measurable or predictable properties of the adsorption system. In the lumped parameter models, however, this analysis of the constants was not possible. This multiplicity of solutions, and the indeterminate nature of some of the coefficients, has enabled the solutions to be applied to systems where the assumptions required for mathematical analysis do not strictly apply. Hence, past workers in an attempt to elucidate the particular mechanism controlling the removal process, have firstly performed experiments under what they believe to be isothermal conditions. Then the results of these experiments have been compared to the solutions given by a few chosen rate mechanisms. Some degree of fit has been produced by manipulation of the value(s) of the constant factors. This procedure has generally been

applied to the concentration of the adsorbate as a function of time in the carrier stream leaving the exit face of the bed. This concentration profile can be readily predicted by the mathematical solutions for any point within the bed. However, the easiest point at which to take measurements is just outside the exit face. The measuring instrument does not then interfere with the flow properties within the bed. Usually the complete concentration profile ($0 \leq c \leq C_0$) has been measured and complete profiles from the analytical solutions fitted over this total concentration range. Whilst the use of this full concentration range aids investigation of the rate process, the interpretation obtained is not conclusive (see Chapter VI). When aiming for this high degree of overall fit, it is not always possible to produce good fit at the lower range of concentration (say 0 - 10% of the inlet concentration). However, it is this lower range of concentrations that is of most interest, if the mechanism under investigation is to be applied to describe the behaviour of an industrial system. For reasons that are obvious (see also Chapter VIII) no industrial system is operated at effluent conditions that approach the inlet conditions (for the passage of adsorbate/carrier fluid through several consecutive beds, the effluent conditions are those leaving the last bed of the series). Yet, production of the full range profile has always served as a suitable starting point in elucidating the removal mechanism. In this chapter full range profiles predicted by the analytical solutions are shown for a particular set of physical parameters (see Chapter VI for their derivation); and for various values of the constants, as defined for the particular cases described in Chapter I.

This method of presentation is not new. Before the wide-spread use of high speed computational machines, the exit concentration profiles for various conditions were presented as series of curves and/or tables

evaluated at suitable constant parameter values. Extrapolation, or interpolation and some simple calculations were then required to produce the exit concentration profile for non-tabulated values. It is now easier and quicker to use the computer programmes described below to produce the profiles. Although the work of this Chapter was carried out on a digital machine, hybrid machines can also be used (31). It is usual to present the exit concentration in a dimensionless form (c/C_0) as a function of time in a dimensionless form (t/t_{0s}), where t_{0s} is the time required to saturate the adsorbent if the rate process were infinite. Profiles for several k values can then be shown for the same mechanism on the one diagram. Where only one k parameter exists, or where two k parameters are interlated by a constant expression, only one diagram is required to illustrate the profiles for a particular mechanism. For two or more k parameters several diagrams are required. In this work k_2 (say) will be held constant for each of several diagrams, whilst the same range of values of k_2 (say) are shown on each diagram. Whilst all the analytical solutions do not require that the adsorbent be fresh ($n_0 = 0$) or that the inlet concentration is constant ($C_0 \neq f_n(t)$), these assumptions have been made here to establish a basis for comparison between mechanisms whose analytical solution does have this rigorous requirement and those that do not.

The constant physical conditions for the bed and adsorbate laden carrier are shown in Table I. ; and were used for all of Cases 7 to 12. The computer programmes were written in ICL FORTRAN and run on the facilities available as part of the University of Manchester Regional Computing Centre. The ICL 1906 A was the machine used.

2.1 The Programming of Cases 1 to 7.

The first seven cases of Chapter I produce exit concentration profiles requiring that the values of one or two constants be specified. A preliminary set of k values differing by factors of ten were used with the programmes and specimen concentration profiles were produced. These specimen profiles were then compared to the profiles obtained experimentally. A reduced range of k values was used so that the profiles illustrated latter contain within them the general shapes of the experimental profiles. Selected k values from within this narrow range were then used to produce the large number of points from which the selected profiles were drawn.

As can be seen from Chapter I, the solutions for cases 2, 4 and 7 involve numerical integration of non-standard functions. The procedure used for the numerical integration is a modified form of Simpson's Rule. This was available as a Library Subroutine `PLINTSMP` compiled and stored within the 1906A. As the routine is stored in machine code a listing of it was not available to the author. The input to this subroutine is in the format (a,b,c,d,e,f) . Where :

- a - lower limit of integration
- b - upper limit of integration ($b > a$)
- c - a function statement which calculates the value of the argument of the integral at all points within the limits of integration.
- d - an accuracy parameter (see below).
- e - an initial step length indicator (see below).
- f - variable for store of value of integral,

$$f = \int_a^b y(x) \cdot dx$$

An initial step length equal to $0.25(b - a)/2^e$ is used. The integration procedure begins at the lower limit of integration and evaluates the integral over the first four intervals by two different procedures. The lack of agreement between the results of these two procedures is compared to an expression involving the accuracy parameter, δ . The integration step length is then altered if necessary; and the integration proceeds towards the upper limit. For a well-behaved function, the absolute error is stated as being unlikely to exceed $\delta.(b-a)/2$. This subroutine had been well tested against known integrals.

Some problems with this routine were encountered. From the analytical solutions presented in Chapter I for Cases 2, 4 and 7 it will be seen that several of the integrands become indeterminate at either the upper or lower limit of integration. The application of De l'Hopital's rule to the relevant terms produced a value, in terms of the determinate variables, for the functions at the troublesome limit. This had then to be programmed into the function statements. It will further be seen that evaluation of the square root terms in the analytical solution is impossible if the value of the integration parameter (ϵ or η) exceeds the upper limit of integration. It was found in preliminary work that the procedure used to alter the integration step made it possible for the integration routine to call for a function value to be evaluated just above its upper limit of integration. When this occurred the programme failed trying to evaluate the square root of a negative argument. As it was not possible to alter the integration routine to prevent it's calling these prohibited function values, the function statements were modified. This consisted of testing the value of the integration parameter, and if it exceeded the upper limit it was re-set to the value of the upper limit. The function value at the upper limit was then evaluated and used in the

integration subroutine. Hence, for values of the integration parameter above the upper limit of integration, the value of the integrand maintained constant. This problem was not encountered at the lower limit. In an effort to minimise the effect of this mis-representation of the function value, several values of the accuracy parameter were tried. It was expected that reducing the accuracy parameter would involve more iterations but produce a more accurate evaluation of the integral. Eight values of the accuracy parameter were used in determining the value of A_2 from FUN2 (E) for Case 2. The results are presented in Table II. It can be seen that the first two results tend towards the values shown for the third, fourth and fifth results which are constant. However, a further reduction in the accuracy parameter gives results six and seven which are equal; but differ greatly from the first five values. Whereas reducing the accuracy parameter more for the eighth result produces a value nearer the first five values than the sixth and seventh. It is not clear which value for the integral is the correct one. The value of FUN2 (E) was then determined for several values of E in the range as shown by Fig.(5). It is immediately apparent that forcing the function values to be constant at and above the upper limit of integration produces great inaccuracy due to the very large function values involved. The values of the other functions for Case 3 and Case 4 were then produced for various values of the integration parameter and shown in Fig.(6) and Fig.(7). The function values from Case 7 were not produced due to the similarity of the solution with that of Case 4. Functions integrated over the range 0 to X fall in value as the integration parameter increases, whereas functions integrated over the range 0 to Y are effectively zero for low values of the integration parameter, becoming very large (positive or negative) at the upper limit.

As there are few problems associated with the lower limit, it was possible to integrate the functions in the form $FUN2(F)$, where $F = Y - E$, over the limit 0 to Y . This produces the large function values at the lower limit, and means that at the upper limit the function value is effectively zero. Five values of the accuracy parameter were used in determining the value of $A2$ from $FUN2(F)$ for Case 2. The results are shown in Table III. Thus, all functions integrated between the limits 0 and Y were reflected about the line $\eta_c = 0.5 Y$ to obtain reproducible results for the values of the integrals, see Fig.(8) for Case 2.

Further notes on the programming of each of the seven cases, and sets of typical effluent profiles are presented below.

2.1.1 Case 1.

A copy of the programme for Case 1 is shown by Fig.(9). As can be seen from equation III, the rate of removal falls to zero as $c \rightarrow 0$; but there is no analytical expression to account for the observed fact that the rate must also tend to zero as $n \rightarrow \infty$. It is thus necessary to include in the programme a criterion for determining at what time the inlet face becomes saturated (t_0). A relationship is also necessary to determine the variation with z and t of those points in the bed that are at saturation capacity. Exit concentration profiles are shown in Fig.(10) for several values of K_1 , where K_1 is defined as $k_1 a \rho_s / \alpha \rho_c$.

2.1.2 Case 2.

A copy of the programmed solution to equation VIII of Case 2 is shown by Fig.(11). The function statements $FUN1$ and $FUN2$ represent the evaluation of the terms to be integrated over X and Y respectively, as defined by equations IX, X and XI. The subroutine $F4INTSMP$ performs the numerical integration; and has been described in 2.1. The subroutines $F4IO$ and $F4I1$ are library routines available within the machine to

calculate the values of the Bessel function with imaginary argument of zero and first order respectively. It can be seen from 1.3.2 that the values of K_1 and K_2 are related by the requirements of the linear isotherm. In particular, as the rate of removal must fall to zero as $c \rightarrow C_0$, $n \rightarrow N_{os}$, then $K_2 = K_1 \times C_0/N_{os}$. It is thus only necessary to illustrate the profiles, as shown in Fig.(12), for various K_1 values. A unique value of K_2 being associated with each K_1 value.

2.1.3 Case 3.

A copy of the programme for Case 3 is shown by Fig.(13). As can be seen from equation XII the rate falls naturally to zero as the bed becomes saturated. This simple programming is all that is necessary. Exit concentration profiles are shown in Fig.(14) for several values of the single parameter K_1 .

2.1.4 Case 4.

A copy of the programme for Case 4 is shown by Fig.(15). The function statements FUN1 and FUN6 represent the evaluation of the terms to be integrated over Y , whereas FUN2 and FUN5 are the terms to be integrated over X . The subroutine F4INTSMP performs the numerical integration, as described in 2.1. The subroutines F4IO and F4II are described in 2.1.2. From equation XIV the removal rate must fall to zero at some adsorbate loading n^* ($< N_{os}$), when the concentration in the bulk fluid is at C_0 . If an initial adsorbate loading greater than n^* is used, then desorption will occur and the effluent concentration will be greater than C_0 . The value of n^* is obviously a function of k_1 and k_2 as $n^* = k_2 C_0 N_{os} / (k_1 C_0 + k_2)$. So that if $n^* = \text{ratio} \times N_{os}$, then the value of ratio ($0 < \text{ratio} < 1$) is given as $k_1 C_0 / (k_1 C_0 + k_2)$. Although the values of k_1 and k_2 are independent for Case 4, the fractional saturation of the bed achieved at

equilibrium gives a means of relating the relative magnitudes of K_1 and K_2 . Hence in Figs.(16) to (21) the exit concentration profiles for six values of K_1 and various K_2 values also show the relative saturation of the bed at equilibrium.

2.1.5 Case 5.

A copy of the programme for Case 5 is shown by Fig.(22). From equation XX it can be seen that the rate equation falls to zero as the bed becomes saturated; but does not fall asymptotically to zero as c tends to zero. So that the form of equation XXI makes it possible for negative concentrations to be produced for ranges of t , z and k values. This is illustrated diagrammatically by Fig.(23), where the time interval $0 \leq t \leq h/V$ is considered. As can be seen, the concentration in the bulk fluid falls to zero at the point z_0 , when $t = t_0 = z_0/V$. For all values of z greater than z_0 , the initial state of the bed is unchanged. When $t > t_0$, the concentration profiles will move through the bed at a velocity less than V , until for some time $t = t^*$ the bulk concentration profile reaches the end of the bed. This is illustrated in Fig.(24). Only when $t > t^*$ will the exit concentration profile rise above a zero value. Using the equality $t_0 = z_0/V$ in equation XXI enables a value for z_0 to be determined as $z_0 = CoV / k_1 (N_0 - m_0)$. If $h \leq z_0$ then equation XXI describes the variation of c with z and t . If, however, $h > z_0$ it is then necessary to modify the programme slightly as shown by Fig.(22); and described in detail in Appendix V. Exit concentration profiles are shown in Fig.(25) for several values of K_1 . Where the exit concentration at $TD = 0.0$ is non-zero, then $h < z_0$ and the unmodified form of equation XXI applies.

2.1.6 Case 6.

A copy of the programme for Case 6 is shown by Fig.(26). As with Case 5, the rate of removal is still finite and non-zero for $c = 0.0$,

so that negative concentration values are possible. From equation XXIII it can be seen that $z_0 = 2.0 C_0 V n_0 / k_0 (N_{os}^2 - n_0^2)$ by arguments similar to those advanced in 2.1.5. So that if $h > z_0$ it is again necessary to modify the programme. The unmodified programme is shown by Fig. (26), and used to produce some of the curves shown in Fig. (27). As the modifications are not simple, reference is made to Appendix VI.

2.1.7 Case 7.

A copy of the programme for Case 7 is shown by Fig. (28). As can be seen from equations XXV to XXIX, its solution is similar to that of Case 4. So that the programming is identical to that of 2.1.4, with minor differences in the terms involving the physical parameters. The rate expression of equation XXIV will be zero when $n = k_1 N_{os} c / (k_2 C_0 + (k_1 - k_2))$. So that as $c \rightarrow C_0$, then $n \rightarrow N_{os}$. Here, unlike Case 4 it is now possible to attain complete saturation of the bed. Further analysis of equation XXIV clearly indicates that, for any initial loading of adsorbate on the adsorbent, desorption is not possible unless the concentration of adsorbate in the bulk fluid is less than $k_2 n_0 C_0 / (k_1 (N_{os} - n_0) + k_2 n_0)$. For an inlet concentration of C_0 , and a non-zero value of n_0 , this condition is most likely to occur at the exit from the bed. So that the minimum value of the exit concentration that can be obtained is equal to the above expression. Hence, for fixed values of C_0 , N_{os} and n_0 ($\neq 0$) the relative values of k_1 and k_2 will determine the minimum initial value of the exit concentration. For $n_0 = 0$ then the minimum initial value of the exit concentration will zero. Figs. (29) to (33) illustrate the exit concentration profiles for five values of K_1 and various K_2 values, chosen so that zero and non-zero initial exit concentrations values are produced.

2.2 The Programming of Cases 8 to 12.

It has been shown in 2.1 how it was necessary to specify the values of one or two parameters (k values) so that the exit concentration profiles could be produced. It was possible to make these solutions more general by grouping together a series of terms into a single parameter. For Cases 8 to 12 it will be seen that this is not directly possible. It is now necessary to specify the values of D_k, k_f, k_e, k_d and k_a ($k_e = k_d / k_d$) when required for each of the cases. So that for Case 12 specification of the values of four parameters must be done. As is described in later work of this thesis, these Cases involving intraparticle variations will be neglected. The major reason (proposed later) is based on the observation that the profiles produced by Cases 8 to 12 can also be produced by using suitable k values in Cases 1 to 7. To illustrate this effect for this work, Case 8 has been programmed and the data from Table I used to produce a series of exit concentration profiles. These profiles are then compared with those produced by Cases 1 to 7 and the degree of fit is commented upon. It was decided to choose Case 8 for particular investigation as it has a solution similar to that of the general case, Case 12; and so serves as a suitable test of the integration procedure. Moreover, it is generally found that for active carbon and non-polar adsorbates, the resistances to mass transfer occur within the intraparticle space and in the external surface film (adsorption occurring very fast). Hence, Case 8 would appear to be the most suitable one of these involving intraparticle effects.

It can be seen from Fig.(34) that the bulk of the programming effort is taken up in evaluation of the integral term of equation XXXI. An illustration of several curves showing the variation, with the value of the integration parameter (λ), of the integrand is given by Masamune

and Smith (12). Similar curves for this work are shown in Fig.(35). The general form is clearly seen to be sinusoidal and stable, the amplitude being rapidly reduced at high values of the integration parameter.

Previous workers (12,28) have used the integration formula of Weddle applied over a finite range of the integration parameter, without making specific use of the sinusoidal form of the integral. The integration routine of this work, programmed as CALC also uses the integration formula of Weddle; but makes use of the sinusoidal form of the integrand. Full details of the programme logic and a complete description of the procedure are given in Appendix VII. The results have been presented by Fig.(36) and Fig.(37) for KF constant with several values of DI, and for DI constant with several values of KF.

Similar procedures can be used for Cases 9 to 12 which would only involve the use of a different form of the function producing routine FUN and minor modifications to the main programme. For the reasons explained earlier in this text these cases will not be discussed further.

2.3 Comparison of Case 8 with Cases 1 to 7.

It is immediately apparent that Cases 1, 5 and 6 can be dismissed as their shapes in no way correspond to those shown in Figs.(36) & (37). Cases 2, 3, 4 and 7 need only be considered. A direct comparison is available by use of the dimensionless concentration CD and the dimensionless time TD which enables the curves for the various Cases to be compared on the basis of shape alone. To this end tracings of the curves of Fig.(36) and Fig.(37) can be placed on the curves shown for Cases 2, 3, 4 and 7 using the values of TD and CD for reference. Any agreement or otherwise is immediately apparent.

Following this procedure identifies two areas of comparison as shown by Fig. (38).

- a) A close agreement between Case 8 and other Cases over small regions of the profile only.
- b) A less precise agreement between Case 8 and other cases over the total range of the profile.

Agreement of the first type above is useful for the initial part of the profiles so that other mechanisms can be used to represent the mechanism of Case 8. This permits analytical solutions of lesser complexity to be used to produce data on breakthrough times as well as giving a good indication of the shape of the initial part of the exit concentration profile. The breakthrough time and initial exit concentration profile being those items of prime importance to a simple study of the suitability of different adsorbents in different physical bed shapes.

Agreement of the second type is of more practical use for any involved study of operating adsorption systems. Although beyond the scope of this present work it can easily be shown that manipulation of parameter values can force simple analytical solutions to closely represent complex solutions. This procedure must however be done on well specified systems where only small scale changes of the parameter values are contemplated. Moreover, any such modified parameters could not safely be used to extrapolate the system behaviour into regions where closeness of fit between simple and complex solutions had not been previously established.

If the above reservations can be satisfied then intraparticle mechanisms can be represented by extra particle parameters and lead to great simplifications in the further analytical treatment of adsorption systems.

C H A P T E R III.

The case of isothermal adsorption has been discussed first to illustrate the nature and solution of the various possible mechanisms that could control the adsorption rate process. It is apparent, however, that for non-zero heats of adsorption, heat will be liberated when the adsorbate is adsorbed. The adsorbate is transferred from the bulk stream to the surface of the adsorbent and then diffuses into the particle. During this diffusion the adsorbate in the pore volume attains an equilibrium (for adsorption itself not rate controlling) with the adsorbate as the internal surface and heat is generated. This heat is removed from the particle into the gas stream from whence it passes to other parts of the bed in the gas stream and into the wall of the container. Heat from the container is then lost to the surrounds, whereas heat retained by the gas stream will affect the adsorption processes further along the bed in the direction of flow.

Two limiting cases are of particular interest - isothermal and adiabatic. If heat transfer rates were infinite, then adsorption would be isothermal. In theory this is of course not possible; but it is approached in a small diameter, uninsulated beds contained by a vessel of high thermal conductivity with a large residence time of the gas stream. A small diameter bed ensures negligible radial variations in temperature so that the gas temperature near the wall is essentially that of the bulk gas flow. A large residence time provides the time necessary for attaining uniform temperature within a small cross section of the bed, which is maintained by the heat losses through the wall area of that cross-section.

If heat transfer to the container wall is zero then the adsorption process is adiabatic. All the heat of adsorption generated within the particle must be retained by the particle and transferred to the gas stream as it passes through the bed. Hence, where appreciable amounts of adsorbate are removed from the gas stream, the heat generated locally causes a sharp rise in the gas temperature which falls away downstream.

Thus a temperature peak is produced within the bed which moves with time through the bed, eventually emerging at the exit from the bed where it is registered by a change in the exit gas temperature. If the gas stream is capable of retaining some of this heat of adsorption during its passage through the entire bed, then whilst the bed remains unsaturated, the exit temperature of the gas will always be in excess of its inlet value. It is apparent that true adiabatic operation is theoretically impossible. However, it is possible to imagine that for beds of large cross-section where the available wall surface per unit depth of bed is small, then adiabatic operation might be approached. An adsorption period of short duration, in not allowing time for heat transfer through the wall, would also tend to promote adiabatic operation.

If heat transfer into the container wall is finite; but heat loss to the surroundings is zero, as might be the case in a well insulated bed, then the process can be described as damped adiabatic. Here the amplitude of the temperature peaks is depressed by the thermal capacity of the container. Heat removed by the container reduces the temperature reached within the bed; and this heat is then returned to the gas stream when its local temperature is lower than the container. This is known as the regenerative heat capacity of the container.

It is thus possible to describe the dynamic behaviour of an adsorption bed in the most general case by the movement and shape of the concentration and temperature profiles as functions of time and position. Of course, one is greatly influenced by the other. If the bed operates isothermally, only the concentration profile assumes importance (as described in Chapter I). The heat and mass fluxes that can be imagined to be present in the fixed bed are shown by Fig.(39) after Coulson and Richardson.

(32). The total fluxes are : -

- N_0, N_1 - are the intraparticle processes. The adsorption step itself and its associated heat of adsorption are subscripted zero. The diffusion of adsorbate into the particle to the point of adsorption; and the counter-movement of heat by conduction through the solid volume are subscripted one.
- N_2 - is the transport of heat and mass between fluid and particle across the surface film around the particle.
- N_3, N_3' - are the radial distribution of heat and mass in the gas, and between solid particles in contact.
- N_4, N_4' - are the axial distribution of heat and mass in the gas, and by conduction and diffusion between particles in contact.
- N_5, N_5' - heat fluxes from the gas to the wall across a boundary film, and by particle contact with the wall.
- N_6, N_7 - heat fluxes in the container wall in the radial and axial directions.
- N_8 - heat losses to the surroundings.

This complete description of the transport processes aids the understanding of the system being considered. However, inclusion of all fluxes in a suitable model has not been regarded as necessary to suitably represent the real system. It is usual to make several assumptions so that a model of the remaining operational fluxes can be constructed and solved - in the general case by numerical methods.

The isothermal case requires that all radial fluxes are zero and the only non-zero axial flux being the mass-flux in the bulk gas due to the bulk gas flow. The adiabatic case requires that fluxes subscripted 5 to 8 are zero. The damped adiabatic case requires that N_8 is zero. Generally, it is usual to assume that N_3', N_4' and N_5' are all effectively zero. That is, transport by point contact is regarded as suitably small compared to

transport by bulk processes. The equilibrium between adsorbate within the particle and on the surface is assumed to be attained instantaneously. While radial adsorbate concentration profiles can exist, it is usually assumed for adsorbents of good thermal conductivity and small particle diameters that there are no radial temperature profiles. Furthermore, heat transfer from the particle surface is across the particle surface film by diffusion processes.

For the isothermal case, the concentration profiles are described by the equations of Chapter I. The temperature profile within the bed and the exit face is described by $\Theta = \Theta_0 = \text{constant}$.

The adiabatic case under the above assumptions has been presented by Carter (33 , 34). The solutions obtained were compared to experimental results for the adsorption of water vapour on activated alumina under both adiabatic and isothermal conditions. A three-dimensional grid with axes of r , t and z was used to solve the difference formulations of the original partial differential equations.

The damped adiabatic case was considered by Meyer and Weber (35). A difference formulation was again set up and solved. The three dimensional grid with axes r , t and z were again used in conjunction with characteristic paths $V = dz/dt$, t and z . This method of characteristics applied to heat and mass transfer has been described by Acrivos (36), and applied to a formulation of the isothermal case by Lee and Weber (37).

3.1 A Description of the General System.

The relevant equations of Meyer and Weber can be set up readily using the nomenclature of this thesis to give the results described below.

In the bulk gas stream within the bed, the material balance for the adsorbate over a unit cross-section is :

$$- \partial(Vc)/\partial z - aM_1 = \partial c/\partial t \text{ ----- LV}$$

This can be compared with equation I in Chapter I. Here possible changes in the interstitial velocity with t and z are taken into account. The rate of removal of adsorbate from the bulk has been re-expressed in terms of its mass flux. An overall material balance takes a similar form,

$$- \partial(Vc)/\partial z - a(M_1 + M_2) = \partial\rho/\partial t \text{ ----- LVI}$$

Equation LVI describes the variation of velocity and bulk gas density in its most rigorous form. By assuming that the bed is initially full of the inert carrier, and that the mass velocity of the inert carrier is constant, then it can be easily shown that :

$$U\rho_c/\alpha = V(\rho - c) = \text{constant} \text{ ----- LVII}$$

A material balance for the adsorbate in the intraparticle space gives :

$$- \frac{1}{r^2} \cdot \frac{\partial(r^2 \cdot \bar{M}_1)}{\partial r} = \frac{\partial \bar{c}}{\partial t} + \frac{\rho_B}{\gamma} \cdot \frac{\partial \bar{q}}{\partial t} \text{ ----- LVIII}$$

This can be compared with equation II from Chapter I. If the bulk fluid is such that $\theta > \theta_w$, and $\theta > \theta_p$ (where θ_p is the uniform surface temperature of the adsorbent particle) the fluid will decrease in enthalpy as it passes through the bed. Heat is transferred to the wall across a film of fluid at the wall. Heat is transferred to the particle across a film of fluid surrounding the particle, also there is the heat transferred in association with the mass fluxes from the bulk to the adsorbent particle. This heat balance between fluid and its surroundings is

$$\partial(\rho H)/\partial t = - \partial(\rho V H)/\partial z - a(M_1 H_1 + M_2 H_2)$$

$$- a \rho_B k_h (\theta - \theta_p) / \alpha \rho_p - \pi d_i k_w (\theta - \theta_w) / \alpha \pi \frac{d_i^2}{4} \text{ ———— LIX}$$

The wall of the bed exchanges heat with the contents of the bed and with the surroundings through any insulation present. For relatively thin walled containers the radial and axial heat fluxes can be neglected. The wall is therefore at a uniform temperature θ_w .

The energy balance for the wall is :

$$\partial \theta_w / \partial t = \pi d_i k_w (\theta - \theta_w) / m \mu_w - \pi d_o k_u (\theta_w - \theta_u) / m \mu_w \text{ — LX}$$

An energy balance within the particle can now be set up on a basis of unit particle volume by considering a thin spherical shell within a particle. So that the heat accumulated by the particle, the adsorbate on the particle and the components in the intraparticle space is equal to the heat generated by adsorption less the heat transferred from the shell by the thermal conductivity of the particle and the fluxes passing through the shell. Hence the balance becomes

$$\begin{aligned} \gamma \cdot \partial (\bar{\rho} \bar{H}) / \partial t + \rho_p \mu_p' \partial \bar{\theta}_p / \partial t = & \left\{ - \rho_p \cdot \partial (\bar{q} Q) / \partial t \right. \\ & + (1 - \alpha) \cdot \frac{k_p}{r^2} \cdot \partial \left(r^2 \cdot \frac{\partial \bar{\theta}_p}{\partial t} \right) / \partial r \\ & \left. - \frac{\gamma}{r^2} \cdot \partial \left[r^2 (M_1 H_1 + M_2 H_2) \right] / \partial r \right\} \text{ ———— LXI} \end{aligned}$$

This effectively defines the heat and mass balances in the absence of radial diffusion effects. The next step is to simplify the above equations by setting up the relevant inter-relationships between the heat and mass fluxes.

The enthalpies of the gas within the pores and in the bulk stream can be related to the temperatures by the equations.

$$\bar{H}_i = \mu_i (\bar{\theta}_p - \theta_u) \quad i = 1, 2 \quad \text{----- LXII}$$

$$H_i = \mu_i (\theta - \theta_u) \quad i = 1, 2 \quad \text{----- LXIII}$$

The enthalpies are thus based on the properties of the surroundings.

The enthalpies of the combined adsorbate and inert streams (related to the composition) can be determined by assuming proportional contributions from each component. So that,

$$H = [c H_1 + (\rho - c) H_2] / \rho \quad \text{----- LXIV}$$

$$\bar{H} = [\bar{c} \bar{H}_1 + (\bar{\rho} - \bar{c}) \bar{H}_2] / \bar{\rho} \quad \text{----- LXV}$$

The effective heat capacity of the adsorbent particles varies with the adsorbate loading and the adsorbate enthalpy.

$$\mu'_p = \mu_p + \partial(w \cdot \bar{q}) / \partial \theta_p \quad \text{----- LXVI}$$

Since $\bar{q} = \bar{q}(z, t)$, then $\partial w / \partial \theta_p$ is the change of the enthalpy of the adsorbate on the adsorbent with the particle temperature, it is of the nature of a specific heat, μ_3 . So that the total specific heat of the bed can be defined by $\mu'_p = \mu_p + \bar{q} \mu_3$.

The heat of adsorption, given as the isosteric heat of adsorption, represents the difference in enthalpy between the adsorbate in the adsorbed state on the adsorbent, and the adsorbate in the free state in the bulk gas stream. Hence :

$$Q = H_1 - w = - \frac{R \theta_p^2}{\bar{c}} \cdot \left[\frac{\partial \bar{q} / \partial \bar{\theta}_p}{\partial \bar{q} / \partial \bar{c}} \right]_{\bar{q}} \quad \text{----- LXVII}$$

It should be noted that the term $(\partial \bar{q} / \partial \bar{\theta}_p)_{\bar{q}}$ represents the variation with adsorbent temperature of the equilibrium adsorption loading (for a constant adsorbate loading). The term $(\partial \bar{q} / \partial \bar{c})_{\bar{q}}$ represents the variation with adsorbate concentration (in the intraparticle space) of the equilibrium adsorption loading (for a constant adsorbate loading). This indicates the general nature of the equilibrium relationship $\bar{q} = \bar{q}(\bar{\theta}_p, \bar{c})$.

This effectively defines the inter-relationship between the properties concerned with the heat transfer processes. These are truly general relationships as they do not depend upon the mechanisms assumed for the heat and mass transport. To complete the specification of the problem it is now necessary to define the mass fluxes in terms of the relevant parameters and to specify appropriate boundary conditions for the problem.

A simplification which does not greatly affect the validity of the argument so far developed arises by considering a single particle when it first comes into contact with the adsorbate laden carrier stream. With a bed initially full of the inert fluid, the flux of adsorbate (\bar{M}_1) from the bulk to the particle must be balanced by the flux of inert (\bar{M}_2) from the particle to the bulk phase. Similarly within the particle \bar{M}_1 must initially be equal, but opposite in sign, to \bar{M}_2 . This initial dynamic process will soon reach steady state, after which time \bar{M}_2 and \bar{M}_2 may be assumed sufficiently small as to be negligible.

It will be apparent from Chapter I of this work that twelve cases can be considered based on physical processes or stochastic derivations for the mass fluxes (\bar{M}_1 and \bar{M}_1) of the adsorbate. Cases 1 to 7 of Chapter I assumed no radial variations within the particle, the rate process being described entirely in terms of the bulk phase parameters. Cases 8 to 12 of Chapter I assumed radial variations within the particle; and in Cases

10, 11 and 12 the possibility of non-attainment of adsorption equilibrium at the particle internal surface was considered. The derivation of the 10, 11 and 12 the possibility of non-attainment of adsorption equilibrium at the particle internal surface was considered. The derivation of the equations of this Chapter has assumed that this equilibrium is attained, which is generally the case for substances readily adsorbed in appreciable quantities. Hence, the mechanisms of Cases 10 to 12 can be neglected. The mechanism of Case 8 where surface film diffusion and intraparticle diffusion determines the mass fluxes has been considered and solved by Meyer and Weber (35). The assumption is often made that the resistance to heat transfer occurs in the surface film surrounding the particle for particles of good thermal conductivity. Radial temperature profiles within the particle are neglected as the particle is essentially isothermal. The mechanisms of Case 9 where intraparticle diffusion only determines the mass fluxes can be considered by letting $x_s = y$ (in the notation of Meyer and Weber); and solving by numerical procedures the resulting equations. This case will not be considered further in this work.

3.2 The Absence of the Intraparticle Effects.

Hence only those mechanisms of Cases 1 to 7 will be considered, so that intraparticle effects do not contribute. This enables the simplification of the equations so far derived as $M_2 = \bar{M}_2 = 0$, $\bar{M}_1 = \text{constant}$, $q = q(z, t)$, $c = c_s = c_s(z, t)$ and $\bar{\Theta}_p = \Theta_p$. The material balance within the particle as shown by equation LVIII now simplifies to,

$$\frac{\rho_B}{\alpha} \cdot \frac{\partial q}{\partial t} + \frac{\partial c}{\partial t} = 0 \quad \text{LXVIII}$$

The heat balance within the particle as shown by equation LXI simplifies by assuming that the nett heat transferred across a spherical shell is now constant. This nett heat flux is equal to the heat

transferred from the exterior surface of the particle $k_h \cdot a \cdot (\theta_p - \theta)$.

So that equation LXI becomes,

$$\begin{aligned} & \delta \mu_1 \delta [c_s (\theta_p - \theta_u)] / \delta t + \rho_p \mu'_p \delta \theta_p / \delta t \\ & = -\rho_p \delta (q \cdot Q) / \delta t - k_h \cdot a \cdot (\theta_p - \theta) \text{---LXIX} \end{aligned}$$

Substitution of equation LXIII into equation LXIV gives

$$\rho H = [c \mu_1 + (\rho - c) \mu_2] \cdot (\theta - \theta_u) \text{---LXX}$$

whilst equation LIX becomes,

$$\begin{aligned} & \delta (\rho H) / \delta t + \delta (V \rho H) / \delta z = \\ & \left\{ - a M_1 \mu_1 (\theta - \theta_u) \right. \\ & \left. - a \frac{\rho_p}{\rho_p} \cdot \frac{k_h}{\alpha} (\theta - \theta_p) - \frac{4}{d_i} \cdot \frac{k_w}{\alpha} (\theta - \theta_w) \right\} \text{---LXXI} \end{aligned}$$

The partial derivations are now of functions of c and θ .

Equations IV, LVII and LIX are unchanged; and when used with equations LXVIII, LXIX and LXXI represent the equations that must be solved (with a suitable expression for the mass flux M_1 , and appropriate boundary conditions) to yield the temperature and concentration profiles as functions of z and t . If the mass flux of adsorbate from the bulk to the particle occurs by diffusion across the particle surface film, then

$$M_1 = k_m \cdot (c - c_s) / \rho \text{---LXXII}$$

The particle balances, equations LXVIII and LXIX are related to the bulk phase balances by the boundary conditions at the

particle surface. For mass transport the boundary condition is $c_s = c_s(q, \theta_p)$ which is the general form of the adsorption isotherms. This is Case 2 of Chapter I. The additional boundary conditions are,

$$\left. \begin{aligned} \theta(t, z) &= \theta(0, z) \\ \theta_w(t, z) &= \theta_w(0, z) \\ \theta_p(t, z) &= \theta_p(0, z) \\ q(t, z) &= q(0, z) \\ c(t, z) &= c(0, z) \end{aligned} \right\} \text{ for all } z \text{ such that } 0 \leq t \leq \int_0^z dz/V$$

$$\left. \begin{aligned} V(t, z) &= V_0 \\ \theta(t, z) &= \theta_0 \\ c(t, z) &= c_0 \end{aligned} \right\} \text{ at } z=0 \text{ for all } t$$

These boundary conditions will be denoted equation LXXV.

3.3 Solution by Numerical Methods.

The most general method, numerical solution, can now be used to solve the six differential equations for the six variables $q, c, V, \theta, \theta_p$ & θ_w . The method used requires that a suitable set of characteristic lines be set up so that the partial differential equations can be reduced to ordinary differential equations along these lines. A modified Euler method can then be set up in computational form to evaluate the variables at points on a suitable z, t mesh by means of difference approximations. A suitable two dimensional grid is shown in Fig.(40) with the three

characteristic lines illustrated for a general point. It will be noted that the particle balance equations LXVIII and LXIX in the absence of radial effects contain derivatives with respect to t only. Hence, for a general variable $f = f(z, t)$ it follows by the chain rule that

$$df/dt = \partial f / \partial t + (\partial f / \partial z) \cdot dz/dt$$

If $V = dz/dt$ is constant along a characteristic path, then along that path

$$df/dt = \partial f / \partial t + V \cdot \partial f / \partial z \text{ ————— LXXIII}$$

Similarly if $z = \text{constant}$ along a characteristic path, then

$$df/dt = \partial f / \partial t \text{ ————— LXXIV}$$

These two relationships mean that equations LV and LXXI can be reduced to ordinary differential equations along characteristic I. Equations LX, LXVIII and LXIX can be reduced to ordinary differential equations along characteristic III. Equation LVII by its very nature must be evaluated along characteristic II. Table IV illustrates these statements.

The computational procedure begins at the first time interval ($i = 1$) $t = \Delta t$, and works in the z direction to the end of the bed ($j = 1, 2, \dots, m$). The next time interval is chosen ($i = 2$) and the calculations again proceed in the z direction. This is repeated until the desired total adsorption time is reached, $t = n \cdot \Delta t$. The initial conditions on the z and t axis are given by equations LXXV.

Evaluation of point 5 (see Fig.(40)) from point 4 along characteristic

II, and evaluation of point 5 from point 3 along characteristic III are straight forward. The evaluation of point 5 from some point 6 along characteristic I requires that the position of point 6 be first found by satisfying the criteria for characteristic I. The values of the variables at point 6 are then found by a quadratic interpolation of their values at the points 1, 2 and 3.

Details of this procedure are shown in Appendix VIII, together with the use of equations LXVI and LXVII to simplify equations LXX. The use of a difference formulation requires that the increments Δt and Δz be specified in advance of computation. Large increments are required if the computing time is to be reduced, however, it is necessary that the difference approximations produce a stable solution. A simple illustration of stability and general discussion of the method can be found in Appendix VIII. The ratio of the increments can be found readily for the condition that

$$\frac{\Delta z}{\Delta t} \cdot \frac{1}{V_0} \leq 1 \quad \text{-----LXXVI}$$

so that the fluid entering the bed with a velocity V_0 reaches the mesh point $z = \Delta z$ in the time $t = \Delta t$. The term $(\rho - \rho_0)$ decreases with increased temperature, so that from equation LXVII V will increase in the z direction. Hence, the value of $(\Delta z / \Delta t) / V$ will change with temperature within the bulk stream. If the value becomes less than 0.5 then in Fig. (40) point 6 will lie outside the span of points 1 and 2. A quadratic equation using another set of 3 points will be required to produce the conditions at point 6. It is conceivable for a dilute bulk stream and little heat generated by adsorption with rapid heat transfer to the surroundings that if $\theta_u < \theta_0$, then the exit temperature of the bulk stream could be less than its inlet temperature. In this case V

at exit would be smaller than V_0 and the ratio $(\Delta z / \Delta t) / v$ could be greater than 1. This case is readily handled by the interpolation method.

Stability criteria for the time interval Δt can be derived from the implicit Euler form of equations LV, LX, LXVIII, LXIX or LXXI. The arguments are presented in Appendix VIII. The most rigid criterion is derived from equation LXXI, which leads to

$$2.0 \rho_c \mu_2 c / (a k_h + 4.0 k_w / d_1) \text{----- LXXVII}$$

3.4 Programming the Solution.

The programme was written in ICL FORTRAN and run in the computing facilities available to the University of Manchester Regional Computing centre. The machine used for this section of the work was the ICL 1906A. No library routines were used. The programme was used only to produce solutions which could be later compared to the solutions obtained by the methods of Chapter IV. The level of programming is, therefore, not sophisticated as the programme is not intended for general usage. The values of the increments dt and dz are found from equations LXXVI and LXXVII, as a result of the calculations shown in Appendix VIII. Numerical expressions were used to represent the functions $c_s = c_s(q, \theta_p)$ and $\rho_c = (\rho - c) = \rho_c(\theta)$. The first term was programmed as a subroutine and called by the main programme as required. The derivations of these expressions are described below.

3.4.1 General Form of the Adsorption Equilibria.

An introductory study of adsorption equilibria is given by Graham (8), who considers the equilibria for monolayer adsorption by the Langmuir and Freundlich isotherms. For multilayer adsorption, equilibria are based on the concept of an adsorption potential. This theory assumes

an attractive force at a solid surface which falls off with distance from the surface but which is independent of temperature. The theory is generally known by the name of its originator Polanyi.

All these equilibrium expressions contain certain constants based on the assumptions made in deriving the expression. It is not usual to evaluate these constants on the basis of their physical interpretation. More usually the chosen adsorbate and adsorbent are allowed to attain equilibrium under several different conditions, and equilibrium measurements taken. The appropriate form of the equilibrium expression is chosen; and the values of the constants determined by fitting the theoretical expression to the experimental results. The values of the constants so obtained will ensure that the expression accurately represents the adsorbate/adsorbent system; but only over the previously used experimental range of values. Extrapolation of the fitted expression is not wise. The variation of the constants with temperature can be handled by either expressions with an Arrhenius relationship or in terms of a low order polynomial relationship.

The early work of Carter (33), (34) made use of a Freundlich isotherm for the equilibrium relationship. This was modified to account for a known single set of conditions, and included the temperature variation by an Arrhenius relationship. The relationship produced had a single constant whose value had to be determined. In later work Carter and Hussain (40) described the equilibrium by the Langmuir isotherm. For the isothermal case this required the evaluation of two constants. In a paper based on theoretical consideration of fixed beds, Amundson et al. (41) assumed the Langmuir relationship to hold and used an Arrhenius relationship to account for variations with temperature. A general expression for isotherms was suggested by Redlich and Peterson (42) which reduces

to the Langmuir equation for a specific value of one of the constants. This expression was used by Meyer and Weber (35) in an expanded form, where temperature variations were expressed in quadratic and exponential terms. The resulting equation possessed eight constants which were evaluated by fitting the equation to equilibrium data at four temperatures. The potential theory has been considered by Kühn (43) who was able to reproduce the characteristic shapes of the main types of isotherms by a single simple equation for isothermal conditions. Later work by Kühn (44) developed some of his earlier assumptions and produced an expression involving temperature of the form:

$$q = A_0 \cdot (\ln(p_0/p))^{A_3} \cdot (A_1 + A_2/\theta)^{A_4} \cdot \theta^{A_5} - A_0 \cdot \theta^{A_5} \cdot (\ln(p_0/p))^{A_3} + A_4$$

The above equilibrium expression is obtained by simplification of the expression shown by Kühn the equilibrium expressions of other authors will be found in the references quoted.

It is usual to choose the form of the equilibrium expression to be the one most convenient for the use to which it is to be put. Thus complex forms of the isotherm expressions are reduced by expansion and/or simplification to a more suitable form. The presence of multiple coefficients ensures, in effect, that the equilibrium expressions chosen will fit the experimental data exceedingly well. In the context of this present work it can be seen that the explicit form $q = q(c_s, \theta)$ and $c_s = c_s(q, \theta)$ are both required. This second relationship arises as a result of choosing Case 2 of Chapter I to describe the mass flux. It would also arise if Case 4 were chosen; but not if Cases 1, 3, 5, 6 and 7 were used. The form of the equilibrium expression most suitable for this interpretation is that used by Meyer and Weber (35), which can be written as :

$$q = A_0 \cdot A_1 \cdot p / (1.0 + A_1 \cdot p \cdot (1.0 + A_2 \cdot p)) \text{-----LXXVIII}$$

$$p = \left\{ - (q - A_0) \pm [(q - A_0)^2 - 4 A_2 q^2 / A_1]^{1/2} \right\} / 2 A_2 q \text{-----LXXIX}$$

The negative sign of the square root term of equation LXXIX is required to satisfy $0 \leq p \leq p_0(\theta_p)$. The constants A_0 , A_1 , A_2 are functions of temperature, given by :

$$A_0 = a_1 + a_2 \theta_p + a_3 \theta_p^2 \text{-----LXXXa}$$

$$A_1 = \exp(a_4 + a_5/\theta_p) \text{-----LXXXb}$$

$$A_2 = a_6 + a_7 \theta_p + a_8 \theta_p^2 \text{-----LXXXc}$$

The values of the a_i , ($i = 1, 2, \dots, 8$) can be found as described by Meyer and Weber. The function $p_0(\theta_p)$ is given by assuming a linear relationship between $\ln(p_0)$ and $1/\theta_p$, so that $p_0(\theta_p) = \exp(a_4 + a_5/\theta_p)$ - as shown by equation LXXXb.

The nomenclature of this work requires that c_s be expressed as a function of q and θ_p . The following relationship will be used :

$$p = P_T \cdot (c_s / \sigma_a) / (\rho_c / \sigma_c + c_s / \sigma_a)$$

from which,

$$c_s = p \cdot \rho_c \cdot (\sigma_a / \sigma_c) / (P_T - p) \text{-----LXXXI}$$

3.4.2 Determination of $\rho_c(\theta)$

For an ideal gas the mass density as a function of temperature can be determined from the ideal gas laws. For most real gases, however,

over a limited temperature range the mass density can be simply expressed as a linear function of the temperature. Tabular values of the density can be fitted to a linear expression of the form $\rho_c = (\text{constant 1}) + (\text{constant 2}) \cdot \theta$ by the procedure known as "least squares". If corresponding tabular values of ρ_c and θ are ρ_{ci}, θ_i ($i = 1, 2, \dots, n$), then the values of constant 1 and constant 2 are found by simultaneous solution of :

$$\begin{aligned} \sum_{i=1}^n \rho_{ci} &= n \cdot \text{constant 1} + \text{constant 2} \cdot \sum_{i=1}^n \theta_i \\ \sum_{i=1}^n \theta_i \rho_{ci} &= \text{constant 1} \cdot \sum_{i=1}^n \theta_i + \text{constant 2} \cdot \sum_{i=1}^n \theta_i^2 \end{aligned}$$

3.5 Results of Computation.

The sole reason for extensively describing the difference formulation of the analytical expressions for the general heat and mass transfer case is to produce an acceptable solution by quasi - analytical means, which can then be compared to solutions produced by the models of Chapter IV. In this manner the accuracy of the models of Chapter IV can be tested. To this end a single mechanism was used to describe the mass flux of adsorbate, and intraparticle effects were neglected. As much of this work has followed that of Meyer and Weber (35), the values of the variables and parameters found by these authors will be used in this computational exercise. These values are given in Table.(V) in the nomenclature of this work. A consistent set of units is used. Two simplifications will be introduced. The first is to assume that the heat of adsorption is constant, and the second is that the specific heat of adsorbate on the adsorbent is that of the adsorbate in its liquid state. The variation of the carrier density with temperature, for a helium carrier follows from 3.4.2 as :

$$\rho_c = 0.016018 \cdot (0.1356385614 - 0.000223826 \cdot \theta)$$

A copy of the computer programme for these calculations, titled HAMAN, is shown by Fig. (4.1). The subroutine ISOT is used to determine the equilibrium relationship between q and c_s as shown in 3.4.

The small values that are required for the time increment to avoid problems of instability mean that several thousand iterations over the complete length of the bed are necessary to cover any really meaningful time interval. The use of a few large distance increments within the bed helps to reduce the total computation time, however, it still remains large. Furthermore, the changes in the exit concentration and temperature are not significant for short adsorption times and long beds as the entry temperature effects are removed by passage through the rest of the bed. It is these exit conditions which merit most attention in a real adsorption system, but they cannot be produced conveniently by this form of the analytical approach. Hence this author has proposed in Chapter IV a simpler model of the general adsorption system which does not have the limitations of the above approach, but which can accurately represent the adsorption system. However, it is necessary to provide a check on this model for the general adsorption system by using the profiles produced by HAMAN as a basis of comparison. The profiles within the bed are most suited for this purpose, and are shown in Chapter IV.

C H A P T E R IV.

The work of Chapter III indicated the setting up of the material and energy balances for a general adsorption process, which was illustrated by the adsorption of methane on activated carbon. The solution of the resulting partial differential equations was carried out by setting up a suitable grid of points at intervals which satisfied the stability criteria. Certain characteristic directions were then defined within this grid so that the partial derivatives were converted to full derivatives. The resulting ordinary differential equations were then interpreted in terms of difference expressions, and these difference expressions used to determine the condition at an unknown node on the grid from knowledge of the nodes in its vicinity.

As will be explained more fully later in this thesis, it is sufficient to use the procedure of Chapter III to produce exit temperature and concentration profiles for an operating industrial system that satisfies the following :

- a) The regeneration of the adsorbent is carried out by indirect means. For example the passage of a heating medium through coils or a container jacket, and the application of a reduced pressure to the adsorption bed to remove the adsorbate. Here, the results of regeneration can be readily expressed as a new set of initial conditions for the next adsorption period.
- b) The regeneration of the adsorbent is carried out by direct means ; but the effects of regeneration can be handled by the mathematical model of Chapter III. For example the passage of a heated inert (perhaps containing trace amounts of adsorbate at inlet) through the system to desorb and sweep away the adsorbate from the adsorbent. Here, as in case a) the results of regeneration can be readily expressed as a new set of initial conditions for the next adsorption period.

c) The regeneration of the adsorbent is carried out by direct means. The effects of regeneration are minimised or removed to produce conditions at the end of regeneration that can be handled by the mathematical formulation of Chapter III. For example the bed may be regenerated by the passage of live steam under pressure through the bed. The desorbed adsorbate being swept out with uncondensed steam. The condensed steam providing the heat of desorption. If there then follows a period where a cool inert (possibly with traces of adsorbate) is passed through the bed to cool it, and simultaneously remove the water from the bed, so that at the end of this period the bed is for all practical purposes dry. The formulations of Chapter III can now be applied using appropriate initial conditions for the next adsorption period.

d) The regeneration of the adsorbent is carried out by direct means. The effects of regeneration are not removed; but their presence does not significantly affect the following adsorption period. For example, the bed may be regenerated by the passage of live steam under pressure through the bed as in c) above without any subsequent cooling and drying. If, however, the time used for regeneration is small compared to the time of the adsorption period, then any dynamic effects of the regeneration process occurring initially during the next adsorption period will be of short duration (compared to the total adsorption time). So the cooling and drying of the bed by the cooler adsorbate laden air will produce adverse effects in the initial part of the adsorption period. However, the effects will be minimised by the continual passage of adsorbate laden fluid through the bed. So that the overall adsorption process can be satisfactorily represented by

the mathematical formulation of Chapter III for the total length of the adsorption period. Initial adverse effects being neglected or allowance made by for example modifying the parameters and for initial conditions of the system.

For systems where the method of regeneration has marked effects upon the system that are not subsequently removed by a stage between the regeneration and adsorption period, then the mathematical formulation of Chapter III is not suitable. It is of course possible to include further heat and mass balances for the particles and the bulk stream to take account of the effects of the regenerative agent. These additional equations can then be treated with the previous equations, and solved in a manner analogous to that of Chapter III.

Further consideration of the process of Chapter III indicated that small values of Δt and Δz may be necessary to ensure stability of the mathematical solution. This means that a large computing effort is required to evaluate the conditions at all points within the bed for all times especially in the case of long beds or long adsorption times. The assumption of isothermality produces solutions shown by Chapter I that may be considerably less complex and can satisfactorily represent the system by choice of appropriate values for the various coefficients. The isothermal case is, of course, invalid where there are appreciable residual effects of the previous regeneration period. Where the bed is long enough to allow the full development and movement of the mass transfer zone; and the length of this zone is not large compared to the total bed length (or where its velocity is suitably small) then conditions preceding and proceeding this zone may be fairly steady. The time involved in computing (to the degree of accuracy required in the mass transfer zone) the conditions either side of this zone, which can be a large fraction

of the total computing time, is thus largely wasted in terms of its contribution to the dynamic processes responsible for the overall system behaviour. In taking these effects into account what is required is an approach that satisfactorily uses large intervals of z and t when little change occurs, with suitable reductions in the complexity of the equations describing the process taking place. Whereas, when large scale changes or rapid changes occur, very small intervals of z and t can represent the system.

A system which has these benefits will now be described. Its inception owes much to the experience gained with the isothermal results of Chapters I and II, and the arguments advanced by Rosenbrock and Storey (45).

It consists essentially of replacing the z, t grid of Chapter III. by a series of stages of variable size (z values) with variable residence times (t values). An initial time interval is specified. The flow of adsorbate laden fluid through the stages is in the positive z -direction. Changes in the values of the variables are described in terms of simple difference equations formed by mass and heat balances over each stage, which is assumed to be isothermal. Where changes are rapid or large, then smaller increments are chosen to represent the system accurately. This system may be illustrated by Fig.(42), for the general case equivalent to that described in Chapter III.

The inlet bulk fluid enters the first stage where it contacts the adsorbent particles and the wall of the container. The simultaneous transfer of heat and mass takes place. The conditions of the exit bulk fluid from the first stage can be simply described in terms of the balance equation $\text{output} = \text{input} - \text{accumulation}$. The accumulation term is described by suitable rate equations applied within the first stage.

The bulk fluid then flows through the remaining (m-1) stages in turn, until it leaves the bed. The next time interval can now be considered, its value being based on the results obtained in the previous time interval. The initial bed conditions ($t=0$, all z) can be simply described for each stage to include the residual effects of the regeneration process. Variations with time in the bulk inlet conditions can be readily handled.

The model will be developed and illustrated by setting it up first for the isothermal case, then for the non-isothermal/non-adiabatic case; and finally for the case where residual effects of regeneration are present that cannot be handled by either of the previous cases. In particular will be considered the situation where there is water present within the adsorbent particle, and its temperature is of the order of the regenerative steam temperature.

The adsorption rate equations used will be those of Cases 1 to 7 from Chapter I, so that intraparticle effects will be neglected. For each stage, where the conditions in the bulk stream are assumed constant over the time interval from t_r to $t_r + \Delta t_r$, then for the adsorbate a mass balance gives :

$$V_r \propto (c_{r-1} - c_r) \cdot (t_r + \Delta t_r - t_r) \\ = (z_r - z_{r-1}) \cdot (n_r + \Delta n_r - n_r)$$

$$\text{So that : } c_r = c_{r-1} - \frac{\Delta z_r \cdot \Delta n_r}{\Delta t_r \cdot V_r \propto} \quad \text{LXXXII}$$

The accumulation within the stage Δn_r can be determined from the appropriate rate equation $dn_r/dt = f(n_r, c_r)$. This is the general form of the rate equation as listed under Cases 1 to 7 of Chapter I.

4.1 Isothermal Case

The individual forms of the seven rate equations are integrated to obtain an expression for Δn_r . For isothermal conditions the general form of the adsorption equilibrium can be reduced to $c_s = c_s(q)$, and the interstitial velocity $V_r = V = \text{constant}$. As the value of n changes within the stage then the value of c_s will also change. However, it is possible for small changes of n to locally linearise the equilibrium relationship to give $c_s = a_0 + a_1 n$. The values of a_0 and a_1 are found by forcing the points (c_s, n_r) and $(c_s + \delta c_s, n_r + \delta n)$ to lie on this line. Here δn is a small constant increment on the value of n_r , and produces a change of δc_s in the value of c_s that lies on the equilibrium curve. This linear relationship would be required for Cases 2 & 4. to replace the more restrictive relationship $c_s = b.n$ used in the analytical solutions. Its use is shown in 4.2. For present purposes it is necessary to keep the assumption used in the analytical solutions so that the results of the model proposed below can be directly compared to the analytical solutions.

Case 1

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot c_r$$

$$\int_{n_r}^{n_r + \Delta n_r} dn_r = k_1 \cdot \alpha \cdot c_r \int_{t_r}^{t_r + \Delta t_r} dt$$

So that : $\Delta n_r = k_1 \cdot \alpha \cdot c_r \cdot \Delta t_r$

Hence from equation LXXXII

$$c_r = c_{r-1} / (1.0 + k_1 \cdot \Delta z_r / V) \text{ ————— LXXXIII}$$

Case 2

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot c_r - k_2 \cdot n_r$$

$$dn_r/dt = k_1 \cdot \alpha \cdot c_r - k_2 \cdot \alpha \cdot n_r$$

this is analagous to $dn/dt + Pn = Q$, which is a first order, linear, differential equation. Its general solution is

$$\int dn = \exp(-\int Pdt) \cdot (\int Q \exp(\int Pdt) dt + \text{constant})$$

With limits of n_r to $n_r + \Delta n_r$, and t_r to $t_r + \Delta t_r$ for n and t respectively. As P and Q are independent of t then it is possible to perform the above integration directly to give

$$n = \exp(-Pt) \cdot ((Q/P) \cdot \exp(Pt) + \text{constant})$$

Using the limits of the integration and defining $t_r = \text{zero}$, then

$$n_r = (Q/P) + \text{constant}$$

$$n_r + \Delta n_r = \exp(-P \Delta t_r) \cdot ((Q/P) \cdot \exp(P \Delta t_r) + \text{constant})$$

These simultaneous equations can be solved for Δn_r to give

$$\Delta n_r = (Q/P) \cdot (1.0 - \exp(-P \Delta t_r)) - n_r \cdot (1.0 - \exp(-P \Delta t_r)) \quad \text{LXXXIV}$$

By substituting equation LXXXIV into equation LXXXII and simplifying,

$$c_r = \left\{ c_{r-1} + n_r \cdot \Delta z_r \cdot (1 - \exp(-k_2 \alpha \Delta t_r)) / (V \cdot \alpha \Delta t_r) \right\} / \left\{ k_1 \cdot \Delta z_r (1 - \exp(-k_2 \alpha \Delta t_r)) / (k_2 \cdot V \cdot \alpha \Delta t_r) + 1.0 \right\} \quad \text{LXXXV}$$

Case 3

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot \text{Nos} \cdot c_r - k_1 \cdot c_r \cdot n_r$$

By arguments similar to Case 2, this gives from equation LXXXIV

$$\Delta n_r = (\text{Nos} - n_r) \cdot (1.0 - \exp(-k_1 \alpha \cdot c_r \cdot \Delta t_r)) \quad \text{LXXXVI}$$

Note that c_r appears in the exponent, hence it is not possible to obtain a direct expression for c_r in terms of the other variables by substitution into equation LXXXII

Case 4.

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot c_r \cdot Nos - (k_1 \cdot c_r + k_2) \cdot n_r$$

By arguments similar to Case 2, this gives from equation LXXXIV

$$\Delta n_r = \left\{ \frac{k_1 \cdot c_r \cdot Nos}{k_1 \cdot c_r + k_2} - n_r \right\} \left\{ 1.0 - \exp \left[- (k_1 \cdot \alpha \cdot c_r + k_2 \cdot \alpha) \cdot \Delta t_r \right] \right\} \quad \text{LXXXVII}$$

Note that c_r appears both in the exponent and in other terms, hence it is not possible to obtain a direct expression for c_r in terms of the other variables by substitution into equation LXXXII.

Case 5.

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot Nos - k_1 \cdot n_r$$

Again by arguments similar to Case 2 this gives

$$\Delta n_r = (Nos - n_r) \cdot (1.0 - \exp(-k_1 \cdot \alpha \cdot \Delta t_r)) \quad \text{LXXXVIII}$$

This can be substituted directly into equation LXXXVII to uniquely define c_r .

Case 6

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot (Nos^2 - n_r^2) / (2.0 n_r)$$

This can be readily integrated directly to give

$$(Nos^2 - (n_r + \Delta n_r)^2) / (Nos^2 - n_r^2) = \exp(-k_1 \cdot \alpha \cdot \Delta t_r)$$

$$\Delta n_r^2 + 2.0 n_r \cdot \Delta n_r - (Nos^2 - n_r^2) \cdot (1.0 - \exp(-k_1 \cdot \alpha \cdot \Delta t_r))$$

$$\Delta n_r = -n_r + \left\{ n_r^2 + (Nos^2 - n_r^2) \cdot (1.0 - \exp(-k_1 \cdot \alpha \cdot \Delta t_r)) \right\}^{1/2}$$

LXXXIX

Which can be substituted directly into equation LXXXII to uniquely define c_r .

Case 7

$$(1/\alpha) \cdot dn_r/dt = k_1 \cdot c_r \cdot N_{os} - [k_2 \cdot C_o + c_r \cdot (k_1 - k_2)] \cdot n_r$$

By arguments similar to Case 2 this gives

$$\Delta n_r = \left\{ \frac{k_1 \cdot c_r \cdot N_{os}}{k_2 \cdot C_o + c_r \cdot (k_1 - k_2)} - n_r \right\} \cdot [1 - \exp\{-\Delta t_r \cdot \alpha \cdot (k_2 C_o + c_r (k_1 - k_2))\}] \quad \text{LXXX}$$

Note that c_r appears both in the exponent (for $k_1 \neq k_2$), and in other terms, hence it is not possible to obtain a direct expression for c_r (unless $k_1 = k_2$, which is Case 3) in terms of the other variables by direct substitution into equation LXXXII. It can be seen that this is the situation for Cases 3 and 4 as well as for Case 7. A procedure has been proposed, and described with the computer programmes, to determine by an iterative process the value of c_r that satisfies the relationship given by equation LXXXII in the general form :

$$c_r = c_{r-1} - \frac{\Delta z_r}{\Delta t_r \cdot V \cdot \alpha} \cdot g(c_r) \quad \text{LXXXI}$$

The computational procedure begins by choosing a time interval Δt and divides the bed into number of equally sized lengths Δz . These are the basic time and distance intervals. They are used whenever changes in the bulk stream are within specified limits. If these limits are violated then other time or distance intervals are chosen. In this way a single stage of Δz_r can be replaced by several smaller stages for the same time interval, or several stages can be lumped together for the same time interval. As illustrated in Chapter II, several of the rate expressions do not fall to zero as $n \rightarrow N_{os}$ and/or $C \rightarrow C_o$, so that capacities in excess of N_{os} and negative concentrations could theoretically be produced. Procedures, therefore, have to be employed to revise the time intervals so that each stage produces valid results. These procedures for changing time and distance increments are quite simple, and have been discussed later with the relevant computer programme for

particular Cases as described in Chapter I.

The initial adsorbate distribution within the bed is specified, as are the conditions in the bulk stream entering the first stage. The desired adsorption mechanism is chosen and the relevant subroutine is used with those cases where the value of c_p cannot be directly determined. The conditions in the bulk fluid leaving the first stage are calculated and become the inlet conditions for the second stage. Conditions within the first stage are updated. The procedure is repeated for the second stage and continued for the complete length of the bed. The next time interval is chosen and computation proceeds through the bed as before. This is repeated until the specified maximum adsorption time has been reached. It is possible to revise the values of Δz and Δt as necessary at any point in the procedure.

4.2 General Heat and Mass Transfer Operations

The procedure described above for the isothermal system will be adapted for the case of heat transfer under the assumptions of Chapter III. Expressions for the simultaneous heat and mass transfer are set up in terms of difference formulations. In the absence of mass transfer effects Ledoux (46) has set up the heat balance difference equations and applied them to the cooling of a bed of broken solids. An equally simple formulation will be used here. In 4.1 it was assumed that conditions within the stage were constant at the exit values of that stage. It was possible to determine the exit conditions uniquely from the inlet conditions and the rate equations either directly or by the use of a simple search procedure, as described later in 4.4.1. The few variables and simple forms of the balance and rate equations enabled the solution to be formulated in this manner. For the general heat and mass transfer system this approach would involve excessive iterative calculations. The easier

approach of assuming that the temperatures within a stage are held constant for the interval Δt , but updated at the end of the interval, will be used.

Hence, the variation of the interstitial velocity uses the relationship given in Chapter III in the form

$$V_{r-1} \cdot \rho_c(\theta_{r-1}) = V_r \cdot \rho_c(\theta_r) \text{-----LXXXXII}$$

So that the interstitial velocity in the stage r is constant at V_{r-1} . Then V_r is calculated for the stage $r+1$ only when the exit temperature from stage r , θ_r , has been determined. Adsorption and heat transfer within the stage r thus occur at a bulk temperature of θ_{r-1} and a particle temperature of θ_{pr} . As Δn_r and Δc_r can be determined uniquely from the mass balance and rate equations of 4.1, the properties of the adsorbate in the bulk and on the particle are average properties. These average properties for the bulk adsorbate concentration is thus $(c_{r-1} + c_r)/2$ and for the adsorbate loading is thus $n_r + \Delta n_r / 2$. Overall heat balances for the bulk stream, particles and the wall are formulated to determine the values of the updated temperatures $\theta_r = \theta_{r-1} + \Delta \theta_r$; $\theta_{pr} + \Delta \theta_{pr}$; $\theta_{wr} + \Delta \theta_{wr}$. So that ultimately V_r can be calculated.

The following heat balances can be set up by considering a cylindrical bed using a basis of unit volume of packed bed. A heat balance over the particles and the bulk stream gives

$$\begin{aligned} & - Q \cdot \Delta n_r + \mu_1 \cdot \Delta n_r \cdot (\theta_{r-1} - \theta_{pr}) - k_h \cdot a \cdot (\theta_{pr} - \theta_{r-1}) \cdot \Delta t_r \\ & = \rho_B \cdot \mu_p \cdot \Delta \theta_{pr} + (n_r + \Delta n_r / 2) \cdot \mu_v \cdot \Delta \theta_{pr} \text{-----LXXXXIII} \end{aligned}$$

A heat balance over the bulk stream gives

$$V_r \cdot \Delta t_r \cdot \left\{ c_r \cdot \mu_1 + \rho_{c_{r-1}} \cdot \mu_2 \right\} \cdot \alpha \cdot \Delta \theta_r =$$

$$\left\{ -\Delta n_r \mu_w (\theta_{r-1} - \theta_{p_r}) + k_{h.o.} (\theta_{p_r} - \theta_{r-1}) \Delta t_r - 4.0 \frac{k_w}{d_i} (\theta_{r-1} - \theta_{w_r}) \Delta t_r \right\} \cdot (z_r - z_{r-1}) \text{-----LXXXXIV}$$

A heat balance over the wall gives

$$4.0 \frac{k_w}{d_i} (\theta_{r-1} - \theta_{w_r}) \Delta t_r = 4.0 k_{u.o.} \frac{d_o}{d_i^2} (\theta_{w_r} - \theta_u) \Delta t_r$$

$$= 4.0 m \mu_w \Delta \theta_{w_r} / (\pi \cdot d_i^2) \text{-----LXXXXV}$$

Equations LXXXIII, LXXXXIV and LXXXXV can be solved directly to yield the values of $\Delta \theta_{p_r}$, $\Delta \theta_r$, $\Delta \theta_{w_r}$ respectively. Hence, the conditions at the end of the time interval for stage r are found directly.

The procedure outlined in 4.1 enables the calculations above, and those for the determination of Δn_r and Δc_r , to be carried out for all stages within the bed at all time intervals of the adsorption period. It is important to note that for the assumption of local isothermal operation the values of Δt_r and Δz_r should be related to the magnitude of the changes in the values of c, θ, n, θ_p (V and ρ_c are related to these variables, but it can be assumed that θ_w is of secondary importance). In practice it has been found that changes in the value of c only are sufficient. The procedures proposed are described later with the relevant computer programme. A single case, i.e. one rate equation of the seven requiring interparticle properties only, has been used to exemplify the method and its workings.

4.3 General Heat and Mass Transfer plus Regenerative Fluid

The initial conditions of the system can be described as those present at the end of the regeneration period. If steam is the regenerative fluid then during the regeneration the steam can be seen as

- a) Occupying part of the interparticle space in the liquid and vapour state

- b) Occupying part of the intraparticle space in the liquid and vapour state.

The steam condenses initially to raise the temperature of the adsorbent bed and its surrounds, and to carry out some desorption. Until the bed and surrounds have reached equilibrium with the steam no steam will penetrate the bed so that no adsorbate will be recovered from the bed. After this time some steam will continue to condense within the bed to supply the necessary heat of desorption and the heat losses through the bed wall. The bed is thus seen to be largely isothermal with the adsorbate being desorbed into the steam and swept from the system when steaming has been undergone for more than several minutes after the first steam breaks through the bed. It is usual to ensure that condensate formed within the bed can be drained off then passed to the adsorbate recovery process. There will, however, be some liquid retained within the pores of the particles and held in the interparticle space by surface tension effects. The larger quantities of liquid formed during the initial heating period can be assumed to have been drained off. Subsequently, any liquid not held by surface tension in the interparticle space can also be assumed to drain away.

Thus at the end of regeneration the bed is at the steam saturation temperature and has a low average loading of adsorbate on the particles. Steam in the vapour state is swept out of the system rapidly by the bulk flow of the adsorbate laden fluid. The fluid temperature initially leaving the bed is hence high. The further flow of cooler adsorbate laden fluid is heated by passage through the bed, so adsorption is not favoured. Adsorption may also be hindered by the blocking of some pores and parts of the particle surface by the water present. It is assumed that while free water is present its removal will be governed by the temperature

difference between the water and the bulk fluid; and by the humidity of the bulk fluid. As the quantity of residual water is reduced, evaporation from within the pores of the particles describes the rate of drying of the bed. When the water content has been further reduced the full pore volume may be available to the adsorbate laden fluid; but water molecules adsorbed on the particle may prevent all the active adsorption sites from being available. For activated carbon the importance of this later step is probably negligible due to its low capacity for adsorbed water.

These combined effects are such that for the initial part of the adsorption period the exit adsorbate concentration may be a substantial fraction of its inlet value. The exit value is likely to fall as adsorption proceeds, only to rise again as the bed becomes saturated with adsorbate. The resulting "U" shape of the exit concentration profile has profound effects on the criteria for economic operation of the adsorption unit. However, these are discussed in later Chapters of this work. For the present purpose it is necessary to describe the processes occurring within the bed allowing for the presence of the steam and water. A brief discussion in simple terms of the evaporation of water from porous solids into a moving air stream is in order.

A full study of the evaporation of a liquid from a porous medium into an external gas stream, involving consideration of the liquid/vapour interface within and outside the porous material, has been carried out by Morgan & Yerazunis (47). Most of the experimental data on the drying of wet porous beds by a moving air stream has been obtained under constant drying conditions. Hence a constant air temperature greater than the wet solids temperature, and a constant initial humidity have been assumed. The fundamental process can be described (48) by considering a slab of high uniform initial moisture content so as to cover the total surface of the

slab with a water film. Contact with the warmer air stream cause evaporation of water from the surface. The water diffuses through the surface film of air and is then removed by the bulk motion of the air. In the general case the temperature of the solids and slab soon approaches the wet bulb temperature as the latent heat of evaporation is usually high compared to the sensible heat of the slab. Thus the heat transferred from the bulk to the slab serves only to evaporate the water and does not affect the temperature of the slab. As the water is evaporated from the surface additional water may flow from the interior of the slab to the surface. This period of constant drying conditions under a constant drying rate is often called the constant rate period. As drying is continued the surface water film breaks down and the drying rate falls. This is associated with an increase in the slab temperature as the amount of heat transferred has less evaporation to perform. Eventually the drying rate will fall to zero as the moisture content of the slab approaches a value in equilibrium with the drying air. The equilibrium moisture content will depend largely upon the air temperature and humidity. The process described above is characterised by a curve of the shape shown by Fig. (43).

This account of the drying process has to be adapted somewhat to describe the processes occurring in the freshly regenerated adsorption bed. Initially the temperature of the particles will be higher than that of the adsorbate stream. Also as activated carbon has a low affinity for water, then only a portion of the particle surface will be covered by water. The diagrammatic representation of Fig(44) is applicable. The porosity of the particles will ensure that some water is taken into the interior by capillary effects. The initial rate of evaporation is thus likely to be high with a rapid cooling of the particles resulting both

from the heat transfer to the bulk fluid and the supply of the latent heat of evaporation. Evaporation will however be limited by the saturation moisture content of the bulk air stream. It is therefore unlikely that there will be a constant evaporation rate for any length of time as the temperature of the bulk fluid and hence its saturation capacity will not be constant. If the particle temperature falls to that of the bulk, but all the water has not been evaporated, then further evaporation based on a mass transfer driving force will reduce the bulk temperature. The exit temperature of the bulk fluid will thus be less than its inlet temperature until evaporation is completed, then the exit temperature will rise. Thus periods of constant evaporation rate are conceivable but generally the rate of evaporation will be a complex function of the system properties.

The above discussion fails deliberately to consider the effects of adsorption occurring simultaneously with the evaporation of water. If, as is possible for active carbon adsorbent, the equilibrium adsorption capacity of the adsorbent is significant at the temperature of regeneration, and the water present does not cover the entire external surface of the particles, then some removal of adsorbate from the bulk stream will occur at the start of the adsorption period. The heat liberated by this adsorption can then contribute to the evaporation of water. If sufficient internal and external adsorbent surface is available, then the blocking effect the water will be negligible, and the particle temperature will effectively control adsorption. In this latter case the cooling and the drying of the adsorbent will have far more effect in promoting the removal of adsorbate from the bulk stream.

This latter case also requires that consideration be given to the equilibrium moisture content of the adsorbent. For high bulk humidities the water retained by the adsorbent at equilibrium will be large and may

reduce the overall adsorption efficiency. Unless, of course, the adsorbate is soluble in water. In which case the solution of adsorbate enhances the overall removal process (49). As the solubility of hydrocarbons in water is usually small this effect can be neglected for these adsorbates. For porous adsorbents where water is not held by chemical bonds the equilibrium moisture content will be the value predicted by the relevant adsorption isotherm for water and the adsorbent. It has long been known that pure activated carbons have a very small capacity for adsorbing water at low relative humidities (50), although the presence of inorganic impurities greatly increases this capacity (51). During the adsorption period the moisture content of the particle will be assumed to reach equilibrium with the humidity of the bulk stream as the bed is dried. As this moisture loading will be constant for the remainder of the adsorption period its effects on adsorption, if any, can be considered as being part of the general activity of the adsorbent. The bed can therefore be considered dry when its free water content has been reduced to zero.

It will therefore be assumed in this work that the presence of free water does not significantly affect the removal process of adsorbate from the adsorbate laden fluid. For a pure adsorbent and a well drained bed this is an acceptable assumption, although its validity must be in question where the process controlling the transfer of adsorbate is one of intraparticle diffusion. Additional heat and mass transport terms must now be formulated to describe the behaviour of the wet system. All resistance to the mass transfer of water is assumed to be in a surface film surrounding the particles. The transfer processes occurring can then be diagrammatically represented by Fig.(45). As the particle temperature is initially greater than the bulk temperature then the heat flux and water flux are in the same direction, and the adsorbate is removed against the temperature gradient. The heat and mass processes for the water

transfer over a general stage r can now be defined as follows. The transfer process for the water evaporating from the particle surface gives

$$ch_r - ch_{r-1} = k_p \cdot a \cdot (ch_s - ch_{s0}) \cdot \Delta t_r \quad \text{----- LXXXXVII}$$

An overall water mass balance gives

$$\Delta z_r \cdot \Delta nh_r = V_r \cdot \alpha \cdot (ch_r - ch_{r-1}) \cdot \Delta t_r \quad \text{----- LXXXXVIII}$$

A heat balance over the particles and the bulk stream gives

$$\begin{aligned} & - \Delta n_r \cdot Q + (\Delta n_r \cdot \mu_4 - \Delta nh_r \cdot \mu_5) \cdot (\theta_{r-1} - \theta_{Pr}) \\ & - k_h \cdot a \cdot (\theta_{Pr} - \theta_{r-1}) \cdot \Delta t_r + \Delta nh_r \cdot Qh \\ & = \rho_B \cdot \mu_P \cdot \Delta \theta_{Pr} + (n_r + \Delta n_r / 2) \cdot \mu_V \cdot \Delta \theta_{Pr} \\ & \quad + (nh_r + \Delta nh_r / 2) \cdot \mu_t \cdot \Delta \theta_{Pr} \quad \text{----- LXXXXIX} \end{aligned}$$

A heat balance over the bulk stream gives

$$\begin{aligned} & V_r \cdot \Delta t_r \cdot \{ c_r \cdot \mu_1 + \rho_{c_{r-1}} \cdot \mu_2 + ch_r \cdot \mu_5 \} \cdot \alpha \cdot \Delta \theta_r \\ & = \{ k_h \cdot a \cdot (\theta_{Pr} - \theta_{r-1}) \cdot \Delta t_r - 4.0 k_w \cdot (\theta_{r-1} - \theta_{w_r}) \cdot \Delta t_r / d_i \\ & \quad - (\Delta n_r \cdot \mu_1 - \Delta nh_r \cdot \mu_5) \cdot (\theta_{r-1} - \theta_{Pr}) \} \cdot (z_r - z_{r-1}) \quad \text{--- C} \end{aligned}$$

A heat balance over the wall gives equation LXXXXIV as before. Equations LXXXXVII and LXXXXVIII determine the values of Δch_r and Δnh_r respectively. These values are used to determine $\Delta \theta_{Pr}$ and $\Delta \theta_r$ from equations LXXXXIX and C respectively. The value of $\Delta \theta_{w_r}$ is determined from equation LXXXXV. The use of equation LXXXXII gives the value of V_r to be used in the appropriate rate expression.

The procedure described earlier in this Chapter is used to initiate and continue calculations through the system for increasing z and t until the specified maximum adsorption time is reached. The magnitude of Δz and Δt are revised as described in more detail when discussing the

computer programs for this section of the work. It should be noted that equation XCVII is still valid if $\text{chos} \geq \text{chs}$ or $\text{chos} < \text{chs}$. The values of chos and chs are separately calculated by a subroutine as functions of temperature only. It is necessary to ensure that the value of Δn_{h_r} calculated above is permissible, so that $n_{\text{h}_r} - \Delta n_{\text{h}_r}$ is never negative. It is easy to restrict the value of Δn_{h_r} to satisfy this constraint. However, it is also then necessary to restrict the value of Δn_{h_r} if this causes the humidity of the carrier fluid to exceed its saturation value. The exit humidity of the fluid must thus be its saturated value at its exit temperature. These problems are simply handled as shown in the relevant computer programme.

4.4 Programming of the Solutions

The programmes were written in ICL FORTRAN and run on the computer facilities available to the University of Manchester Regional Computing Centre. The machine used for this section of the work was the ICL 1906A. No library subroutines were used. The computational effort was not difficult but required a moderate amount of computing time whenever frequent changes in the values of Δz and Δt were called for. Certain aspects of the mathematical form of the solution are described below. These required elucidation before the programmes could be written.

4.4.1 Determination of c_r

From section 4.1 for Cases 3, 4 & 7 the value of c_r cannot be explicitly determined as Δn_r was a complex function of c_r . In these instances it is possible to express equation LXXXII in the form

$$c_r / C_o = c_{r-1} / C_o - (\Delta z_r / (C_o \cdot \alpha \cdot V_r \cdot \Delta t_r)) \cdot g(c_r) \text{ ————— CI}$$

Division by C_o renders the equation dimensionless. It is possible to choose by trial and error values for c_r that successively produce better agreement between both sides of the equality of equation CI until some

desired accuracy criteria is satisfied. However, use will be made here of the fact that c_r must lie between c_{r-1} and zero. The term DEL will be defined as

$$\text{DEL} = \left\{ \frac{c_r}{C_0} - \frac{c_{r-1}}{C_0} + \frac{\Delta z_r}{C_0 \cdot \alpha \cdot V_{r0} \cdot \Delta t_r} \cdot g(c_r) \right\}^2 \quad \text{--- CII}$$

Hence DEL is always positive but will have its minimum value of zero when the required value of c_r is chosen. The problem is now essentially one of carrying out a univariate search in the bounded interval $c_{r-1} \leq c_r \leq 0$ to minimise the value of the objective function DEL by choice of c_r . The most efficient univariate search technique, the Fibonacci method (52), will be used. For an objective function where the minimum does not lie near the limits of search, a n-point search will produce two previously determined search points equally spaced on either side of the n-1 search point. As a point value of c_r is required and not a range of values the final point of the search technique will not normally be used. The exception being when one of the points on either side of the n-1 point lies at the search limit. Here the n point will be placed at the limit involved and its value of DEL determined. This ensures that the minimum (i.e. correct value of c_r) will have been located to within the range of three equally spaced points. A quadratic interpolation can be used over these three points to produce an interpolated minimum point by analytical means (53). The value of DEL is next determined at this minimum point. If the value of DEL is sufficiently close to zero then the desired value for c_r has been found, and the computational procedure returns to the stage of the model under investigation in the main programme. If the value of DEL does not satisfy the accuracy criteria, the point of the three original points that is furthest from the interpolated point is rejected, and a further quadratic interpolation is carried out on the remaining points and the previously

interpolated one. Hence, the Fibonacci procedure finds the interval for the value of c_p as efficiently as possible ; and successive use of the interpolation procedure further reduces the search interval until the minimum is located. This procedure has been programmed as the subroutine FIBS and is shown by Fig. (46); and calls the routine DEL to determine the value of the relevant form of equation CII. The routines DEL for Cases 3, 4 and 7 are shown in Fig. (47).

4.4.2 Determination of $\rho_c(\theta)$

This has previously been described in Chapter III (see 3.4.2) for a helium carrier gas. A similar procedure is used to represent the variation of ρ_c for air, in the temperature range $20^\circ - 100^\circ\text{C}$. The expression is $\rho_c = 0.00125941517 - 0.00000320602 \cdot \theta$ (gms/cm³)

4.4.3 Determination of chos(θ) and chs(θ_p)

It is usual to represent the variation of chos with temperature by a humidity chart. It is more convenient for computational purposes to express this variation in an analytical form (54) to give

$$\text{chos} = \frac{p_o \cdot \rho_c \cdot \frac{\sigma_w}{\sigma_o}}{p_T - p_o} \quad (\text{gms/cm}^3)$$

This is also the same relationship as for chs. However, chos and chs are evaluated at different temperatures, that is for different values of p_o and ρ_c as they are also functions of temperature. The dependance of ρ_c on temperature is given by 4.4.2. As p_o is the saturation vapour pressure it can best be expressed as a function of temperature in the form

$$p_o = \exp(13.64146496 - 5089.94836672 / \theta) \quad (\text{atms})$$

where the numerical constants are found by fitting an expression of the above form to data of $\log_{10}(p_o)$ versus $1/\theta$ by the procedure of 3.4.2.

4.4.4 Linearisation of Adsorption Equilibria

The adsorption equilibria has been described in 3.4 in general

terms. Cases 2 and 4 of the analytical solutions for the isothermal case were developed for a linear isotherm with its intercept at the origin. Although the models for Cases 2 and 4 were developed in this Chapter for adsorption equilibria in the form $c_s = a_0 + a_1 \cdot n$, they can only be compared to the analytical solutions when $a_0 = 0$. The models for general heat and mass transfer with and without water present are operated at constant adsorbate concentration in the bulk fluid within each stage. However, the loading of adsorbate on the adsorbent varies with time within the stage. Only when the transfer of adsorbate uses the mechanisms of Cases 2 or 4 of Chapter I will this variation of the adsorbate loading affect the transfer processes. Values of a_0 and a_1 must therefore be supplied. As the temperature within a stage is held constant for the time interval being used, then the adsorption equilibria expressed in the form of equation LXXIX can be illustrated diagrammatically by Fig.(48). The initial adsorbate loading on a stage is n_1 , which produces a vapour concentration at the particle surface of c_1 . During the adsorption process the value of the adsorbate loading will increase. From the programmes described in 4.5 below it will be seen that a maximum change of adsorbate concentration in the bulk fluid of C_0/L is allowed for each stage (L is the number of stages that the bed length is divided into). This change in the bulk fluid concentration is approximately equal to Nos/L for the adsorbate loading. So that as is shown in Fig.(48) a loading of $n_1 + \delta n = n_2$; ($\delta n = Nos/L$) produces a vapour concentration at the particle surface of c_2 . It is then easy to show that a line through the points (n_1, c_1) and (n_2, c_2) has the form $c = a_0 + a_1 \cdot n$ where

$$a_0 = (c_1 - n_1) \cdot (c_1 - c_2) / (n_1 - n_2) \quad a_1 = (c_1 - c_2) / (n_1 - n_2)$$

These values of a_0 and a_1 are calculated for each stage and each time interval whenever Case 2 or Case 4 is the rate mechanism, and used as

shown in 4.1.

4.5 Programming of the Isothermal Models (Cases 1 to 7)

Comments on the programming of the models for Cases 1 to 7, and copies of the programmes are given below. Several of the programmes are similar as can be imagined from the forms of the equations shown in 4.1. The subroutine FIBS is common to Cases 3, 4 & 7, and has been described in 4.4.1. For Case 1 it is necessary to ensure that the adsorbate loading does not exceed the saturation capacity N_0 . For Cases 5 & 6 it is necessary to ensure that the bulk adsorbate concentration does not become negative. The procedures for doing these operations are simple, and can be seen from the relevant copy of the MOD series of programmes.

It was found in preliminary work that division of the bed into forty intervals of width 0.25 cm. produced suitable agreement between the analytical solutions and the model formulations in a reasonable time on the computer. For all useful adsorbents the length of the mass transfer zone is much less than the total bed length. The occurrence of large-scale changes in the bulk concentration can thus take place across a few stages at positions within the bed that vary with time. All the programmes, therefore, tested the concentration change across each stage. If the change was greater than $0.025 C_0$ then the model solutions were applied across successively smaller intervals within the stage, until the concentration change over all these reduced intervals was less than $0.025 C_0$. The change in adsorbate loading across the stage is then determined by applying the mass balance over the complete stage (thus averaging out the adsorbate loading) without taking into account the calculations of the bulk concentrations within the stage.

Earlier work on the analytical solutions, and small scale experimental work determining concentration profiles for dilute adsorbate concentrations indicated that concentration changes of the order of

0.5% of the inlet concentration were insignificant. When the bulk fluid concentration falls below 0.5% of the inlet concentration within the bed then the effluent from the bed is set at zero adsorbate concentration. The adsorbate within the bulk fluid then assumes a linear profile over the remaining stages. The loading of each remaining stage is increased by a constant quantity given by the mass balance using the linear bulk concentration profile.

All programmes use equally sized stages within the bed, and have a constant initial adsorbate loading for each stage. This is written as part of the programmes but does not restrict the applicability of the programmes. Likewise, only the bulk fluid concentration at the bed exit is printed out, although the concentrations and loadings at all stages within the bed are calculated. It is easy to alter the printout to produce any other desired information.

The results shown below are produced from the data values shown in Table I, and were used in producing the analytical profiles shown for Chapter II. The model profiles shown below have been determined for a few values of the constant(s) and compared with the corresponding profiles from Chapter II.

4.5.1 Model for Case 1.

A copy of the programme for MOD1 is shown by Fig.(49). If the calculated adsorbate loading of a stage is above the saturation loading then the time interval is reduced until the adsorbate loading is equal to its saturation value. This reduced time interval can be calculated directly as shown, and replaces the previous value of the time interval. The time interval reverts to its original value for the next complete iteration of the system. Record is made of the stage at which the adsorbent becomes saturated, and calculations are not in future carried out over these saturated stages. Typical exit profiles calculated by MOD1 are compared in Fig.(50) to the profiles determined by Case 1 using

the same data.

4.5.2 Model for Case 2

A copy of the programme for MOD2 is shown by Fig.(51). It is identical to that of 4.5.1 except that the form of the rate equation prohibits loadings in excess of the saturation capacity. Hence part of the programming of MOD1 is not required. Typical exit profiles calculated by MOD2 are compared with those of Case 2 in Fig.(52).

4.5.3 Model for Case 3

A copy of the programme for MOD3 is shown by Fig.(53). Use is made of the subroutines FIBS and DEL as described in 4.4.1. The accuracy criteria used in FIBS ensures that the concentration in the bulk is found to within 0.1% of the inlet value. Use of the nine point Fibonacci search produces three points spanning an interval of the order of 4% of the bulk concentration value entering the stage. The remaining accuracy is found by the interpolation procedure. Typical exit profiles calculated by MOD3 are compared with those of Case 3 in Fig.(54).

4.5.4 Model for Case 4

A copy of the programme for MOD4 is shown by Fig.(55). The programme is identical to that of 4.5.3; but uses a different DEL subroutine. Typical exit profiles calculated by MOD4 are compared to those of Case 4 in Fig.(56).

4.5.5 Model for Case 5

A copy of the programme for MOD5 is shown by Fig.(57). If the calculated bulk adsorbate concentration leaving a stage is negative, then the time interval should be reduced. It is difficult to determine the new value for the time interval (unlike that shown by MOD1). It is, however, easy to determine the point (z value) within the stage at which

the bulk concentration would be zero for the time interval DT . It is then possible to assume that this stage operates at zero exit bulk concentration for all of the time interval DT ; and the change in the adsorbate loading calculated by the mass balance is averaged over the complete stage. For all subsequent stages the bulk concentration is zero. The next time interval over the complete bed is then considered. Typical exit profiles calculated by MOD5 are compared with those of Case 5 in Fig. (58).

4.5.6 Model for Case 6

A copy of the programme for MOD6 is shown by Fig. (59). The programme is identical to that of 4.5.5 but uses a different form of the model calculations. Typical exit profiles calculated by MOD6 are compared with those of Case 6 in Fig. (60).

4.5.7 Model for Case 7

A copy of the programme for MOD7 is shown by Fig. (61). The programme is identical to that of 4.5.3 and 4.5.4 but with a different form of the DEL subroutine. Typical exit profiles calculated by MOD7 are compared with those of Case 7 in Fig. (62).

4.5.8 Conclusions on comparison between MOD and CASE results

Where the exit concentration profiles show a smooth rise, go through a point of inflexion and then exhibit a smooth approach to the value of the inlet concentration (Cases 2,3,4 & 7) the MOD and CASE profiles show a maximum deviation in mid-range of approximately 4% of the inlet value. For a fixed value of TD the maximum error is of the order of 2% of the calculated CD value.

Where the exit concentration profiles show a smooth rise that has a continually increasing gradient so that the profile does not approach a value of $CD = 1$ asymptotically (Case 1) the MOD and CASE profiles show a maximum deviation at values of CD approaching unity of

approximately 10%. The deviation is greater at higher values of K_1 due to the more perpendicular shape of the profiles at the higher concentrations. For values of CD upto 0.5 the maximum error is of the order of 3%.

Where the exit concentration profiles show a sharp rise initially but the gradient of the profiles falls to zero approaching a value of CD of unity (Cases 5 & 6) the MOD and CASE profiles show a maximum deviation at low values of CD of approximately 10%. Although as with Case 1 this deviation is far less for lower K_1 values and is due again to the more perpendicular shape of the profiles as the mass transfer rate is increased.

In general the agreement between the CASE and MOD results is very good, although there are exceptions largely where the rate of mass transfer becomes large. It was found that closer agreement could be obtained by using more elements in the MOD formulations; but the use of more computation time and doubts about the accuracy of the numerical integration procedures used in some of the CASE formulations rendered this step of lesser value. It should also be noted that for industrially useful systems only the initial part of the exit concentration profile is required so that with the exception of CASES 5 & 6 the agreement between MOD and CASE results is excellent in this low concentration range. Furthermore, analytical solutions shown by the CASE profiles are based on very simple forms of the parameters capable of expressing the state of the adsorption system. The small loss of accuracy that is associated with the MOD results is but a small inconvenience in view of the far wider range of parameters that the MOD formulation can utilise successfully. This aspect is of particular value when the cases of simultaneous heat and mass transfer are considered in an attempt to produce a model that is truly representative of an industrially operated adsorption system.

4.6 Programming of General Heat & Mass Transfer Operations

The programming of GENHAM (describing an adsorption system in the absence of moisture) and WETBED (describing the wet adsorption system) is similar to the form of the model used for the MOD series of adsorption systems (isothermal). In essence the formulation of MOD 2 is used to determine the values of c and n leaving each element of the system. However, whereas MOD 2 used an adsorption isotherm of the form $c = \text{constant} \times n$ in the two programs considered below a general form of the adsorption isotherm is used to allow for non-isothermal conditions and is linearised (as described earlier) over small sections. This partial linearisation slightly alters the form of the equations used to determine the new c and n values. A comparison between the programme for MOD 2 and either of GENHAM or WETBED programmes (described below) shows these modifications.

The change in the particle temperature within the element is next evaluated using either equation LXXXXIII or equation LXXXXIX as is appropriate. A check is placed on the magnitude of this change to ensure that the model is not invalidated by the occurrence of large scale temperature effects within a single element (in the same way that a check was placed on the calculated value of c). For a bed of forty elements with a maximum temperature change of 80°C a maximum temperature change of 2°C was allowable for each element. If the calculated particle temperature change exceeds 2°C the system time interval is reduced accordingly and calculations repeated until no element shows a change in particle temperature of more than 2°C . This does not involve excessive computation time as the largest temperature changes take place on entry to the system where the cool dry carrier fluid meets the hot (or hot and wet) particles of the bed. Thus once the time interval has been reduced to satisfy the temperature constraint over the first element it is found that this time interval is satisfactory for the remainder of the bed. It

was found that this required a reduction in the time interval of the order of one hundred or more depending on the particular values of the heat and mass transfer coefficients. In order that this did not then mean that an excessive number of iterations had to be performed to reach the preset maximum adsorption time, it was necessary to include a means of increasing the value of the time interval. When a change in the value of the particle temperature of 0.5°C or less occurred over each bed element the time interval was doubled. A check is made to ensure that the time interval so produced does not exceed the input value of the maximum time interval.

In the programme WETBED calculations of the change in the moisture content of the particles and the bulk fluid are calculated before evaluating changes in the value of the particle temperature. These calculations are described in detail below in 4.6.2. The calculations are not necessary in the programme GENHAM. In WETBED a check is made to ensure that the bulk fluid entering the element is not saturated prior to determination of the changes in moisture content of the bulk fluid and the particles as determined by mass transfer considerations. The changes predicted by mass transfer considerations only are now checked against more practical requirements.

The change in the temperature of the bulk fluid is next determined using either equation LXXXIV or equation 7 as appropriate. No check is made on the magnitude of this change.

In both programmes the change in the wall temperature is now calculated using equation LXXXV. No check is made on the magnitude of this change.

This concludes the calculation for a single element. The next bed element is considered and the same calculations repeated. When one full iteration is successfully completed all the parameters are updated and the next time iteration begun. Arrangements are made to print out at set intervals certain of the outlet physical properties and the full parameter

profiles within the bed.

4.6.1 The programme GENHAM

Just as the MOD series of programmes were tested by comparison with the CASE series of programmes, so the programme HAMAN (see Chapter III) based on the analytical numerical solution of the relevant partial differential equations provides a means of testing the validity of the results obtained from the programme GENHAM. A copy of the programme GENHAM is shown by Fig. (63). When used in comparison with HAMAN it is necessary to modify GENHAM slightly. All that is required is the programming that includes the change of the time interval based on the lower limiting value of the change in the particle temperature be removed. This is done because the very small time intervals used with HAMAN are below this lower limit. Using the same data values it is possible to compare the results of HAMAN and GENHAM in terms of both exit concentration and temperature profiles, and the profiles within the bed at fixed points in time. Such suitable profiles are shown in Fig. (64) to Fig. (67).

From Fig. (64) the exit concentration profiles for HAMAN and GENHAM show similar divergence to the profiles produced for the CASE and MOD series described earlier. This is to be expected as GENHAM and MOD are based on the same model approximating the system. The CASE results are truly analytical, whereas the HAMAN results are based on a difference approximation that has been found by other authors to satisfactorily represent the analytical solution.

From Fig. (65) the exit temperature profiles show an initial divergence to a maximum temperature difference of the order of 0.05°K . This magnitude of divergence is negligible. However, it is of interest to show that the divergence is a genuine property of the GENHAM and HAMAN results. It arises from the need to allow for the enthalpy change of the adsorbate as it is transferred from the bulk fluid to the particle, and the

different iteration procedure used in the GENHAM and HAMAN programmes. In the HAMAN programme, based as it is on very small time intervals, the heat of adsorption is not transferred to the bulk fluid as quickly as it is generated so that the adsorbate and carrier fluid experience an increase in enthalpy as they pass from the bulk fluid to the particle. This enthalpy is provided by the bulk fluid which is thus cooled below its inlet temperature. When sufficient adsorbate has been adsorbed on the particle its temperature has been raised sufficiently so that the nett heat loss from the particle raises the bulk fluid temperature. The exit bulk temperature then increases. In the GENHAM programme the far longer residence time of the bulk fluid within a particular element of the bed smooths out any initial variations as a result of the far larger heat fluxes involved. The exit temperature profile therefore rises smoothly from its inlet value.

From Fig.(66) showing the concentration profiles within the bed at various times it can be seen that the profiles for GENHAM and HAMAN are in good agreement. The profiles show a slight variation that is barely perceptible at small time values, but which builds up slowly and moves forward through the bed at increased time values leaving good agreement between the profiles to the rear of the variation. Further work indicated that even for long beds this variation was slight.

From Fig.(67) this same variation is again noted, as is its movement forward through the bed with increasing time values, when the temperature profiles within the bed are considered. The variation on the profiles at the exit face of the bed clearly indicate the variation in the exit temperature profiles as shown by Fig.(65).

The programme GENHAM divided the adsorption bed of length 6.0 cms into 40 elements of equal size and used a time interval of 0.001 min. It required 15 secs of machine time and 3 secs of programme control time by the

GEORGE operating system in use on the machine. The programme HAMAN used the same bed length divided into 20 elements (21 nodes) of equal size and used a time interval of 0.0000735614 mins. It required 162secs of machine time and 4secs of the GEORGE time. The programme GENHAM thus uses one tenth of the machine time required by HAMAN and produces results that compare very favorably with the restricted analytical approach. The real benefit of the programme GENHAM lies in its being able to produce the profiles shown by Figs. (64) to (67) for a 40.0 min adsorption period at a usage of computer time that is of the order of 10^3 less than that required by HAMAN to produce the same profiles. This is simply achieved by increasing the time interval to 0.1mins when using GENHAM. It is moreover now possible to investigate quickly and cheaply (with reference to the cost of computer time) the effects of variations in the initial conditions of the system and to study the effects of changes in the shape of the adsorption isotherm on the adsorption performance of the system. Of particular interest to this work is the effect on the system performance of an elevated initial particle temperature as might result from the use of some inert hot fluid used to regenerate the system for further adsorption duty. This leads naturally onto a discussion of the effects of removal of any condensed regenerative agent that is present in the system at the start of an adsorption period (see 4.6.2 below).

Several runs were carried out with GENHAM using an initial particle temperature of 373°K uniform throughout the system but varying the mass and heat transfer coefficients. This general series served to illustrate the response of the system to changes in the parameters in an effort to produce conditions that might be representative of the industrial system described in Chapter VII. Originally the equation describing the form of the adsorption isotherms was used unmodified as shown with the programme HAMAN. However, it was found that this formulation had a low adsorption

capacity when saturated with adsorbate and was relatively insensitive to temperature. What was needed was a more representative expression for the adsorption isotherms of a general hydrocarbon on activated carbon. In order to maintain the general applicability of the programme it was decided to modify the available isotherm expression rather than use an isotherm expression for a particular hydrocarbon and a particular adsorbent. This simply required increasing the maximum adsorbate capacity on the adsorbent (multiplication by a chosen factor) and including a term in the subroutine ISOT that increased the temperature sensitivity of the subroutine. These modifications are not based on any published work but were found to be the simplest ones available that produced the desired results yet maintained the general applicability of the model. It was also found possible to modify the ISOT subroutine so that a degree of irreversibility could be introduced into the adsorption process. This required simply a reduction (by a chosen factor) of the adsorbate pressure above the adsorbent surface. This series of operations produced what is called in this work the Standard Isotherm Subroutine and is shown as part of Fig.(63). The shape of the isotherms at various temperatures and for a very wide range of co-ordinate values are shown in Fig.(68). The isotherms are essentially those used by Meyer & Weber (35) who only use the portion of the isotherms that is convex. The more complete shape is included here for completeness of the present work which uses higher CAP values.

This standard isotherm subroutine cannot of course be used when comparing the results of HAMAN and GENHAM. The isotherm formulation used by Meyer & Weber must be applied unmodified.

Using the standard isotherm subroutine it was possible to select a series of heat and mass transfer coefficients that produced temperature effects which could be regarded as typical of an industrial adsorption

unit (see Chapter VII). The bed depth was increased to 40.0 cms and the adsorption time to a maximum of 40 mins. The complete data (with the exception of KM - the overall adsorbate mass transfer coefficient) are shown in Table VI. The programme GENHAM was run with several values of KM and the data of Table VI to illustrate the effect of changes in the mass transfer coefficient. The system thus represented is one where a cool, dry, adsorbate laden bulk fluid comes into contact with a hot, dry, adsorbate free particulate bed. The resulting dimensionless exit concentration profiles are shown in Fig.(69) for five values of the mass transfer coefficient. All profiles show what will be referred to later as a characteristic "U" shape, where the adsorption is adversely affected by the initially hot bed and produces a very high exit concentration that falls as the bed cools. When an equilibrium adsorbate loading on the particles is reached the exit concentration begins to rise and so produces a "U" shaped profile. The exit concentration profiles shown are particularly sensitive to the value of KM when KM is less than 1.0, as it was found that profiles for KM equal to 10.0, 100.0, 1000.0 and 10000.0 were identical when plotted to that of $KM = 1.0$. For the exit concentration profiles shown in Fig.(69) there was little variation in the exit temperature profile. The exit temperature profile is shown in Fig.(72) for $KM = 0.1$, but is representative of the profile for other values of KM .

The very steep initial parts of the profiles shown in Fig.(69) clearly indicate the advisability of cooling a hot adsorption bed prior to the introduction of an adsorbate laden bulk fluid when it is desired to recover the adsorbate from the bulk fluid. It also indicates that in a system whose isotherms are particularly sensitive to temperature changes care should be taken to ensure good mass transfer and the avoidance of any localised 'hot spots' within the system. The use of a system which contains an inert fluid whose evaporation aids heat transfer offers an interesting

operating alternative.

4.6.2 The programme WETBED

A copy of the programme WETBED is shown by Fig. (70). As has been stated an attempt has been made to describe the simultaneous mass transfer of adsorbate from the bulk fluid to the particle, and of mass transfer of water from the particle to the bulk fluid, together with their associated heat transfer effects.

The elemental approach used means that water is transferred to the bulk fluid by a driving force that is the difference between the humidity at the particle surface and the humidity of the bulk fluid. The reverse driving force is also possible so it is necessary to test that the inlet bulk humidity to an element is below the saturation humidity of that element. If not the reverse transfer takes place to remove water from the bulk fluid. It is also necessary to ensure that the transfer of water does not produce a humidity in the bulk fluid that is in excess of its saturation capacity. All saturation humidities are determined by the subroutine HUMID. Finally it is necessary to ensure that the total moisture transferred from the particle does not exceed its initial moisture loading. A water mass transfer coefficient (overall) is used to control the rate of transfer.

The heat effects associated with the water transfer are easily incorporated into the calculations for determining the temperature changes over an element. It was however found desirable to limit the amount of water transferred if this produced particularly large scale changes in the value of DTP (the change in the particle temperature) so that the model used to represent the overall system was not invalidated. In all other aspects the programme WETBED is similar to the programme GENHAM.

The additional data required were easily found from the generally available sources of data on water. It was assumed that the inlet bulk fluid

had zero water content, although this is not a necessary condition, and a value for the initial water loading on the particles was found from experimental work (see Chapter VII). The additional data values are shown in Table VII. For the purposes of comparison the value of $KM = 0.1$ was chosen and the programme WETBED was run using two different values of KF , viz. $KF = 0.0001$ and $KF = 0.00001$. The standard isotherm subroutine was used as was the data of Table VI.

The exit concentration and temperature profiles are shown by Fig. (71) and Fig. (72) respectively. Included on both figures is the profile for the programme GENHAM with $KM = 0.1$. The effects of the presence of the water are immediately apparent. In Fig. (71) the initially sharp drop in the exit concentration has been completely removed so that the profiles for WETBED now rise from the horizontal axis. All points on the profile for the wet bed are significantly less than the points on the profile for the dry bed. From Fig. (72) the smooth drop in exit temperature for the dry bed system has been replaced by profiles which show a considerable amount of initial sub-cooling below the inlet temperature before a gradual rise to a constant exit temperature. These effects are to be expected as the initial rapid evaporation of water from the particles requires more enthalpy than can be provided by the heat of adsorption liberated on the particles. The additional enthalpy is provided by the bulk fluid whose temperature thus falls.

It is of interest to note that in Fig. (71) the profile with the larger water mass transfer coefficient lies above (i.e. is a worse exit concentration profile) that profile with the smaller water mass transfer coefficient. The more rapid removal of water from the bed allows the effects of the liberation of the heat of adsorption to be illustrated sooner as adversely affecting the removal of adsorbate from the bulk fluid. This is amply illustrated by Fig. (73) where the particle temperature is shown as a function of the bed depth for various times during the adsorption operation.

Three adsorption times of 5, 15 and 40 mins. were chosen as showing sufficient changes between profiles. For the sake of clarity the profiles at 40 mins. have not been drawn singly but shown by means of their envelope. The initial large variations in profile shape thus disappear for large adsorption times as might be expected when all the water present had been removed. The effect of a ten-fold change in the value of KF is clearly illustrated by the initial profiles which differ by upto 20°C for the same point in the bed. It should also be noted that even at high adsorption times sufficient adsorption is still taking place to ensure that the temperature profile within the bed is from 5 to 15°C above the inlet bulk fluid temperature. The adsorbate loading as a function of bed depth (not shown here) indicates that the inlet face of the bed has not reached its equilibrium loading so that the so called 'adsorption wave' has a length in excess of 40 cms. and is not fully developed after a period of 40 mins. This variation from what is generally regarded as the appropriate theoretical situation can be explained satisfactorily. It is, however, first necessary to briefly consider the situation where the presence of water offers some resistance to the adsorption process.

The simplest procedure that can be used to produce this resistance is to modify the adsorption isotherm subroutine to include a term that reduces the maximum adsorption loading in accordance with the amount of water present on the adsorbent particles. It is necessary to ensure that the modification exerts its full effect when the water content of the particles is highest (i.e. at very low adsorption times) and exerts no effect when the bed is dry. One possible way of writing this restriction is shown by the Blocked Isotherm Subroutine of Fig. (70a), where the second line of the Standard Isotherm Subroutine has been modified. The term N_{UMIN} represents the initial moisture loading of the bed ($= n_{h_0} = N_{HST}$), and the term N_{UMP} represents the actual moisture loading of the particular element being

considered. The numerical factor (in this case 0.95) represents the degree of blocking initially present.

The exit concentration profile using this 95% blocked isotherm has been shown dotted in Fig. (71). As can be seen the profile has resumed its characteristic "U" shape and is marginally worse than the unblocked profile. Its exit temperature profile does not significantly differ from the unblocked case thus illustrating the very small heat effects involved. This blocked form of the WETBED programme should now be truly representative of an adsorption system initially containing residual amounts of an inert regenerative agent. Comparison with the work of Chapter VII for an operating industrial system is at best only fair.

It is the belief of the author that whilst this present work is generally representative it lacks a specific application. The system that is considered in later Chapters shows less pronounced changes with the presence of water at the start of the adsorption period. In this aspect these other adsorption systems behave somewhat mid-way between the GENHAM and the blocked WETBED systems shown here. However, use of the appropriate isotherm subroutine and determination of the appropriate blocking function should make the use of the blocked WETBED programme truly representative of a system whose heat and mass transfer coefficients are known. It is the author's belief that the inclusion of the effects of moisture on the adsorbent and the proposed model of an adsorption system are significant steps forward in the further understanding of adsorption systems. This significance is in no way diminished by the incomplete correlation between theory and the practical systems described later - rather it highlights the scope of the work still to be done on such practical systems.

CHAPTER V.

The analytical approach to the adsorption phenomena has been considered in previous Chapters. In Chapter VI certain specific results obtained by this and other authors are presented for active carbon adsorbents and hydrocarbons or related species as adsorbates. However, the analytical approach is not complete without some consideration of what happens to an adsorbent that has been saturated to a high degree with adsorbate. Basically, two particular cases can be considered. Namely the case where the adsorbent is used once and then disposed of together with its attached adsorbate; and the case where some attempt is made to recover the adsorbate.

Several examples of the disposable use of adsorbents are available to-day, e.g. small scale water purifiers, filter tips on cigarettes, domestic oven hoods and some air conditioning systems, all use activated carbon or a similar adsorbent. It can be readily seen that while the total amount of adsorbent used for such purposes is likely to increase, only small quantities of adsorbent are used in each application. This factor coupled with the multitude of adsorbates that are likely to be adsorbed in each application, makes large scale regeneration of the spent adsorbent economically infeasible; and would produce several recovered adsorbates for which no suitable market existed. It is, therefore, of little importance to consider the regeneration of such adsorbent materials.

Where attempts are made to recover the adsorbate, or alternatively to remove the adsorbate and re-use the adsorbent, it is usual to have large amounts of adsorbent involved, often of the order of several tons. An initial distinction should be made between the terms "regeneration" and "reactivation". In this work the term regeneration will be regarded as synonymous with desorption; but will cover much more than just the desorption of the adsorbate from the adsorbent. Therefore, regeneration is

that operation whereby the adsorbate is removed from the adsorbent; and the adsorbent made ready to perform further adsorption duty, all these operations occurring in situ within what can be called the adsorption system. Reactivation on the other hand will be regarded as closely allied with some or all of those operations that produced an active adsorbent from inactive raw materials. Hence when the adsorptive power of the adsorbent falls significantly (i.e. the adsorbent becomes deactivated), the adsorbent is removed from the adsorber system and suitably re-processed to restore its activity. This re-processing is often the same sequence of operations that are used to activate the inert raw materials, and so often results in a diminution of the adsorbent mass. Reactivation will not be considered in this work, although if the adsorbent is rapidly deactivated by the conditions of the adsorbate laden fluid, the reactivation is of major importance in determining how to operate the system economically.

This work will, therefore, concentrate on those processes of regeneration where there is but little change in both the mass of adsorbent and its adsorption activity. It is possible to divide this case one stage further by considering two inter-related aspects of regeneration :

- a) Where regeneration is carried out primarily to restore the adsorptive capacity of the adsorbent, so that any recovered adsorbates are of little value or use, e.g. in the large scale removal of general odours from the atmosphere of industrial premises, or the drying of petroleum based vapours.
- b) Where regeneration is carried out primarily to recover significant quantities of a valuable adsorbate; and the restoration of the adsorbent capacity is a side factor enabling the adsorbent to perform this valuable service once more, e.g. in the large scale

recovery of volatile solvents used by a particular chemical process and discharged from the process at a low concentration in an inert carrier fluid.

These two subdivisions do of course overlap, where for example the atmosphere of industrial premises contains a single toxic material, which if recovered could be used again on the premises. However, there is this basic distinction between them as to whether the adsorbate on the adsorbent is of major importance. This distinction will be referred to later in this Chapter; and will be seen to be highly significant when the optimisation criteria of Chapter VIII are proposed. The work of this Chapter investigates more closely the regeneration processes available, their usage; and their side effects.

5.1 Regeneration - General Consideration.

It has been shown above that it is necessary to regenerate the adsorption bed either to recover the adsorbate or render the adsorbent suitable for re-use. The question of when to regenerate is an important one and has been left to Chapter VIII for more intense investigation. It depends basically on some definition of the adsorption break through time. It is evident from the adsorbate effluent concentration profiles of Chapter II that this time cannot be defined as that time when the effluent concentration just becomes non-zero; but must be the time when the effluent concentration reaches a certain specified value. So that at this time the mass transfer zone has started to emerge from the exit face of the bed. For convenience this time will be given the symbol τ_a , and the profiles within the bed at $t = \tau_a$ for the adsorbate concentration in the bulk fluid, and the adsorbate loading on the adsorbent can be shown diagrammatically by Fig. (74). For convenience (and convenience only) it will be assumed that the system is isothermal at this time.

The bed thus has non-zero, non-constant (with respect to z) loading of adsorbate on the adsorbent, and is filled with bulk fluid of non-constant adsorbate concentration. Before considering specific methods of regeneration, as described below in 5.2 and 5.3, the behaviour of a simple regenerative fluid will be discussed.

This simple regenerative fluid enters the bed at what was the exit face during adsorption, with a zero adsorbate concentration and at the same temperature as that of the bed. During its passage through the bed its adsorbate content will increase as adsorbate is transferred from the particles to the regenerative fluid, so that the adsorbate concentration in the regenerative fluid leaving the bed as a function of time is shown by Fig. (75a). Also, the concentration of adsorbate laden regenerative fluid within the bed as a function of time can be described by Fig. (75b); and the variation of the adsorbate loading on the adsorbent as a function of time can be described by Fig. (75c). These figures are diagrammatically correct, and serve to illustrate several points.

- a) The regenerative fluid passes in the opposite direction to the flow of adsorbate laden carrier fluid, so that the exit part of the bed during the adsorption period always has a low adsorbate loading thus producing low exit concentration values for the length of the adsorption period.
- b) The adsorbate loading within the bed shows a profile that is pushed back towards the inlet face of the bed during regeneration. If the regeneration period is long enough then this profile will be pushed completely out of the bed. While this profile is moving, between times t_2 and t_5 , the amount of adsorbate removed per unit time is constant. For $t > t_5$ the recovery rate of adsorbate falls ultimately to zero.

c) From Fig. (75a) and the notes under b) above, for $t > t_s$ the law of diminishing returns operates, whereby successive equal quantities of regenerative fluid remove less and less adsorbate. This has a profound effect on determining how long to regenerate; and is discussed in more detail in Chapter VIII.

Is it now possible to describe this simple regeneration model by an analytical expression? Clearly, if the regenerative fluid is the same as the carrier fluid used during adsorption, then the mass balance equations and the adsorption rate expressions of Cases 1 to 12 of Chapter I will be applicable. However, only a few of the rate expressions are capable of being both applied and solved analytically, due to the complexity of the initial conditions for the bed and the failure of the mathematical methods to provide analytical solutions. The models formulated in Chapter IV are, however, ideally suited to this purpose of describing the simple regenerative system and the more complex regenerative models proposed later in this Chapter.

For this simple regenerative model it is evident that the equilibrium expression is the same for both adsorption and regeneration, hence the concentration of adsorbate in the regenerative fluid leaving the bed will at best be several orders of magnitude of its inlet value during the adsorption period. This state of affairs is of little practical use if it is desired to recover the adsorbate for further use. However it is quite satisfactory if the primary aim is to restore the adsorptive capacity of the adsorbent. Thus if the adsorbate was water in a carrier fluid of methane, then using a regenerative fluid of air, the air/water fluid could be safely discharged to atmosphere during regeneration. Effective regeneration of the adsorbent is then obtained. To obtain a concentration of adsorbate in the regenerative fluid leaving the bed that enables satisfactory recovery of the adsorbate it is necessary to consider methods of regeneration other than by this simple means.

5.2 Regeneration by a Heated, non-Condensable Inert.

This method is generally used where it is desired to regenerate the adsorbent for future use, and where the adsorbate is not necessarily recovered. The example already given (removal of water from methane) is typical of this application, where the adsorbent is usually activated alumina, silica gel or a molecular sieve. As these adsorbents are outside the scope of this work, great detail will not be presented here for their usage. However, they form the simplest system that can be dealt with; and illustrate the effect of heating the regenerative fluid. A heated regenerative fluid will supply the required heat of desorption, however, the effect of temperature on the equilibrium relationship is of far more importance. A set of general non-linear isotherms are shown diagrammatically by Fig.(76). In the nomenclature of Chapter I, for an adsorption isothermal temperature of Θ_a , the maximum loading on the adsorbent is N_{os} given by an inlet concentration of C_o . For a bed at a loading of N_{os} , and a regenerative fluid of temperature Θ_p then the maximum concentration of adsorbate leaving with the regenerative fluid is C_p (note that C_p is greater than C_o). If the regenerative fluid is at Θ_c then the maximum adsorbate concentration in the regenerative fluid is C_c (note that C_c is greater than C_p). Hence, a heated regenerative fluid effects an increase in the adsorbate concentration. This means that far less fluid is required (if heated) to regenerate a bed, than was passed through it during the adsorption period. Also, regeneration can be carried out in a time less than that required for the adsorption period, under the same flow conditions.

In practice the regenerative fluid is often not at zero adsorbate concentration at inlet; but has an inlet concentration of C_o' . Moreover, it is usual to cool the bed at the end of regeneration before

proceeding with the next adsorption period, so that efficient adsorption occurs at the start of the period. Thus, the adsorbate loading on the bed will not be reduced to zero, but rather to a value of Nos' at the start of adsorption; and a three stage cycle viz. adsorption/regeneration/cooling is used.

The regeneration and cooling stages can be expressed mathematically by the different equations set up in Chapters III and IV to cover adsorption phenomena, or more conveniently by the mathematical models proposed in Chapter IV. As cooling is carried out prior to adsorption the heat effects of the regeneration process are largely removed from the system, so that there is little interaction between the regeneration and adsorption periods. Operation of the three cycle system thus is more complex practically; but offers several simplifications when described mathematically, over the comparable two cycle systems described below:

5.3 Regeneration by a Heated, Condensible Inert.

This method is generally used where it is desired to recover the adsorbate in large quantities. The adsorbate and regenerative fluid can be condensed and separated by density difference or separated in the vapour phase by distillation and condensed separately. Where the adsorbate is non-hydrolysed it is usual to use steam as the regenerative agent.

As the adsorbent bed and its surrounds are much cooler than the steam, on entry to the bed all the steam will condense initially. The heat of condensation serving to raise the temperature of the bed. Successive amounts of steam will raise the temperature of the bed locally until some of the steam no longer condenses. This uncondensed steam will move further into the bed and then condense. In this manner no

steam and its associated desorbed adsorbate vapours will leave the bed in the vapour phase until the bed has been heated sufficiently to allow the passage of steam through its entire length. There is thus some time τ_b , the regeneration breakthrough time, before which no adsorbate and steam pass through the bed. If the bed is well drained then some of the condensed steam will have associated with it some condensed adsorbate; and this will be produced before the breakthrough time τ_b . To reduce this time τ_b it is possible to use superheated steam. The heat of superheat will thus contribute to heating the bed and its surrounds before any of the steam condenses. This will mean less water present within the bed and a smaller value for τ_b . For $t > \tau_b$, then the adsorbate profiles in the vapour phase and on the adsorbent can be described diagrammatically as shown earlier in Fig.(75b) and (75c). For $t < \tau_b$ the temperature profile within the bed can be described as shown by Fig.(77c); and the temperature profile for the adsorbate/regenerative agent leaving the bed as a function of time can be shown by Fig.(77b). In these two diagrams the superheated steam has a temperature of θ_s' and a saturation temperature of θ_s , whereas the bed initially has a uniform temperature distribution of θ_a . It will be seen that shortly before breakthrough occurs the temperature begins to rise due to heat conduction within the bed in the direction of regenerative fluid flow. At breakthrough the temperature climbs rapidly to the saturation steam temperature, and thereafter only slowly to the asymptotic value of the superheated steam temperature. The curve shown in Fig.(77a) illustrates the variation of the overall rate of adsorbate recovery with time. Prior to breakthrough the rate is zero, climbing slightly as condensates drain out of the bed, until at breakthrough the rate climbs rapidly and linearly (indicating a constant amount of adsorbate recovered per unit time). The overall rate then

passes through a maximum and begins to decline as the amount of adsorbate recovered in successive time intervals falls off. Here again is illustrated the law of diminishing returns in action, with the amount desorbed per unit mass of steam supplied falling ultimately to zero. It is necessary to decide how long to regenerate as the recovery of adsorbate falls with time. Full consideration as to determine how long is given in Chapter VIII. For the purposes of the later work of this Chapter it is sufficient to assume that at the end of regeneration the bed has a fairly uniform high temperature, and a fairly uniform distribution of water held within the bed.

This description of the regenerative process can be readily handled by the model formulation of Chapter IV with the inclusion of a term that relates the heat transferred from the bulk fluid to the wall and to the particles with the amount of steam necessary to supply such heat as superheat and heat of condensation. It is difficult to express in any meaningful analytical way the amount of water that drains from the bed and hence the amount of water that remains within the bed. The work of Chapter VII and the reasoning applied earlier in Chapter IV have to a large extent removed the requirement of analytical precision for this aspect. However, until items such as these are resolved complete description of the regenerative operation will not be possible. Fortunately this difficulty has not hindered this work, for as will be shown in Chapter VII and used in Chapter VIII a complete description of this part of the process is of secondary importance to the results of the adsorption operation. It is only necessary for this part of the work to indicate that a uniform high temperature within the bed could be obtained at the end of regeneration; and that the value of γ_b is largely independent of the adsorbate loading at the end of the previous adsorption period.

Both these assumptions are logically arguable by considerations similar to those which produced Fig.(75) and Fig.(77); and have been experimentally verified as described in Chapter VII.

The above describes the use of superheated steam alone without external heating to perform the regeneration. It is possible to carry out regeneration by a combination of external heating and superheated steam at different pressures or by use of external heating alone and subjecting the adsorbent bed to different pressures. Some very early work by Berl and Schwebel (56) concluded that the best technical procedure was a combination of external heating and steam under vacuum. The external heating would take care of heat losses to the surroundings, a reduced pressure would aid the desorption process; and the passage of steam at zero inlet adsorbate concentration would effectively sweep away the adsorbate. No doubt this is the best technical procedure measured in terms of ease of adsorbate recovery, however, the provision and running of vacuum equipment would be costly if adsorption were carried out at atmospheric pressure or above. The external heating medium in supplying heat to the bed would greatly increase the thermal content of the container wall. This heat would have to be removed before efficient adsorption could take place. Hence, the regeneration of fixed beds seldom uses these sophisticated procedures.

The general method of regeneration described above using steam as the regenerative medium does, however, have the side effect not present in 5.2, namely that of water within the bed at the end of regeneration; and ways must be found of dealing with this water.

5.3.1 Two or Three Cycle Operations.

As described briefly in 5.2 it is possible to use a cooling stage between the regeneration and adsorption periods. Use of such a

stage on a steam regenerated bed would not only cool the bed, but also remove by evaporation some or all of the water present within the bed. Clearly, if the adsorbate is to any large degree capable of being hydrolysed then it would be unwise to use steam as the regenerative medium in the first place. However, it is often cheaper and more convenient to use steam than any substitute. Hence, adsorbates such as ethyl acetate will undergo slow decomposition to acetic acid and ethanol. The ethyl acetate is not only lost; but the acetic acid produced gives corrosion problems. It would in this case be advisable to dry the bed prior to adsorption of ethyl acetate in an effort to reduce the acetate/water contact time. On the other hand, for adsorbates such as ethanol and other hydrophilic compounds the presence of water will tend to enhance removal of the adsorbate by solution in the water. Here it might be unwise to dry the bed, if the poorer adsorption at higher temperatures is more than offset by solution in the water present. As the bed would cool and dry in the two cycle operation anyway as a result of the passage of cool adsorbate laden carrier fluid, these effects of hydrolysis and solution would be but temporary.

For the general case where the adsorbate is unreactive with water, then a comparison between the two and three cycle system is readily available. Providing the water does not significantly reduce the adsorption capability of the adsorbent, then the difference is solely one of temperature effects. Fig.(78) illustrates these differences, the temperature and concentration profiles being for $z = h$ in all cases. The temperature profiles for cooling and steaming are identical for both the two and three cycle case. The exit adsorbate concentration profiles are identical towards the end of the adsorption period, but for the two cycle case the total adsorption period is slightly longer due to its initially lower overall rate of adsorption (a longer time

therefore being required to reach the same average adsorbate loading as the three cycle case). The time difference between complete cycles for the three and two cycle cases is shown by Δt . These diagrams are illustrative only; and represent equally sized and operated adsorption units. It is also assumed that while one adsorber is steaming or steaming plus cooling, a similar unit is performing adsorption duty. If the time taken to regenerate and cool in the three cycle system is longer than the adsorption time, then a third adsorption unit would be required to maintain continuous operation. If the time taken to regenerate in the two cycle system is longer than the adsorption time then again a third unit would be required. Changes in the feeds and/or the operating conditions can possibly remove the need for the additional units described above. Each application must be considered separately.

So that if the same number of units are required for both two and three cycle operations, the two cycle system would carry out more adsorption and regeneration periods than would the three cycle system for the same total time. This means that the two cycle system is subject to more rapid changes in temperature. These thermal "shocks" can lead to a more rapid degradation of the adsorbent.

The main difference between the two and three cycle systems described below is essentially the factor that predetermines which cyclic system is more suitable for a particular application. It is essentially a balance between the different capital and running costs of the two and three cycle system. The three cycle system requires that equipment (piping, valving, etc.) be provided to carry out the cooling operation. The two cycle system requires none of these provisions. The three cycle system requires that auxiliary fans and control operations be carried out for the cooling period. These are essentially capital

costs, and are not present in the two cycle system. However, the two cycle system has higher operating costs associated with the initial loss of adsorbate from the system. If this initial loss is likely to be at concentrations that either exceed the legal discharge limit or are offensive to those in the discharge area, then it is necessary to perform some cooling operation on the bed. If the initial discharge concentration is acceptable, then a strict cost comparison can be carried out. In general terms it can be seen that for a costly adsorbate, then cooling would be advisable and hence a three cycle system used. If adsorbate loss costs are small then a two cycle system can be used. A detailed comparison will of course depend the particular system under consideration, and is beyond the scope of this work. For the purposes of the remaining part of this work a two cycle system will be considered as described in more detail in Chapter VII.

5.4 The Regeneration Effects on Cyclic Operations.

From Fig.(78) it can be seen that for a two cycle system the effects of regeneration influence at least the initial part of the adsorption period. If the adsorption cycle is of short duration then the effects of regeneration may well influence most of the adsorption period. For example by reference to Fig.(78), if the horizontal portion of the effluent concentration profile is completely eliminated then the profile becomes essentially "U" shaped. The effects of regeneration are therefore not completely removed before the bed becomes saturated. Here the adsorbate lost cost becomes a major factor in efficient operation of the overall system. Although the detailed implications of this effect are left to Chapter VIII, it is convenient to review some general effects here.

One effect of the regenerative process will be to reduce the

adsorbate loading within the bed to give some non-constant (with respect to z) loading at the end of regeneration. It is not usually economically feasible to completely regenerate the bed, due to the law of diminishing returns operating on the regeneration process. Similarly, at the end of the adsorption period the adsorbate loading is unlikely to be the smooth profile that is produced analytically under the assumptions of isothermality and an initial zero adsorbate loading. These general shaped profiles may be illustrated by Fig. (79a); and are useful in illustrating the concept of the average adsorbate loading \bar{N} , where at any point in time \bar{N} is defined as $(1/h) \int_0^h n \cdot dz$. It is now more convenient to discuss the effects of regeneration in terms of this average adsorbate loading. For the purposes of the work described below the term "adsorbate loading" will be used to mean the average adsorbate loading defined as above. The typical variation of the adsorbate loading with time during the adsorption period can then be described as shown by either Fig. (79b) or (79c), depending on the shape of the profile of the outlet adsorbate concentration in the bulk fluid.

Zone I From the start of the adsorption period not all the adsorbate is removed, however, the rate of removal improves with time. Thus the adsorbate loading increases with successively larger values of $d\bar{N}/dt$.

Zone II The exit adsorbate concentration has now fallen to a constant value, so the amount removed remains constant. Thus the adsorbate loading increases linearly with time.

Zone III Here the exit adsorbate concentration begins to rise until its breakthrough value is reached and the adsorption period is terminated. Thus the adsorbate loading increases with successively smaller values of $d\bar{N}/dt$, as less adsorbate is removed per unit time interval.

If the exit adsorbate concentration profile does not illustrate this level period (i.e. the profile is "U" shaped) then as shown by Fig. (79c) only Zones I and III are shown in the adsorbate loading/time relationship. If the exit adsorbate concentration profile is known or can be drawn from suitable measurements, then the variation of \bar{N} with t can be simply described as $\bar{N} = \bar{N}_0 + \int_0^t (C_0 - c) \frac{V_a}{h} dt$, where c is exit adsorbate concentration and \bar{N}_0 is the initial adsorbate loading.

Having described in some detail the adsorption period, it is now possible to consider the effects of the regeneration operation on the combined adsorption/regeneration processes. The principles used in the above descriptive section of this work will be used again in Chapter VIII to illustrate optimum procedures for the operation of adsorption systems. However, for present purposes it can clearly be seen that the regeneration operation affects not only the value of \bar{N}_0 but also the value of C_0 (see Fig. (78b)). In general terms regeneration for longer periods will reduce the value of \bar{N}_0 ; but the increase in the bed temperature and the presence of additional moisture (possibly moving further from the particle surface into the intraparticle space) will increase the value of C_0 . As these two factors are obviously inter-related, it should be possible in some general way to describe their interaction. Although the precise nature of the interaction depends upon the nature of the adsorbate, adsorbent and regenerative fluid conditions, this author feels that the following description is generally applicable.

Consider first several consecutive adsorption and regeneration cycles; but that adsorption is terminated when the adsorbate loading reaches some constant specified value. The regeneration time is then altered so that different values of \bar{N}_0 are achieved. For this system to produce meaningful results it is necessary to stipulate that all the

adsorption cycles are of sufficient duration to completely dry and cool the bed, so that the effects of regeneration are not present for the full adsorption period. The operations of adsorption and regeneration can now be expressed in terms of a single parameter, the adsorbate loading \bar{N} . The above series of adsorption regeneration operations can now be described by Fig. (80). To satisfy the above requirements it is necessary to perform a certain minimum amount of regeneration to \bar{N}_{lim} so that the smallest value of C_e will be greater than the minimum exit adsorbate concentration by several orders of magnitude. The concentration profile beginning at \bar{N}_{lim} then falls to the equilibrium concentration C_{eqvil} (at a loading of \bar{N}_{eqvil}) momentarily before rising again as breakthrough occurs. If regeneration is carried out so that the adsorbate loading is reduced from \bar{N}_{lim} to some general value \bar{N}_0 , then the resulting concentration profile has an initial value of C_e that lies on the path illustrated by Fig. (80). It can be seen that reducing the adsorbate loading beyond \bar{N}_{lim} requires successive increases in the time of regeneration. The smallest loading \bar{N}_{min} can be obtained under the conditions of the regenerative fluid only after prolonged steaming. As the law of diminishing returns is operating the reduction of \bar{N} by a fixed amount requires more steam as the value of \bar{N} decreases. Hence, the locus of C_e from C_e for $\bar{N} = \bar{N}_{lim}$ to C_e for $\bar{N} = \bar{N}_{min}$ shows that the value of C_e rises slowly at first as regeneration is "easy", but rises steeply as the adsorbate loading is reduced to \bar{N}_{min} . All the concentration profiles should fall to C_{eqvil} at some adsorbate loading less than \bar{N}_{eqvil} ; and will then rise as breakthrough occurs. All the concentration profiles should be of the same shape for loadings greater than \bar{N}_{eqvil} , for each adsorption cycle at this loading meets the same bed conditions.

Consider now what would occur if the above requirements were again used, with the exception that regeneration produces adsorbate loadings greater than \bar{N}_{lim} at the end of the regeneration period. The value of C_g would be reduced further from its value at \bar{N}_{lim} ; but the concentration will now not fall to C_{equl} . It is, therefore, necessary to include the requirement that during the adsorption period, the bed is cooled and dried by the time \bar{N} reaches \bar{N}_{tot} . This requirement then enables the several adsorption/regeneration cycles to be considered separately, so that Fig. (81) is applicable. The profiles are all now "U" shaped; but the requirement of producing a cool dry bed means that the concentration profiles should follow some or all of the profile for $\bar{N} = \bar{N}_{lim}$ where the concentration rises during breakthrough. The limiting condition is reached when $\bar{N} = \bar{N}_{clim}$, as this profile now becomes identical with the profile for \bar{N}_{lim} only when $\bar{N} = \bar{N}_{tot}$. It is truly limiting in that if regeneration produced loadings greater than \bar{N}_{clim} , then the assumptions made above would not be satisfied. Hence, it would no longer be possible to consider successive adsorption/regeneration cycles separately. It is not necessary to consider adsorbate loadings greater than \bar{N}_{clim} , as all real operating two cycle systems require that either the bed be well regenerated for re-use or large quantities of adsorbate are recovered. To satisfy either of these requirements implies that the adsorbate loading must be significantly reduced during regeneration, so that the descriptions of the system given above are applicable.

It will be shown in Chapter VIII how the information of Figs. (80) and (81) can be used in economic evaluations of the system. The work of this Chapter will be completed by some considerations as to how information on the locus of C_g might be obtained. Clearly it is

possible to produce the C_e vs \bar{N} relationship by either analytical or practical means. Analytical means such as those described in Chapter IV could handle the operation of regeneration successfully in as far as determination of the values of \bar{N}_0 for various regeneration conditions would be possible. However, as mentioned earlier in this Chapter, there is no analytical procedure for determining the moisture held within the bed at the end of regeneration. The presence of moisture was handled by the model formulated in Chapter IV only on the assumption that it did not interfere with the adsorption process. The only interference with the adsorption process was the adsorbent temperature. Clearly in the general case this assumption is not valid, so the analytical procedure fails. However, if this assumption were valid, then it would be possible to predict the value of C_e for various values of \bar{N}_0 . Consider though the complexity of the model and the number of parameters that have to be specified before an analytical solution can be produced. If temperature was the only parameter of interest it would be possible (and simple to perform) to take a sample of the adsorbent heated to a known uniform temperature, and with a known adsorbate loading, and pass the adsorbate laden carrier fluid through a bed containing the sample. The exit adsorbate concentration of the carrier fluid as it emerges from the bed would then be the desired value of C_e . The above description is not rigorous, but it serves to illustrate the point that practical work with adsorbent/adsorbate systems is far easier to perform (and likely to be more applicable) than analytical treatment of the same systems. Chapter VII describes the experimental work carried out by this author on several systems; and verifies the general conclusions to the arguments presented in this Chapter.

C H A P T E R V I

No theoretical treatment of the adsorption phenomena in practice can be considered complete without some discussion of the work of other authors in their attempts to relate theory and practice. Indeed it is fortunate that the theory has so many aspects and the practice so many separate applications for there is no shortage of published work on these aspects. It is difficult to choose suitable work for discussion in any attempt to be both comprehensive and particular.

Early investigators were concerned primarily with expressing the equilibrium relationship between adsorbate on the adsorbent and adsorbate in the free state. There is the evidence of Danby et al. (21) however that indicates that interest was also shown in other practically important relationships determined for systems typical of the time, and capable of comparison with theoretical predictions. This refers of course to the variation of the exit adsorbate concentration with time, bed length, inlet flow rate and inlet concentration. Later investigators turned naturally to more sophisticated pursuits in expressing adsorption equilibrium relationships as well as further elucidation of the influence of adsorbent properties on the adsorption process. In coming completely up to date attention is now focused on the whole range of theoretical considerations in an effort to precisely tie theory and practice together by including details of the design and operation of adsorption systems.

6.1 Basic Adsorption Data

Although a certain amount of rationalisation of published work has taken place recently there still exists a need to be specific when single systems are considered. It is hoped to present below some of the more relevant results relating to adsorption systems of the type considered in this work.

6.1.1 Adsorption Isotherms

Adsorption isotherms for low molecular weight volatile organic

compounds have been determined by several authors. The adsorbates ethyl acetate, toluene, benzene and carbon tetrachloride were used in the practical work described in later Chapters of this work. In all cases the adsorbent was activated carbon. Pearce & Hanson (57) found that the adsorption of ethyl acetate at temperatures between 0° and 76°C can be predicted by a Langmuir type adsorption isotherm at pressures no greater than 200 mm Hg. Dubinin & Timofeev (58) as well as McBain et al. (59) also found Langmuir type adsorption isotherms for toluene as did Josefowitz & Othmer (60) for benzene. The adsorption of carbon tetrachloride was studied by Danby et al. More recent work by Thomas & Qureshi (61) and Thomas & Lombardi (62) has relieved this author of determining the properties of the adsorbents used in the systems described in Chapter VII of this work, and their behaviour towards some of the above adsorbates.

It is no longer necessary to produce a valid model for use with experimentally produced adsorption isotherms. It is sufficient to fit an empirical expression to the regions of the isotherms of most interest, and use the fitted isotherms for computation purposes.

6.1.2 The Adsorbent

Sufficient generalisations on adsorbents have been made earlier in this work. This author is indebted once more to the work of Thomas and his associates (61,62) for listing the relevant adsorbent characteristics. Turuizumi (63) has stated that carbon prepared from coconut shells has a tridisperse pore size distribution with maximum diameters of 15° , 100° and 10000 \AA . Such a carbon would show the rate of adsorption changing with time in three steps for non-polar gaseous adsorbates ($0^{\circ} - 20^{\circ}\text{C}$, 1atms pressure). This change in the rate of adsorption would not normally be detected in any of the adsorption systems described below.

6.1.3 The Adsorption System

Where theoretical considerations are so complex it is not surprising that many authors have used small scale adsorption systems to determine

parameter values for use in theoretical models. Such experimental systems have also found use in determining the effects of changes in the parameters on the system performance. Experimental work can be divided into two sections.

- (a) Where it is not required to elucidate the adsorption mechanism that is rate controlling, usually because the mechanism is known. Dedrick & Beckmann (64) were able to show the effects of varying the inlet adsorbate concentration, the adsorption temperature, and the adsorbent particle size for the adsorption of a single organic compound from dilute aqueous solution onto activated carbon. Smith et al. (65) using a similar system showed the effects of variation of the adsorbent pore structure. In both systems it was known that the rate of transport within the adsorbent was controlling, although precise mathematical expression of this fact was not necessary to aid the experimental work.
- (b) Where it is required to elucidate the adsorption rate controlling mechanism. Masamune & Smith (66) used the adsorption of ethyl alcohol vapour from a helium carrier onto activated alumina to illustrate the effect of particle size and adsorption temperature on the overall adsorption process. Talbot (67) assumed that the surface film was controlling the non-isothermal desorption of ethylene from a moving bed of activated carbon. The value of the mass transfer coefficient was then determined as was its variation with temperature.

Finally there are those experimental systems where an effort is made to do more than just measure parameter values. A valuable piece of work carried out by Jones (68) attempted to determine the most efficient physical arrangement of the adsorption bed for a system under a particular set of flow conditions. This work simply varied the length and diameter of beds packed with different sizes and shapes of adsorbent particles.

Once these basic physical data are available it is next desirable to shed light on the rate controlling process if this is not known.

6.2 Elucidating the Adsorption Mechanism

The most commonly used adsorption mechanisms have been described in Chapter I of this work. In all some twelve cases were possible, but most authors have tended to restrict their investigations to a single mechanism. However, Kostecki et al. (22) used six possible expressions to calculate the adsorption rate coefficient from data produced by the liquid phase adsorption of water from benzene on activated alumina. Of more relevance is the work of Thomas & Qureshi (61) on the isothermal adsorption of low concentrations of toluene onto active charcoals in the region of 100°C. They showed that surface adsorption and mass transfer within the porous structure of the adsorbent are important and can only be ignored when the adsorbent particle size is less than 0.08 cm in diameter. The importance of the particular adsorbent is clearly shown by Shen & Smith (69) with the adsorption of benzene and hexane on silica gel at 130°C. Here the rate is controlled by intraparticle diffusion for particle diameters as small as 0.000575 cm. Surface diffusion was found to account for more than 90% of the intraparticle transport. This division of the intraparticle transport processes has also been observed by Masamune & Smith (9) for particles of porous glass larger than 0.01 cm when adsorbing nitrogen from a helium carrier. Diffusion in the gas within the pores is thus clearly established as offering less resistance to the transport of adsorbate than surface diffusion (also called surface migration).

For small particles at low adsorbent temperatures Masamune & Smith (66) concluded that the overall rate was determined by the process of physical adsorption at the particle surface. However the use of very small particles in an industrial system is usually ruled out on the grounds of excessive pressure drop across a bed of the required amount of adsorbent.

Further work by Jones (70) with industrial sized carbon adsorbent particles discusses four possible rate controlling mechanisms for the adsorption of benzene vapour from air at 25°C. It was concluded that

diffusion of vapour into the particle as the rate controlling mechanism gave the best description of the observed results. The adsorption mechanism for the systems considered in this work is thus apparent.

However in Chapter II it was concluded that these intraparticle effects could be represented by use of suitable parameter values for other non-intraparticle mechanisms. Here lies the dilemma in the present state of knowledge of adsorption systems. It is certainly more valid academically to determine precise values for diffusion coefficients and use them in the correct model of the system. Unfortunately the need to set up the mathematical solution in terms of a mesh for bed distance, particle radial distance, and adsorption time produces a costly computational solution if the heat effects are also to be included. Particular reference should be made on this point to the work of Rimmer & Bowen (71). The cost of obtaining such a solution for industrial operating systems has thus hindered the application of theory to practice and reduced the practical value of the theoretical investigations. It is hoped that the earlier work of this author presented in Chapters I to IV goes some way towards improving the practical value of theoretical studies. However it is truly necessary to consider the impact to date of theoretical work in the practical design, construction and operation of adsorption systems.

6.3 Adsorption Theory in Practice

Several review articles with a simplified description of the use of adsorption theory in practice have appeared from time to time both in England and the U.S.A. The work of Carter (72,73) and Barry (74) has often been published in this form. Detailed description of particular industrial operating units are not surprisingly rarely published; but are usually short on details when they actually appear. Articles like that of Robson (75) are no longer available to the general reader. The description of a fluid adsorbent bed for the removal of volatile organic vapours given by Avery & Boiston (76) is more typical of published information. Advice is offered on

the choice between a static and fluidised bed, and some of the factors that affect performance are considered; but overall the article is short on precise detail.

When however the author can blend theory and practice to produce a none too specific article some useful generalities can appear. Harris (77) describes simply the purification of liquids using granular activated carbon and taking into account operating factors of the system and laboratory evaluations to decide on the most suitable adsorbents. The work of Brooking & Walton (78) with molecular sieve adsorbents describes regeneration systems and deals non-specifically with the industrial useful factors of operating time, bed life, flow changes, pressure drop, and operating utilities. The present large scale use of adsorption systems for gas drying is reflected in the literature, whether it is the purely theoretical design process of Gregory (79) or the more practical adsorbent selection aspects of Colley (80).

Regretably adsorption theory still finds little direct application to industrial systems. The words of Coulson & Richards (32) are only too apt when considering the process design of industrial sorption equipment. The complexity of the phenomena occurring in non-isothermal equipment has led to widespread use of empirical design methods. They do of course present their own empirical design methods and make use of the concept of 'capacity at break point'. This concept as they rightly say does appear elsewhere in other guises. It is a pity perhaps that the simplicity of the concept and its application hides more worthwhile theory. Collins's (81) standard design practice uses the 'length of unused bed' and the 'equilibrium section' concept. Whilst Webber (82) prefers the use of 'rate of advance of adsorption front' and gives brief details on its use in design procedures, Mc Carthy (83) for his work using the comparable concept of 'mass transfer zone' did not consider it a good design tool. It is no wonder that such generalised simplifications are not universally applicable. Yet in all fairness the

theoretical developments to date do leave some relevant practical aspects uncovered.

Adsorption from high adsorbate concentration carrier fluids is a single case where there exists a possible future use of adsorbents. Here according to Bowen (84) the relevant theory and available mathematical studies break down, although the theory can be applied to the concentration front at low values as the front moves through the bed. The associated experimental work of Bowen & Donald (85) considers the effects of the adsorbent structure on high concentration feeds when factors such as capillary condensation due to multimolecular adsorption are likely to be present and further confound theoretical representation

When difficult practical considerations have been minimised and the theory greatly extended there is still a future for the practical application of adsorption theory. The analysis by Needham et al. (86) of a large amount of dynamic adsorption data using a number of the existing mathematical models gives some idea of the future trends. Although many models could be used to fit the data to varying degrees, the incompatibility of a model with proven physical realities makes the ability of the model to fit the data of empirical significance only. However as Rimner & Bowen (71) conclude it is not necessary to set up rigorous equations as a prerequisite for the design of fixed bed adsorbers if academic satisfaction is neglected. The publishing of work such as that of Chen et al. (87) covering the full range of limited theoretical model building with small and large scale experimental studies, and hinting at operational optimisation studies is surely indicative of future advances to be made.

The further contribution of this author to future advances is concluded by consideration of aspects that have appeared in print only too frequently, but which have singularly failed to be rigorously defined. How does one know when the best adsorbent is in use on an industrial system? How

should one determine what is the best operating policy and how should proposed changes in the operating procedure be evaluated? Solutions to these problems are offered in later Chapters of this work. As an introduction (and in common with other authors) the practical systems used by this author and some relevant results are first presented.

C H A P T E R VII.

For practical aspects of this work the author had access to three adsorption systems. A detailed description of the systems and the results obtained from them are given below in 7.1, 7.2 and 7.3. As the systems had several aspects in common, it is more convenient to describe these similarities here and deal with their differences later. The three systems were :

- a) A large scale industrial system for the recovery of mixtures of toluene and ethyl acetate vapours from warm, moist air.
- b) A pilot scale package adsorption unit that could be used to remove any volatile adsorbate from a carrier of air.
- c) A small scale experimental unit where the effects of different adsorbents, adsorbates and operating conditions could be investigated.

The adsorbent used in all three systems was activated carbon in the form of granules supplied by Sutcliffe Speakman Ltd. The adsorbent used for the industrial unit^{***} was changed from time to time, whereas the package unit was supplied with adsorbent 208 C (a coal based adsorbent). A range of adsorbents of differing mesh sizes and origins (including 208 C) were available for use on the experimental unit, although all were activated carbons.

The method of regeneration for all units was to pass live steam under pressure through the adsorbent in the reverse direction to that of the adsorbate laden air flow. The steam and recovered adsorbate(s) were then condensed by heat exchange with cold water and the condensates fed to a separate vessel. The adsorbates were separated from the water by density difference. Due to the significant solubility of ethyl acetate in water, the industrial unit processed the aqueous phase from the

*** Authors Note: The terms industrial unit, package unit and experimental unit will be used in this text to denote the systems described above under a), b) and c) respectively .

separation operation to remove further quantities of adsorbate. This operation was not carried out with the other two units. On the industrial unit the organic phase from the separation operation was contacted with a solid drying agent before being returned to storage for eventual re-use. This operation was not carried out with the other two units.

All units operated with fixed adsorbent beds. The industrial unit used a bed of annular construction with a cylindrical section on top of the annulus (see 7.1). In this way approximately six tons of adsorbent were used to produce a maximum bed depth of 18 inches and a large cross-sectional area. The other two units had cylindrical beds. The amount of adsorbent in the package unit was not varied, although it was possible to do so with some difficulty. The amount of adsorbent and physical dimensions of the adsorbent bed could be changed at will on the experimental unit.

The adsorbates used on all systems were volatile organic liquids at 20°C, 760 mm Hg. Operations on the industrial unit were restricted to a mixture of toluene and ethyl acetate. The adsorbate for the package unit had to be non-combustible (see 7.2) so carbon tetrachloride was chosen. Although there were no restrictions on the adsorbate for the experimental unit only benzene, ethyl acetate and toluene were separately used. Benzene was used initially as little work had been published at that time on the other adsorbates. While mixture of ethyl acetate and toluene would have been representative of the industrial system, the theory of multiple adsorbates is not well understood and problems were associated with ethyl acetate in the presence of moisture. For these reasons ethyl acetate and toluene were used separately. It would have been advantageous to use carbon tetrachloride on the experimental unit, however, the detection device used by the author did not register the presence of the

carbon tetrachloride or other non-combustible materials. The work on the package unit thus assumed secondary significance compared to work on the other two units.

7.1 The Industrial Unit

The industrial unit was located on the premises of British Sidac Limited (St. Helens Works), who were kind enough to allow the author and several other post graduate students access to operating plant. Some results of work carried out at this time have already been published. The work of Koo (88) is of particular relevance to this work. At the St. Helens Works, British Sidac produce cellulose film from a raw material of processed wood pulp by a series of chemical processes. The final stage in these processes is to spin the cellulose into a continuous film some six to eight feet wide. This operation takes place in a spinning machine and the resultant film wound onto a former is called a mill roll. The cellulose film can be used in this form, although its properties and uses can be improved by coating one or both sides with a suitable polymeric material. It is the coating process that is of direct relevance to this work. The uncoated mill roll is passed through the coating machine where the coating substance dissolved in suitable solvents is spread evenly across the film. The solvents are evaporated into a stream of air moving counter-currently to the movement of the film, and the solvent laden air (SLA) removed from the machine. The moisture content of the film is corrected by contact with live steam. The coated film is then cooled and rewound onto a former. A diagram of the spinning and coating processes is shown by Fig. (82). As the air is passed the length of the coating machine it carries the steam used for moisture correction as well as the evaporated solvents when it leaves the machine.

The economics of the process demand that the solvents used in the

coating stage be recovered as far as possible. For safe operation of the coating process it is necessary to pass enough air through the coating machine to produce a solvent content in the exit stream less than the lower explosive limit of the particular solvents. In this particular unit 50 to 70% of the lower explosive limit (LEL) was aimed for. This produced a SLA stream with a maximum solvents content of about 1% by volume.

At the St. Helens Works the cellulose film was coated either in a horizontal coating machine (described by Fig. (82)) or in a vertical coating tower. In both operations the same results were achieved. The SLA from the horizontal machine was fed to a static fixed bed adsorption plant manufactured by Sutcliffe Speakman Limited, whereas the S.L.A. from the vertical tower was fed to a rotating fixed bed adsorption plant manufactured by OECA Limited. There were provisions to cross-link these arrangements; but these were not used during the course of this author's investigations. The solvents were different in each coating plant as a different polymeric coatings were used. A description of the general operations involving a vertical coating tower is given by Inskeep and Van Horn (89) for the production of cellophane. A rotating fixed bed arrangement for adsorption duty is described with a diagram in Coulson and Richardson (32), as is the general layout out of the static fixed bed arrangement described below.

British Sidac operated four horizontal coating machines (machines 1, 2, 3 and 6) using an ethyl acetate/toluene solvent mixture that was fed to two separate plants (Plant A and Plant B) consisting of three adsorbers each. The arrangement is shown by Fig. (83). Each plant operated independantly and continuously using constant adsorption and regeneration cycle times. All valve changes, etc., were operated by pneumatic signals. The timing of the signals was done by an electric drive operating through a

gearbox on to a shaft with a set of cams . It was possible to alter the adsorption cycle time by selecting different gear ratios. As only a small number of gear ratios were possible, the timing could not be varied either continuously or over a wide range. The regeneration cycle time was permanently fixed at half the adsorption cycle time, so that when Adsorber 1 began regeneration, Adsorber 2 was mid-way through its adsorption period and Adsorber 3 has just begun adsorbing. When Adsorber 1 completed regeneration, Adsorber 2 was completing its adsorption period and Adsorber 3 was mid-way through its adsorption period. The plant thus operated a two cycle system as described in Chapter V, with two adsorbers in use for adsorption duty at any particular time.

The mixed SLA from two coating machines was piped to the associated adsorption plant. The SLA passed through a filter and the primary cooler before entering the adsorber building then was passed through the fan, and was delivered through the secondary cooler to whichever two adsorbers were in their adsorption cycle. A single fan was thus used to draw the SLA from two coating machines. The SLA ducting was equipped with slide valves so that a coating machine could be isolated from the fan if desired.

The solvent free air (SFA) emerged from the adsorbent in the centre of the annular bed, was ducted under the floor and vented to atmosphere from the roof of the building. An illustration of the bed shape and some relevant dimensions are shown in Fig.(8₄).

Steam for regeneration was fed into the centre of the annular bed and passed through the adsorbent into the space between the exterior adsorbent support wall and the wall of the container. Any condensate formed in this space was drained away. The steam/adsorbate vapours displace the liquid in the seal line and pass into the condenser and condensate cooler. The liquid mixture passes into the seal tank and over-

flows into the pump tank where it is pumped to the gravity settler. This arrangement is illustrated in Fig.(85) for a single adsorber; but all three adsorbers in a Plant were connected to the one system for handling the regeneration products. An expanded view of the base of each adsorber is shown in Fig.(86). When the regeneration ends, reduction in the steam pressure as the main steam valve closes causes the seal line to be re-filled, so that during adsorption no SLA is carried over into the regeneration system.

7.1.1 Measurements taken on the Industrial Unit

It is possible to measure three quantities on the industrial unit that are of importance to this work, these are :

- a) The temperature near the exterior surface of the adsorbent bed. This would indicate the bed temperature near the inlet face during adsorption and near the exit face during regeneration.
- b) The adsorbate level in the SFA leaving the adsorber. This can be done for each individual adsorber.
- c) The relative amounts of adsorbates and water produced on steaming each adsorber. This indicates the performance of the adsorber during regeneration.

The first quantity is recorded continuously on circular charts (24 hour per revolution) and is also shown on a meter mounted on each adsorber. As the meter gives more easily read values, temperatures shown by the meters were noted by the author at short time intervals during the regeneration cycle of each adsorber. Typical temperature versus time profiles are shown by Fig.(87) and Fig.(88) for the regeneration period. It can be seen that the steam breaks through the bed after 5-6 minutes; but that the bed does not attain a relatively uniform high temperature until

some 10 minutes from the start of regeneration. As the total regeneration time is 20 minutes (fixed by the adsorption cycle time) a substantial amount of the steam used for regeneration is required to heat the bed to its regeneration temperature. There is some evidence of a slight amount of superheat present in the steam. The unit was designed for operation using 15 psig steam; but was actually operated with 5 psig steam during the author's investigations. The saturation temperature of 5 psig steam is c. 108°C , whereas bed temperatures of 106°C to 113°C were measured.

It was also possible to produce temperature versus time profiles for the adsorption period using the same procedure as above. Three distinct types of profile were found, although Type I (see Fig.(89)) was by far the most common.

Type I : Here the temperature falls from 110° to 65°C in the first 10 minutes of adsorption, to 55°C in the second 10 minutes and levels off at 50°C after 40 minutes when the adsorption cycle is terminated.

Type II : (See Fig.(90)). Here the temperature falls from a maximum temperature of 106°C to 55°C in the first 10 minutes of adsorption, to 45°C after 30 minutes adsorbing and then shows a sudden drop to 40°C by the time the adsorption cycle is terminated.

Type III (See Fig.(91)). Here the temperature profile follows closely that of Type II, although starting from a maximum temperature of 112°C . Thus any effect of differences in the initial temperature seems to be ruled out. However, after adsorbing for 30 minutes the temperature rises again to reach 50°C by the time the adsorption cycle is terminated.

These differences in profile shape were noted for all six adsorbers over a period of time under different operating conditions; but with a

SLA inlet temperature of the order of 35°C . This author believes that these profiles illustrate variations in the conditions of the SLA. With reference to Fig. (83) it is seen that the SLA for each adsorption plant comes from two coating machines. Non-constant operating conditions of the coating machines, e.g. when the film breaks or when coating mixes are changed, will produce variations in the solvent content of the SLA. The air flow rate and the SLA inlet temperature are unlikely to vary greatly as the coating machine is not isolated during these short term stoppages. Indeed it is necessary to maintain the air flow through the machine to prevent the formation of a hazardous atmosphere within the machine. It is also necessary to maintain the temperatures and moisture levels within the machine in preparation for the next coating run. Hence, it is only the adsorbate level that is likely to change for periods of from 10 minutes upwards. It can be seen from Fig. (91) that in this case the Type III profile was produced only for a single adsorption cycle, earlier and later cycles showing a Type I profile.

It is now possible to describe the shapes of the three types of profiles in terms of the adsorbate level of the SLA. A Type I profile occurs under normal operating conditions where, during the initial cooling and drying, the temperature falls at a reduced rate due to the generation of the heat of adsorption. When the bed is dry adsorption is still taking place so that the heat of adsorption serves to maintain the temperature of the bed above the SLA inlet temperature. For Type II and Type III profiles the initial part of the adsorption period occurs under a reduced SLA adsorbate concentration. As there is less heat of adsorption generated then the temperature of the bed falls at a faster rate than for Type I profiles. In Type II at the latter part of the adsorption period there is a further decrease in the adsorbate concentration of the SLA, so that the bed

temperature drops towards the SFA wet bulb temperature. For the latter part of the adsorption period with a Type III profile there is an increase in the adsorbate concentration of the SLA, so that the heat of adsorption liberated increases the bed temperature. These effects of Type II and Type III behaviour will only display themselves clearly at the latter stages of the adsorption period, as up to this time they will be masked by the temperature effects the water being evaporated from the bed. It is therefore possible to conclude that under normal full load running conditions the temperature profile is reproducible and of Type I shape. The effect of the heat of adsorption in slowing the temperature changes in the bed during drying is clearly appreciable; so that under normal operating conditions it is not possible to cool the bed below some equilibrium temperature which is appreciably in excess of the inlet SLA temperature.

The second measurable quantity described at the beginning of 7.1.1 is the adsorbate level in the SFA. A small sample pipe was used for this purpose fitted to the side wall of the section of the adsorber shell that emerged beneath the adsorbent level. It was necessary to drain the condensation products from this line before the SFA could be sampled. The work described by Koo (88) using gas phase chromatography to analyse vapour samples should be referred to for further details and a comprehensive series of results obtained. This author used the portable MSA Combustible Gas Meter, described in 7.3 to measure the combined level of the adsorbates in the SFA as a check on the earlier work of Koo, and to establish the suitability of using the meter for this application. Two problems were encountered. The first (also found by Koo) was a difficulty in obtaining readings at the start of the adsorption period. The mixture of SFA and residual steam that is the initial sample does not make manual sampling methods very convenient. The second problem was that while the

combined toluene and ethyl acetate levels were measured by the meter, their value was for most of the adsorption time of the same order as the accuracy of the meter. The high adsorption efficiency recorded by Koo was thus verified. The portable MSA meter was found unsatisfactory for this work, although it is believed by this author that the principal used by the meter is satisfactory. The difficulty being the non-continuous application of the meter operation. This problem was successfully countered on the experimental unit by using a continuous recording device that operated on the same principle as the portable meter.

In order to illustrate the general nature of the SFA concentration profiles here, several of the values produced by Koo have been shown in Figs. (92) and (93). The curves shown in these figures have been drawn through the arithmetic mean points of the values for each of the several time points. They illustrate the general "U" shape of the curves; and give some idea as to the relative magnitudes of inlet and outlet adsorbate concentrations that are being dealt with. The lower level of values for Plant B does not reflect the performance of the adsorbers; but rather that coating machine 6 (see Fig. (83)) has a lower solvent production rate than coating machines 1, 2 and 3. It should be noted that the ethyl acetate is adsorbed more rapidly initially (possibly due to water solubility); but that at the end of the adsorption period the toluene is being adsorbed more rapidly. The adsorption time was fixed by determining when there was detectible amounts of organics in the SFA. The detecting instrument most commonly used was the human nose.

The third measurable quantity described at the beginning of 7.1.1 is the proportion of water and organics produced during regeneration. It was not possible to sample the regeneration products until they had been condensed and cooled. The presence of the liquid in the seal lines also tends to distort the true performance of the unit. The nearest point at

which liquid sampling could be carried out was where the contents of the seal tank overflowed into the pumping tank. When steam has broken through the adsorption bed the resulting turbulence and short residence time in the pipework means that the liquid samples taken are likely to represent the products of the regeneration operation. However, when regeneration ends most of the regeneration products will be steam with small amounts of adsorbates. This mixture will fill the seal lines, and settle out in the seal tank to form an upper organics layer and lower aqueous layer. Hence, at the start of the next regeneration the products of regeneration will first displace the liquid already present in the seal lines and so the overflow from the seal tank will have a high organics content falling rapidly as the lower aqueous layer is displaced from the tank. The level of organics will then rise again rapidly as the true composition of the regeneration products emerges from the seal tank. Hence, a plot of the weight ratio of organics to water in the overflow from the seal tank should show two peaks when plotted as a function of time. This was found to be the case as shown by Fig. (94). The curves were obtained from samples of the liquid overflow that were allowed to settle. The two layers were carefully separated and analysed by the staff of the analytical laboratory of the Chemical Engineering Department, U.M.I.S.T. to determine the composition of each layer. The components in each layer were then summed to give the total volumetric quantities of each component. Multiplication by the density of each component gave its weight in the total sample. The weight ratios of toluene and ethyl acetate then followed directly.

In Fig. (94) the vertical line A indicates the point at which steam first entered the adsorber. If a steam breakthrough time of 5 minutes is used, then the vertical line B indicates the time at which steam and

adsorbate begin to be condensed and so displace liquid in the seal lines. It would be expected that sometime within the interval A - B, due to condensate draining from within the bed before breakthrough, an adsorbate peak value should occur. This peak value should represent the composition of the upper organics layer that had begun to settle out in the seal tank. This is in fact clearly seen in Fig.(94). As more products of regeneration are condensed and displace liquid in the seal lines and the seal tank the adsorbate concentration falls; but rises again as the initial products of regeneration reach the overflow from the seal tank. The larger peak occurring some 12 minutes after regeneration begins indicates the composition of the initial products of regeneration. It can thus be seen that the system has a lag time of the order of 7 minutes. Close to the end of the regeneration cycle the flow of steam is reduced as the steam valve closes, and samples at this point were taken when there was very little overflow from the seal tank. In some instances there was no overflow at all. Compositions determined from samples taken at this time are therefore likely to be non-representative due to the small sample size. It is now possible to illustrate the general shape of the adsorbate level in the regeneration products by means of the curve shown dotted on Fig. (94). This curve is by way of illustration only, as the time lags and mixing effects of the industrial unit make it impossible to be determined precisely. As the shape of curves similar to those shown by Fig.(94) is of importance to the work of Chapter VIII, it was necessary to use another unit to produce the information. The package unit described below was found to be of most use in determining this information.

7.2 The Package Unit

This was supplied by Sutcliffe Speakman Limited to the Department of Chemical Engineering, U.M.I.S.T. and was used by the author for the

work described below, as well as forming part of an undergraduate teaching laboratory. The unit was designed to handle a fixed volumetric quantity of 250 c.f.m. of solvent laden air. Its adsorbate capacity was specified as a maximum of $\frac{3}{4}$ gallon per charge, using a normal solvent laden air temperature in the region of $85^{\circ} - 90^{\circ}\text{F}$. By way of comparison, the Industrial unit described in 7.1 had a design capacity of 50 gallons per charge from a SLA flow of 16000 c.f.m. at a temperature of $90^{\circ} - 100^{\circ}\text{F}$.

The package unit could be operated for any desired adsorption and regeneration time. Changeover between cycles was achieved by use of a manual control lever whose operation is described below. A diagram of the unit is shown by Fig.(95), and some dimensions of the adsorbent bed are given in Fig.(96a). Solvent laden air is drawn through a filter bag and air heater by the centrifugal fan which delivers the SLA to the adsorbent bed. The SLA flow enters the bed tangentially beneath the lower perforated adsorbent support and passes upward through the adsorbent. The S.F.A. flows through the open adsorber outlet valve and is discharged to atmosphere via a duct. There is no valve on the inlet SLA line between the fan and the adsorbent bed. When the adsorbate breaks through the bed the manual control lever is moved to bring the unit into its steaming cycle. In moving the manual control from the adsorbing to the steaming position the fan is stopped, the adsorber outlet valve is closed and the steam and water supply plunger valves are opened. At the end of the steaming cycle the manual control is returned to the adsorbing position. This action opens the adsorber outlet valve, closes the steam and water valves and starts the fan.

The SLA was generated separately and could comprise any volatile liquid as the adsorbate. It consisted essentially of a solvent feed

container and a solvent evaporator. A sketch of the evaporator is shown by Fig. (96b). It consists of a steam heated platen completely hooded and ready for connection by suitable trunking to the recovery part of the apparatus described above. The adsorbate liquid from storage flows through a normally closed solenoid valve that opens during adsorption in conjunction with the fan, and drips onto the heated surface. The Vaporised adsorbate is mixed with air drawn through the vents in the hood by the fan and passes through the top of the hood to the recovery apparatus. In the event of fan failure or shut down the adsorbate is automatically shut off. A fine control over the adsorbate flow into the evaporator was achieved by using a $\frac{1}{2}$ inch needle valve in place of the thermostatically controlled valve that was supplied with the unit. Under normal operating conditions the valve was set to deliver $\frac{3}{4}$ gallon of liquid in 15 to 20 minutes. This used only one-tenth of the heated platen surface; but ensured both that the adsorbate was readily vaporised and that no adsorbate splashed out through the vents in the hood.

The package unit was located in a flameproof area, and drew the air for the SLA stream from its surroundings. As the hood on the vaporiser was open to atmosphere it was deemed prudent to operate the heated plate using a low steam flow rate with a low adsorbate flow rate and non-combustible adsorbate. This immediately ruled out any small scale replication of the industrial unit either in terms of the adsorbates used or the adsorbate concentration in the SLA at inlet. Work is currently in hand to remove these restrictions and will possibly be reported elsewhere at a later date. It was, therefore, decided to use carbon tetrachloride as the adsorbate.

The adsorbent was regenerated by passing live steam at 20-25 psig, into the space above the adsorbent bed. After some 10 to 12 minutes the steam and desorbed solvent break-through the bed and are condensed by a

spiral copper cooling coil. The liquid regeneration products are discharged by gravity into the separation vessel, where the upper water layer and lower carbon tetrachloride layer can be run off continuously. It is necessary to fill this vessel before using the apparatus so that carbon tetrachloride fills the lower section up to its outlet level and the water layer occupies the rest of the vessel. Hence, the liquids serve as a seal when the SLA enters the bed during adsorption. During regeneration, as the liquid regeneration products displace their own quantities of organics and water it is possible to obtain an immediate measure of the products of regeneration. The problems found on the industrial unit in determining the composition of the products of regeneration are thus not encountered in the package unit.

7.2.1 Measurements taken on the Package Unit.

The adsorbate flow rate was adjusted as described above so that the adsorbent would become saturated for an adsorption time of 15 to 20 minutes. If traces of carbon tetrachloride were detected in the SFA before $\frac{3}{4}$ gallon of the adsorbate had been supplied then adsorption was terminated. The detection device was similar to the one used on the industrial unit. No great accuracy was required for this part of the work in determining the adsorbate content of the SFA. It was sufficient to know that the bed was saturated with adsorbent so that regeneration could begin. It was found that several adsorption periods were necessary before the regeneration operation began to recover significant quantities of adsorbate. This is a factor that should be classified prior to further work on this unit and the experimental unit. Where the design capacity is stated as $\frac{3}{4}$ gallon as was the case for this unit, this is the dynamic capacity of the adsorbent. That is the amount of adsorbate which, when adsorbed in excess of some minimum adsorbate loading, \bar{N}_{\min} can

be recovered by the regeneration operation. It is unlikely that N_{min} will be zero for a good commercial adsorbent, so that it is necessary to provide an initial loading (the static adsorbate loading) of adsorbate on the adsorbent before any adsorbate can be recovered. Hence while this static loading is being established successive regeneration operations will recover progressively greater amounts of adsorbate. This is clearly shown by Fig. (97) for four successive regeneration cycles 1, 2, 3 and 4 where approximately four litres of carbon tetrachloride were used for each adsorption cycle. In all cases the regeneration cycle time was kept at 20 minutes, so that the number of cycles necessary to achieve the static loading was not excessive.

When the bed had achieved its static loading conditions it was found that three litres of carbon tetrachloride could be adsorbed before breakthrough was detected. Successive adsorption and regeneration cycles were then found to give reproducible results when operated under constant conditions. In particular, the results of regeneration were as shown by Fig. (98) for successive cycles. It was found that the steam flow through the bed tended to displace the condensate, so that quantities of adsorbate free water were recovered before the steam emerged from the bed carrying the adsorbate. The zero point on the time axis therefore corresponds to when measurable quantities of water were first obtained, whereas true breakthrough did not occur until the time indicated. After breakthrough occurs water is recovered at a constant rate (linear portion of water curves), so that an estimate of the steam flow rate is readily available (no steam flow indicator was included with the package unit). A value of approximately 300 gm per minute is obtained by this method. By way of comparison the industrial unit had a steam flow rate of 33,000 lbs/hour (c.25 kg per minute). It is also possible to estimate the amount of water held within the bed in the liquid and vapour state, as being the

difference between the total steam supplied and the total water recovered during the constant rate period after breakthrough. This gives a value of approximately 1000 gm of water held within the bed, or a loading of 0.0134 gms of water per cubic centimetre of packed bed.

7.3 The Experimental Unit.

This simple apparatus was constructed of QVF glass of 1" I.D. The adsorbent bed consisted of a mesh support for the adsorbent granules and a large diameter, well lagged QVF tube into which the adsorbent was placed. By varying the diameter of the tube and the packed height of adsorbent the effects of different bed sizes could be investigated. As it had not proved possible to represent the operations of the industrial adsorption unit with the package unit, it was hoped to do this on the experimental unit. This essentially meant reproducing the operating conditions of the industrial unit suitably scaled down for experimental purposes. The SLA temperature and flow velocity were directly reproducible, however, the adsorbate concentration produced some problems. It was decided to use a single adsorbate, toluene, at an inlet concentration equal to the combined concentrations of toluene and ethyl acetate that were used on the industrial unit. The adsorbent used was 207B activated carbon manufactured by Sutcliffe Speakman Limited, as this was believed to be the one in current use on the industrial system. Regeneration was performed by saturated steam at 20-25 psig, and was carried out until sufficient adsorbate had been recovered (see below).

A diagram of the experimental unit is shown in Fig.(99). The flow rate of solvent free air from the fan is measured by the rotameter. The liquid adsorbate vapour is pumped at constant rate from a reservoir and drips onto the heated ceramic rings where it is vaporised. Heat is provided by an electric heating tape wound round the exterior surface and well lagged. The apparatus was run for several minutes before any

solvent was vaporised to allow the vaporiser section to be heated. The inlet temperature of the SLA is also produced by this heater which was controlled by a rheostat. It was found possible to control the SLA temperature to within 1°C . The warm SLA passes through the well lagged glassware; but is not admitted to the adsorbent bed until its temperature and adsorbate concentration had reached their constant inlet values. The main valve was then opened and the SLA passed through the adsorbent. The solvent free air was discharged from the top of the apparatus into a fume extract hood after the outlet adsorbate concentration had been recorded. To regenerate the bed the steam supply was introduced via a flexible connection through a removable bung located in the top section of the bed. A solid bung in the bottom of the bed is replaced by one carrying the inlet tube of a water cooled glass condenser. The condensed regeneration products are collected in measuring cylinders. The apparatus was constructed in this manner to allow rapid changeover between the adsorption and regeneration cycles, yet keep the level of sophistication to a minimum. Solvent laden air could be continually generated and vented to the extractor hood whilst regeneration was in progress so that constant inlet SLA conditions were maintained. Likewise, when a suitable steam flow rate had been obtained from the mains, the steam could be continually discharged to drain whilst adsorption was in progress. Hence, consecutive cycles of adsorption and regeneration could be carried out (as on the industrial unit) under constant operating conditions but using only a single adsorption bed.

The detection device use for the early parts of this work (the results of which are described in 7.3.1) was a portable MSA Combustible Gas Indicator. This was suitable for use within hazardous atmospheres and gave readings of the combustible gas concentration as a percentage of its lower explosive limit (LEL). In the range 0 to 10% LEL there is a

linear relationship between the % LEL and the toluene concentration in air expressed as a percentage by volume. The 0 to 10% LEL range was used when measuring the toluene concentrations in the SFA. The instrument had a second range of 0 to 100% LEL which was used when measuring the toluene concentration in the SIA. As this second range was not linear with respect to volume percentages, a constant inlet SIA concentration of 60 to 75% LEL as measured by the instrument was used for the adsorption periods; but the true concentration of toluene in air was calculated from measurements of the toluene and air flow rates. All readings were taken and plotted in terms of % LEL for the toluene in the SFA. They can be readily converted to Vol % by multiplying by the value of the LEL for toluene in air (given as 1.27 Vol % by Schefflan and Jacobs (90)).

7.3.1 Measurements taken on the Experimental Unit.

An adsorbent bed depth of 18 inches was used initially as this was the same thickness as the annular section of the industrial unit. The general experimental procedure was to first wet the bed by passage of steam through it as in regeneration. The series of adsorption and regeneration cycles could then be initiated. Fresh samples of adsorbent were used for each set of runs so that it was necessary to first build up the static adsorbate loading (see 7.2.1) on the adsorbent before reproducible results could be obtained. With the experimental conditions as described by Table VIII the results shown by Figs. (100) to (106) were obtained. Run 2 was the first adsorption period. The adsorption periods were labelled by even number runs, whereas the regeneration periods were labelled by odd number runs. All the adsorption runs were terminated when the exit concentration of toluene was 7-8 % LEL, with the exception of Run 2 which was terminated at 3 % LEL. The regeneration conditions were kept constant but the regeneration time varied depending on the ease

with which the adsorbate appeared to be recovered. So that if the recovery rate of toluene was low the regeneration time was small. As the total amount of toluene recovered during each regeneration was recorded, the data of Figs. (100) to (106) could be plotted as % IEL versus total adsorbate loading. This has been done as shown by Fig. (107), which clearly indicates the range of adsorbate loadings over which the runs were carried out. Also shown is the fact that the concentration profiles were not reproducible although of the similar shape for later runs. This would indicate that the static adsorbate loading had yet to be reached. As the latter profiles were taking in excess of one hour to produce and were not yet reproducible it was decided to reduce the bed height to 15 cms (c. 10ins) and repeat the experimental procedure beginning again with fresh adsorbent.

An earlier series of tests using benzene as an adsorbate and several different adsorbent samples had shown that the major effect of changes in the bed length was to alter the adsorption breakthrough time. The shape of the exit concentration profile was changed but little. It was, therefore, believed that reducing the bed length, so that the static adsorbate loading could be reached in less time, would not detract from the validity of the results.

Using the reduced bed height a series of adsorption and regenerating cycles were carried out under identical conditions until calculations showed the adsorbate loading at the start and end of successive cycles to be constant. A set of three adsorption cycles (Runs 1, 3, 5) were then carried out from the same initial adsorbate loading. The regeneration cycle recovering approximately the quantity of toluene adsorbed in the previous adsorption cycle. The regeneration time was reduced to produce an initial higher adsorbate loading and one adsorption cycle was carried out to remove the effect of this change in regeneration

conditions. A set of three adsorption cycles (Runs 9, 11, 13) were then carried out from the same new initial adsorbate loading. Finally, the initial adsorbate loading was reduced below that used for Runs 1, 3, 5 over two regeneration cycles. Two adsorption cycles were used to remove the effects of this change in regeneration conditions, and a further set of three adsorption cycles (Runs 19, 21, 23) were performed from a constant initial loading. The exit toluene concentration as a function of time for these three sets of runs is shown in Figs. (108) to (110). The three curves shown by Figs. (108) to (110) were then plotted against the adsorbate loading as shown by Fig. (111). These experimental results shown in Fig. (111) should be compared with the theoretical curves produced by the arguments of Chapter V and shown by Fig. (80). The author believes these experimental results support the arguments proposed in Chapter V, and indicate the importance of the regeneration operation in cyclically operated adsorption systems. The importance of regeneration is emphasised further in Chapters VIII and IX.

C H A P T E R VIII

Although the advantages of operating processes continually have resulted in a decline in the number of batch process applications, there still exist important operations which can only be performed by non-continuous procedures. These processes involve the use of cyclic operations involving periodic shutdowns for discharging, cleanout or reactivation. The most generally well known example is that of a batch reactor. This is a true batch operation in that no product is obtained until the unit is shut down for discharging. In semicontinuous cyclic operations, product is delivered continually while the unit is in operation, but the rate of delivery diminished with time. It becomes necessary, therefore, to shut down the operation periodically in order to restore the original conditions for high production rates.

The operations of adsorption and regeneration of the fixed bed units described in this work fit into the above general description. An individual adsorber is a true batch system in that no adsorbate is recovered until completion of the adsorption cycle and the start of the regeneration operation. Hence, the regeneration time can be considered as "down time" in the adsorption operation. The adsorber must be shut down for regeneration as its adsorption duty decreases when the adsorbate breaks through the bed. However, a system of adsorbers operating consecutively has the characteristics of a semi-continuous operation, where adsorption takes place continually but the outlet adsorbate concentration, and hence the adsorption duty of the system, varies in a cyclic manner.

If the regeneration operation is considered separately then this too is a true batch system in that no adsorbate is recovered while the unit is shut down for adsorption duty. So that the adsorption time can be considered as "down time" in the regeneration operation. However, a system of regeneration operations has the characteristics of a semi-continuous operation, where adsorbate is recovered continuously but the

amount recovered varies in a cyclic manner.

It is usual to illustrate these cyclic variations as a function of time. So that for the two semi-continuous operations described above (adsorption and adsorbate recovery) the cyclic variations can be illustrated by Fig. (112a) and (112b). A more convenient representation of the cyclic nature of an individual unit is shown by Fig. (112c), where the total adsorbate loading has been shown as a function of time. The process rates have been shown in Fig. (112a) and (112b) to illustrate the general property of cyclic systems where for part of the operation the rate is above the average rate; and for part of the cycle the rate is below the average rate. Clearly, the longer the cycle time, the lower the average rate value will be as it is defined by the total production for the cycle divided by the total cycle time.

In both batch and semicontinuous processes two rates are involved. The average rate can be readily defined and is described above. The second rate is the instantaneous rate which is the actual value of the rate at each instant in time. It is also known as the differential rate as it is the slope of the tangent to the total production versus time curve. The instantaneous rates have been shown as the solid lines in Fig. (112a) and (112b). The maximum occurs in the instantaneous adsorption rate due to the shape of the effluent concentration versus time curve, where the efficiency of adsorption increases initially as the adsorbent is cooled and dried by the process stream.

The work of Chapter VII has indicated the close inter-relation between the adsorption and regeneration cycles of a single unit. This can be further emphasised from the above arguments, as overall it is necessary for the average adsorption rate to equal the average adsorbate recovery rate in this system. This inter-relation has resulted in the term Combined Operations being used to describe these systems (91).

It is the purpose of this Chapter to investigate the particular combined operation of adsorption/regeneration in more detail than has been previously available. A detailed economic evaluation of the separate adsorption and regeneration cycles is presented initially; and is followed by an analysis of the combined cycles and their interaction. The criteria described below are of a general nature in that they can be applied to most batch operations, although they have been adapted specifically for the adsorption system. This sort of evaluation has not been presented by other authors except in vague terms (91, 92). The efforts of other authors to describe operating criteria have been discussed in Chapter VI as part of the influence of theoretical considerations on practical adsorption units.

8.1 The System Variables

Prior to the formation of suitable economic criteria for the operating adsorption system, it is necessary to discuss those quantities which influence the behaviour of the system. For a particular system these quantities (variables) will be fixed at set values (state variables) or will be allowed to have values within a constrained range (decision variables). There is also likely to be variables whose values are not known and are subject to change in some generally predictable manner (parameters).

For the adsorption cycle the input variables can be listed as:-

- a) The inlet adsorbate concentration.
- b) The inlet SLA temperature.
- c) The inlet SLA flow rate
- d) The initial temperature distribution within the bed
- e) The initial adsorbate distribution within the bed

f) The initial moisture distribution within the bed.

g) The adsorption cycle time.

- a parameter for the adsorption cycle would be the activity of the adsorbent, which is known to fall in use; but is not quantitatively predictable. The state variables have been omitted from the above list but include such items as the nature of the adsorbent, the nature of the adsorbate and carrier fluid, and the method of contacting the adsorbent and the adsorbate.

The analytical sections of this work have attempted to present the transformation equations, whereby conditions within the bed and at its exit can be uniquely defined at all times given a set of values for the variables, and making some suitable assumptions. In particular the values of the output variables described below can be determined via the transformation equations. For the adsorption cycle the output variables can be listed as :-

aa) The outlet adsorbate concentration.

bb) The outlet SFA temperature.

cc) The temperature distribution within the bed.

dd) The adsorbate distribution within the bed.

ee) The moisture distribution within the bed.

The regeneration operation has been crudely considered in this work, but no analytical formulation of its effects has been presented. It is still possible, however, to consider those variables relevant to the regeneration operation. For the regeneration cycle the input variables can be listed as :-

h) The regeneration fluid temperature at inlet.

i) The regeneration fluid flow rate at inlet.

j) The initial temperature distribution within the bed.

- k) The initial adsorbate distribution within the bed.
- l) The initial moisture distribution within the bed.
- m) The regeneration cycle time.

The state variables would be the nature of the regeneration fluid, adsorbent and adsorbate, and the method of contacting the adsorbent and the regenerative fluid. Clearly the output variables of the adsorption cycle cc), dd) and ee) at the end of adsorption are identical to the input variables for the regeneration cycle j), k) and l) respectively.

The output variables for the regeneration cycle can be listed as:-

- hh) The recovered adsorbate flow rate.
- ii) The recovered regeneration fluid flow rate.
- jj) The temperature distribution within the bed.
- kk) The adsorbate distribution within the bed.
- ll) The moisture distribution within the bed.
- mm) The regeneration fluid breakthrough time.

The output variables jj), kk) and ll) at the end of the regeneration cycle are identical to the input variables for the adsorption cycle d), e) and f) respectively.

The interaction of the adsorption and regeneration cycles is shown diagrammatically by Fig. (113) which also indicates the information flows within the system. The simplified analytical approach used in this work has meant that all input and state variables, and parameters were assumed constant. Even so, there is still a long way to go before the use of dependable transformation equations will enable complete analytical investigation of the system. However, it can be seen from investigations of this general nature those outputs that contain information which is of use in an objective economic assessment of the overall system. It is therefore possible to set up meaningful objective functions that represent various economic criteria for the system, using information that can be

produced from the system either by analytical or practical means. These objective functions are discussed below prior to an assessment of the effects of changes in the input variables.

8.2 Economic Assessment (Cycles Independent)

If those variables which are common to both the adsorption and the regeneration cycles have no significant effect upon the performance of the cycles, then under continuous steady operation the effects of successive adsorptions and regenerations will be reproducible. The adsorption and regeneration operations can then be considered separately. The economic analysis of each cycle is therefore independent of the conditions of operation of the previous cycle; and is greatly simplified. This is of course not likely to be typical of the industrial adsorption/regeneration operation. However, it will be closely approached in those cyclic systems where the effects of the previous cycle are rapidly dissipated during the initial period of the cycle under consideration.

It will be assumed that during the adsorption operation the only variable not held constant is the adsorption cycle time. Then the output variable of prime significance, the exit adsorbate concentration, can be described graphically as a function of the adsorption cycle time. This representation has been used before in this work; but is shown again for comparative purposes in Fig. (114a). The residence time of adsorbate laden fluid within the bed has been included for completeness, although for industrial adsorption operations it is small enough to be neglected. As the total amount of adsorbate adsorbed at any time t is given by :-

$$W_1 = V \alpha \int_{h/V}^t (C_0 - c) . dt + C_0 h \alpha$$

- then it is possible to represent the variation of c with W_1 as shown by Fig. (114b). Also, as the total amount of adsorbate lost at any time is

given by :-

$$W_2 = V \propto \int_{h/V}^t c \cdot dt$$

.. and the total adsorbate loading on the adsorbent is given by $L + W_1$, then the variation of c with L can be expressed by the variation of W_2 with L as shown by Fig. (114c).

It can be seen the adsorption cycle time is constrained in that it must lie in the range $0 \leq t \leq t_{\infty}$, where the total amount adsorbed reaches a maximum at t_{∞} . Conversely, the total weight of adsorbate lost tends to infinity at $L \max$ for $t > t_{\infty}$. It is, therefore, usual to terminate the adsorption cycle at some time $t_a \leq t_{\infty}$, where the adsorbate loading has a value of L_a , as maximising the total amount adsorbed is not a suitable objective for operating adsorption units. If the adsorbate has little value, but cannot be discharged at its inlet conditions, then the criteria for choosing t_a is that time at which the exit adsorbate concentration reaches its specified upper limit. Hence, the adsorption unit operates solely as a machine for reducing the adsorbate level in the carrier to an acceptable limit. The criteria described above are operating criteria and involve no economic assessment.

If the price of a unit weight of adsorbate is $\pounds p_a$ then a series of cost curves can be constructed from the information of Fig. (115). At any time t the total value of adsorbate in the feed stream is $C_0 V \propto t p_a$ and the total value of adsorbate lost in the effluent stream is $W_2 p_a$. These total values may be expressed as functions of t as shown by Fig. (115a). The difference between these two curves represents the value of the adsorbate held on the adsorbent as shown by Fig. (115b). The difference between the total value of adsorbate adsorbed and the total value of the adsorbate in the effluent represents the nett profit of the

adsorption operation as shown by Fig. (115c). The broken line 3 represents the point where the maximum amount of adsorbate has been adsorbed and thereafter the adsorbate effluent concentration is equal to the feed concentration. So that at some later time, shown by line 4, the total adsorbate lost will equal the total amount adsorbed. The maximum nett adsorption profit occurs as shown by line 2 at some time during the cycle before the adsorbent is fully saturated. The maximum nett adsorption profit rate occurs at all times less than the residence time, and so is clearly not an acceptable objective.

If the costs associated with the down time of the adsorption operation (the regeneration cycle) are small, and the adsorption capacity is not significantly affected by the regeneration cycle. Then the adsorption cycle time should be chosen to maximise the nett adsorption profit. This is likely to be achieved on a cyclic unit where the adsorption time is large compared to the regeneration time and the adsorbate is valuable. If, however, the exit concentration at this time violates a constraint, possibly the legal limit or the purity tolerance of the carrier stream, then the maximum nett adsorption profit cannot be achieved. The optimum operating policy would now require adsorption until the constraint was met.

If the regeneration operation is considered separately, and it is assumed that the regeneration cycle time is the only variable not held constant, then a similar analysis to the above can be performed. Here the output variable of prime significance is the amount of adsorbate recovered. The total weight of adsorbate recovered W_4 and the total weight of steam required to recover this adsorbate W_3 , are shown as functions of time by Fig. (116a). No adsorbate is recovered until after the steam breakthrough time. This time cannot be neglected in any economic analysis. It is possible to plot W_3 against W_4 as shown by

Fig. (116b), where W_3^0 is the steam supplied up to breakthrough. The maximum amount of adsorbate capable of being recovered under the conditions of regeneration is shown by W_4^0 . As the total adsorbate loading at any particular time is $L_4 = W_4$, then W_3 can also be shown as a function of L as in Fig. (116c). The minimum adsorbate loading L_{\min} is achieved at time t_{\max} where the total amount of adsorbate recovered is a maximum. If the cost of steam is negligible compared to the value of the adsorbate, and the regeneration operation does not significantly affect the adsorption period, then for $t = t_{\max}$ the maximum amount of adsorbate would be recovered. As the average adsorbate recovery rate is $(1/t) \int_0^t W_4 dt$, then for times less than t_{\max} the average recovery rate will be higher, as the instantaneous recovery rate has fallen to zero at t_{\max} . The maximum average adsorbate recovery rate will be achieved at some time t_B , where the line A through the origin is a tangent to the adsorbate curve. This is an application of the well known tangent rule (93). The criteria described above require no economic assessment.

If the cost per unit weight of steam supplied is $\pounds p_s$, then a series of cost curves can be produced from the information of Fig. (116). The total cost of steam used $W_3 p_s$ and the corresponding total value of adsorbate recovered $W_4 p_s$ can be shown as functions of the regeneration time by Fig. (117a). Two curves for the steam cost, A and B, have been shown. If the adsorbate cost is small compared to the cost of steam, or if the amount of adsorbate recovered is low, then the total steam cost B will always lie above the total adsorbate curve. If the adsorbate cost is large compared to the cost of steam and the adsorbate is easily recovered in quantity, then the total steam cost A will intersect the total adsorbate curve. The difference between the total value of the adsorbate recovered and the total cost of steam required to achieve this recovery is the nett profit of the regeneration operation. This nett profit has been

shown as a function of time by Fig. (117b). The nett profit is initially negative (a loss) increasing linearly up to the breakthrough time shown by line 1. As adsorbate is recovered the nett profit increases so that for the steam cost curve A the nett profit becomes positive, passes through a maximum and decreases again. For steam cost B the nett profit never becomes positive, so that the regeneration cycle always runs at a loss. The regeneration time should therefore be chosen by line 3 so that the nett regeneration cost is minimised.

For steam cost A the nett profit function shows two breakeven points at 2 and 6. Here the value of the adsorbate recovered is exactly balanced by the cost of steam used to recover it. So that for a positive regeneration profit the cycle time is constrained to lie within these limits. The maximum nett profit of regeneration occurs at 5; and the maximum average profit rate at 4, as found by application of the tangent rule. If the total steam cost curve becomes a tangent to the total adsorbate curve of Fig. (117a), then the maximum regeneration profit becomes equal to the maximum average profit rate. Both have a zero value, so that the time of coincidence is also the break even time.

This completes considerations of the adsorption and regeneration cycles separately. It should be noted that those instances where possible operating criteria did not involve any economic considerations can readily be converted into economic conditions by attaching suitably large cost values to the desired response. In this manner the shadow prices serve to ensure that the economic assessment produces the desired response.

8.2.1 Effects of Changes in the Input Variables.

If the requirement that the input variables to the adsorption and regeneration cycles are constant is relaxed, but the assumptions of 8.2 are maintained so that the cycles can be considered separately, then

the effects of the input variables can be considered for each cycle. Only the general implications of particular changes in the values of the variables will be considered. The precise results of the changes can only be determined by experimental or analytical means.

For the adsorption cycle a reduction in the SLA inlet temperature will provide a greater temperature driving force initially so the bed should cool more quickly. It is therefore probable that the initial adsorbate losses will be reduced. This saving may be extended throughout the adsorption cycle if the adsorption process is significantly affected by the temperature change. Any reduction in the adsorbate lost cost must of course be balanced by the additional cost of cooling the SLA further by the apparatus available, or by some alternative arrangement. It was found in operating the industrial unit described in Chapter VII, that the SLA temperature could not be lowered beyond some limit. For although the adsorption bed was cooled rapidly by the passage of the SLA, the evaporation of water took place at a slower rate. It was therefore necessary to supply sufficient sensible heat with the SLA so that the bed could be dried by the end of the adsorption period. Otherwise, moisture build up within the bed was found to progressively reduce the adsorption efficiency.

Changes in the inlet SLA flow rate and the inlet adsorbate concentration can only be considered independent if the total adsorbate flow rate is not constant. For example, use of a larger SLA flow rate with the same inlet adsorbate concentration could only be achieved if the change in the SLA flow rate affected the rate of adsorbate generation. In the industrial unit of Chapter VII this could be brought about by running the coating machines with a higher through-put. If the inlet adsorbate concentration is held constant, then an increase in the SLA flow rate would cool the adsorbent quicker and so perhaps produce a

reduction in the adsorbate lost costs. However, the increased power requirements to move the greater flow rate would increase the running costs of the system. If the mass transfer processes were controlled by the external particle film resistance, then changes in the flow rate might enhance the adsorption operation. The constant inlet adsorbate concentration would mean that adsorbate was supplied at a greater rate so that there would be a reduction in the adsorption cycle time to give the same outlet concentration. If this reduced time meant that the bed was not sufficiently dried then the adsorption process would not be aided by changes in the SIA flow rate.

For a constant SIA inlet flow rate, the effects of any change in the inlet adsorbate concentration can only be evaluated by experiment or analytical techniques. However, it is likely that an increase in the inlet concentration will produce a greater generation of the heat of adsorption. So that the cooling of the bed may be initially retarded; but the drying of the bed promoted. However, the greater heat generated may mean a higher adsorbent temperature in the dry bed so that adsorption is not favoured. The available time for adsorption could be affected in several ways. Although the adsorbate supply rate has been increased, the higher concentration in the bulk phase would tend to increase the adsorbate loading on the adsorbent, so that the adsorption time could remain approximately the same, increase or decrease.

For the regeneration cycle changes in the inlet steam temperature and flow rate must be considered. A higher steam temperature should produce a lower adsorbate loading on the adsorbent, and may increase the rate at which the adsorbate is recovered. If the steam is saturated at the higher temperature then the breakthrough time is unlikely to be greatly affected. The larger temperature difference between the adsorbent and its surroundings would increase the rate of heat loss and

hence the rate of condensation within the bed. If the steam is superheated at the higher temperature then it is likely that the breakthrough time will be reduced so that adsorbate is recovered sooner. The amount of condensate within the bed may also be reduced. In both cases the bed temperature will be raised. The use of a large degree of superheat is not found to be desirable as the lack of water at the start of the subsequent adsorption cycle slows down the rate of cooling of the bed.

A higher steam flow rate will increase the rate at which heat is supplied to the bed, so that breakthrough might occur sooner. The higher flow rate may increase the desorption rate and hence increase the adsorbate recovery rate.

However, any improvements in the amount of adsorbate recovered or its rate of recovery must be offset against increases in the steam costs either to provide a higher temperature or a greater flow rate.

It can thus be seen that an economic balance must be struck between the effects of changing the values of the variables and the costs of achieving these changes. The nature of this economic balance will depend to a large extent on the particular system under investigation. The principles outlined in 8.2 can only serve as a guide to the criteria that might be used to objectively determine what the best set of conditions are. They are of course subject to what has been termed intangible and practical considerations (94).

Particularly relevant to this work is the steam cost, which is likely to have been arrived at by some suitable accounting procedure, possibly peculiar to the location where it is used. Changes in the steam flow rate and/or its properties are unlikely to be capable of quantitative costing, so that optimisation of the process by theoretical considerations may only serve as a base point for cost or design analysis. To be of any real value the analysis should be based upon the combined

cyclic series of operations, with the interaction effects included.

8.3 Economic Assessment (Cycles Interacting)

It is now necessary to consider not only the effects of the operating characteristics of the separate cycles, but also the interrelations between the cycles that arise as shown by Fig. (112). Some preliminary work on this interaction has been presented in Chapter V and VII of this work, where its physical nature has been described. The economic nature of the interaction must now be considered. For simplicity the assumptions used in 8.2 will be applied again, so that it is only necessary to consider changes in the adsorption and regeneration cycle times. It will be assumed that these times are independent of each other and can take any finite values. The implications if this assumption does not hold are discussed in Chapter IX after the economic analysis has been presented here.

It has been shown that the effects of regeneration influence the value of the adsorbate exit concentration during adsorption as well as the recovery of the adsorbate. Similarly, although it has not been shown, it can be imagined that the adsorption cycle influences the regeneration cycle to some degree. Although adsorption can be terminated by examination of the adsorbate exit concentration profile, the property that most affects the regeneration can be seen to be the adsorbate loading. It can be imagined for instance, that the greater the total adsorbate loading, then the larger the change in loading that can be achieved by the regeneration operation, and hence the ease with which the adsorbate can be removed is enhanced.

Although variations in the cycle times are being considered, it is more enlightening to consider the interaction between the cycles in terms of a common variable. The total adsorbate loading will be used for this

purpose. The main factors in the adsorption and regeneration cycles have already been shown as functions of the total adsorbate loading by Fig. (114c) and Fig. (116c) respectively. If the data shown in these figures is converted to a cost basis, then it is possible to describe the operations of adsorption and regeneration as a single diagram as shown by Fig. (118). For continuous stable operation of the two cycle system then the solid curves A and B must be reproducible and lie within a lower loading L_1 and an upper loading L_4 . Hence, the amount of adsorbate adsorbed during the adsorption cycle must be exactly balanced by the amount of adsorbate removed during the regeneration cycle. The value of this amount of adsorbate is constant and common to both cycles, so that the objective of maximising the total system profit reduces to its dual objective; that of minimising the total system costs. Under the assumptions made earlier, the only variable components of the system cost (i.e. functions of time) are the cost of adsorbate lost during adsorption and the cost of steam used during regeneration. The objective function for the combined cycles is therefore simply expressed as the (Total Steam Used Cost + The Total Adsorbate Lost Cost) / $(L_4 - L_1)$. The cycle times (and hence values of L_4 and L_1) should thus be chosen to minimise the operating costs per unit adsorbate loading.

Clearly it is not necessary to know the absolute value of the adsorbate loading shown in Fig. (118), as the loading range is sufficient. Thus, it is quite straight forward to produce the information shown by Fig. (118) from original data of the exit adsorbate concentration versus time, and the amount of adsorbate recovered versus time profiles. These profiles being the simplest ones that can be produced by measurements of an industrial plant. As the same optimum conditions will be obtained either by graphical or analytical methods, graphical procedures will be used in this work. They have the advantages that the application of the

optimisation procedure is readily seen, and the information produced in the region of the optimum acts as a guide to the sensitivity of the optimum value for changes in the variables.

It is now necessary to consider how the objective function changes with variations in the adsorbate loading range. Referring to Fig. (118), if the adsorbate loading is increased above L_L by further adsorption then the total adsorbate lost cost curve A can be extended as shown by the dotted line. Similarly, if the adsorbate loading is reduced below L_L by further regeneration, then the total steam used cost curve B can be extended as shown by the dotted line. This is only one half of the picture, as changes in the adsorbate loading at the end of one cycle affect the total cost curve for the next cycle.

Consider first the regeneration cycle. The value of the initial adsorbate loading is unlikely to affect the breakthrough time as this is largely dependant upon the heating duty of the steam (little duty is required for the adsorbate due to the relatively small changes in its concentration). Hence, it may be assumed that the value $W_3^0 p_s$ is constant for all adsorbate loadings. This cost is now effectively the changeover cost that must be incurred whenever regeneration is carried out, irrespective of the change in adsorbate loading. It is, therefore, a fixed operating cost for the regeneration cycle. The problem now remains one of determining how the cost of steam used in excess of the changeover cost will vary with the initial value of L . It can be safely assumed that once the bed has reached its regeneration temperature then the cost of steam used to remove an additional unit of adsorbate will depend only upon the value of L . This relationship is already available as shown by Fig. (118) for $L \leq L_L$, where the cost of steam used to remove an additional unit of adsorbate is the differential (or instantaneous) steam cost $dB/dL = p_s \cdot dW_3/dL$, and is the gradient of the solid curve B. If

dB/dL is plotted against L as shown by Fig. (111a), then it is possible to extrapolate the curve beyond L_h to give the variation of dB/dL across the total possible adsorbate loading range L_{min} to L_{max} . The total steam cost for operation between any general adsorbate loading L_a to L_b ($L_b > L_a$) is now given by

$$B_T = B^o + \int_{L_a}^{L_b} (dB/dL) \cdot dL$$

The adsorption cycle can now be considered. The work described under Chapter V and experimentally verified in Chapter VII is of direct relevance. Referring to Fig. (80), it was argued that if the regeneration operation reduced the adsorbate loading below \bar{N}_{lim} , then the exit adsorbate concentration values above \bar{N}_{equil} were independent of the initial adsorbate loading. Hence, if \bar{N}_{equil} is represented by L_3 in Fig. (111), the differential adsorbate lost cost dA/dL is given at loadings in excess of L_3 by the shape of the solid curve A, $dA/dL = p_s \cdot dW_2/dL$. If the exit adsorbate concentration profile as a function of time can be produced either analytically or experimentally for high values of c/C_o , then the value of dA/dL for loadings up to L_{max} can be determined. It is now possible to plot dA/dL versus L for loadings in the range L_3 to L_{max} , as is shown by Fig. (111b). The problem now remains as to the variation of dA/dL for loadings in the range L_{min} to L_3 . This situation can be clarified by use of the arguments that produced Fig. (80) and which can be used to produce Fig. (120) relevant to the work of this Chapter, where the changes in the adsorbate lost concentration profiles have been compared by using the time t_E at which the concentration begins to increase once more.

If the exit adsorbate concentration profile as a function of time is identical for all adsorbate loadings less than L_2 , then a Type I

situation occurs as represented by Fig. (120a). Here the value of c_e is constant and the area (FGHJ) equals the area (ABDE). If these profiles are separated by a time interval Δt , then the difference in the total adsorbate loading can clearly be seen to be $(C_0 - c_{\text{equil}})V \propto \Delta t$. The additional cost of adsorbate lost over this loading is $p_a c_{\text{equil}} V \propto \Delta t$, so that as $\Delta t \rightarrow 0$, the differential adsorbate lost cost is $da/dL = c_{\text{equil}}$.

$p_a / (C_0 - c_{\text{equil}})$, which is constant. Its value can now be drawn on Fig. (120b) for $L_{\text{min}} \leq L \leq L_2$, and extrapolated to L_3 as in the loading range L_2 to L_3 the total adsorbate lost cost is a linear function of the adsorbate loading. Hence a period of constant differential adsorbate lost cost is obtained as shown by curve I in Fig. (119b). The value of the adsorbate lost at the start of the adsorption cycle is now independent of the initial adsorbate loading, and equal to :

$$\int_{t_A}^{t_E} c(t) V \propto dt = \int_{t_F}^{t_J} c(t) V \propto dt = A^0$$

Where A^0 is now effectively the change-over cost that must be incurred whenever adsorption is carried out, irrespective of the adsorbate loading as long as it is initially less than L_2 .

If the exit adsorbate concentration profile as a function of time varies with the initial adsorbate loading (less than L_2), then a Type II situation occurs as represented by Fig. (120b). Here the initial value of the exit adsorbate concentration is not constant but a function of time $c_e(t)$. The difference in adsorbate loadings between the curves starting at t_F and t_A is clearly $C_0 V \propto \Delta t - \{ \text{Area FGDE} - \text{Area ABDE} \} V \propto$ whereas the cost of adsorbate lost over this loading is $p_a \{ \text{Area FGDE} - \text{Area ABDE} \} V \propto$. As the curve BD is common to both Type I and Type II cases, then for the Type II case as $\Delta t \rightarrow 0$, the value of the differential adsorbate lost cost tends to the constant value found for the Type I case

at an adsorbate loading of L_2 . Hence, a constant value of the differential adsorbate lost cost is common to both Type I and Type II in the adsorbate loading range L_2 to L_3 .

The difference in adsorbate loadings between the curves starting at t_K and t_F is clearly $CoV \propto \Delta t - \{ \text{Area KLDE} - \text{Area FGDE} \}$, whereas the cost of adsorbate lost over this loading is $p_a \{ \text{Area KLDE} - \text{Area FGDE} \}$. An assessment of the size of the differential adsorbate lost cost can be obtained moving the curve GD so that it becomes PH, as shown in Fig. (120b). Then the difference between Area KLDE and Area FGDE can be expressed as $c_{equil} \Delta t + \Delta \text{Area}$, which is shown shaded. The magnitude of ΔArea will depend on the lack of agreement between the curves and hence serves to indicate the effects of changes in the regeneration operation. A small value of ΔArea will imply that the adsorption process is only slightly affected by the conditions of regeneration. The total cost of adsorbate lost in the loading range from t_K to t_F per unit change in adsorbate loading is now :

$$\frac{p_a c_{equil} V \propto \Delta t - \Delta \text{Area } p_a V \propto}{(Co - c_{equil}) V \propto \Delta t - \Delta \text{Area } V \propto}$$

- which is greater than $p_a c_{equil} / (Co - c_{equil})$ for all values of Δt . Hence, as $\Delta t \rightarrow 0$ the differential adsorbate lost cost will have a value in excess of the constant value found for the range L_2 to L_3 , for adsorbate loadings less than L_2 . This behaviour is illustrated by curve II in Fig. (119b). Obviously the adsorption changeover cost is now not constant, but differs by an amount equivalent the area of PLDH. As this area is small compared to the total area ABDE, then the changeover cost can be assumed constant.

The total adsorbate lost cost for the adsorption cycle operating between any general adsorbate loading L_a to L_b ($L_b > L_a$) is now given by:

$$A_T = A^0 + \int_{L_a}^{L_b} (dA/dL) \cdot dL$$

which is similar to the relationship by which the total regeneration costs are determined.

8.3.1 The Overall Economic Objective.

In the above economic assessment it has been assumed that some constant price p_a can be attributed to a unit weight of adsorbate present in the exit from the adsorber. This would generally be the case where the purpose of the adsorption unit was to recover a valuable adsorbate for re-use. If, however, the purpose of the adsorption unit was to reduce the concentration of the adsorbate leaving the unit to below some specified value c_{exit} , then a variable value of p_a can be used. Operations which produced an exit concentration less than c_{crit} would have a small constant adsorbate cost associated with them. Operations above c_{crit} would use an increasing adsorbate unit cost or penalty price. The penalty price would be determined by the cost factors associated with handling concentrations greater than c_{crit} outside the adsorption unit. It would still be possible to produce the differential cost curves shown in Fig. (119).

It is therefore possible to determine the value of $(A_T + B_T) / (L_b - L_a)$ for operations with limiting adsorbate loadings of L_a and L_b having any values between L_{min} and L_{max} , by integration of the appropriate section of the differential cost curves. If the two differential cost curves are first summed then only a single integration is necessary for the combined curve as shown by Fig. (121a). Hence, the total operating costs per unit adsorbate loading can be determined for a particular value of the adsorbate loading range, $(L_b - L_a)$. The determination of suitable values for L_a and L_b , and hence the loading range can be carried

out as described below.

Consider two general loadings L_a and L_b (again $L_a < L_b$) where the combined differential cost curve has a value of D_a at L_a , and a value of D_b at L_b . The cost of obtaining a unit change in the adsorbate loading at L_a is shown shaded, as is the cost of obtaining a unit change in the adsorbate loading at L_b . Clearly if these two shaded areas are not equal then the loading can be reduced at the point with the larger area, and increased at the point with the smaller area so that the loading range is held constant; but the total operating costs reduced. This procedure can be applied successively until the two areas are equal, that is when the adsorbate loadings L_a and L_b are chosen so that both intersect the combined curve at the same value of the differential cost. The total operating costs per unit adsorbate loading can now be directly calculated by this method for several different values of the loading range. This data is shown by Fig. (121b), where the loading range that produces the minimum total operating costs per unit loading can be found directly.

For a shallow operating cost curve then the minimum point may not be clearly defined. A further graphical procedure can be used so that a point of intersection with the operating cost curve is obtained. This requires a brief investigation of the relationship between the average cost per unit loading and the differential (or instantaneous) cost per unit loading. If for the same adsorbate loading range L , the average cost per unit loading has the value X and the instantaneous cost per unit loading has the value Y . Then if the loading range is increased to $L + 1$, the new average cost is $(LX + Y) / (L + 1)$ or $[(L + 1)X + (Y - X)] / (L + 1)$, that is $X + (Y - X) / (L + 1)$. Clearly if $Y > X$ the average cost increases, whereas if $Y < X$ then the average cost decreases with an increase in the adsorbate loading. Hence, while the instantaneous cost is less than the average cost, the average cost will fall with an increase

in the loading range. Whereas when the instantaneous cost is greater than the average cost the average cost will be increased with an increase in the loading. Hence the minimum average cost must be obtained when the instantaneous and average costs are equal. This is the point of intersection that is shown in Fig. (121b), and gives a precise value for the optimum loading range and the minimum operating cost. The operating conditions for the adsorption and regeneration cycles can be obtained by working back from the optimal loading range as shown in Chapter IX.

C H A P T E R IX.

A worked example of the optimisation procedure described in 8.3.1 is given below using experimentally determined conditions from the industrial unit described in Chapter VII. This illustrates the principles of the optimisation procedure better than any discussion, and serves to indicate the possible gains to be made by the use of such procedures. It is necessary to view the results obtained with some caution as is explained later. The likely effects of non-constant operating conditions and the limitations of the practical constraints can then be considered.

9.1 The Available Data.

The industrial unit operates two adsorption systems, Plant A and Plant B dealing with an SLA containing the adsorbates toluene and Ethyl Acetate. As two adsorbers are on stream at any one time the volumetric SLA throughput can be divided equally for each bed. Sampling of the SFA leaving both plants by the method of Koo (88) enables the separate outlet concentration curves for the two components to be drawn, as shown by Fig. (122) and Fig. (123). As has been noted earlier the outlet values for Plant B are constantly lower than those for Plant A due to the lower feed concentration used on Plant B. The data for Plant A will be used exclusively for the rest of this example. The information presented by Fig. (122) can be converted into cumulative cost and weight values as functions of time as shown by Table X, where the inlet SLA conditions are also given. The cumulative cost data for the individual adsorbates can now be produced as shown by Fig. (124). For this analysis it will be assumed that the sum of the individual adsorbate lost costs describes the total adsorbate lost cost for the adsorption cycle, as shown by the combined curve in Fig. (124). The data for the curves is given in Table X.

From the measurements taken on the industrial unit, and with the aid of the results for the package unit (see Chapter VII) it was possible

to determine the cumulative amounts of toluene and ethyl acetate recovered during the regeneration period. The total value of the recovered adsorbates is shown in Fig. (125) from the data given by Table IX.

The data presented above includes values for total weights of adsorbate adsorbed and recovered. If it is assumed that the adsorption cycle begins and the regeneration cycle ends at the same absolute solvent loading L_0 , then the total adsorbate lost cost and the total steam used cost can be drawn as functions of the adsorbate loading. This is shown in Fig. (126) and Fig. (127) respectively. From these two figures it can be seen that suitable values for the adsorption change-over cost, A^0 , and the regeneration changeover cost, B^0 , are £0.018 and £0.102 respectively. The differential costs can now be determined at several values of the adsorbate loading from the shapes of the respective total cost curves. This has produced the data shown in Table XI, from which Fig. (128) has been drawn showing the individual and combined differential cost curves.

Several values of the differential cost for the combined curve can now be chosen in the range 0.7 to 2.0, and the area under the combined curve having these cost values as limits can be found. The intercepts of the constant differential cost lines and the combined cost curve gives the values of the upper and lower adsorbate loading. Hence, the adsorbate loading range for each calculated area can be determined. Any suitable integration procedure can be used to evaluate these areas. This author feels that the trapezium rule is quite accurate enough over loading intervals of 10 lbs; and has used this method with an expanded loading axis so that the combined curve is flattened somewhat. The areas so evaluated represent the total variable operating costs of the system. The two constant changeover costs should be added to these values to give the total operating cost which are then divided by the

loading range to yield the objective function values. This is shown by Table XII. The average and differential costs can now be plotted against the adsorbate loading range as in Fig. (129), and the optimum point determined. An optimum loading range of 360 lbs with an operating cost of £0.00117 per lb of adsorbate loading is thus found for the cycle.

It is now possible to work backwards through the calculations to determine the operating conditions for the adsorption and regeneration cycles. However, it can readily be seen from the production of the differential cost curves (see Fig. (128)) that the existing system operating conditions were non-optimal. The differential steam cost having been shown to be far greater than the differential adsorbate lost cost. An equal differential cost of £0.00117 per lb gives a lower adsorbate loading of $L_0 + 84$ lbs and an upper loading of $L_0 + 444$ lbs. For the adsorption cycle this means initial exit concentrations of £0.004 Vol % for ethyl acetate and 0.0042 Vol % for toluene; and final exit concentrations of 0.0034 Vol % for ethyl acetate and 0.0015 Vol % for toluene. The exit concentration values are found by extrapolation of the concentration profiles used for this example; and hence are liable to some error. True values can be found experimentally.

A preliminary comparative analysis can now be carried out between the existing operating conditions and the proposed optimal operating conditions. This is shown in Table XIII, where the optimal operation of an adsorption unit produces a reduction of £0.033 per hour. This gives an estimated annual saving of £850 for a three unit plant, or a 6.5% reduction in the operating costs. The implications of operating the industrial unit to achieve these savings are examined below in an attempt to decide how far optimal operation can be approached.

9.2 Operating Limitations.

The optimal conditions predicted above must clearly be viewed

in the light of their ability to be achieved. This can be sub-divided into two parts. Firstly those operations which are not cost dependant, for example the cycle times; but which are related to the optimal conditions. Secondly, those operations which have cost data associated with them.

It is easier to deal with the second set of operations first. Into this category can be placed the adsorbate cost and steam cost. The above analysis has used constant cost values per unit of adsorbate and steam, as well as constant flow rates for these components. Some brief points were made in Chapter VIII about the use of a penalty price for the adsorbate if its presence in the SFA detrimentally affects other systems; and about the reliability of an accounting cost for the steam. It is necessary to reconsider these points here. It was seen from 9.1 that the differential steam cost was in excess of the differential adsorbate lost cost under the present operating conditions. The optimal solution, therefore, showed that the steam usage per cycle should be decreased at the expense of increased adsorbate losses. If the adsorbate is purchased from an external agent then its unit cost is unlikely to vary if the flow rate is changed or if the increased adsorbate losses require extra adsorbate to be bought in. The nett result of the optimisation will appear to the plant manager as an actual increase in the annual cost of bought-in material that has to be set against some savings in the steam cost which the plant manager is unlikely to physically see.

If the steam usage on the adsorption plant is only a minor part of the total works steam usage, then any changes in the steam usage will have negligible effects on the steam supply cost. In this case the steam price will effectively be constant, and may in fact be costed at less than the full steam cost. With a large excess of generated steam

available changes in the steam requirement for the adsorption unit can be charged at zero unit cost. Hence, when the steam cost becomes insignificant the optimum policy is to minimise the adsorbate lost cost by choice of the operating conditions. This illustrates the general condition that when the price of an item is reduced more of that item is used under optimal conditions.

If the steam usage on the adsorption unit is a significant part of the total works steam usage, then changes in the steam usage should be associated with a variable unit steam cost. So that the total steam cost used in the optimisation procedure of 9.1 would be given by the integral of the differential steam generation cost over the range of variations in total steam consumption that is of relevance. The linear variation shown in Fig. (125) would thus no longer be representative. However, once the variation of the steam cost was known the optimisation procedure could be directly applied.

The above analysis has used a constant adsorbate unit cost so that changes in the adsorbate use were not considered. If the adsorbate unit cost varies, for example if the adsorbate is produced on an associated plant and separated from other products by adsorption, then this variation must be taken into account. Here the cost of producing additional quantities of adsorbate must be considered when costing the adsorbate lost from the adsorption unit. The unit cost of adsorbate lost from the adsorption unit then becomes equal to the marginal cost of producing this unit of adsorbate on the associated plant (if all other effects remain constant). Once more, however, if the variation of adsorbate costs is known, then the optimisation procedure can be directly applied.

In the first category described at the start of this section were put operations not cost dependant. The optimisation example of 9.1 was carried out using constant steam and adsorbate flow rates. The

adsorption cycle time was therefore determined from dividing the adsorbate loading range by the adsorbate supply rate. Similarly, the regeneration cycle time was determined from dividing the steam used cost for the optimal cycle by the cost of steam per unit time. Hence, while the adsorption cycle time was but slightly affected, the regeneration cycle time was reduced by some 25%. If the flexibility of the adsorption plant is such that the adsorption and regeneration cycle times can be set to any desired values, then the optimal conditions can be achieved. However, where the cycle times are not independent or can only be set to certain specific values, it is necessary to choose the cycle times to produce the best approach to optimality that can be obtained. In such cases investigation of all possible changes in the operating conditions must be considered in order that any more viable optimum policy might be arrived at. The particular situation of the industrial unit described in Chapter VII is worthy of further investigation in this light.

9.3 A better optimum policy for the Industrial unit ?

The general optimising procedure described by the example above fails to take account of the particular constraints of the Industrial Unit as operated by British Sidac Ltd. at their St. Helens works. The adsorption plant is capable of being run as both a three unit system and as a two unit system. The two unit system is in use only during maintenance of the third unit. The adsorption cycle time is restricted to a limited number of values by a series of gears and thus is not infinitely variable. The regeneration cycle time is fixed at half the adsorption cycle time for the three unit system and is equal to the adsorption cycle time for the two unit system. The two unit system is in use so infrequently that it is sufficient to assume that for all normal operating conditions the regeneration time is no longer a variable in the optimising procedure once the adsorption cycle time has been specified. As the regeneration cycle time can no longer be

considered a decision variable to maintain the total degrees of freedom of the system requires that one of the quantities previously designated a state variable must now become a decision variable. The choice is between regenerative steam flow rate and regenerative steam temperature. Clearly from an operating point of view the steam temperature is less variable than its flow rate so the choice of steam flow rate as the new decision variable is established.

The steam has still to perform its function of reducing the adsorbate loading on the adsorbent to the point where the adsorbent is capable of carrying out its adsorption duty. So that a criteria is immediately available as a constraint that must be satisfied by all choices of steam flow rate. The cost of steam used to go beyond this constraint (i.e. to reduce the adsorbate loading further) must again be offset by any savings in the adsorbate lost cost, so the objective is still one of minimising the system operating costs. The use of a constant steam flow rate must first be considered as no equipment exists at present on the operating plant for varying the steam flow rate during regeneration. Altering the steam flow rate is unlikely to change the absolute quantity of steam required to perform the initial heating of the bed and its surrounds. Nor are there likely to be significant changes in the steam used to compensate for heat losses when the bed is regenerating. What is likely to be affected is the rate at which the adsorbate is recovered from the unit and hence the differential steam cost. The production of a differential steam cost curve for each level of steam flow used is straightforward based upon measurements from the operating plant. For each steam flow rate used an optimum value of the average system operating cost can be obtained by the procedure of Chapter VIII. The best steam flow rate to use is then easily chosen as the one which produces the lowest optimum average operating costs.

This analysis of the steam usage is incomplete in two aspects.

- a) The possibility exists of considering variable steam flow rates during regeneration.

- b) There is an implicit assumption in all the above analysis that altering the steam flow rate but not its temperature, pressure or degree of unsaturation will in fact alter the rate at which the adsorbate is recovered.

The use of a variable steam flow rate is a practical possibility but it must first be shown that the cost of equipment required to control the flow rate can in fact be offset against some savings either in steam usage or in a prolonging of the life-span of the adsorbent due to less thermal aggravation. Any variation in flow rate must however still ensure that the bed is properly regenerated for further adsorption duty.

The second aspect, b) above, must still be considered even if the steam rate is varied. A deeper view is needed in the mechanisms whereby the adsorbate from being adsorbed on the internal surface of the adsorbent is swept out of the bed by the steam flow. If the rate controlling step is the transfer of adsorbate from the external particle surface across a stagnant film to the bulk steam flow, then any increase in the steam interstitial velocity will promote the removal of adsorbate. It is necessary to consider also the effect of any liquid water covering part of the external particle surface, as this would offer a resistance to the removal of adsorbate greater than that of a stagnant gas film. Diffusion of adsorbate through this water would then mean that although regeneration was diffusion controlled it would be relatively insensitive to temperature changes for as long as the adsorbent remained appreciably wet. A reduction of the steam flow rate if it also reduces the water content of the bed would then promote the recovery of the adsorbate. If the rate controlling step is the diffusion of the adsorbate from the interior particle surface to the external surface then this will be more sensitive to steam temperature but will be completely independent of steam flow rate. Therefore at all steam flow rates that provide the necessary heat requirements the rate of adsorbate recovery (weight of

adsorbate per unit time) would be the same function of the regeneration time only shifted along the time axis to allow for the shorter breakthrough times associated with increased steam flow rate. With a constant steam temperature there would then exist a minimum regeneration time after breakthrough needed to sufficiently regenerate the bed. Thus adsorbate recovery would be unaffected by the steam flow to the extent that any steam in excess of that needed for heat duty and to sweep the bed of adsorbate would be wasted. The cost of generating the unused steam and the cost of condensing it would be operating costs that it was not necessary to incur. The first step in the recovery process, that of desorption at the interior particle surface, is again independent of the steam flow rate as long as it performs its heat duty.

It could be argued that the steam performs the function of physically displacing the adsorbate on the particle surface and so promotes desorption. However, it is readily demonstrable that although some steam would be adsorbed the capacity of a good quality activated carbon for adsorbed moisture is low. It could also be argued that the steam displaces adsorbate from within the pores of the particle and so aids desorption. This is acceptable and must occur to some extent. Yet it is not possible to argue that this same steam in the pores hinders the passage of adsorbate during the adsorption period. The smaller steam molecules will more readily diffuse out of the pores into the moving air stream than the larger adsorbate molecules will diffuse into the particle. The sole detrimental effect of water during the adsorption cycle is in its existence in the liquid state held to the particle surface by the effects of surface tension. The bed drying that is so necessary for efficient adsorption is the removal of this liquid water and not of any water in the vapour state within the particles.

From the above discussion it is apparent that there is no single satisfactory answer as to what steam flow rate to use for the best regeneration. Each individual system must be assessed first to determine which effect contribute most to the recovery of adsorbate.

On the operating industrial unit studied in this work it is believed that the two diffusion processes are the rate controlling steps so that continuous uniformly high steam flow rates at present in use are not the best operating policy. A better steam policy in this case (requiring the use of control equipment) would appear to be the initial use of a high flow rate pulse until breakthrough occurs and for a short period thereafter to ensure complete and thorough heating of the bed. Then a low steam flow rate for the remainder of the regeneration cycle time. Ideally the steam flow rate in this second stage should be profiled to minimise the cost of recovering the adsorbate. An operationally simpler procedure would be either to use a uniformly low steam flow rate (a step reduction in flow) or to gradually reduce the steam flow rate down from its initial value (a linear reduction in flow say).

Under these conditions the initial high rate corresponds to the fixed steam used cost of the general optimising procedure. However, as the recovery of adsorbate is now independent of the steam flow rate (the effects of saturated or wet steam wetting the adsorbent may well mask this fact) the cost of the remaining steam used is no longer a function of the adsorbate loading. The total steam cost thus becomes a fixed operating cost for the system and forces the optimisation procedure to concentrate solely on the adsorption cycle (see below). The need to sufficiently regenerate the bed now requires that enough time be available for regeneration. The final adsorbate loading for the start of the adsorption cycle is now fixed in this manner. Variations in the adsorbate loading at the end of adsorption (start of regeneration) would require no change in the steam policy as long as such variations are only a small part of the total adsorbate loading (initial high driving force at start of regeneration). This point has been dealt with further below.

The above conclusions effect a simplification in the optimising

procedure although the objective remains the same. It is now only necessary to choose the adsorption cycle time when the differential adsorbate lost cost equals the average cycle cost as before. There is no differential steam cost to consider. A further simplification results at the cost of a slight loss in accuracy.

Consider that for a well operated system the exit adsorbate concentration is a very small percentage of its inlet value. The cost of adsorbate lost per unit change in loading can be equated to the cost of adsorbate lost per unit time or more importantly to the value of the exit concentration itself.

In time Δt the adsorbate supplied is $C_o.V.\alpha.\Delta t$ and this is approximately equal to the change in adsorbate loading over this time. Using the figures in the text gives an adsorption rate of 10 lbs of adsorbate per minute or one pound adsorbed in 6 secs. Integrating the adsorbate exit concentration over 6 sec. intervals can be approximated by assuming a constant concentration c . The differential (or instantaneous) adsorbate lost cost then will be approximately $(c.V.\alpha.\Delta t.P_g)/(C_o.V.\alpha.\Delta t)$ which is dependant only on the value of c if all other terms are constant.

The previous theoretical and practical work of this text relevant to the industrial system has indicated that for a sufficiently regenerated bed, under constant SLA inlet conditions, the right hand half of the typical U - shape exit adsorbate concentration profile is of fixed shape. Moreover, if regeneration always leaves the bed in the same state, then the left hand half of the concentration profile is also of fixed shape. Under these conditions the calculations of the average cycle costs are dependant solely on the value of the exit adsorbate concentration. Once the complete exit concentration profile has been produced on the operating unit a single calculation will yield the value of c at which the general optimising criteria

is satisfied. The industrial unit should be operated until the exit concentration rises to this predetermined value at which point adsorption ceases and regeneration commences. Equipment is commercially available to record the exit adsorbate concentration as demonstrated earlier in this text. The adsorption cycle time is now in fact chosen indirectly. An automatic control system is now feasible based on the above criteria.

The most important single assumption in the above discussion is that of the constancy of C_0 . It is also the one variable that is most likely to change on the operating plant. The SIA inlet temperature and moisture content remain fairly constant even in the complete absence of any adsorbate, as for example during the repair of film breakage on a coating machine. It is proposed that a control system be installed to adjust the carrier air flow rate to maintain a uniformly high inlet adsorbate concentration during normal running of the coating machines that provide the SIA. The inlet concentration should be as high as possible giving due consideration to safety requirements and the effects of non-normal running of the coating machines.

As the SIA is fed to two adsorbers in different parts of their adsorption cycles it is necessary to provide sufficient air flow at all times to at least dry out the wetter of the two beds. The poor adsorptive capacity of a cold, wet bed is well known to the author from his experiences on the pilot unit described earlier in the text. It is therefore desirable to place a lower limit on the air flow rate. An upper limit is provided by the rating of the fan. Operation of the coating machines at maximum rate of solvent evaporation must be such that with full air flow the safety constraint on the inlet adsorbate concentration is not violated. This latter requirement is in fact part of the present operating conditions. Running at the minimum air flow rate in times of coating machine failure will mean non-optimal inlet adsorbate concentrations. The possibility then exists of a very gradual rise in the outlet adsorbate concentration such that, due

to the possible long duration of this rise, appreciable quantities of the adsorbate would be lost before the preset exit concentration was reached. It is thus desirable, when operating at the minimum air flow rate, to use an adsorption cycle longer than the normal one. This allows extra cycle time for satisfactory drying of the beds. The beds change from adsorbing to regenerating when the increased cycle time has elapsed.

The final considerations of this particular operating unit involve the temperature and moisture content of the SLA. The SLA temperature is the result of its passage through the two coolers of the plant and its moisture content is set by conditions in the coating machines. The adsorption equilibria is favoured by lower temperatures but the adsorption rate is greatly hindered by poor drying of the bed. Clearly the inlet temperature should be high enough to prevent condensation of moisture within the bed during the latter stages of adsorption. The constraint is thus that the solvent free air (SFA) temperature is in excess of its wet bulb temperature. During the initial stages of the adsorption cycle the SFA will be saturated with water at a high temperature as a necessary part of the bed cooling/drying operation. Operating experience and the continuous monitoring of the SFA exit temperature for each unit has shown that there exists a 'critical' SLA inlet temperature below which the SFA temperature drops sharply and the adsorption performance deteriorates. This critical value is of the order of 50°C , although the range $45^{\circ} - 50^{\circ}\text{C}$ is satisfactory. The Figs. (88) to (91) used in the text illustrate the operating temperature profiles near the inlet face of the bed and so offer evidence of normal running conditions. It is envisaged that should the proposed changes in the operating conditions outlined above be implemented then an inlet SLA temperature of 50°C would form an initial estimate of the best inlet temperature. Any reduction in the wetness of the bed that results from operating changes would of course allow a lower temperature to be used safely. A programme of planned experiments

is proposed to chose the best operating temperature under normal running conditions. On the minimum air flow rate in the absence of significant quantities of adsorbate in the SLA additional heat to dry the beds might be supplied by allowing the SLA inlet temperature to rise above its normal value by reducing the cooling carried out. It is expected that the need for this procedure or otherwise would also be established by the programmed experiments, as would the need to increase the adsorption cycle time when running at minimum air flow rate.

In concluding this discussion of a particular case the proposed changes are listed below. It is the belief of the author that the implementation of these changes and the use of the optimising procedure would effect significant savings in adsorbate losses and steam used.

- a) Objective is to minimise operating costs.
- b) Control air flow rate to maintain uniformly high inlet adsorbate concentration.
- c) Adsorption cycle time is chosen by time taken to achieve specified exit adsorbate concentration.
- d) Regeneration cycle time is half adsorption cycle time using a variable steam flow rate.
- e) A series of programmed experiments should be carried out to find the effects of non-normal operating conditions and to determine suitable values of any modifications to the inlet adsorbate laden air temperature and the adsorption cycle time.

Unfortunately comparative cost data of the effects of these changes and the present operating costs are not at present available.

A P P E N D I C I E S

APPENDIX I

Substitution of equation (IV) into equation (III) gives

$$(1/\alpha) \frac{\partial n}{\partial t} = \frac{k_f a \rho_B \cdot Co}{\alpha \rho_c} \exp \left\{ - \frac{k_f a \rho_B \cdot z}{\alpha \rho_c V} \right\}$$

which can be readily integrated over the interval 0 to $t < t_0$ giving

$$\int_{n(z,0)}^{n(z,t)} \frac{dn}{n(z,t)} = \frac{k_f a \rho_B \cdot Co}{\alpha \rho_c} \exp \left\{ - \frac{k_f a \rho_B \cdot z}{\alpha \rho_c V} \right\} \cdot \int_0^t dt$$

with n a general function $n(z,t)$ and we define $n(z,0) = n_0(z)$, then

$$n = n_0(z) + \frac{k_f a \rho_B \cdot Co}{\alpha \rho_c} \exp \left\{ - \frac{k_f a \rho_B \cdot z}{\alpha \rho_c V} \right\} \cdot t \quad \text{--- 1}$$

for $t=0$, all z , equation (1) reduces to $n = n_0(z)$ which is the initial

distribution of adsorbate on the adsorbent. For $n_0(z) = n_0 = \text{constant}$, then

as at $z=0$, $t=t_0$, and $n = Nos$, so that equation (1) becomes

$$Nos = n_0 + \frac{k_f a \rho_B \cdot Co \cdot t_0}{\alpha \rho_c} \quad \text{--- 2}$$

If from t_0 to $t_0 + dt$ the profile of n developed within the bed moves a distance dz , then assuming that the concentration of adsorbate leaving the bed in the fluid remains zero, a mass balance gives

$$Co \cdot V \cdot \alpha \cdot dt = (Nos - n_0) \cdot dz \quad \text{--- 3}$$

which with (2) becomes

$$dz = \left(\alpha V \rho_c / k_f a \rho_B t_0 \right) \cdot dt \quad \text{--- 4}$$

For the fully developed c profile moving through the bed uniformly with a shape described by equation (IV) of the text, then at time $t (> t_0)$ the bed is saturated for a length z_0 and the c profile for $z \geq z_0$ is seen to be

$$c = Co \exp \left\{ - \frac{k_f a \rho_B \cdot 1}{\alpha \rho_c V} (z - z_0) \right\} \quad \text{--- 5}$$

But integration of (4) gives

$$z_0 = \frac{\rho_c \alpha V}{k_f a \rho_B t_0} (t - t_0) \quad \text{--- 6}$$

so that substitution of (6) in (5) gives

$$c = Co \exp \left\{ - \frac{k_f a \rho_B \cdot z}{\alpha \rho_c V} + \frac{k_f a \rho_B}{\alpha V \rho_c} \left(\frac{\rho_c \alpha V (t - t_0)}{k_f a \rho_B t_0} \right) \right\}$$

which simplifies for $t \geq t_0$ to give equation (V) of the text.

APPENDIX II

By making the changes of variable $m = (N_0 - n)$; $x = z/v$ and $y = (t - z/v)$ then equation (I) of the text reduces to $(\partial m / \partial y) - (\partial c / \partial x) = 0$, and equation (XX) of the text reduces to $\partial m / \partial y = -k_4 m$.

It is therefore implied that there exists a function $f(x, y)$ such that

$$df = m dx + c dy \quad (m = \partial f / \partial x \text{ and } c = \partial f / \partial y)$$

$$\text{hence, } \frac{\partial^2 f}{\partial y \partial x} + k_4 \frac{\partial f}{\partial x} = 0 \quad (1)$$

Let $f(x, y) = \phi(x, y) \cdot \exp(-k_4 y)$, so that (1) reduces to $\partial^2 \phi / \partial x \partial y = 0$,

$$\text{so that } \phi(x, y) = p(x) + q(y)$$

$$\text{then } m(x, y) = \exp(-k_4 y) \cdot \partial \phi / \partial x \quad (2)$$

$$\text{and } c(x, y) = -k_4 \phi \cdot \exp(-k_4 y) + \exp(-k_4 y) \cdot \partial \phi / \partial y \quad (3)$$

If the boundary conditions are constant, and can be defined by

$$m(x, 0) = N_0 - n(x, 0) = N_0 - n_0, \text{ for } y = 0$$

$$c(0, y) = C_0, \text{ for } x = 0$$

$$\text{So that in equation (2) } N_0 - n_0 = \partial \phi(x, 0) / \partial x$$

$$\text{hence, } \int_0^x (N_0 - n_0) dx = \phi(x, 0) = (N_0 - n_0) x \quad (4)$$

$$\text{and in (3) } C_0 = -k_4 \phi(0, y) \cdot \exp(-k_4 y) + \partial \phi(0, y) / \partial y \cdot \exp(-k_4 y) \quad (5)$$

The solution to (5) is obviously, $\phi(0, y) = C_0 y \exp(k_4 y)$, where $\phi(0, 0) = 0$

Then from the expression for $\phi(x, y)$ it follows that $\phi(0, y) = q(y)$ and

$$\phi(x, 0) = p(x), \text{ hence:}$$

$$f(x, y) = C_0 y + (N_0 - n_0) \cdot \exp(-k_4 y) \cdot x$$

$$\partial f / \partial x = m = (N_0 - n_0) \cdot \exp(-k_4 y)$$

$$\partial f / \partial y = c = C_0 - k_4 \cdot x \cdot (N_0 - n_0) \cdot \exp(-k_4 y)$$

Reverting to the original variables z and t gives equation (XXI) of the text.

By making the change in the variable as in Appendix II for $x=z/v$ and $y=c(t - z/v)$, then equation(I) from the text reduces to $(\partial n/\partial y) + (\partial c/\partial x) = 0$; and equation(XXII) from the text reduces to $\partial n/\partial y = k_1/n - k_1 n$, where $k_1 = k_0 \text{Nos}^2/2$ and $k_2 = k_0/2$.

It is therefore implied that there exists a function $f(x,y)$ such that $df = n dx - c dy$ ($n = \partial f/\partial y$ and $c = -\partial f/\partial x$), hence:

$$(\partial f/\partial x) \cdot (\partial^2 f/\partial x \partial y) = k_1 - k_2 (\partial f/\partial x)^2 \quad (1)$$

$$\text{Let } k_1 - k_2 (\partial f/\partial x)^2 = \phi(x,y)$$

$$\text{so that } \partial f/\partial x = k_2^{-1/2} (k_1 - \phi(x,y))^{1/2}$$

$$\text{and } \partial^2 f/\partial x \partial y = 0.5 k_2^{-1/2} (k_1 - \phi(x,y))^{-1/2} \cdot (-\partial \phi/\partial y)$$

$$\left(\frac{\partial f}{\partial x}\right) \cdot \left(\frac{\partial^2 f}{\partial x \partial y}\right) = \frac{-1}{2 k_2^{1/2}} \cdot \frac{\partial \phi}{\partial y} \cdot [k_1 - \phi(x,y)]^{-1/2} \cdot \frac{1}{k_2^{1/2}} [k_1 - \phi(x,y)]^{1/2}$$

$$\left(\frac{\partial f}{\partial x}\right) \cdot \left(\frac{\partial^2 f}{\partial x \partial y}\right) = -\frac{1}{2 k_2} \cdot \frac{\partial \phi}{\partial y} = k_1 - k_2 \cdot \left(\frac{\partial f}{\partial x}\right)^2 = \phi$$

$$\text{So that } \partial \phi/\partial y = -2 k_2 \phi \quad (2)$$

With the boundary conditions used in Appendix II then

$$n(x,0) = n_0 = k_2^{-1/2} (k_1 - \phi(x,0))^{1/2}$$

$$\text{So that } \phi(x,0) = k_1 - k_2 n_0^2 \quad (3)$$

As the solution of (2) is $\phi = p(x) \cdot \exp(-2 k_2 y)$, then it follows that

$$k_1 - k_2 n_0^2 = p(x), \text{ so that } \phi(x,y) = (k_1 - k_2 n_0^2) \cdot \exp(-2 k_2 y), \text{ and}$$

$$f(x,y) = \left(1/k_2^{1/2}\right) \cdot \int_0^x [k_1 - (k_1 - k_2 n_0^2) \cdot \exp(-2 k_2 y)]^{1/2} dx + s(y)$$

$$f(x,y) = s(y) + \frac{1}{k_2^{1/2}} [k_1 - (k_1 - k_2 n_0^2) \cdot \exp(-2 k_2 y)]^{1/2} \cdot x$$

$$\partial f/\partial y = \partial s/\partial y + \frac{x}{2 k_2} \left\{ [k_1 - (k_1 - k_2 n_0^2) \cdot \exp(-2 k_2 y)]^{-1/2} \right\} \cdot$$

$$\cdot [2 k_2 (k_1 - k_2 n_0^2) \cdot \exp(-2 k_2 y)]$$

Using the second boundary condition of Appendix II, $\partial s/\partial y = -C_0$, therefore replacing k_1 and k_2 by their original values gives:

$$c = C_0 - \frac{x \cdot k_0^2 (\text{Nos}^2 - n_0^2) \cdot \exp(-k_0 y)}{4 \left[\frac{k_0^2}{k} (\text{Nos}^2 - (\text{Nos}^2 - n_0^2) \cdot \exp(-k_0 y)) \right]^{1/2}}$$

APPENDIX IV

By making the change of variables $x=z/v$, $y=c(t - z/v)$ then equation(1) reduces to $\partial n/\partial y + \partial c/\partial x = 0$, and equation(XXIV) from the text reduces to

$$\partial n/\partial y = k_1 c (N_0 - n) - k_2 n (C_0 - c) \quad (1)$$

Again there exists a function $f(x,y)$ such that $df = n dx - c dy$ and equation(1) becomes

$$\begin{aligned} \frac{\partial^2 f}{\partial x \partial y} &= -k_1 \frac{\partial f}{\partial y} \left(N_0 - \frac{\partial f}{\partial x} \right) - k_2 \frac{\partial f}{\partial x} \left(C_0 + \frac{\partial f}{\partial y} \right) \\ \frac{\partial^2 f}{\partial x \partial y} + k_1 N_0 \frac{\partial f}{\partial y} + k_2 C_0 \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y} \frac{\partial f}{\partial x} (k_1 - k_2) &= 0 \end{aligned} \quad (2)$$

If $\phi(x,y)$ is defined such that

$$f(x,y) = \frac{-1}{(k_1 - k_2)} \ln \left[\phi(x,y) \cdot \exp(-k_1 N_0 x - k_2 C_0 y) \right]$$

Then it can be shown that equation (2) reduces to

$$\partial^2 \phi / \partial x \partial y - k_1 k_2 N_0 C_0 \phi = 0 \quad (3)$$

Use of the boundary conditions for the problem as set out in Appendix II gives

$$-C_0 = \frac{k_2 C_0}{(k_1 - k_2)} - \frac{1}{(k_1 - k_2)} \frac{\partial \ln(\phi(0,y))}{\partial y} \quad (4)$$

$$n_0 = \frac{k_1 N_0}{(k_1 - k_2)} - \frac{1}{(k_1 - k_2)} \frac{\partial \ln(\phi(x,0))}{\partial x} \quad (5)$$

Equations (4) and (5) can be solved as ordinary differential equations after defining $\phi(0,0) = 1$ to give

$$\phi(0,y) = \exp \left(\int_0^y (k_2 C_0 + (k_1 - k_2) \cdot C_0) d\eta \right)$$

$$\phi(0,y) = \exp \left(\int_0^y (k_1 C_0) d\eta \right) \quad (6)$$

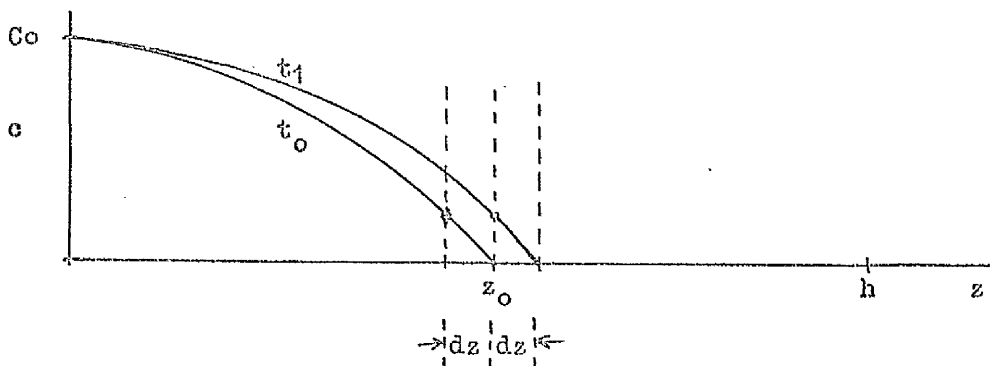
$$\phi(x,0) = \exp \left(\int_0^x (k_1 (N_0 - n_0) + k_2 n_0) d\xi \right) \quad (7)$$

Equations (3), (6), and (7) are now in a form analogous to those used by Amundson to give the solution to Case/4. Hence, following the method of Amundson this particular solution for Case/7 is as shown by equations (XXV) to (XXIX) in the text.

From the notation used in the text, for $t = t_0$ then $c = 0$ at $z = z_0$, where the value of z_0 can be readily found as shown in the text. It is necessary to determine the shape of the c profile for times greater than t_0 and at distances greater than z_0 . It can clearly be seen that for all $z \leq z_0$ and $t > t_0$ then equation XXI applies directly. In particular at $z = z_0$ for $t > t_0$:

$$c = C_0 - k_1 \frac{z_0}{V} (N_{os} - n_0) \exp\left(-k_1 \alpha \left(t - \frac{z_0}{V}\right)\right)$$

If for some time $t_1 = t_0 + dt$ the point of zero adsorbate concentration moves a distance dz to $z_0 + dz$, then the fluid in moving this distance encounters fresh bed. The profile shape produced will then be similar to that of the profile at t_0 when the fluid encountered fresh bed. This is explained diagrammatically below.



The profile for t_1 , $z_0 \leq z \leq z_0 + dz$ is the same as that for t_0 , $z_0 - dz \leq z \leq z_0$. Hence a value of dz can be obtained, as:

$$\begin{aligned} k_1 \cdot (z_0 - dz)/V \cdot (N_{os} - n_0) \cdot \exp\left(-k_1 \alpha \left(t_0 - (z_0 - dz)/V\right)\right) \\ = k_1 \cdot z_0/V \cdot (N_{os} - n_0) \cdot \exp\left(-k_1 \alpha \left(t_0 + dt - z_0/V\right)\right) \end{aligned}$$

Which accounts for the equal values of c found for the two profiles. This can be simplified as $t_0 = z_0/V$ to give:

$$dz = z_0 \left(1.0 - \exp\left(-k_1 \alpha (dt - dz/V)\right)\right) \quad (1)$$

By procedures similar to those outlined above it is possible to show that for successive time increments dt the point of zero adsorbate concentration moves equal successive distance increments dz . Hence the shape of the profile that is found in the region of z_0 moves through the bed as a constant shape with a constant velocity, vel , where $vel = dz/dt$. It is possible to expand equation (1) as a power series and divide by dt so that:

$$vel = z_0 \left\{ k_1 \alpha (1 - vel/V) - \frac{(k_1 \alpha)^2}{2!} (dt - 2dz/V + dz \cdot vel/V) + \dots \right\}$$

For $dz \rightarrow dt \rightarrow 0$, then $vel = k_1 \alpha z_0 / (1.0 + k_1 \alpha z_0 / V)$

and the profile at $z > z_0$ becomes the profile at z_0 evaluated at different times. The point of zero adsorbate concentration will now reach the end of the bed at a time t^* , where $t^* = t_0 + (h - z_0)/vel$.

The adsorbate concentration profile at $z = h$ is thus zero for $t \leq t^*$, and

$$c = C_0 - k_1 \cdot z_0 / V \cdot (N_0 - n_0) \cdot \exp(-k_1 \alpha (t - t^*)) \quad \text{for } t > t^*$$

This expression can be rearranged slightly to give the equation shown in the programme of Fig.(22).

It is possible to check the above functional relationship for the solution to Case 5 by use of the model proposed in Chapter IV. Close agreement is found to verify the above somewhat intuitive approach.

APPENDIX VI

Following the arguments proposed in Appendix V for Case 5 it is possible to imagine a similar situation occurring for Case 6 when $n_0 \neq 0$, so that z_0 is non-zero. Hence, it can be shown that dz is related to the other parameters by:

$$dz = z_0 (1.0 - (A/B) \cdot \exp(-k_0 \alpha (dt - dz/V))) \quad (1)$$

where:

$$A = \{N_{os}^2 - (N_{os}^2 - n_0^2) \cdot \exp(-k_0 \alpha dz/V)\}^{\frac{1}{2}}$$

$$B = \{N_{os}^2 - (N_{os}^2 - n_0^2) \cdot \exp(-k_0 \alpha dt)\}^{\frac{1}{2}}$$

It is noted that equation (1) of this Appendix differs but slightly from its equivalent form in Appendix V. However, the difference is significant. The non-linear driving force means that for successive time increments the point of zero adsorbate concentration does not move successively equal distance increments. The simplifications used in Appendix V cannot therefore be applied.

Moreover, for an adsorbent that is initially free of adsorbate ($n_0 = 0$) the value of z_0 is zero. The above procedure cannot now be applied as whenever the adsorbate laden bulk fluid meets fresh bed the adsorption rate is infinite. The simple intuitive approach used so far now fails. This non-availability of a complete analytical solution is not serious as the model proposed in Chapter IV is not subject to these limitations. The model can be used to produce profiles not obtainable analytically, whereas the available analytical solution can be used to test the validity of the model. This approach has been used to complete the set of curves shown in Fig.(27), and referred to in the text (see 2.1.6).

APPENDIX VII

Application of Weddle's integration formula as performed by other authors has required the setting of a constant small value for the integration parameter, and successive application of the formula until a finite range of the integration parameter had been covered. This procedure is quite easy to programme and provided the range and value of the integration parameter are suitable, will yield reliable results.

The procedure used by this author although making use of the Weddle integration formula does not keep the above factors constant. Examination of the shape of the integrand shown by Fig.35 clearly indicates possible causes of inaccuracy in the simple approach. The association of the largest function values with the smallest range of the integration parameter for a single cycle may not be well represented by use of a fixed increment of the integration parameter. Hence, this author makes use of a variable increment related to the size of the initial cycle. This author also uses the contributions of successive pairs of cycles to the total value of the integral to determine when to stop the integration. Hence the possibility of losing significant figures from the value of the integral found using a fixed total integration range is avoided.

Thus a more accurate estimation of the value of the integral is produced, as well as providing a more economical programme when the magnitude of the cycles are small and can be represented by larger increments with fewer cycles evaluated. The approach also permits the user to decide on the accuracy required by direct change of the programme parameters, instead of relying on choosing "suitable" values for the increment of the integration parameter and the total integration range.

The integration routine can now be described by referring to Fig.34 and the introductory notes above.

This form of the programme produces between 150 and 200 increments upto the maximum or minimum point of the first cycle by starting with a fixed initial step size DL of 0.1 and modifying the value of DL until this criteria is satisfied. It was found in earlier work that the number of increments used above produced satisfactory accuracy and reproducibility of the final profiles. The dimension A is used to store the function evaluations and can be updated whenever the value of DL is changed so that the relevant previous function evaluations are not lost. Hence a change in the value of DL does not involve complete evaluation of a further 200 points (say).

When the turn point occurs within the required number of increments the value of DL is held constant, and the integration routine of Weddle is applied to the function values that have been produced and stored in A. Further function values can then be evaluated and stored in B when all the previously determined points from A have been used. The Weddle integration formula is then applied to the function values in B.

When each function value is produced it is checked to determine whether the cycle has ended or not as shown by a negative sign to the product of the function value just determined and the previous one. The function values now determined in B will vary between two and seven. If less than seven they are integrated by application of Simpsons Rule and/or the Trapezium Rule.

The cumulative total of these successive integrations is the value of the integral for the first cycle AR(1)

Using the same value of DL the integral of the second cycle is found as described above in terms of using B only. This produces the value AR(2). The sum of AR(1) and AR(2) is DELAR and represents the contribution of

one pair of cycles to the value of the integral.

If this contribution is less than 0.5% of the value of the integral so far determined then it is assumed that the value of the integral has converged to its desired value. The integration routine is then left converged to its desired value. The integration routine is then left.

If the value of DELAR is significant then the next pair of cycles must be evaluated using a suitable value of DL.

The above description outlines the basic simplicity of the operation, however, it is necessary to include certain checks in the programme to ensure the routine operates satisfactorily.

- a) It is possible for the first cycle to be incompletely represented, i.e. the absolute value of AR(1) is less than the absolute value of AR(2); but successive pairs of cycles are well behaved with decreasing amplitude. The maximum amplitude of the first cycle is therefore stored as RAMP1 and is compared to the function value formed during the second cycle. If any function value of the second cycle exceeds RAMP1 then the programme reverts to its start with the second cycle becoming the first and the contribution of the first cycle is stored in AREA. Thus, the value of DL is adjusted to the shape of the second cycle, and the routine can proceed satisfactorily.
- b) It is possible for the amplitude of the second cycle in a pair of cycles to be so small that the number of function evaluations using the same value of DL as for the first cycle is less than seven. When this occurs the value of DL is reduced and the cycle re-evaluated. For all other pairs of cycles the value of DL is only changed after each pair of cycles has been evaluated, as described below.

- c) Changes in the value of DL are related to the size range of the integration parameter used in the previous two cycles, and stored in RJ11 and RJ12. As the amplitude of successive cycles decreases rapidly a non-linear estimation of the size range of the integration parameter is produced, and the value of DL chosen so that about 20 points (i.e. function evaluations) are present as a minimum in the first cycle of the next pair. It is likely however that more than 20 points will be produced whenever the sign of the function value shows rapid changes.

All function values are determined by calling the routine FUN with the desired values of the parameters and the integration variable L. It should be noted that the analytical form of the function programmed in FUN as shown in (12) contains several typographical errors.

APPENDIX VIII

Using the properties of the characteristic lines, and the relationships shown by equations LXXIII and LXXIV, the following results are obtained. Along characteristic I

$$dc/dt = -a.k_m(c - c_s)/\rho \quad (1)$$

$$d\theta/dt = \left[-a.k_h(\theta - \theta_p)/\alpha - 4.k_w(\theta - \theta_w)/d_i.\alpha - a.k_m(c - c_s)\mu_1(\theta - \theta_w)/\rho \right] / (c\mu_1 + (\rho - c)\mu_2) \quad (2)$$

Along characteristic II

$$v(\rho - c) = \text{constant} \quad (3)$$

Along characteristic III

$$d\theta_w/dt = \pi d_i k_w(\theta - \theta_w)/m\mu_w - \pi d_o k_u(\theta_w - \theta_u)/m\mu_w \quad (4)$$

$$dq/dt = -\alpha(dc/dt)/\rho_B \quad (5)$$

$$\begin{aligned} \gamma.\mu_s.c_s.(d\theta_p/dt) + \rho_p(\mu_p + q\mu_v)(d\theta_p/dt) &= -\rho_p Q(dq/dt) \\ &- k_h.a(\theta_p - \theta)/\rho_p/\rho_B \quad (6) \end{aligned}$$

If the heat of adsorption varies little with surface coverage of the adsorbate on the adsorbent, then a simplification results as Q and μ_v can be assumed constant.

Equations 1, 2 and 4 can be converted to difference expressions by use of a modified Euler method (2nd order Runge-Kutta formula) expressed as (39)

$$y_{k+1} = y_k + h y'_k + \frac{h^2}{2} y''_k$$

$$\text{where } y' = dy/dx = f(x, y)$$

$$\text{so that } y'' = df/dx = \partial f/\partial x + (\partial f/\partial y).(dy/dx)$$

$$\text{or } f' = f_x + f_y . f$$

$$\text{hence, } y_{k+1} = y_k + h f_k + 0.5 h^2 (f_{xk} + f_{yk} . f_k) \quad (7)$$

Expressing equations 1, 2 and 4 in the form of equation (7) leads to

$$c_{k+1} = c_k + \Delta t . f_k + 0.5 \Delta t^2 (f_{xk} . (-a.k_m/\rho)) \quad (8)$$

where f_k for (8) is defined by equation (1)

$$\begin{aligned} \theta_{k+1} &= \theta_k + \Delta t . f_k + 0.5 \Delta t^2 (f_{xk} . (-a.k_h/\alpha - 4.k_w/\alpha d_i \\ &- \frac{a.k_m(c - c_s)\mu_1}{\rho} / (c\mu_1 + (\rho - c)\mu_2)) \quad (9) \end{aligned}$$

where f_k for (9) is defined by equation (2)

$$\bar{\theta}_{k+1} = \bar{\theta}_{k} + \Delta t \cdot f_k + 0.5 \Delta t^2 (f_k - (N \Delta z k_w / m \mu_w - N \Delta z k_u / m \mu_u)) \quad (10)$$

where f_k for (10) is defined by equation (4)

Equations (5) and (6) can be converted to difference expressions by use of the ordinary forward difference approximation $df/dx = (f_{k+1} - f_k)/h$, so that

$$\rho_B (q_{k+1} - q_k) / \alpha = (c_k - c_{k+1}) \quad (11)$$

$$(\gamma \mu_s c_s + \rho_p \mu_p + \rho_p q \mu_v) (\bar{\theta}_{k+1} - \bar{\theta}_k) = - \rho_p Q (q_{k+1} - q_k) - k_h a \Delta t (\bar{\theta}_{k+1} - \bar{\theta}_k) \rho_p / \rho_c \quad (12)$$

It will be noted that equations (11) and (12) involve the forward differences of two variables. However, c_{k+1} can be calculated directly by equation (8), so that in equation (11) the value of q_{k+1} is uniquely defined. Using this value of q_{k+1} in equation (12) produces a unique value for $\bar{\theta}_{k+1}$.

The computational procedure can then be easily seen by reference to Fig. (40)

where the value of the variable at the nodes is represented by, for example, the notation $\bar{\theta}(i,j)$. For convenience the value $(\Delta z / \Delta t) / V$ has been chosen at unity. For the first time interval Δt the fluid travels a distance Δz so that along characteristic I the bulk fluid temperature and concentration at (2,2) are evaluated from conditions at (1,1). The velocity at node (2,2) is evaluated along characteristic II based on the constancy of the product inlet velocity by inlet adsorbate free carrier density, and using the temperature of the bulk fluid just found for (2,2). The properties of the particles and the container (i.e. those fixed in distance) are evaluated along characteristic III giving their values at (2,1); but using the concentration change $c(2,2) - c(2,1)$ and temperature change $\bar{\theta}(2,2) - \bar{\theta}(2,1)$ with other values evaluated at (1,1). This illustrates the point that although bulk concentration and temperature changes occur over a fixed distance increment within the bed, the fluid movement carries these changes further down the bed.

The value of c_s at (i,j) is determined from the isotherm expression using the values of $q(i,j)$, $\bar{\theta}(i,j)$ and ρ_c .

The calculations are repeated for (2,3) once the variables have been evaluated at some intermediate point (1,z). Where, by definition of the characteristic I, $V = (2.0.\Delta z - z)/\Delta t$, so that $z = 2.0.\Delta z - V.\Delta t$. For the general node (i,j) the intercept is the point ((i-1). Δt ,z), where $z = j.\Delta z - V.\Delta t$ and V is evaluated at the node (i,j-1).

The quadratic approximation $y = a_0 + a_1 z + a_2 z^2$ will be used to determine the value of the property y at the intercept point z. The coefficients are defined in terms of the known property values y_1, y_2, y_3 at the nodes

$z_1 = z_2 - \Delta z, z_2, z_3 = z_2 + \Delta z$ and are

$$a_2 = (y_1 - 2y_2 + y_3)/2\Delta z^2$$

$$a_1 = (y_2 - y_1)/\Delta z - a_2(2z_2 - \Delta z)$$

$$a_0 = y_2 - a_1 z_2 - a_2 z_2^2$$

As the mesh must be set up in advance of computation of the variables it is necessary to first specify the values of Δz and Δt . Suitable values of Δt can be determined from equations (8), (9) and (10) by the simple procedure set out below.

The forward difference formula $dy/dt = f_k = (y_{k+1} - y_k)/\Delta t$ can be stated as $(y_{k+1} - y_k)/\Delta t \cdot f_k > 0$. Expressing equations (8), (9) and (10) in this form gives the requirement that,

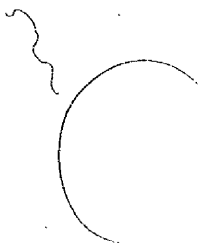
$$0.5 \Delta t (a k_m / \rho) < 1 \quad (13)$$

$$0.5 \Delta t (a k_h / \alpha + 4 k_w / \alpha d_i + a k_m (c - c_s) \mu_1 / \rho) / (c \mu_1 + (\rho - c) \mu_2) < 1 \quad (14)$$

$$0.5 \Delta t (\pi d_i k_w / m \mu_w + \pi d_o k_u / m \mu_w) < 1 \quad (15)$$

Once the physical constants for the system have been defined the values of Δt computed from the equations (13), (14) and (15) can be compared and the smallest value used for the time interval. The appropriate value of Δz is then given as $\Delta z = V.\Delta t$. It should be noted that (14) has the variables c and c_s in its formulation. Clearly if the heat flux associated with the mass flux of adsorbate is small then the smallest value of Δt in (14) is when $c = c_s = 0$, and equation (14) simplifies somewhat.

Following the arguments of 3.5 of the text, the work of Meyer and Weber has been followed. So that the values of the physical constants are those used by Meyer and Weber in their work. These values have been shown in Table. (v). Substitution into equation (15) gives $\Delta t = 1.72 \text{ mins (0.0286 hrs)}$, from equation (14) $\Delta t = 8.55 \times 10^{-5} \text{ mins (1.5} \times 10^{-4} \Delta t = 0.0214 \text{ hrs)}$, from equation (13) $\Delta t = 6.23 \times 10^{-4} \text{ mins}$. Hence, as was found by Meyer and Weber the value of Δt is that given by equation (14).



NOMENCLATURE

Any consistent set of units can be used unless otherwise specified. The following abbreviations have been used: M = weight, T = time, L = length, Q = thermal energy, θ = temperature. All the computer programmes reproduced in the text used the following units: grammes, minutes, centimetres, calories, degrees Kelvin, for M, T, L, Q, θ respectively. Any nomenclature not defined below has been defined in the text at the relevant point and applies solely to that section of the work where it is used.

α	Fractional void volume of packed bed	(L^3/L^3)
γ	Fractional void volume of adsorbent particles	(L^3/L^3)
ρ	Density of bulk fluid in interparticle space	(M/L^3)
$\bar{\rho}$	Density of bulk fluid in intraparticle space	(M/L^3)
ρ_B	Density of packed bed	(M/L^3)
ρ_C	Density of adsorbate-free bulk fluid	(M/L^3)
ρ_P	Density of adsorbate-free adsorbent particles	(M/L^3)
θ	Bulk fluid temperature	(θ)
θ_P	Adsorbent particle temperature	(θ)
θ_u	External temperature	(θ)
θ_w	Container wall temperature	(θ)
μ_1	Specific heat of adsorbate in bulk fluid	$(Q/M\theta)$
μ_2	Specific heat of adsorbate-free bulk fluid	$(Q/M\theta)$
μ_3	Specific heat of adsorbate on adsorbent	$(= \mu_v) (Q/M\theta)$
μ_4	Specific heat of water in bulk fluid	$(Q/M\theta)$
μ_5	Specific heat of water on adsorbent	$(Q/M\theta)$
μ_P	Specific heat of adsorbate-free adsorbent particles	$(Q/M\theta)$
μ'_P	Specific heat of adsorbate-laden adsorbent particles	$(Q/M\theta)$
μ_w	Specific heat of container	$(Q/M\theta)$
σ_a	Gramme molecular weight of adsorbate	$(gm/mole)$
σ_c	Gramme molecular weight of adsorbate-free bulk fluid	$(gm/mole)$
σ_w	Gramme molecular weight of water	$(gm/mole)$
η, λ	Integration parameters	
$\alpha_1, \alpha_2, \Omega_1, \Omega_2, \psi_1, \psi_2, \phi_1, \phi_2$	Functions defined in the text	

a	Specific surface of adsorbent particles	(L^2/L^3)
c	Adsorbate concentration in bulk fluid in interparticle space	(M/L^3)
\bar{c}	Adsorbate concentration in bulk fluid in intraparticle space	(M/L^3)
c_s	Adsorbate concentration in bulk fluid at exterior surface of adsorbent particle	(M/L^3)
C_0	Initial value of adsorbate concentration in bulk fluid leaving the bed	(M/L^3)
C_0	Inlet adsorbate concentration in bulk fluid	(M/L^3)
C_{H_0}	Inlet water concentration in bulk fluid	(M/L^3)
d_i	Internal diameter of container of packed bed	(L)
d_o	External diameter of container of packed bed	(L)
D_i	Effective diffusivity in intraparticle void volume based upon the spherical area perpendicular to the radial direction	(L^2/T)
f', g', F, G	Functions defined in the text	
h	Total adsorbent bed length	(L)
H	Enthalpy of bulk fluid in intraparticle space	(Q/M)
H_1	Enthalpy of adsorbate in bulk fluid in interparticle space	(Q/M)
H_2	Enthalpy of adsorbate-free bulk fluid in interparticle space	(Q/M)
\bar{H}	Enthalpy of bulk fluid in intraparticle space	(Q/M)
\bar{H}_1	Enthalpy of adsorbate in bulk fluid in intraparticle space	(Q/M)
\bar{H}_2	Enthalpy of adsorbate-free bulk fluid in intraparticle space	(Q/M)
k_0, k_1, \dots, k_9	Constants defined in text	
k_a	Adsorption rate constant	(L^3/MT)
k_d	Desorption rate constant	(T^{-1})
k_e	Adsorption equilibrium constant $(= k_a/k_d)$	(L^3/M)
k_f	Inert fluid film mass transfer coefficient	(M/L^2T)
k_h	Adsorbent particle film heat transfer coefficient	$(Q/L^2T\theta)$
k_m	Bulk fluid film mass transfer coefficient $(= k_c = k)$	(M/L^2T)
k_p	Effective thermal conductivity of adsorbent particles	$(Q/LT\theta)$
k_u	Container wall exterior film heat transfer coefficient	$(Q/L^2T\theta)$
k_w	Container wall interior film heat transfer coefficient	$(Q/L^2T\theta)$
L	Inlet flow rate of adsorbate-free bulk fluid	(L^3/T)

m	Weight of unit length of container wall	(M/L)
M_1	Mass flux of adsorbate in interparticle space	(M/L^2T)
M_2	Mass flux of adsorbate-free fluid in interparticle space	(M/L^2T)
\bar{M}_1	Mass flux of adsorbate in intraparticle space	(M/L^2T)
\bar{M}_2	Mass flux of adsorbate-free fluid in intraparticle space	(M/L^2T)
n	Adsorbate loading on unit volume of packed adsorbent	(M/L^3)
\bar{n}	Adsorbate loading on unit volume of adsorbent particles	(M/L^3)
n_0	Initial adsorbate loading on unit volume of packed adsorbent	(M/L^3)
nh_0	Initial water loading on unit volume of packed adsorbent	(M/L^3)
Nos	Saturation adsorbate loading on unit volume of packed adsorbent	(M/L^3)
p	Partial pressure of adsorbate in bulk fluid	(mms. of mercury)
P_0	Saturation vapour pressure of adsorbate in bulk fluid	(mms. of mercury)
P_T	Total pressure of bulk fluid	(mms. of mercury)
q	Adsorbate loading on unit mass of adsorbate-free adsorbent	(M/M)
\bar{q}	Equilibrium adsorbate loading on unit mass of adsorbate-free adsorbent	(M/M)
\bar{q}_{os}	Saturation adsorbate loading on unit mass of adsorbate-free adsorbent	(M/M)
Q	Isosteric heat of adsorption	(Q/M)
Q_h	Latent heat of vaporisation of water	(Q/M)
r	Intraparticle radial distance from particle centre	(L)
R	Radius of spherical adsorbent particle	(L)
t	Time	(T)
U	Fluid velocity in empty bed	(L/T)
V	Fluid velocity through interstices of packed bed	(L/T)
z	Distance	(L)

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TABLE.(I).

Symbol in Text	Symbol in Programms	Value
Co	CO	0.000030
Nos	NOS	0.082
n ₀	NO	0.0
V	V	3650.0
α	AL	0.362
ρ_a	ROHB	0.50
ρ_p	ROHP	1.135
R	R	0.13
h	H	10.0

The units of the above terms are as defined in the nomenclature.

TABLE.(II).

Value of accuracy Parameter	Value of integral A2 from Case 2
100.0	2.757569×10^4
10.0	2.757562×10^4
1.0	2.757561×10^4
0.1	2.757561×10^4
0.01	2.757561×10^4
0.001	6.895432×10^4
0.0001	6.895432×10^4
0.00001	2.933318×10^4

N.B. In TABLE.(II) and TABLE.(III) the accuracy parameter refers to the term 'd' of page 32 of the text.

TABLE. (III).

Value of accuracy Parameter	Value of integral A2 from Case 2
100.0	2.756187×10^4
10.0	2.758108×10^4
1.0	2.757466×10^4
0.1	2.756838×10^4
0.01	2.756915×10^4
0.001	2.757243×10^4

TABLE. (IV).

Characteristic Line	Constant Parameter	Variables evaluated along characteristic
I	V	c, θ
II	t	V
III	z	q, θ_p, θ_w

TABLE (V).

Symbol in Text	Symbol in Programme	Value
k_m	KM	0.36060449 g/(min)·(cm ²)
k_h	KH	0.58773 cal/(min)·(cm ²)·(K)
k_w	KW	0.22605 cal/(min)·(cm ²)·(K)
k_u	KU	0.001708 cal/(min)·(cm ²)·(K)
μ_1	MU1	1.2425 cal/(g)·(K)
μ_2	MU2	0.54 cal/(g)·(K)
μ_p	MUP	0.111131 cal/(g)·(K)
μ_v	MUV	1.1 cal/(g)·(K)
m	MASS	12.753566 g/cm
-	TST	300.2 K
-	TWST	300.2 K
-	TPST	300.2 K
θ_i	TOUT	300.2 K
v_o	VO	4078.224 cm/min
θ_o	TO	300.2 K
Co	CO	0.13766688 x 10 ⁻⁴ g/cm ³
h	H	6.0 cm
-	TIME	0.08 min
Q	HEAT	260.44015159 cal/g
d_i	DI	2.24536 cm
d_o	DO	2.667 cm
a	A	13.090551 cm ² /cm ³
α	AL	0.37
γ	GA	0.421
ρ_p	ROHP	0.716 g/cm ³
ρ_B	ROHB	0.450105 g/cm ³

Table VI

Definition	Symbol	Value	Units
Initial wall temperature	TWST	373.0	$^{\circ}\text{K}$
Initial particle temperature	TPST	373.0	$^{\circ}\text{K}$
n_0	NST	0.0	see Nomenclature
Inlet bulk velocity	VO	4078.224	cm/min
Inlet bulk temperature	TO	300.2	$^{\circ}\text{K}$
C_0	CO	0.000014	see Nomenclature
h	H	40.0	"
Maximum time interval	DT	0.1	min.
Total adsorption time	TTIE	40.0	min.
k_h	KH	0.001	see Nomenclature
k_w	KW	0.0002	"
k_u	KU	0.02	"
μ_1	MU1	1.2425	"
μ_2	MU2	0.54	"
μ_3	MU3	1.1	"
μ_w	MUW	0.108353	"
μ_p	MUP	0.111131	"
m	MASS	12.753566	"
α	AL	0.37	"
γ	GA	0.421	"
a	A	13.090551	"
d_i	DI	2.24536	"
d_o	DO	2.667	"
e_u	TOUT	300.2	"
ρ_p	ROEP	0.716	"
ρ_B	ROHB	0.450105	"
Nos	NOS	0.01	"
Q	HEAT	260.44015	"

Table VII

Definition	Symbol	Value	Units
Q_h	HVAP	540.0	see Nomenclature
μ_4	MU4	1.0	"
μ_5	MU5	0.451	"
CHO	CHO	0.0	"
nh_o	NHO	0.01342	"

Table VIII

Inlet air flow rate	15.63 litres/min
Toluene liquid feed rate	0.54 gms/min
Inlet adsorbate concentration (70% IEL)	0.89 vol%
Inlet SLA temperature	35°C
Regeneration steam flow rate	11.0 gms/min
Regeneration steam temperature	110°C
Regeneration breakthrough time	6.25 mins
Weight of adsorbate-free adsorbent	364 gms
Diameter of bed	5.08 cms

Table IX

Time (mins)	Cumulative Values				Adsorbate loading in excess of L_0 (lbs)	Total cost of steam used (£)
	Eth. Ac. recovered (lbs)	Toluene recovered (lbs)	Eth. Ac. recovered (£)	Toluene recovered (£)		
0.0	0.0	0.0	0.0	0.0	395.0	0.0
2.5	0.0	0.0	0.0	0.0	395.0	0.057
5.0	13.4	10.56	0.55	0.12	371.0	0.115
7.5	66.05	61.45	2.71	0.71	267.5	0.172
10.0	109.32	113.58	4.48	1.31	172.1	0.230
12.5	141.16	153.64	5.79	1.78	101.2	0.287
15.0	164.28	181.72	6.74	2.10	49.0	0.345
17.5	179.45	198.75	7.36	2.30	16.8	0.402
20.0	186.90	208.10	7.67	2.41	0.0	0.459

Eth. Ac. = Ethyl Acetate

Table X

Time (mins)	Exit concentration of Eth. Ac. (vol %)	Exit concentration of Toluene (vol %)	Cumulative Values				Adsorbate loading in excess of I_0 (lbs)
			Eth. Ac. lost to atmos. (lbs)	Toluene lost to atmos. (lbs)	Eth. Ac. lost to atmos. (£)	Toluene lost to atmos. (£)	
0	0.00400	0.00420	0.0	0.0	0.0	0.0	0.0
5	0.00090	0.00173	0.197	0.330	0.00809	0.00382	25.9
10	0.00070	0.00133	0.292	0.521	0.01187	0.00603	79.1
15	0.00071	0.00120	0.376	0.682	0.01536	0.00789	132.2
20	0.00079	0.00114	0.469	0.831	0.01910	0.00962	184.5
25	0.00095	0.00112	0.576	0.975	0.02347	0.01130	237.6
30	0.00119	0.00112	0.706	1.116	0.02880	0.01297	289.2
35	0.00164	0.00115	0.877	1.328	0.03581	0.01466	342.1
40	0.00243	0.00122	1.122	1.418	0.04590	0.01640	395.0

Ethyl acetate (Eth. Ac.) inlet concentration 0.456 vol %
 Toluene inlet concentration 0.494 vol %
 Inlet air flow rate 4966 cu ft per min
 Inlet air temperature 35°C

Table XI

Adsorbate loading (lbs)	Differential Costs $\times 10^3$		Total Differential costs $\times 10^3$ (£/lb)
	Adsorbates lost (£/lb)	Steam used (£/lb)	
L_0	0.093	4.960	5.053
$L_0 + 50$	0.093	1.460	1.553
$L_0 + 100$	0.093	0.960	1.053
$L_0 + 150$	0.110	0.760	0.870
$L_0 + 200$	0.123	0.630	0.753
$L_0 + 250$	0.147	0.550	0.697
$L_0 + 300$	0.188	0.530	0.718
$L_0 + 350$	0.258	0.530	0.788
$L_0 + 400$	0.336	0.530	0.896
$L_0 + 440$	0.583	0.530	1.113
$L_0 + 480$	1.457	0.530	1.987
$L_0 + 490$	2.380	0.530	2.910

Extrapolated
Values

Table XII

Total Differential cost $\times 10^3$ (£/lb)	Loading range (lbs)	Total variable cost $\times 10^3$ (£)	Total fixed cost $\times 10^3$ (£)	Total cycle cost $\times 10^3$ (£)	Total cost per unit loading $\times 10^3$ (£/lb)
2.0	444.0	423.8	120.0	543.8	1.225
1.8	435.0	406.7	120.0	526.7	1.210
1.6	424.0	388.0	120.0	508.0	1.198
1.4	404.0	358.0	120.0	478.0	1.182
1.2	367.0	309.9	120.0	429.0	1.170
1.0	310.0	247.2	120.0	367.0	1.184
0.8	192.0	141.0	120.0	261.0	1.360

Table XIII

Item	Present cycle	Optimum cycle
Adsorbate loading range (lbs in excess of L_0)	0 to 395	84 to 444
Adsorbate handled per cycle (lbs)	395	360
Adsorbate supply rate (lbs/min)	9.88	9.88
Adsorption cycle time (min)	40.0	36.4
Exit concentration of ethyl acetate at end of adsorption period (vol %)	0.00243	0.0034
Exit concentration of toluene at end of adsorption cycle (vol %)	0.00122	0.0015
Differential adsorbate lost cost at end of adsorption period (£/lb)	0.00037	0.00053
Total adsorbate lost cost for adsorption cycle (£)	0.0623	0.0728
Steam supply for regeneration flow rate (lbs/hr)	3820	3820
Regeneration cycle time (min)	20.0	15.2
Total steam cost for regeneration cycle (£)	0.4590	0.3482
Differential steam used cost at end of regeneration cycle (£/lb)	0.00496	0.00104
Total operating costs for combined adsorption and regeneration cycles (£)	0.5213	0.4210
Total hourly operating costs (£/hr)	0.5213	0.4880

Fig.1a.

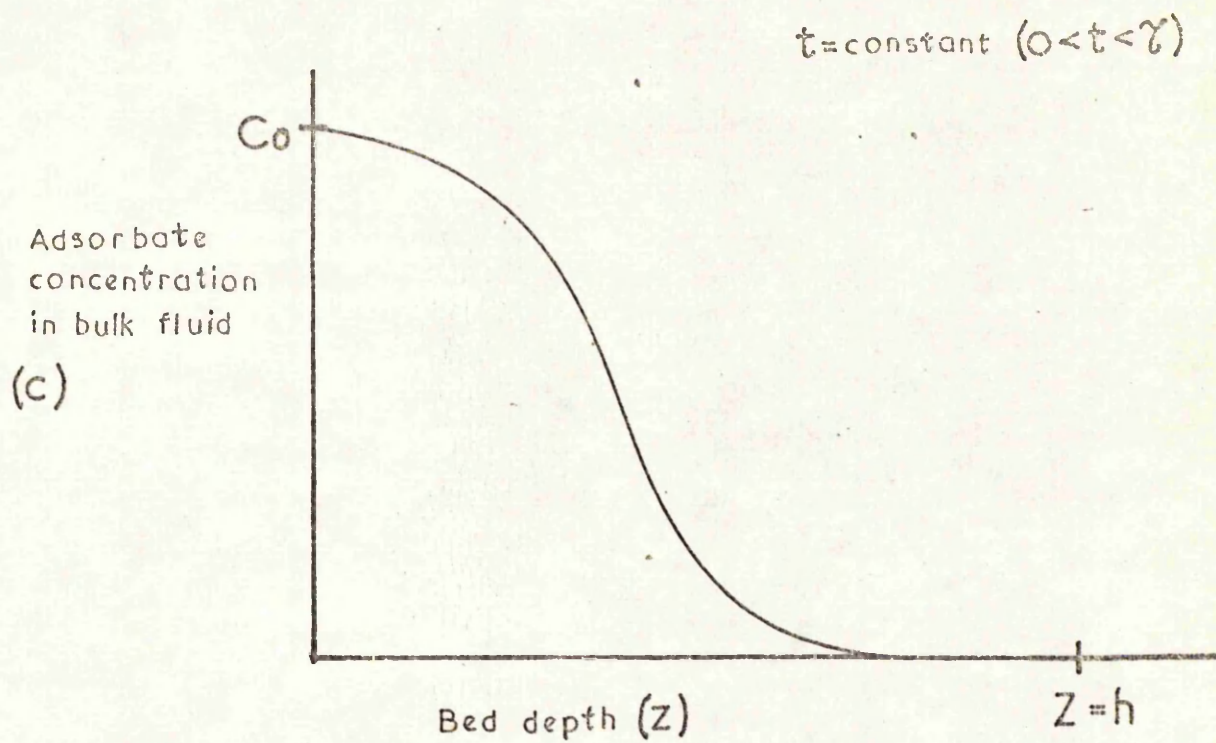


Fig.1b.

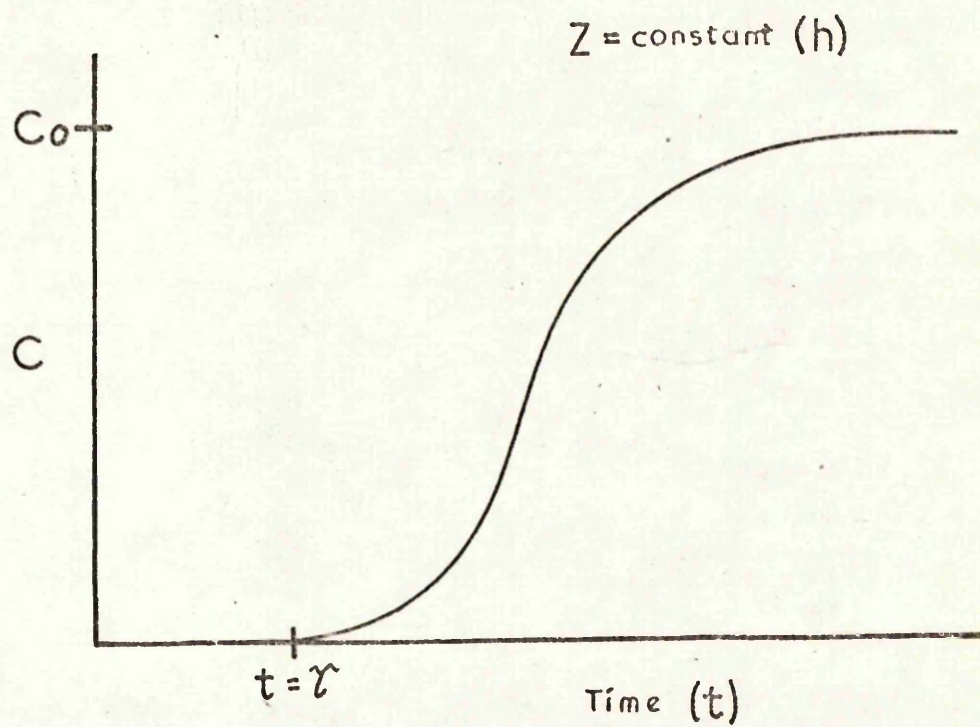


Fig.2a.

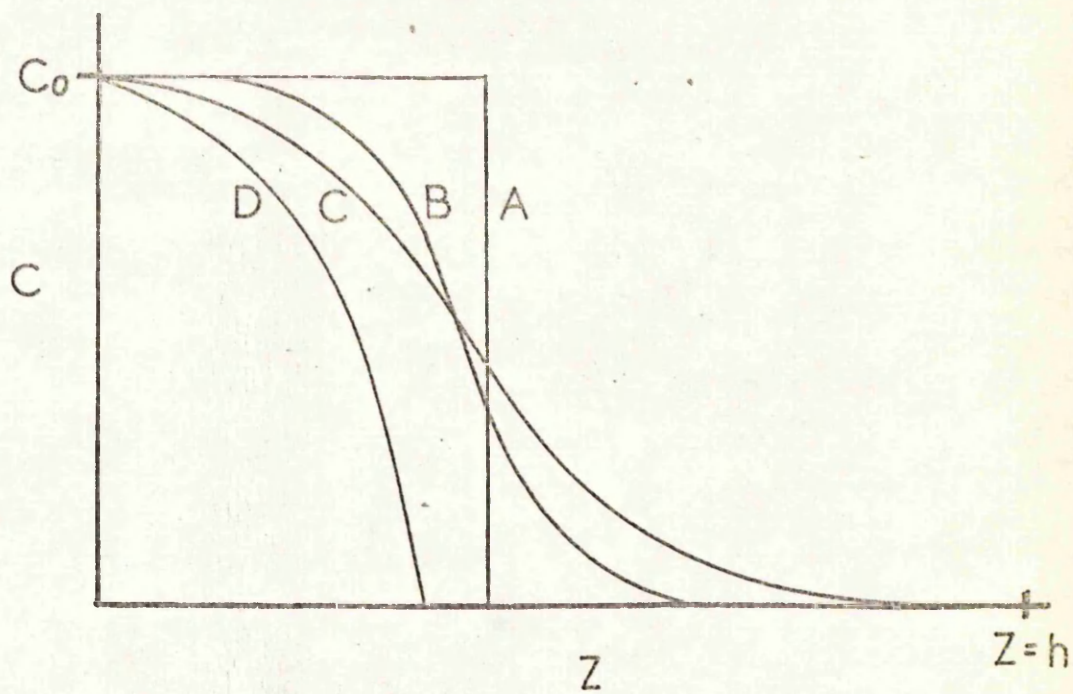


Fig.2b.

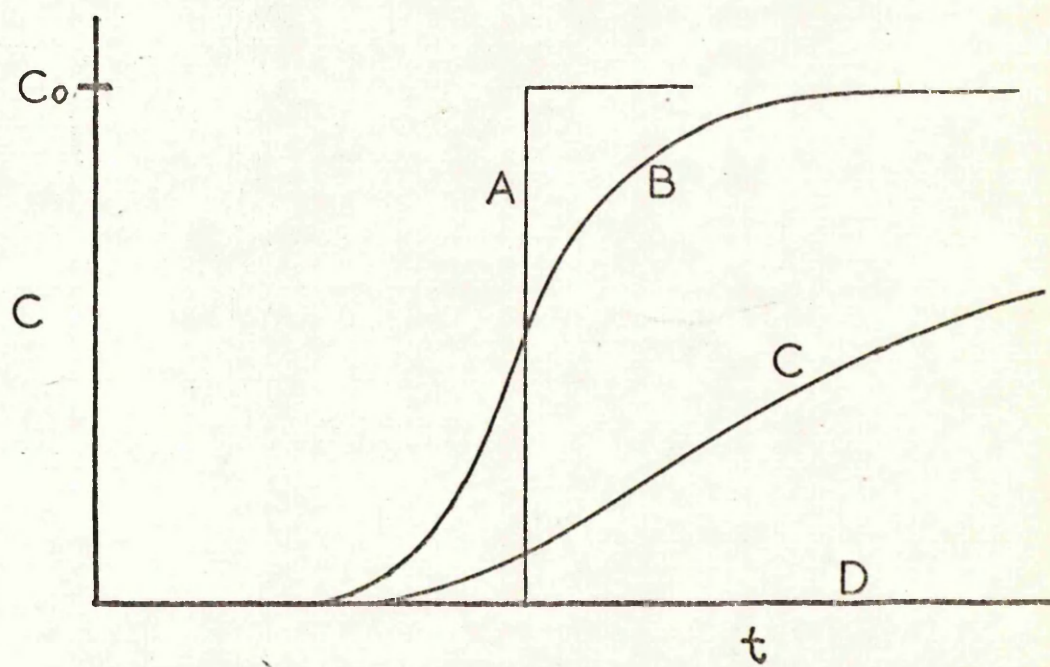
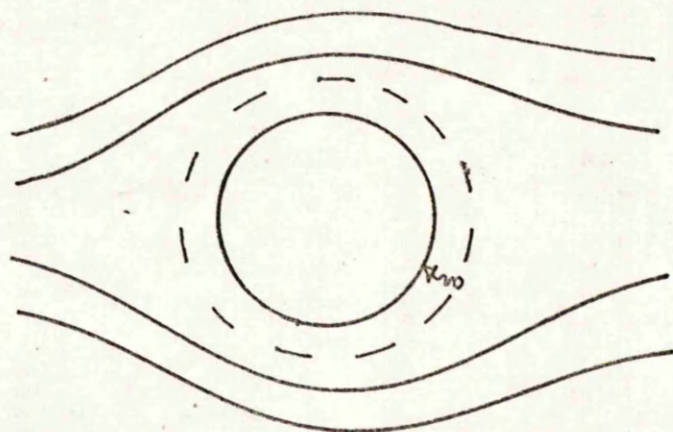
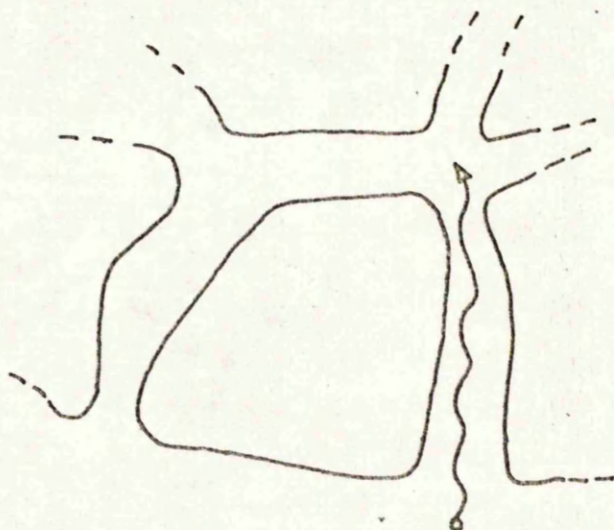


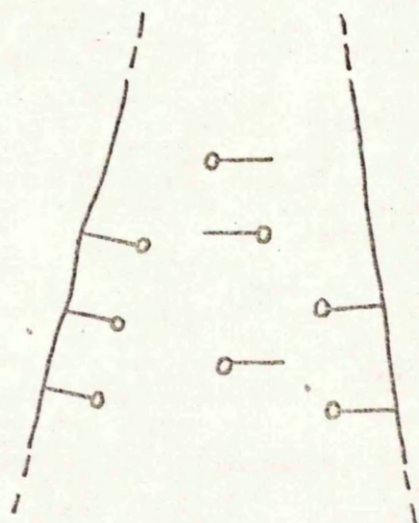
Fig.3.



Diffusion from the bulk fluid across a surface film to the exterior of the particle



Diffusion from the exterior of the particle into the intraparticle void volume



Physical adsorption on the interior surface of the particle

Fig.4.

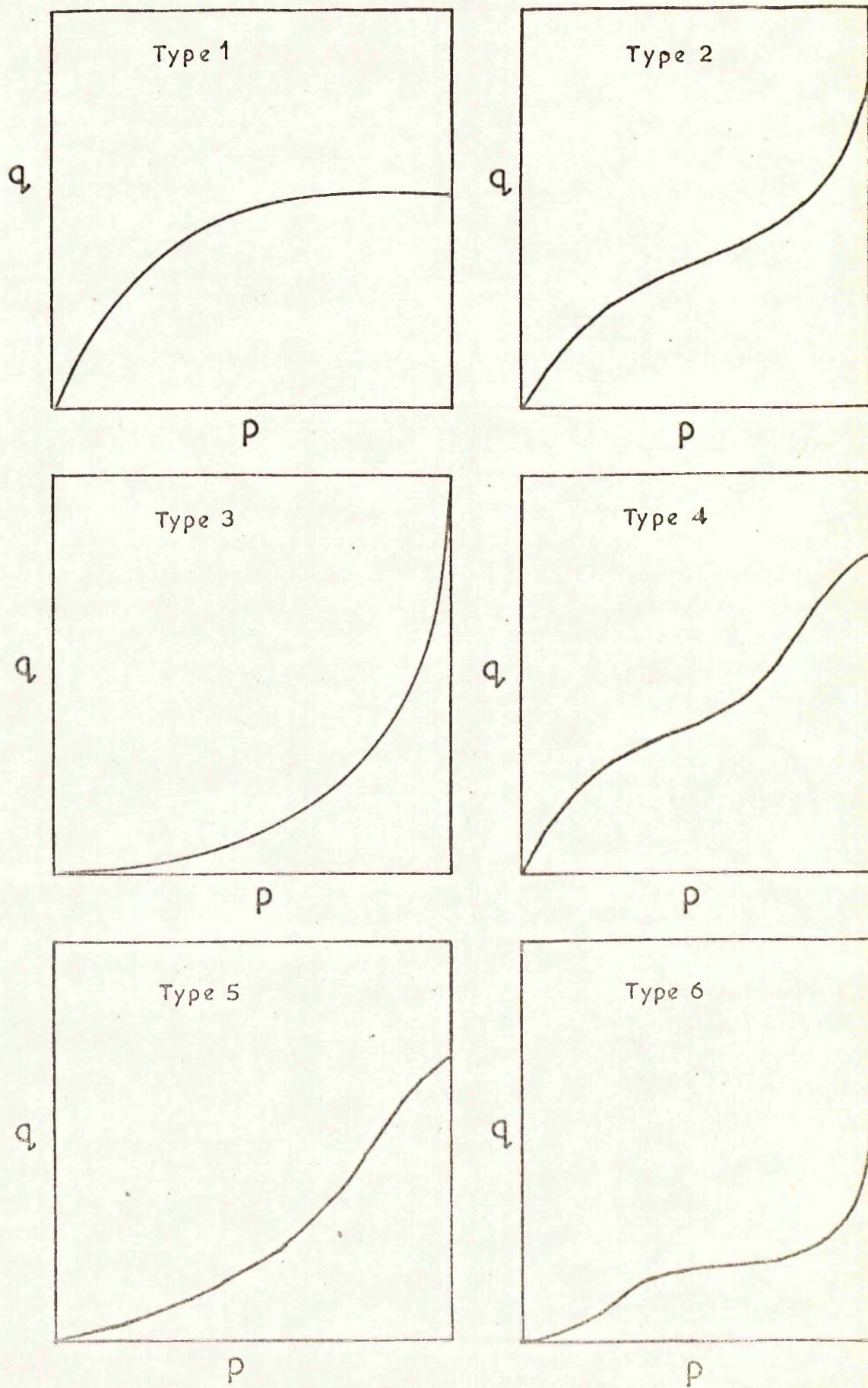


Fig.5.

CASE/2

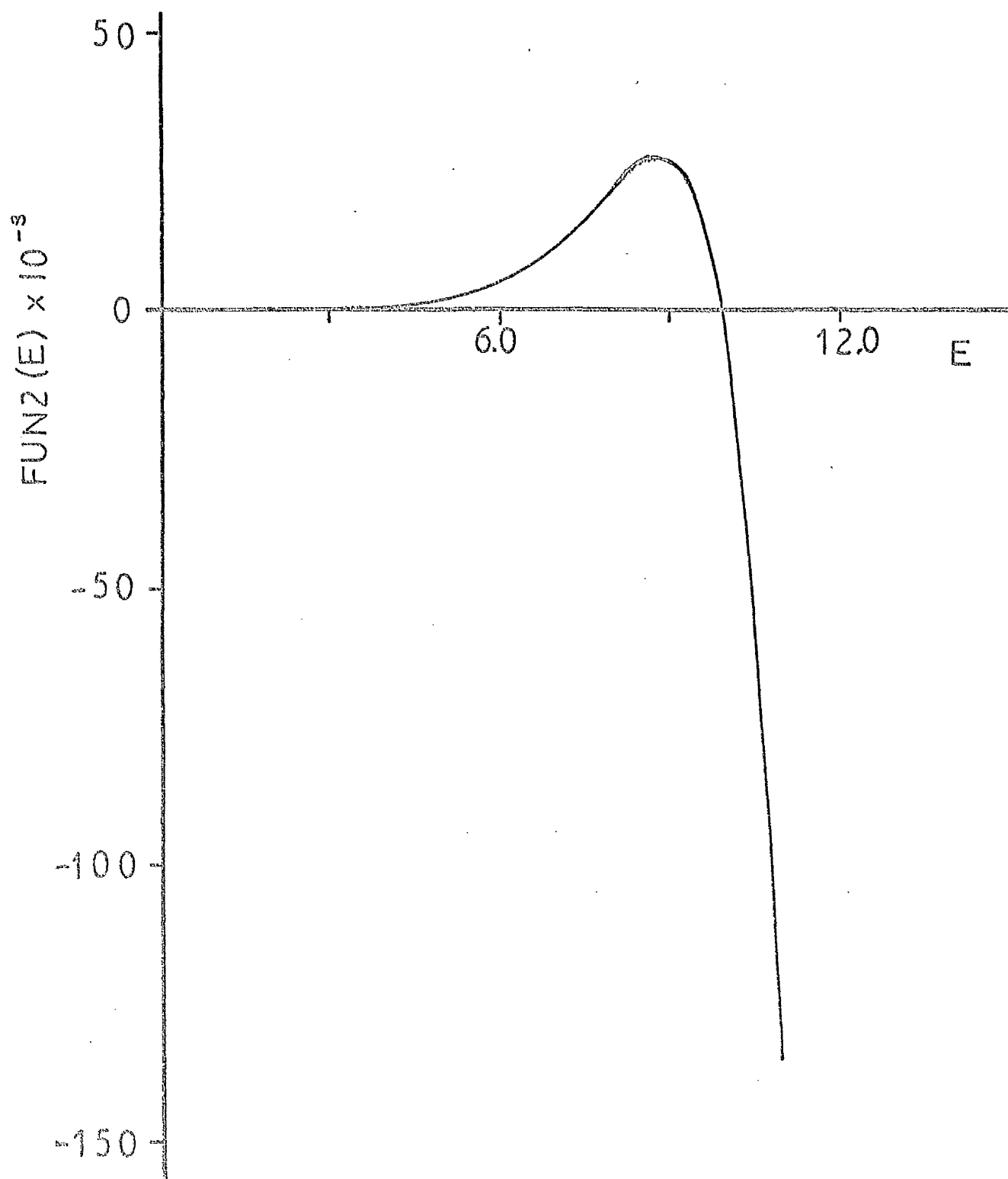


Fig.6. CASE/4

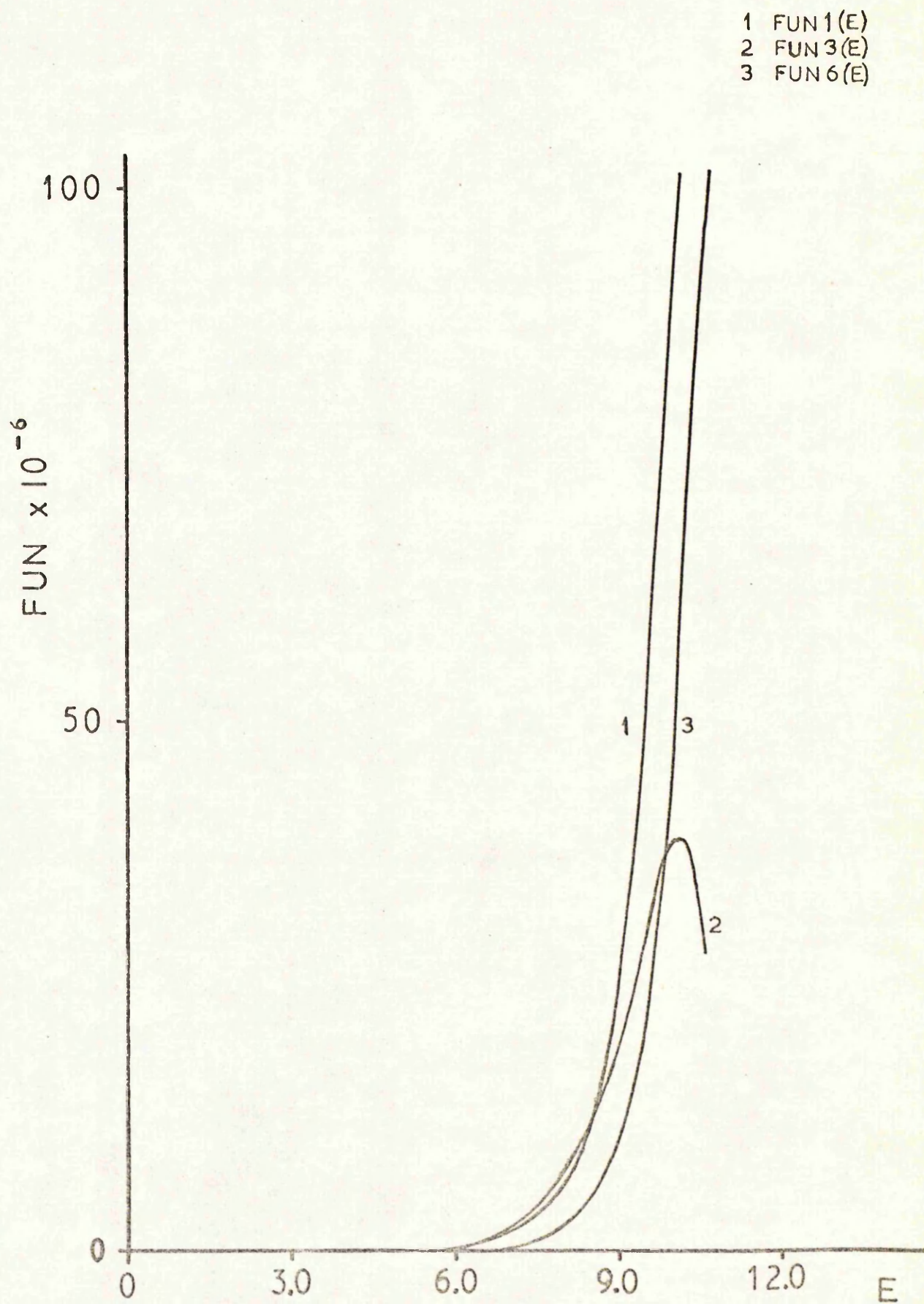


Fig.7a. CASE/2

- 1 $No = 0.04$
- 2 $No = 0.08$
- 3 $No = 0.12$
- 4 $No = 0.16$

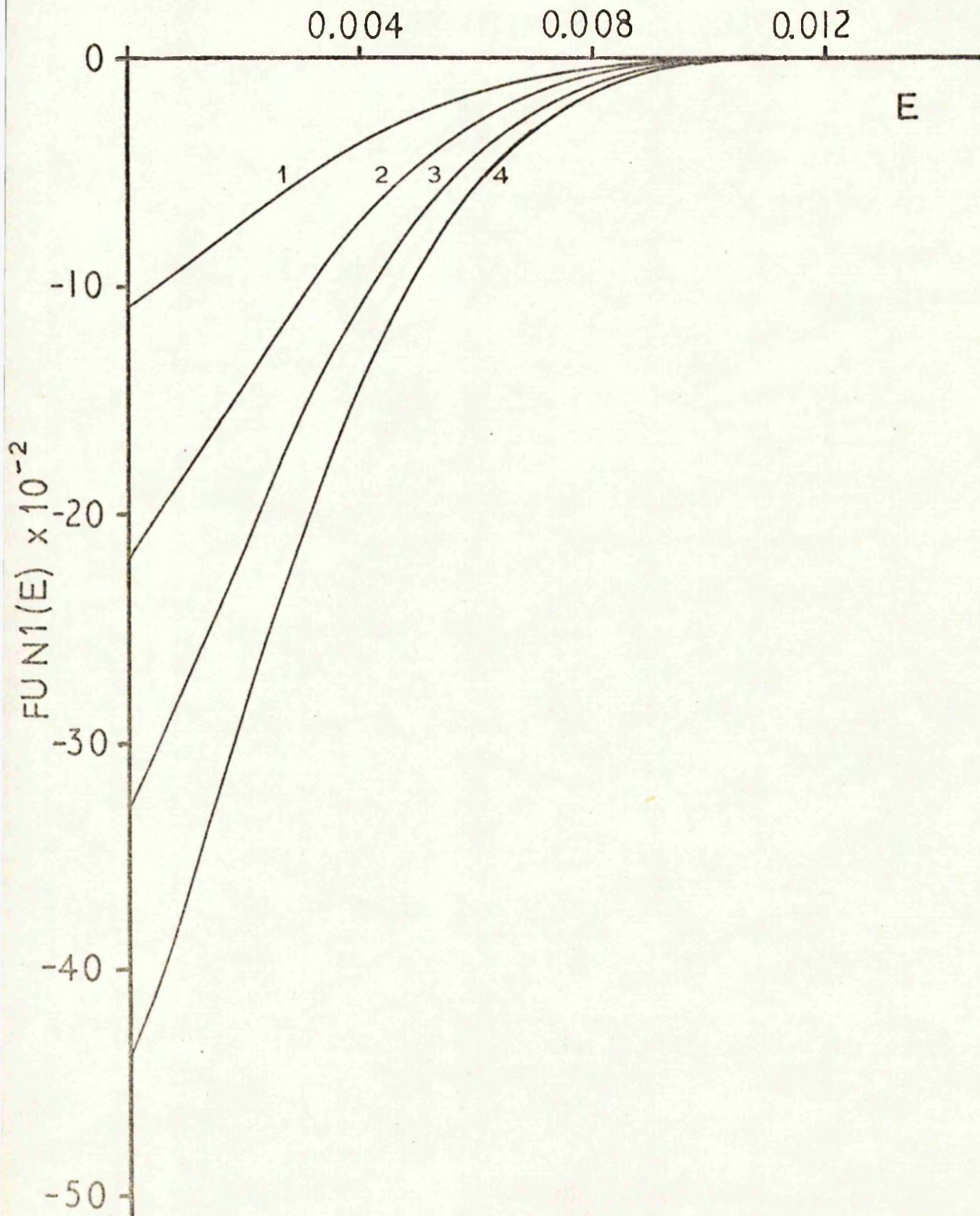


Fig.7b. CASE/4

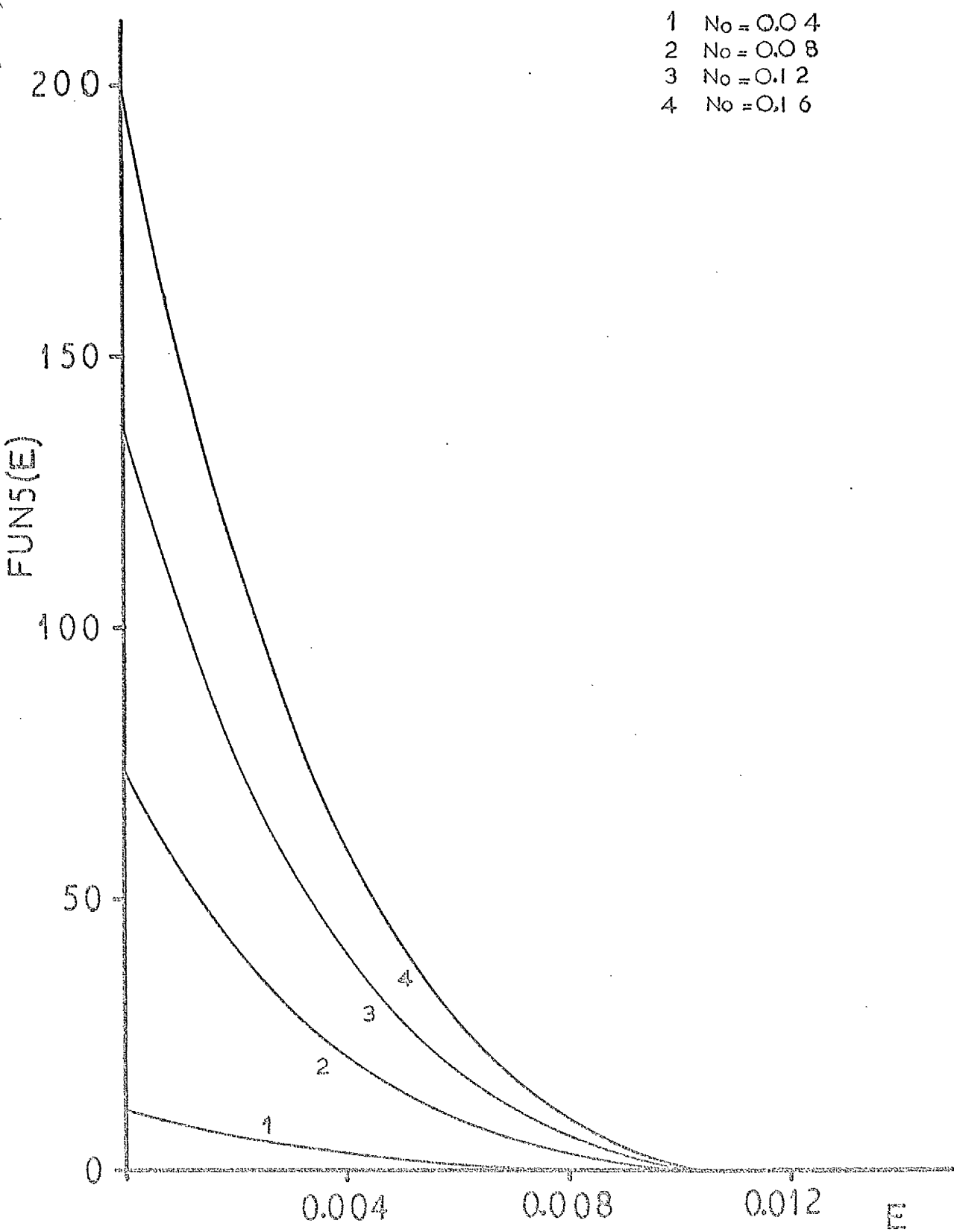


Fig.7c.

CASE/4

- 1 $No = 0.04$
- 2 $No = 0.08$
- 3 $No = 0.12$
- 4 $No = 0.16$

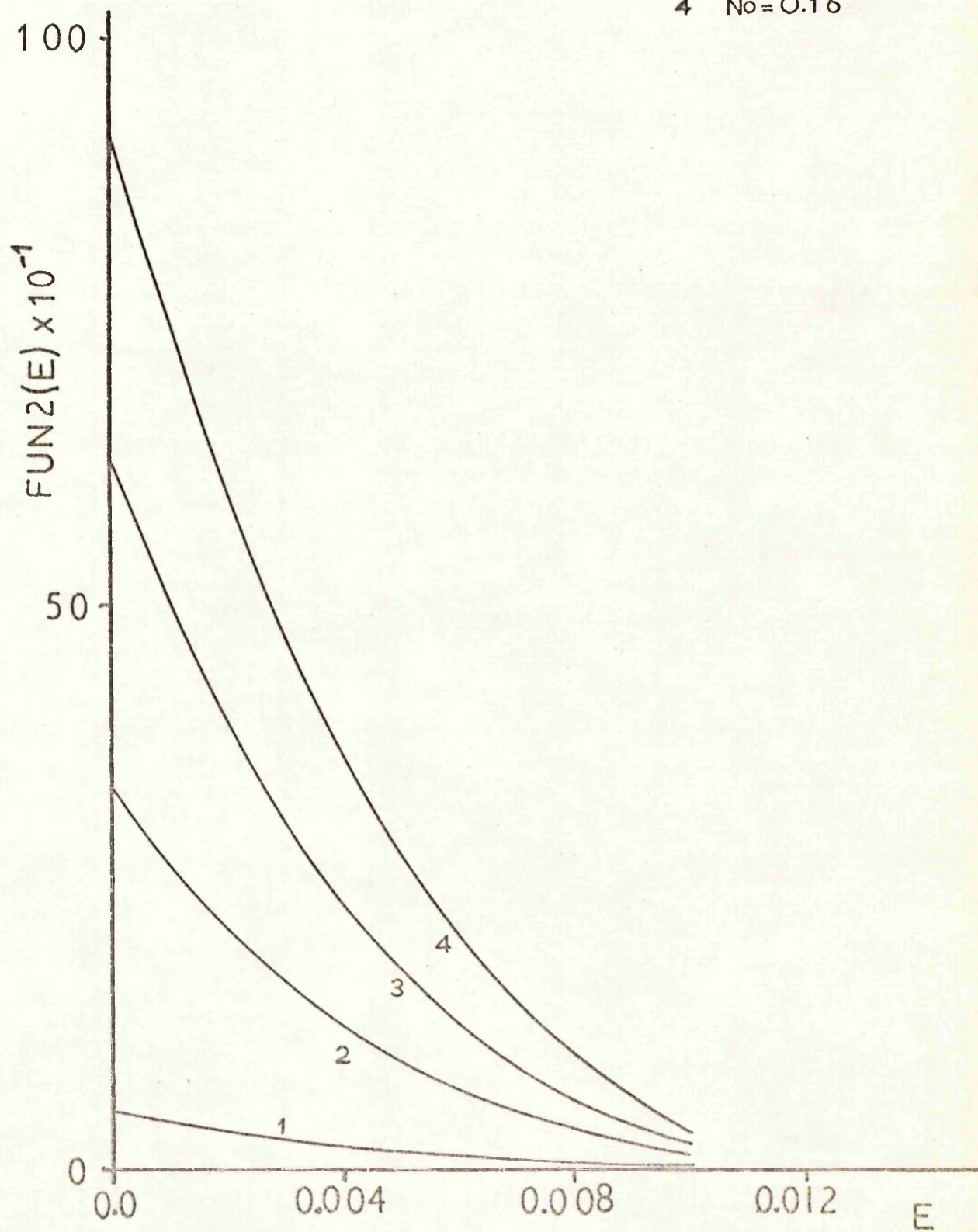


Fig. 8.

CASE/2

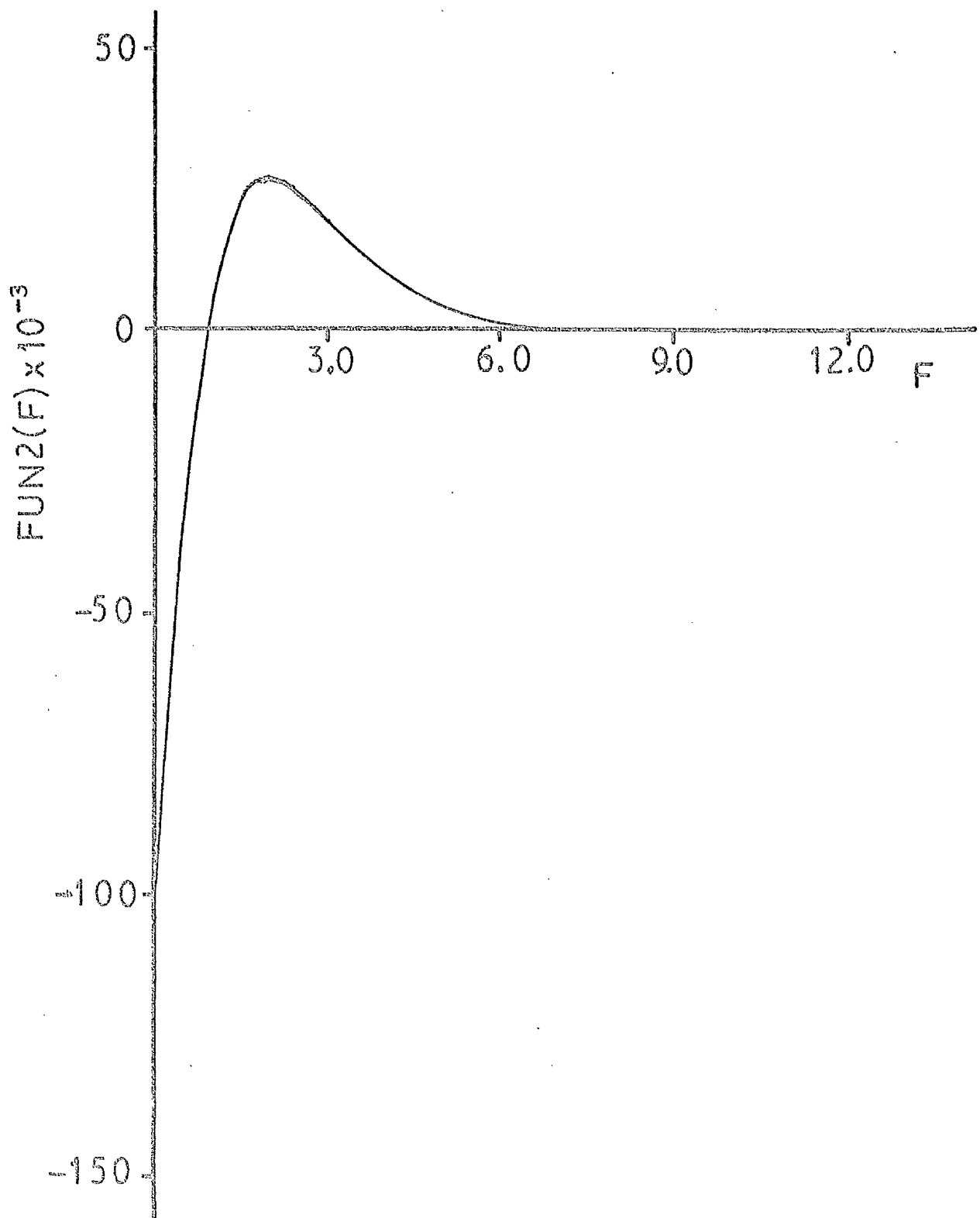


Fig.9.

```

      READ FROM(CR/S1900)
      MASTER CASE/1
      READ N,NO,NOS,K1
      READ(1,50) CO,NO,NOS,AL,V
      READ(1,53) H
      READ(1,54) TM,DT
      X=H/V
      TOS=(NOS*X)/(CO*AL)
      CONST=1000.0
21    CONST=CONST+1000.0
      IF(CONST=2001.0) 0,0,20
      K1=CONST
      TO=(NOS-NO)/(CO*K1*AL)
      T=DT
2    T=T+DT
      IF(T=TM) 0,0,1
14    CONTINUE
      TD=T/TOS
      WRITE(2,51) TD
      Y=AL*(T-X)
      IF(Y) 0,3,3
      T=X+0.1/AL
      GO TO 14
3    IF(T=TO) 0,0,5
      CD=EXP(-K1*X)
      GO TO 4
5    IF(K1*X=T/TO+1.0) 0,0,6
      CD=1.0
      GO TO 4
6    CD=EXP(-K1*X+T/TO+1.0)
4    WRITE(2,52) CD
      GO TO 2
1    CONTINUE
      GO TO 21
20   CONTINUE
50   FORMAT(5F12.6)
51   FORMAT(F8.4)
52   FORMAT(10X,F12.9)
53   FORMAT(E10.4)
54   FORMAT(2E10.4)
      STOP
      END

```

Fig.10. CASE/1

- 1 $K_1 = 10000.0$
- 2 $K_1 = 20000.0$
- 3 $K_1 = 30000.0$
- 4 $K_1 = 40000.0$

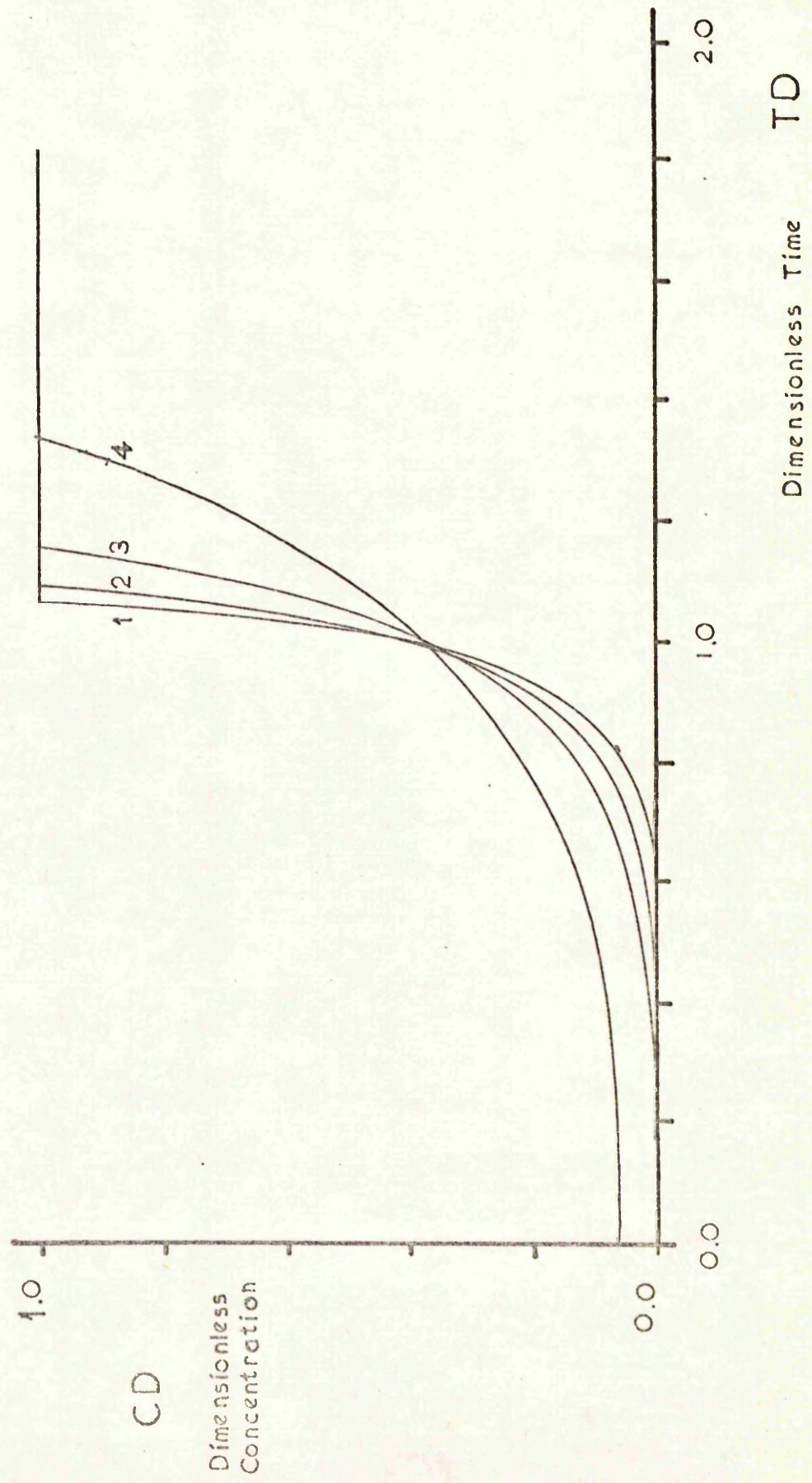


Fig.11.

```

MASTER CASE2
REAL K1,K2,NO,NOS
COMMON K1,K2,Y,X,CO,NO
EXTERNAL FUN1,FUN2
READ(1,50) CO,NO,NOS,AL,V
READ(1,53) 4
READ(1,54) TM,DT
X=H/V
TOS=(NOS*X)/(CO*AL)
TSTORE=DT
21 READ(1,55) K1
   IF(K1) 20,0,0
   WRITE(2,56) K1
   K2=K1*CO/NOS
   T=DT
   STORE=0.0
   DT=TSTORE
2   T=T+DT
   IF (T-TM) 0,0,1
14  CONTINUE
   TD=T/TOS
   IF(TD-1.0) 12,12,0
   DT=DT/5.0
12  CONTINUE
   WRITE(2,51) TD
   Y=AL*(T-X)
   IF(Y) 0,3,3
   T=X+0.1/AL
   GO TO 14
   CD=0.0
   GO TO 4
3   IF (Y) 0,0,5
   A2=0.0
   GO TO 10
5   CALL F4INTSMP(0.0,Y,FUN2,1.0,3,A2)
   A2=A2*1000.0
10  IF (X) 0,0,6
11  A1=0.0
   GO TO 9
6   IF(NO) 11,11,0
   CALL F4INTSMP(0.0,X,FUN1,1.0,3,A1)
9   AS=EXP(K1*X+K2*Y)
   C=((K2*(A1+A2))-CD*(1.0+K2*Y)*EXP(K2*Y))/AS
   CD=C/CO
4   WRITE (2,52) CD
   IF(CD-0.75) 0,0,21
   IF(STORE-CD) 0,0,21
   STORE=CD
   IF((1.0-CD)-0.0001) 1,0,0
   GO TO 2
1   CONTINUE
   GO TO 21
20  CONTINUE
50  FORMAT (5F12.6)
51  FORMAT(F8.4)
52  FORMAT(10X,F12.0)
53  FORMAT(F10.4)
54  FORMAT(2F10.4)
55  FORMAT(F13.6)
56  FORMAT(F13.6)
STOP
END

```


Fig.11.continued

```

FUNCTION FUN1(E)
REAL K1,K2,NO
COMMON K1,K2,Y,X,CO,NO
IF (X=E) 0,0,97
E=X
97 CONTINUE
DUM=2.0*SQRT(K1*K2*Y*(X=E))
CALL F410(DUM,V1)
CALL F411(DUM,V2)
IF (Y=0.0) 0,0,98
TOT=K1*(X=E)=1.0
GO TO 99
98 TOT=(SQRT((K1*(X=E))/(K2*Y))*V2-V1)*EXP(DUM)
99 TOT=TOT*NO*(1.0+K1*E)*EXP(K1*E)
FUN1=TOT
RETURN
END

```

```

C FUNCTION FUN2(F)
ALL FUNCTION VALUES REDUCED BY 0.0001
REAL K1,K2
COMMON K1,K2,Y,X,CO
IF (Y=F) 0,0,102
F=Y
102 IF (F) 0,0,100
TOT=(K1*X=1.0)*(-CO)*(1.0+K2*Y)*EXP(K2*Y)*0.0001
GO TO 101
100 DUM=2.0*SQRT(K1*K2*X*F)
CALL F410(DUM,V1)
CALL F411(DUM,V2)
TOT=((SQRT((K1*X)/(K2*F))*V2)-V1)*EXP(DUM)*0.0001
TOT=TOT*(-CO)*(1.0+K2*(Y=F))*EXP(K2*(Y=F))
101 FUN2=TOT*10.0
RETURN
END

```

Fig.12. CASE/2

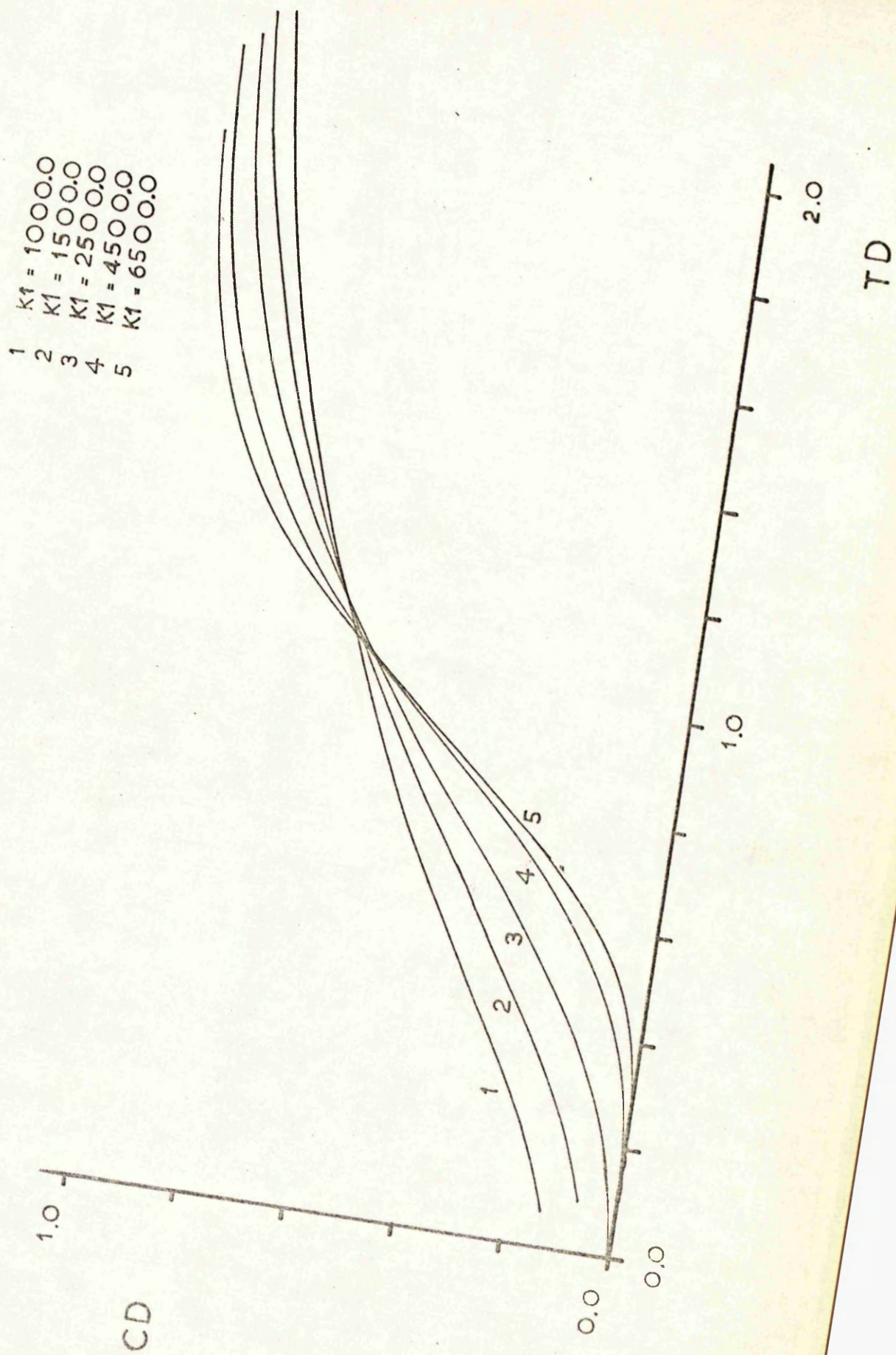


Fig.13.

```

      READ FROM(CR/S1900)
      MASTER CASE/3
      REAL K1,NO,NOS
      READ (1,50) CO,NO,NOS,AL,V
      READ(1,53) H
      READ(1,54) TM,DT
      X=H/V
      TOS=(NOS*X)/(CO*AL)
      CONST=40000.0
21    CONST=CONST+30000.0
      IF(CONST=100001.0) 0,0,20
      K1=CONST
      T=DT
2    T=T+DT
      IF (T=TM) 0,0,1
14    CONTINUE
      TD=T/TOS
      WRITE (2,51) TD
      Y=AL*(T-X)
      IF(Y) 0,3,3
      T=X+0.1/AL
      GO TO 14
3    DUM=EXP(K1*X*(NOS-NO))+EXP(K1*CO*Y)=1.0
      CD=(EXP(K1*CO*Y))/DUM
4    WRITE (2,52) CD
      IF((1.0-CD)=0.0001) 1,0,0
      GO TO 2
1    CONTINUE
      GO TO 21
20    CONTINUE
50    FORMAT (5F12.6)
51    FORMAT(F8.4)
52    FORMAT (10X,F12.9)
53    FORMAT(F10.4)
54    FORMAT(2F10.4)
      STOP
      END

```


Fig.14. CASE/3

1 K1 = 10000.0
 2 K1 = 15000.0
 3 K1 = 20000.0
 4 K1 = 30000.0
 5 K1 = 40000.0
 6 K1 = 70000.0

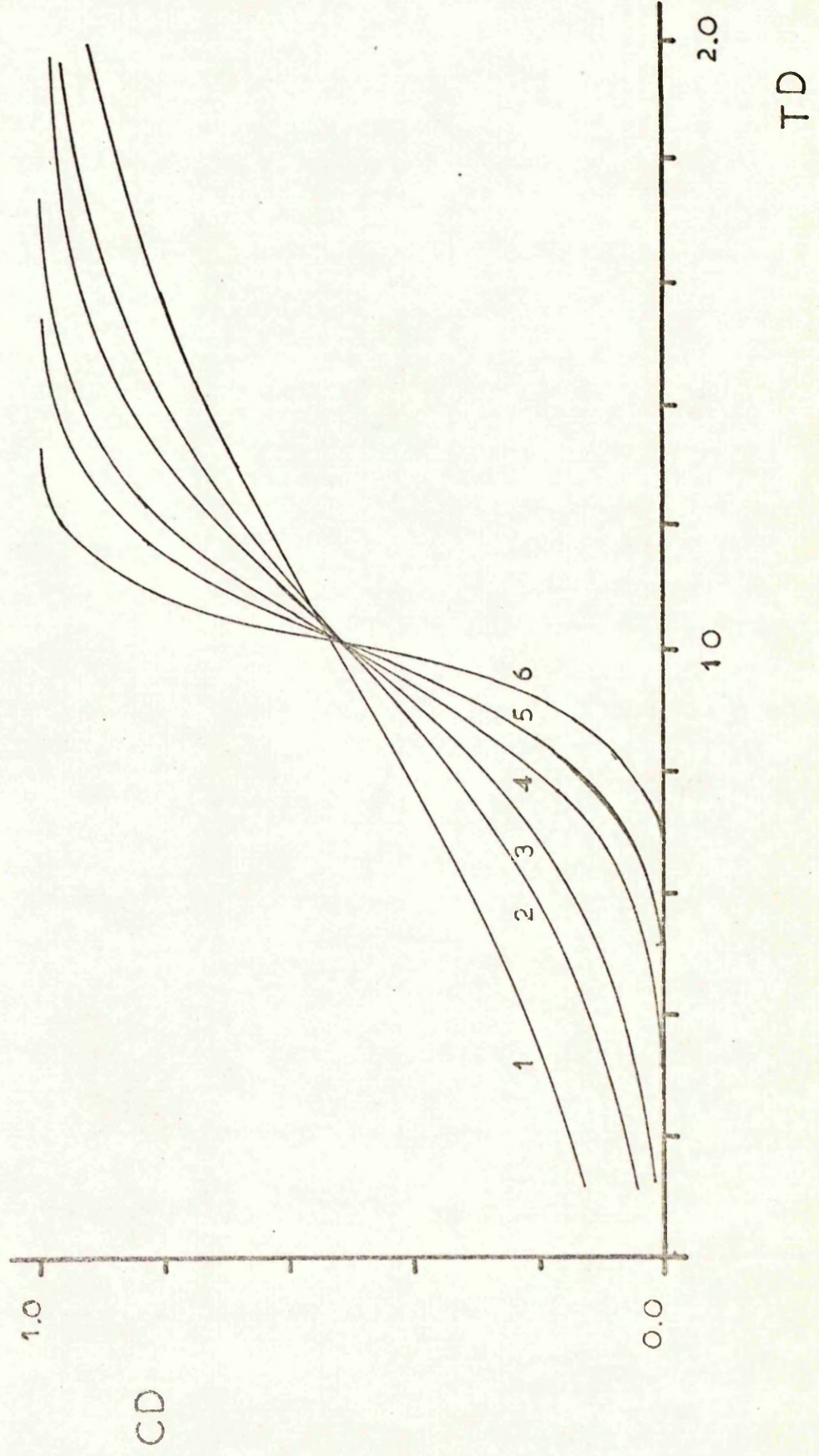


Fig.15.

```

MASTER CASE/4
REAL NO,NOS,K1,K2
COMMON K1,K2,Y,X,CO,NO,NOS
EXTERNAL FUN1,FUN2,FUN5,FUN6
READ(1,50) CO,NO,NOS,AL,V
READ(1,53) H
READ(1,54) TM,DT
X=H/V
TOS=(NOS*X)/(CO*AL)
21 READ(1,55) K1,K2
   IF(K1) 20,0,0
   K2=K1*CO*(1.0=K2)/K2
   WRITE(2,56) K1,K2
   T=DT
2   T=T+DT
   IF(T=TM) 0,0,1
14  CONTINUE
   TD=T/TOS
   WRITE(2,51) TD
   Y=AL*(T-X)
   IF(Y) 0,3,3
   T=X+0.10/AL
   GO TO 14
   CD=0.0
   GO TO 4
3   DUM=2.0*SQRT(K1*K2*NOS*X*Y)
   CALL F410(DUM,V1)
   A1=V1*EXP(DUM)
   CALL F411(DUM,V2)
   V2=V2*EXP(DUM)
   IF(Y) 0,0,0
   A7=K1*K2*NOS*X
   GO TO 5
9   A7=V2*SQRT((K1*K2*NOS*X)/Y)
5   IF(X) 0,0,6
   A3=0.0
   A8=0.0
   GO TO 7
6   CALL F4INTSMP(0.0,X,FUN2,1,0,3,A3)
   CALL F4INTSMP(0.0,X,FUN5,1,0,3,A8)
7   IF(Y) 0,0,8
   A2=0.0
   A9=0.0
   GO TO 13
8   CALL F4INTSMP(0.0,Y,FUN1,1,0,3,A2)
   CALL F4INTSMP(0.0,Y,FUN6,1,0,3,A9)
   A2=A2*1000000.0
   A9=A9*1000000.0
13  C=(K2/K1)+(A7+A8+A9+(K1*CO+K2)*EXP((K1*CO+K2)*Y))/(K1*(A1+A2+A3))
   CD=C/CO
4   WRITE(2,52) CD
   IF(CD=0.98) 0,0,1
   GO TO 2
1   CONTINUE
   GO TO 21
20  CONTINUE
50  FORMAT(5F12.6)
51  FORMAT(F8.4)
52  FORMAT(10X,F12.9)
53  FORMAT(F10.4)
54  FORMAT(2F10.4)
55  FORMAT(2F13.6)
56  FORMAT(F13.6,10X,F13.6)
STOP
END

```

Fig.15.continued

```

C      FUNCTION FUN1(F)
      FUNCTION VALUES DIVIDED BY 1000000,0
      REAL K1,K2,NC,NOS
      COMMON K1,K2,Y,X,CO,NO,NOS
      DUM=2,0*SQRT(K1*K2*NCS*X*F)
      CALL F41Q(DUM,V1)
      TOT=V1*EXP(DUM)*(K1*CO+K2)*EXP((Y=F)*(K1*CO+K2))*0,000001
      FUN1=TOT
      RETURN
      END

```

```

      FUNCTION FUN2(E)
      REAL K1,K2,NC,NOS
      COMMON K1,K2,Y,X,CO,NO,NOS
      DUM=2,0*SQRT(K1*K2*NOS*Y*(X=E))
      CALL F41Q(DUM,VALUE)
      TOT=VALUE*EXP(DUM)*K1*(NOS=NO)*EXP(E*(NOS=NO)*K1)
      FUN2=TOT
      RETURN
      END

```

```

      FUNCTION FUN5(E)
      REAL K1,K2,NC,NOS
      COMMON K1,K2,Y,X,CO,NO,NOS
      DUM=2,0*SQRT(K1*K2*NOS*Y*(X=E))
      CALL F411(DUM,VALUE)
      IF (Y=0,0) 0,0,104
      TOT=K1*K2*NOS*(X=E)
      GO TO 105
104    TOT=VALUE*EXP(DUM)*SQRT((K1*K2*NOS*(X=E))/Y)
105    TOT=TOT*K1*(NOS=NO)*EXP(K1*E*(NOS=NO))
      FUN5=TOT
      RETURN
      END

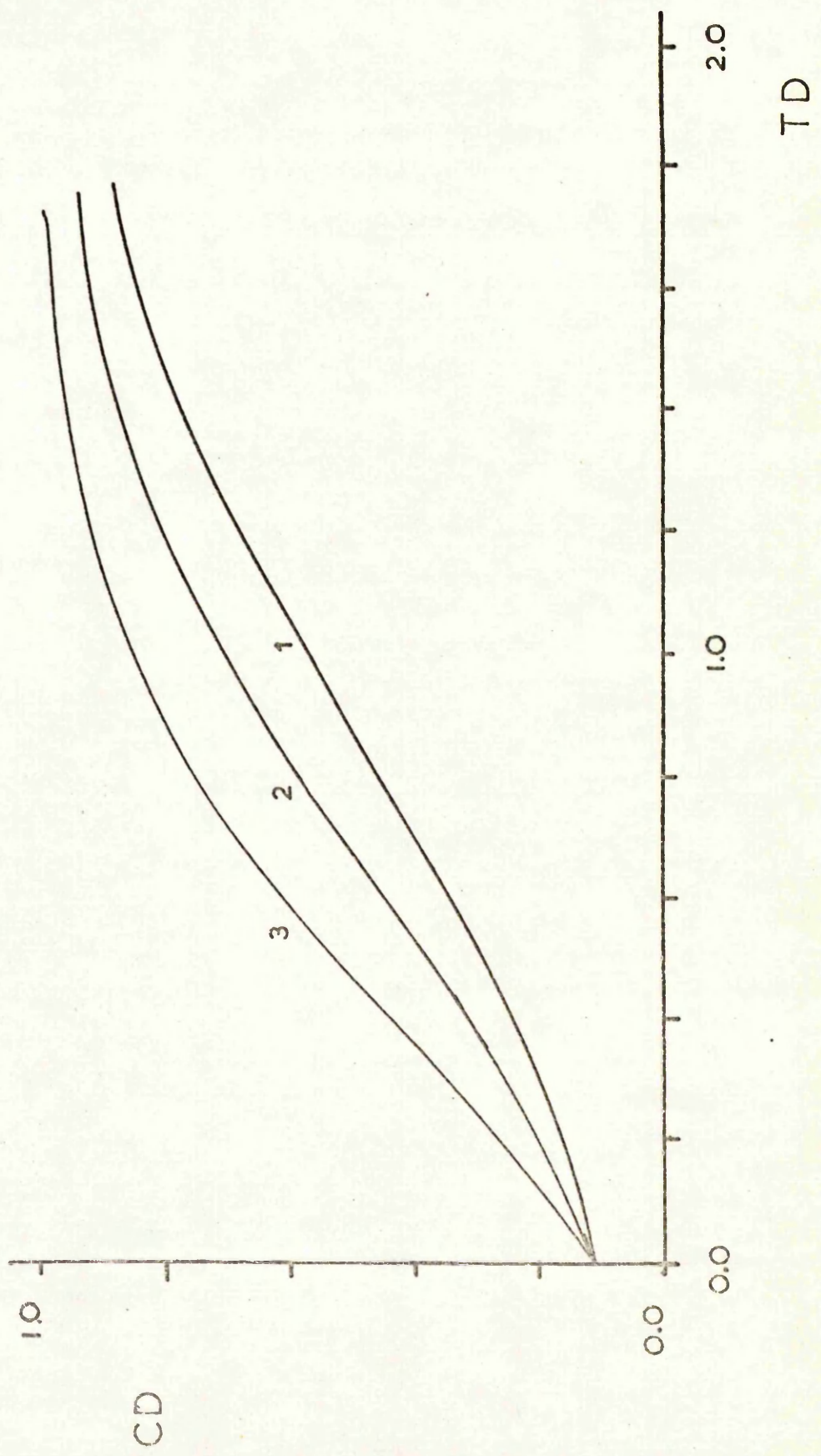
```

```

C      FUNCTION FUN6(F)
      FUNCTION VALUES DIVIDED BY 1000000,0
      REAL K1,K2,NC,NOS
      COMMON K1,K2,Y,X,CO,NO,NOS
      IF (F) 0,0,102
      TOT=K1*K2*NCS*X
      GO TO 103
102    DUM=2,0*SQRT(K1*K2*NOS*Y*F)
      CALL F411(DUM,V2)
      TOT=V2*EXP(DUM)*SQRT(K1*K2*NOS*X/F)
103    TOT=TOT*(K1*CO+K2)*EXP((Y=F)*(K1*CO+K2))*0,000001
      FUN6=TOT
      RETURN
      END

```


Fig.16. CASE/4



1	K1 = 100000.0	K2 = 0.015789	(r=0.95)
2	K1 = 100000.0	K2 = 0.100000	(r=0.75)
3	K1 = 100000.0	K2 = 0.245455	(r=0.55)

Fig.17. CASE/4

1	K1 = 15000.0	K2 = 0.023684	($r = 0.95$)
2	K1 = 15000.0	K2 = 0.150000	($r = 0.75$)
3	K1 = 15000.0	K2 = 0.368182	($r = 0.55$)

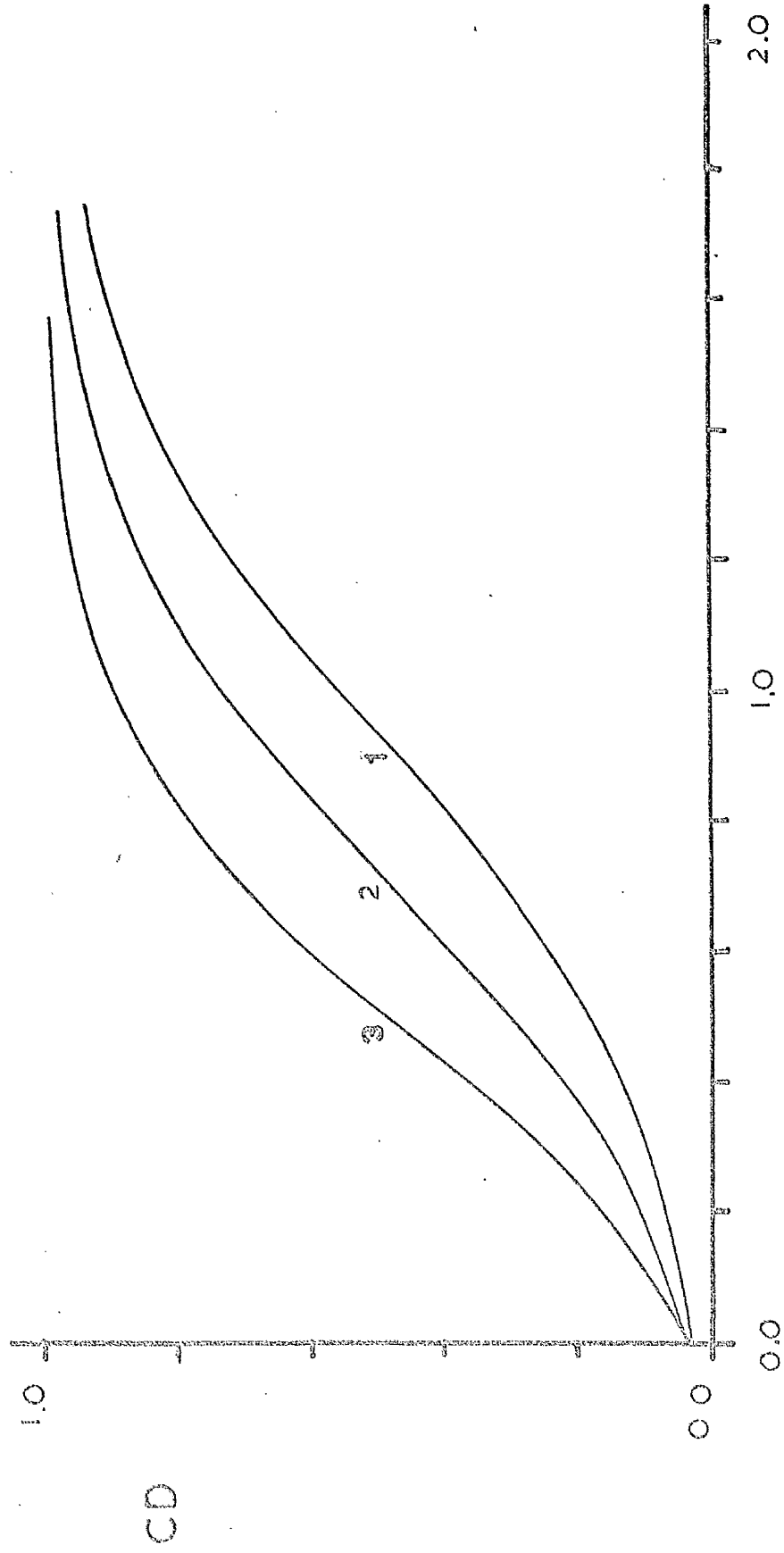
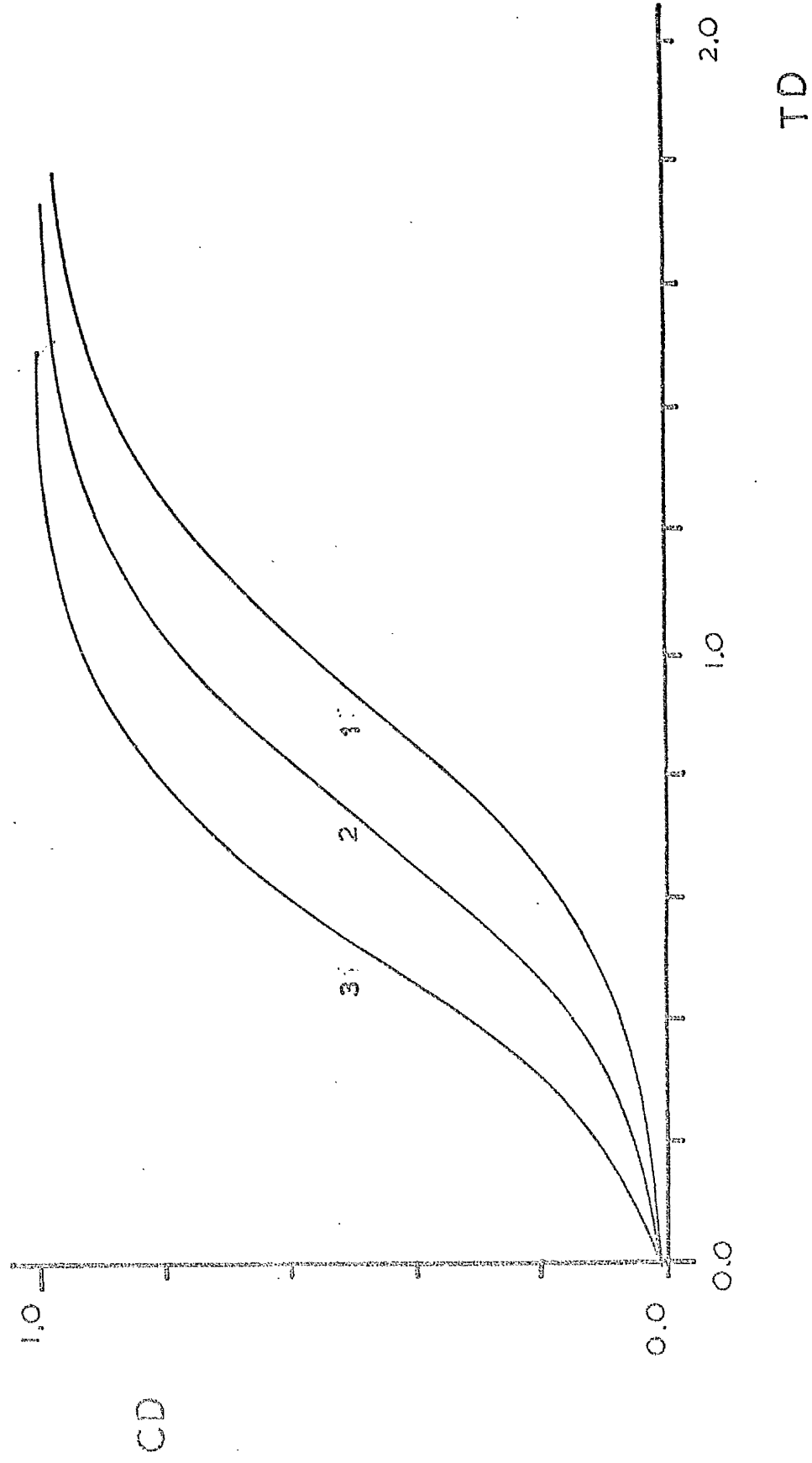


Fig.18. CASE/4

1	K1=200000.0	K2=0.031579	($r=0.95$)
2	K1=200000.0	K2=0.200	($r=0.75$)
3	K1=200000.0	K2=0.490909	($r=0.55$)



1	K1 = 25000.0	K2 = 0.039474	($r = 0.95$)
2	K1 = 25000.0	K2 = 0.250	($r = 0.75$)
3	K1 = 25000.0	K2 = 0.613636	($r = 0.55$)

Fig.19. CASE/4

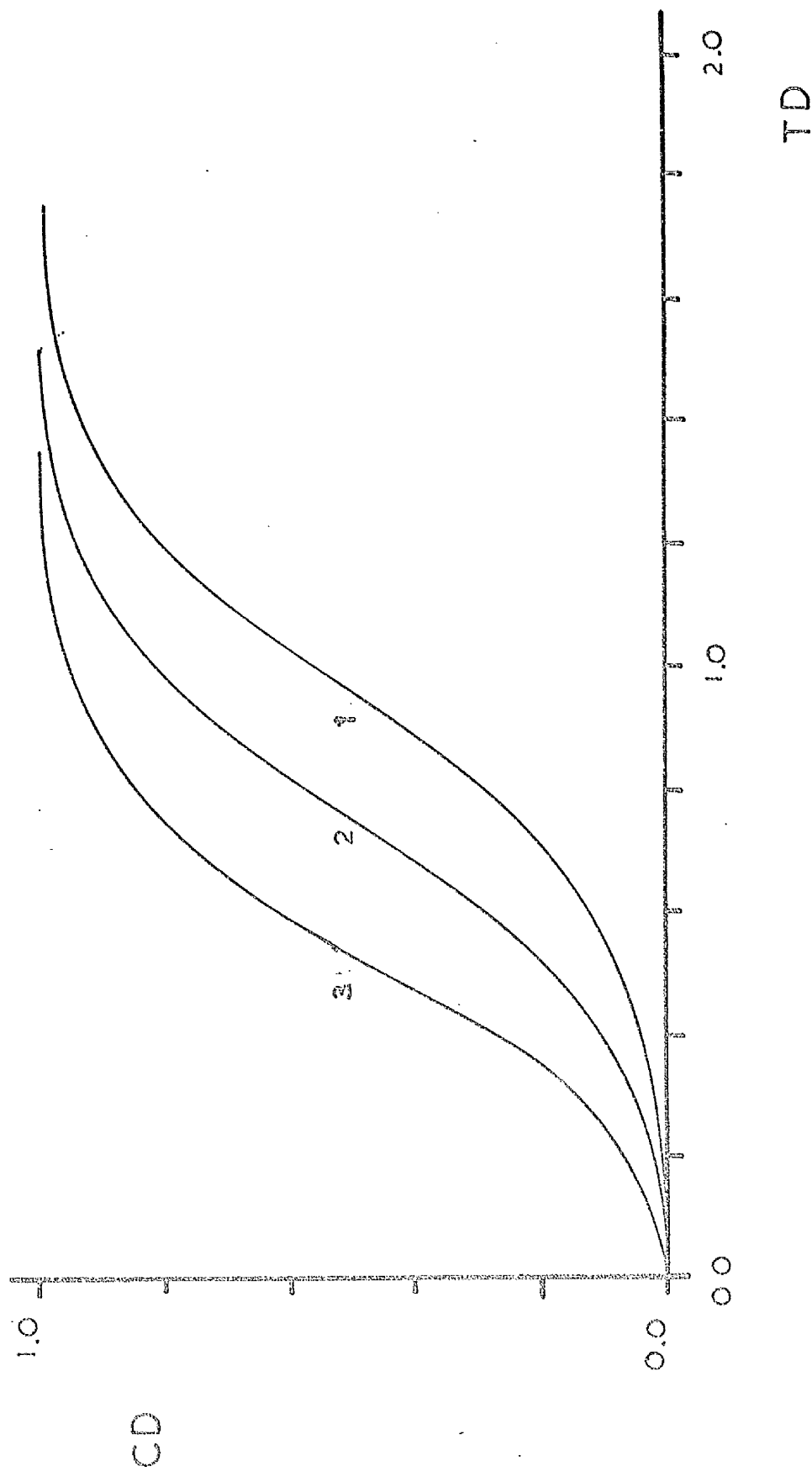
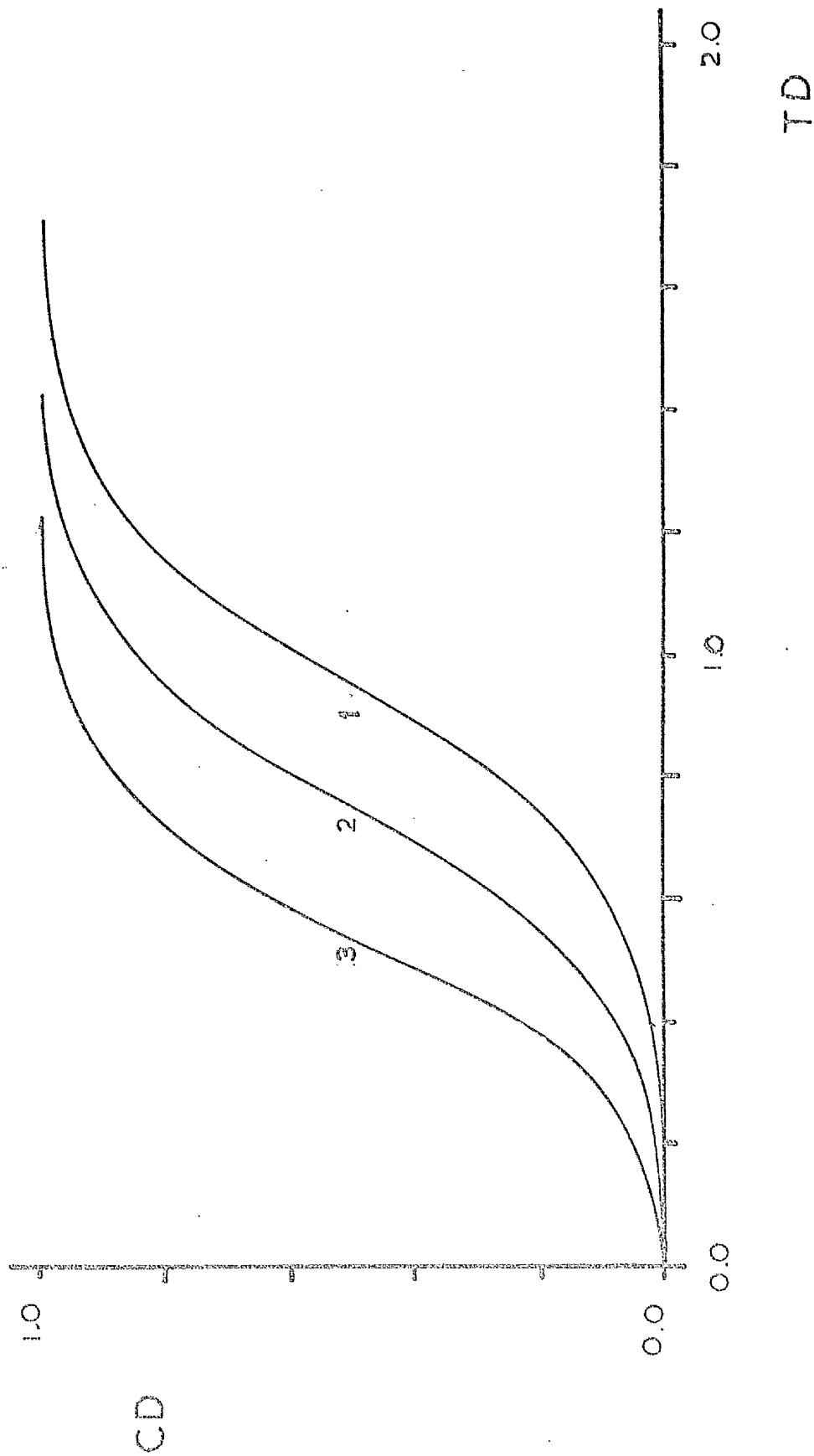


Fig.20. CASE/4

1	K1=300000.0	K2=0.047368	($r=0.95$)
2	K1=300000.0	K2=0.300	($r=0.75$)
3	K1=300000.0	K2=0.736364	($r=0.55$)



1	K1 = 35000.0	K2 = 0.055263	($\nu = 0.95$)
2	K1 = 35000.0	K2 = 0.350	($\nu = 0.75$)
3	K1 = 35000.0	K2 = 0.859091	($\nu = 0.55$)

Fig.21. CASE/4

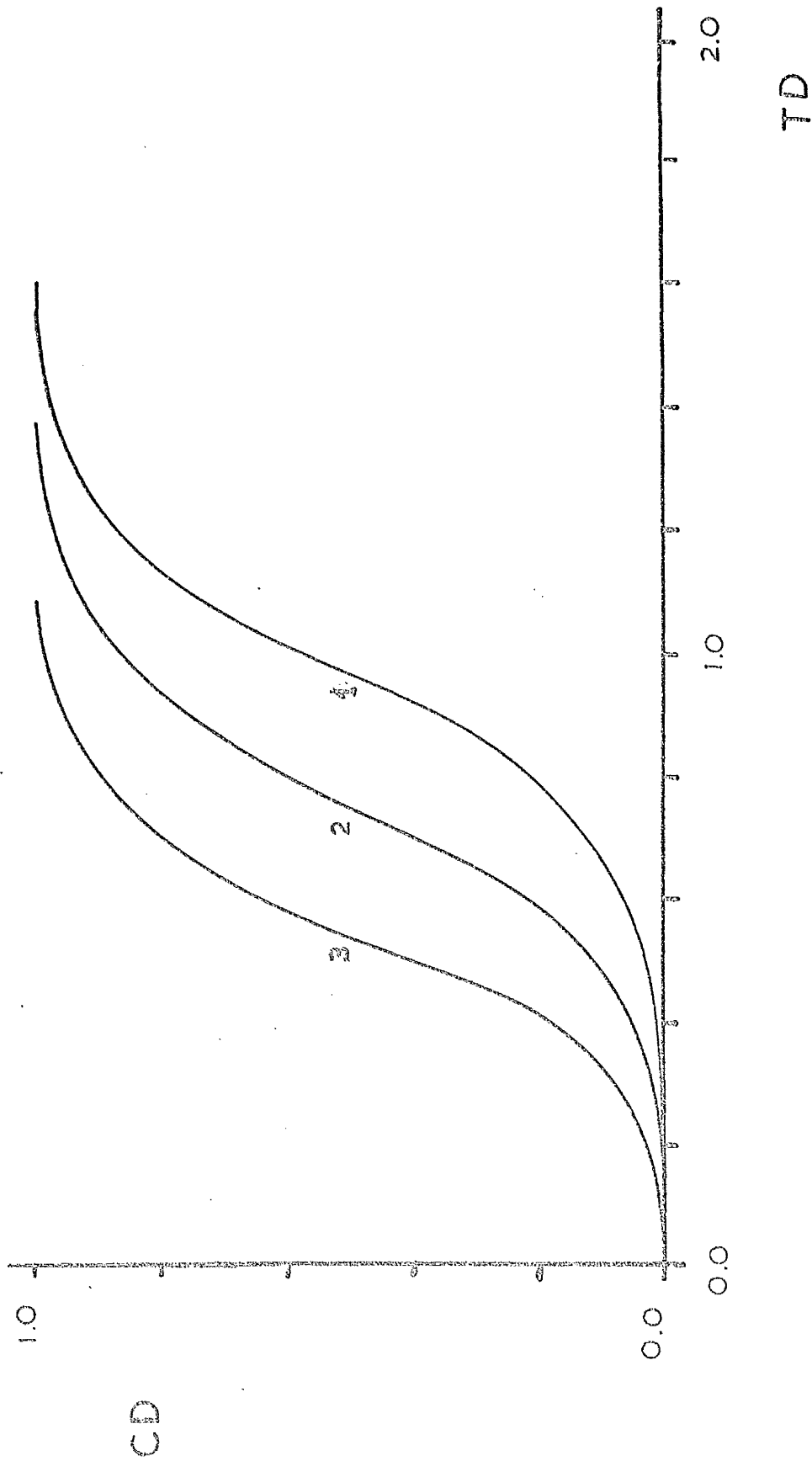


Fig. 22.

```

READ FROM(CR/S1900)
MASTER CASE/5
REAL NO,NOS,K1
READ(1,50) CO,NO,NOS,AL,V
READ(1,53) H
READ(1,54) TM,DT
X=H/V
TOS=(NOS*X)/(CO*AL)
1 READ(1,55) K1
IF(K1) 20,20,0
WRITE(2,55) K1
ZO=CO*V/(K1*(NOS=NO))
TO=ZO/V
IF(ZO=H) 40,40,0
ICH=1
GO TO 41
40 ICH=-1
VEL=ZO*K1*AL/(1.0+ZO*K1*AL/V)
T1=(H-ZO)/VEL
TST=T1+TO
41 CONTINUE
IF(ICH) 42,0,0
C PROFILE ZERO OUTSIDE BED
T=DT
2 T=T+DT
IF(T=TM) 0,0,1
A TDET/TOS
WRITE(2,51) TD
Y=AL*(Y=X)
IF(Y) 0,3,3
Y=X+0.1/AL
GO TO 4
3 C=CO-K1*X*(NOS=NO)*EXP(-K1*Y)
CD=C/CO
WRITE(2,52) CD
GO TO 2
42 CONTINUE
C PROFILE ZERO WITHIN BED
T=DT
21 T=T+DT
IF(T=TM) 0,0,1
TDET/TOS
WRITE(2,51) TD
IF(T=TST) 0,5,5
CD=0.0
GO TO 6
5 C=CO-K1*(ZO/V)*(NOS=NO)*EXP(-K1*AL*((T=T1)-(ZO/V)))
CD=C/CO
6 WRITE(2,52) CD
GO TO 21
20 CONTINUE
50 FORMAT(5F12.6)
51 FORMAT(F8.4)
52 FORMAT(10X,F12.7)
53 FORMAT(F10.4)
54 FORMAT(2F10.4)
55 FORMAT(F13.6)
STOP
END

```

Fig.23.

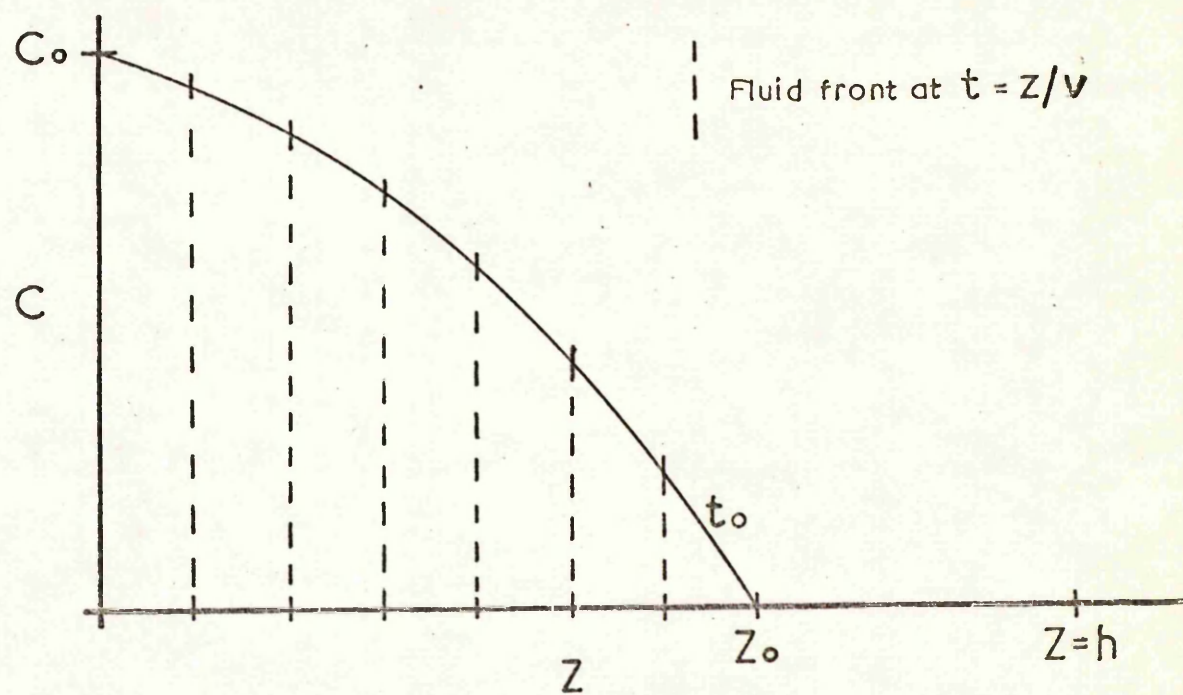


Fig.24.

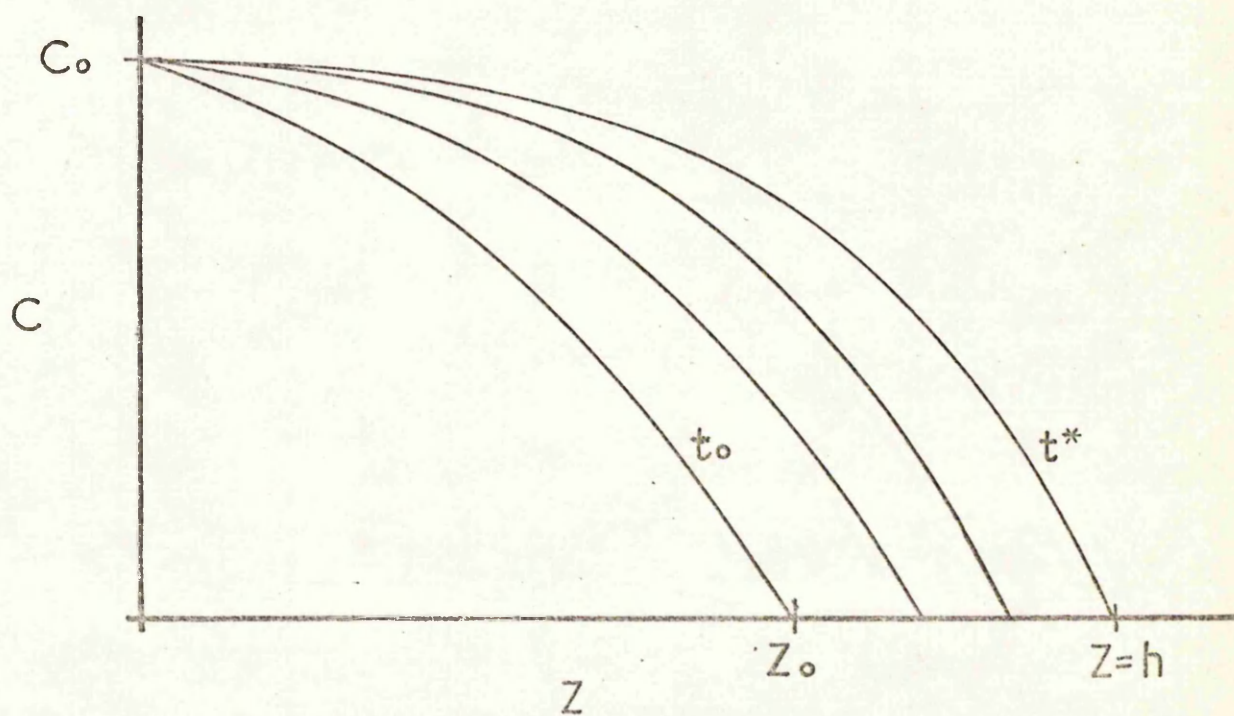


Fig.25. CASE/5

- 1 $K1 = 0.15$
- 2 $K1 = 0.30$
- 3 $K1 = 0.60$

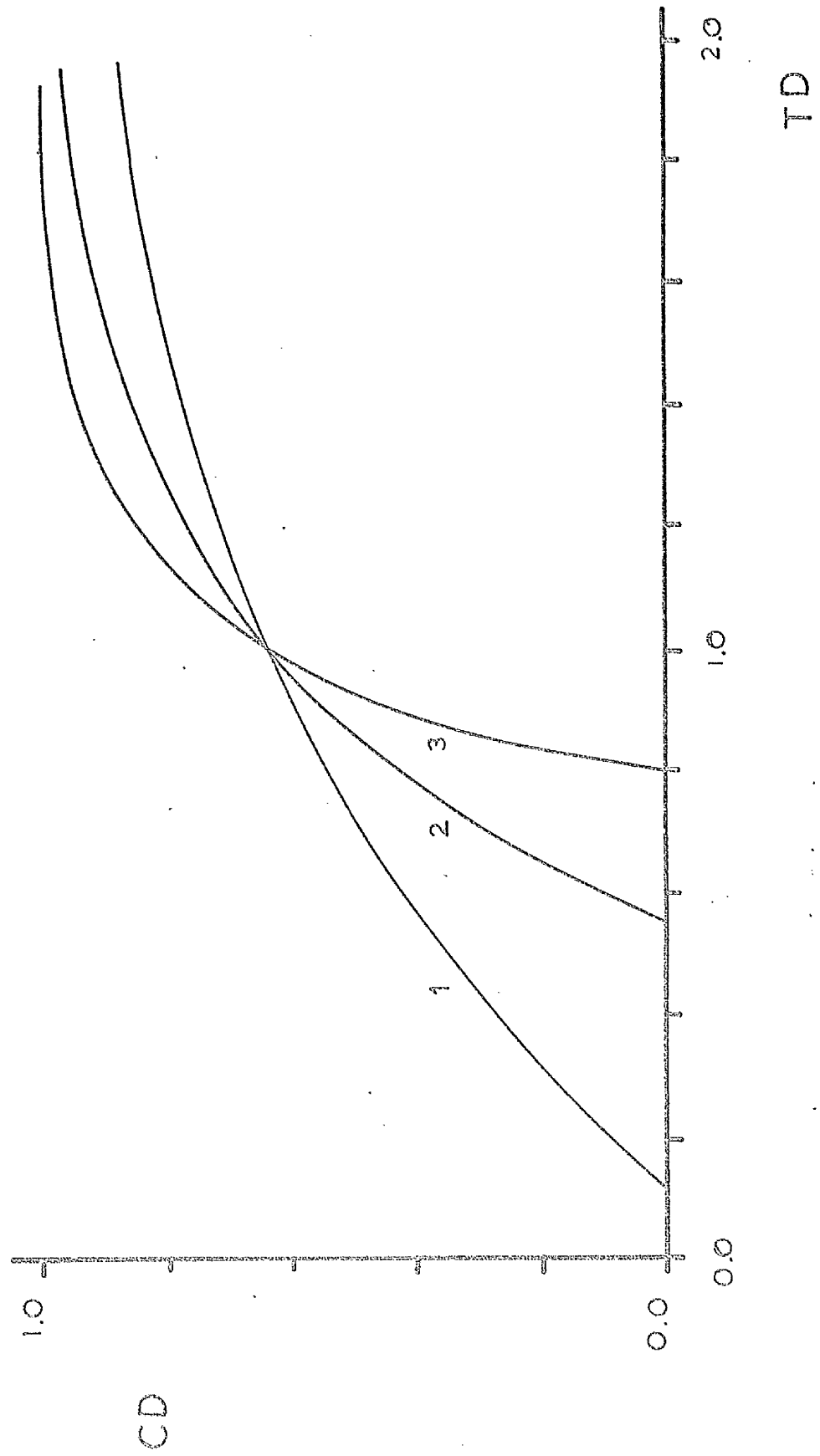


Fig.26.

```

      READ FROM(CR/S1900)
      MASTER CASE/6
      RFAL NO,NOS,K1
      READ(1,50) CO,NO,NOS,AL,V
      READ(1,53) H
      READ(1,54) TM,DT
      X=H/V
      TOS=(NOS*X)/(CO*AL)
1     CONTINUE
      READ(1,51) K1
      IF(K1) 20,20,0
      K1=2.0*CO*V*NO/(K1*H*(NOS**2-NO**2))
      WRITE(2,51) K1
      T=-DT
2     T=T+DT
      IF(T-TM) 0,0,1
10    CONTINUE
      TD=T/TOS
      Y=AL*(T-X)
      IF(Y) 0,11,11
      T=X+0.1/AL
      GO TO 10
11    CONTINUE
      DUM=SQRT(NOS**2-(NOS**2-NO**2)*EXP(-K1*Y))
      CD=1.0-0.5*K1*H*(NOS**2-NO**2)*EXP(-K1*Y)/(DUM*CO*V)
      WRITE(2,52) TD,CD
      GO TO 2
20    CONTINUE
50    FORMAT(5F12.6)
51    FORMAT(F13.6)
52    FORMAT(F13.6,10X,F13.6)
53    FORMAT(F10.4)
54    FORMAT(2F10.4)
      STOP
      END

```


Fig.27. CASE/6

1	$K1=0.003257$	3	$K1=0.01$	} MOD/6
2	$K1=0.001629$	4	$K1=0.05$	
		5	$K1=0.15$	
		6	$K1=0.30$	

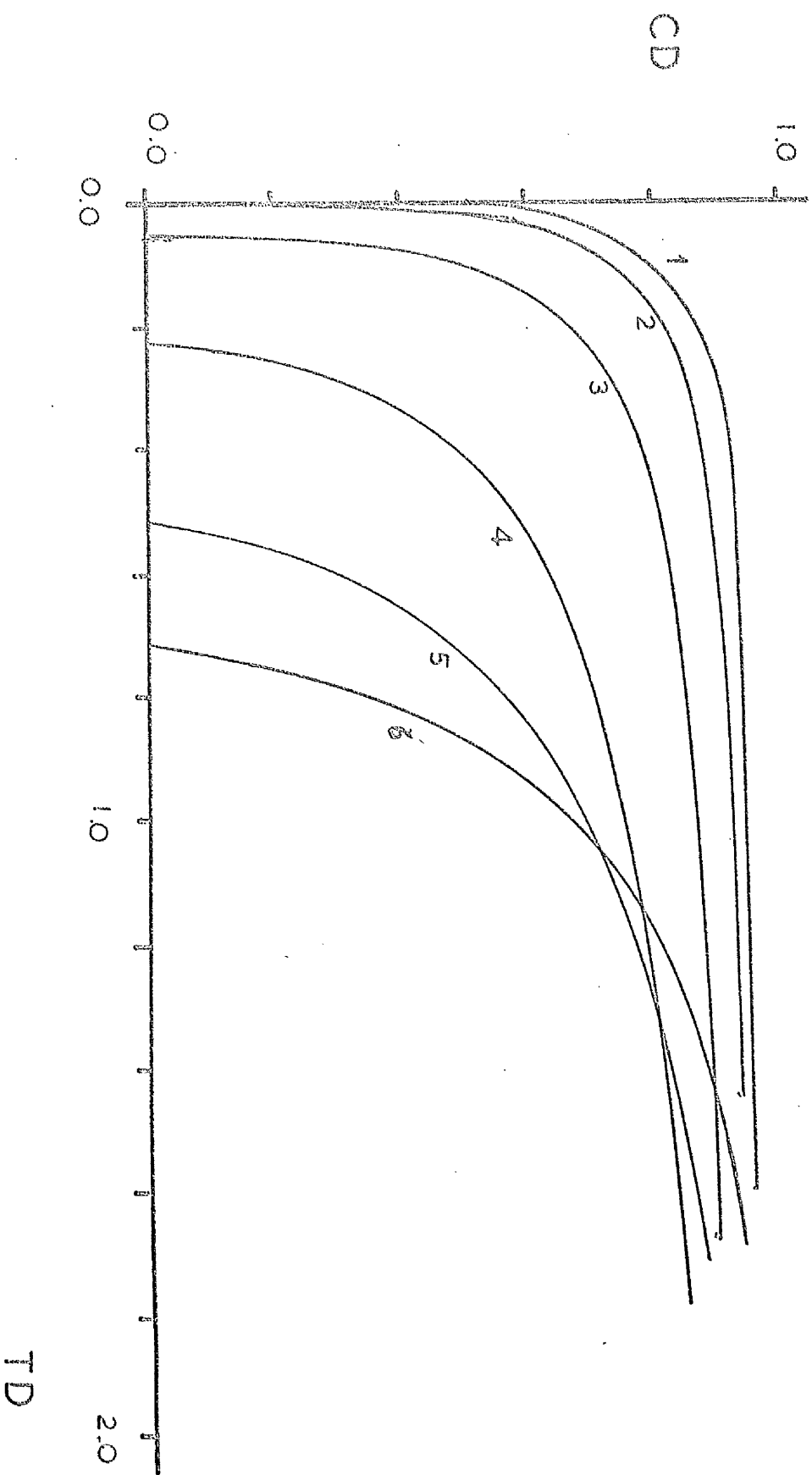


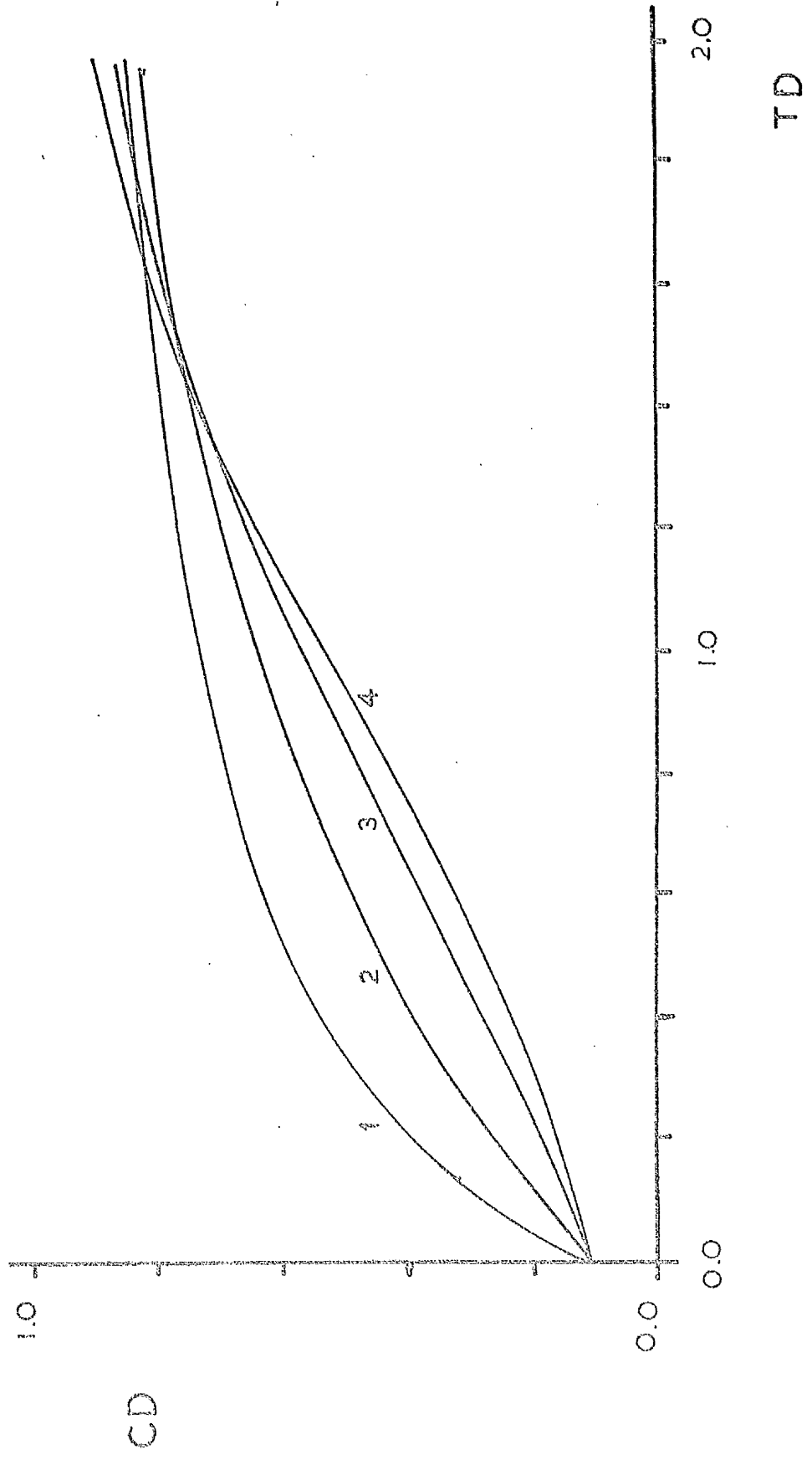
Fig. 28.

```

MASTER CASE7
REAL NO,NOS,K1,K2
COMMON K1,K2,Y,X,CO,NO,NOS
EXTERNAL FUN1,FUN2,FUN5,FUN6
READ(1,50) CO,NO,NOS,AL,V
READ(1,53) H
READ(1,54) TM,DT
X=H/V
TOS=((NOS*NO)*X)/(CO*AL)
21 READ(1,55) K1,K2
   IF(K1) 20,0,0
   WRITE(2,56) K1,K2
   T=DT
2   T=T+DT
   IF(T=TM) 0,0,1
14  CONTINUE
   TD=T/TOS
   WRITE(2,57) TD
   V=AL*(T-X)
   IF(V) 0,3,3
   T=X+0.10/AL
   GO TO 14
   CD=0,0
   GO TO 4
3   DUM=2,0*SQRT(K1*K2*NOS*CO*X*Y)
   CALL F4IQ(DUM,V1)
   A1=V1*EXP(DUM)
   CALL F4IQ(DUM,V2)
   V2=V2*EXP(DUM)
   IF(Y) 0,0,9
   A7=K1*K2*NOS*CO*X
   GO TO 3
9   A7=V2*SQRT((K1*K2*NOS*CO*X)/Y)
5   IF(X) 0,0,6
   A3=0,0
   A8=0,0
   GO TO 7
6   CALL F4INTSMP(0,0,X,FUN2,1,0,3,A3)
   CALL F4INTSMP(0,0,X,FUN5,1,0,3,A8)
7   IF(Y) 0,0,8
   A2=0,0
   A9=0,0
   GO TO 13
8   CALL F4INTSMP(0,0,Y,FUN1,1,0,3,A2)
   CALL F4INTSMP(0,0,Y,FUN6,1,0,3,A9)
   A2=A2*1000000,0
   A9=A9*1000000,0
13  C=((K2*CO/(K1*K2))*((A7+A8+A9*K1*CO*EXP(K1*CO*Y)))/((K1*K2)*(A1+A2
1+A3)))
   CD=C/CO
4   WRITE(2,58) CD
   IF((1,0-CD)=0,0001) 1,0,0
   GO TO 4
1   CONTINUE
   GO TO 21
20  CONTINUE
50  FORMAT(5F12,6)
51  FORMAT(1F8,4)
52  FORMAT(10X,F12,9)
53  FORMAT(1F10,4)
54  FORMAT(2F10,4)
55  FORMAT(2F13,6)
56  FORMAT(1F13,6,10X,F13,6)
STOP
END

```

Fig.29. CASE/7



1	K1=10000.0	K2=60000.0
2	K1=10000.0	K2=20000.0
3	K1=10000.0	K2=5000.0
4	K1=10000.0	K2=500.0

Fig.30. CASE/7

1	K1=15000.0	K2=60000.0
2	K1=15000.0	K2=20000.0
3	K1=15000.0	K2=5000.0
4	K1=15000.0	K2=500.0

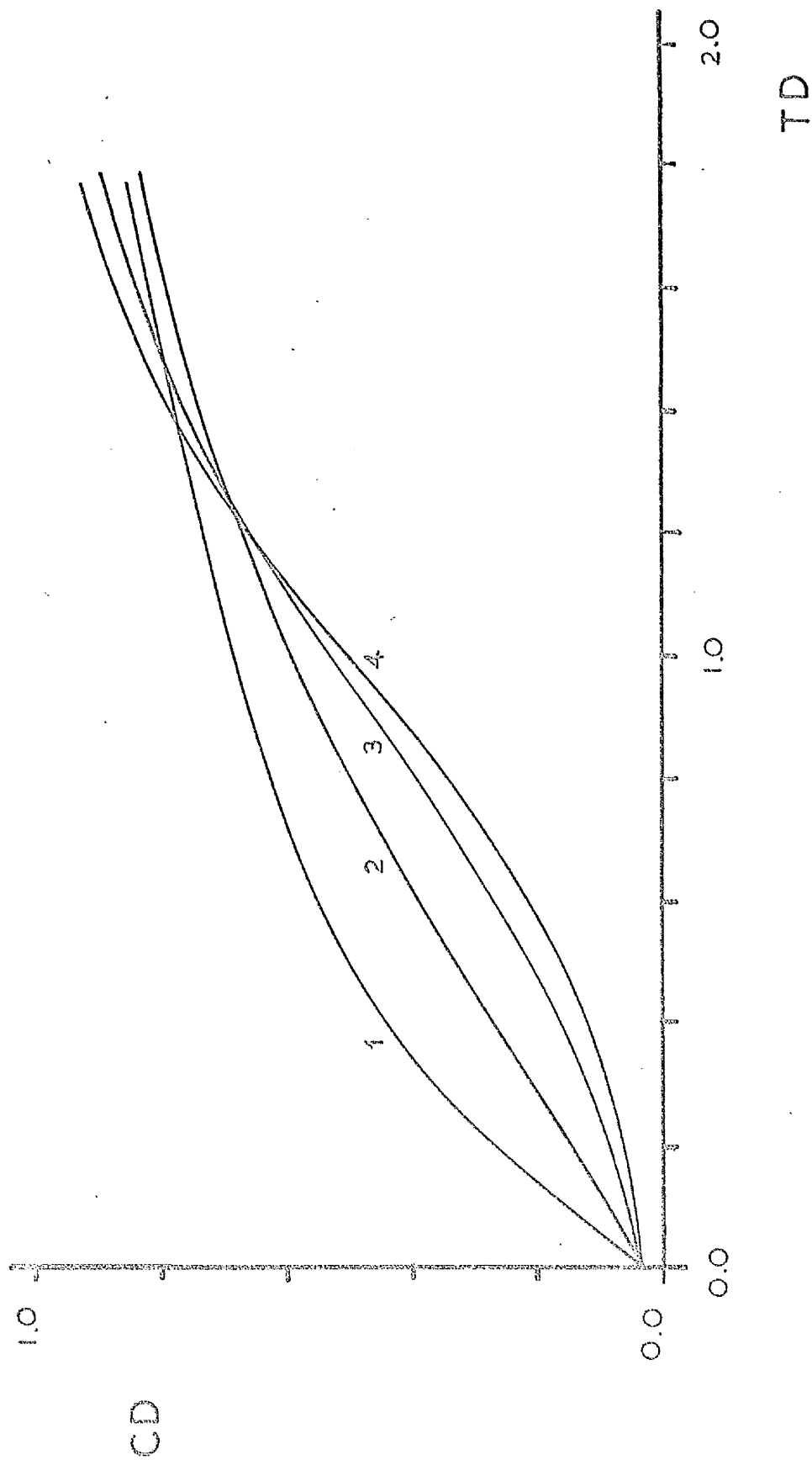


Fig.31. CASE/7

1	K1 = 20000.0	K2 = 30000.0
2	K1 = 20000.0	K2 = 5000.0
3	K1 = 20000.0	K2 = 500.0

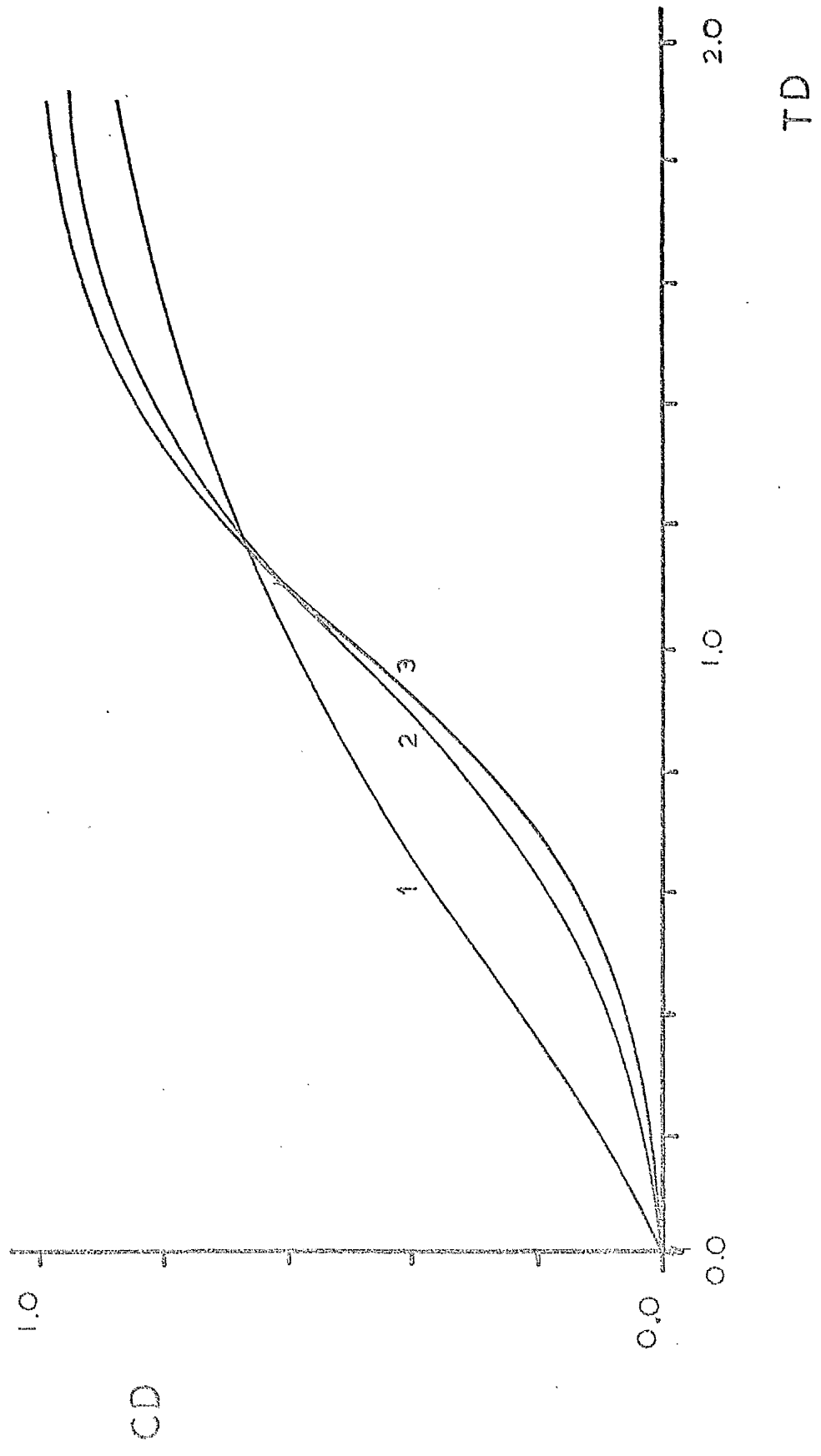


Fig.32. CASE/7

1	K1 = 25000.0	K2 = 200000.0
2	K1 = 25000.0	K2 = 50000.0
3	K1 = 25000.0	K2 = 500.0

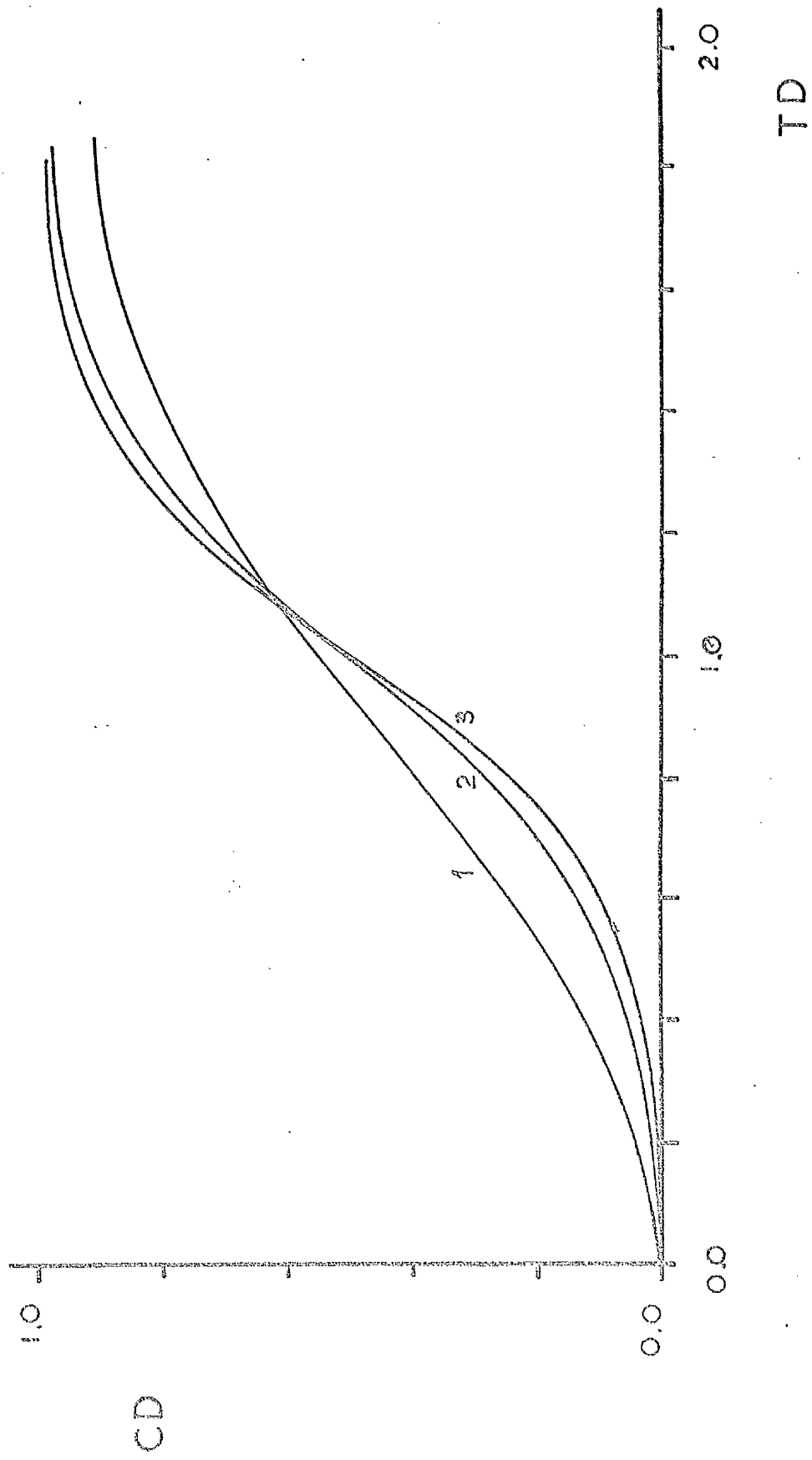


Fig. 33. CASE/7

1	K1 = 35000.0	K2 = 20000.0
2	K1 = 35000.0	K2 = 10000.0
3	K1 = 35000.0	K2 = 500.0

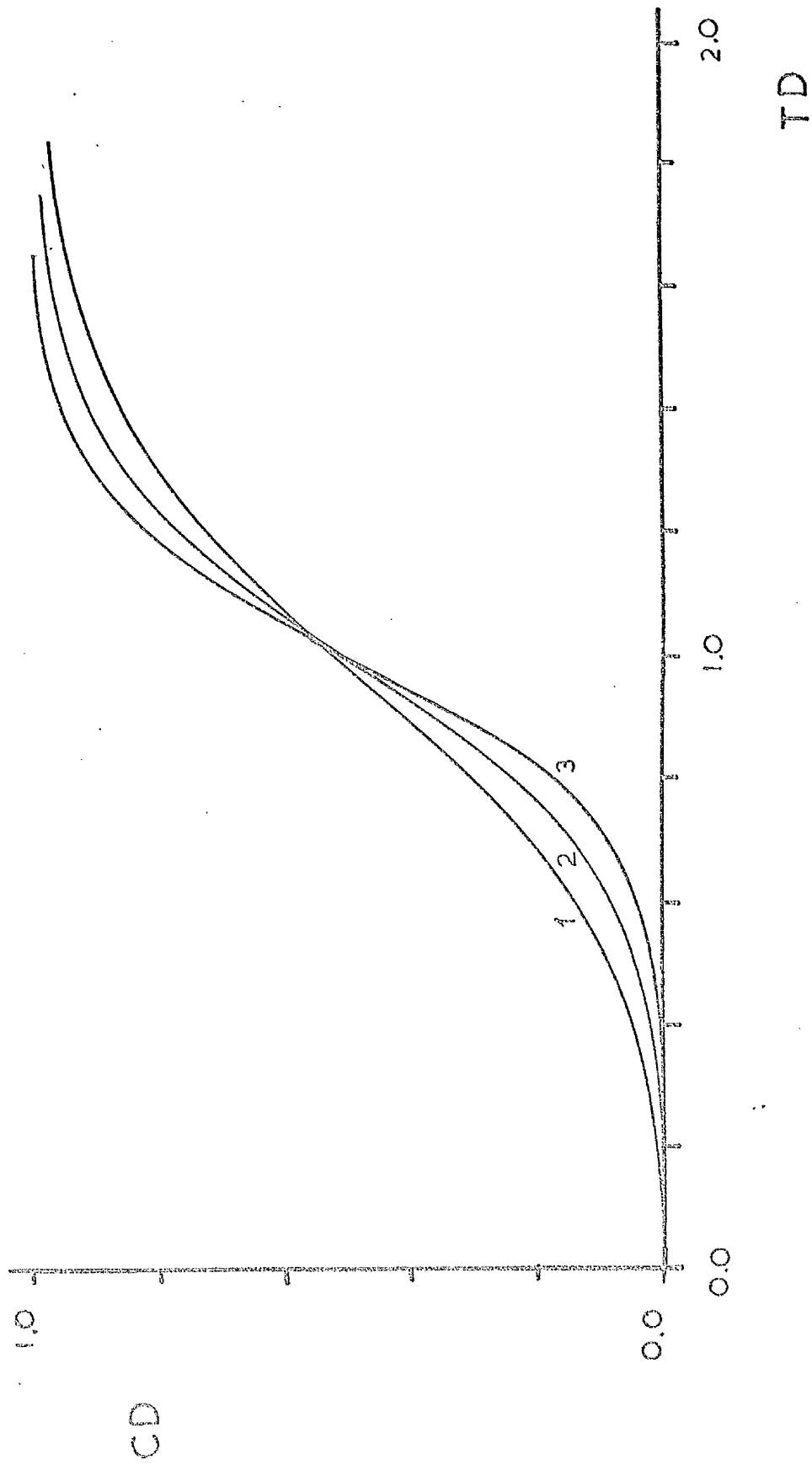


Fig. 34.

```

      READ FROM(CR/S1900)
      MASTER CASE8
      EXTERNAL FUN,CALC
      REAL NOS,K1,K2,KE
      READ(1,50) CO,NOS,AL,V,ROB,ROP,R
      READ(1,53) H
      READ(1,54) TM,DT
      X=H/V
      TOS=(NOS*X)/(CO*AL)
      KE=NOS/(CO*POB)
21    READ(1,55) K1,K2
      IF(K1) 20,0,0
      WRITE(2,56) K1,K2
      T=DT
2    T=Y+DT
      IF(T=TM) 0,0,1
      TD=T/TOS
      WRITE(2,51) TD
      Y=AL*(T-X)
      IF(Y) 0,3,3
      CD=0.0
      GO TO 4
3    V1=(ROB*X*K1)/(ROP*AL*R*R)
      V2=(Y*K1)/(AL*R*R*ROP*KE)
      V3=K1/(K2*R)
      CALL CALC(AREA,V1,V2,V3)
      CD=0.5+(2.0*AREA/(4.0*ATAN(1.0)))
4    WRITE(2,52) CD
      GO TO 2
1    CONTINUE
      GO TO 21
20   CONTINUE
50   FORMAT(5F12.6)
51   FORMAT(F8.4)
52   FORMAT(10X,F12.9)
53   FORMAT(F10.4)
54   FORMAT(2F10.4)
55   FORMAT(2F13.6)
56   FORMAT(F13.6,10X,F13.6)
      STOP
      END

```

```

SUBROUTINE FUN(VAL,V1,V2,V3,L)
REAL L
TH1=-L
TH2=L
SAM=COSH(2.0*TH2)=COS(2.0*TH1)
FI1=((TH1*SYN(2.0*TH1)+TH2*SINH(2.0*TH2))/SAM)=1.0
FI2=(TH2*SIN(2.0*TH1)-TH1*SINH(2.0*TH2))/SAM
SAM=(1.0+V3+FI1)**2+(V3+FI2)**2
GA1=(FI1+V3*(FI1**2+FI2**2))/SAM
GA2=FI2/SAM
AL1=3.0*V1*GA1
AL2=2.0*V2*L+L=3.0*V1*GA2
VAL=(EXP(AL1)*SIN(AL2))/L
RETURN
END

```


Fig.34.continued

```

SUBROUTINE CALC(AREA,V1,V2,V3)
REAL L
DIMENSION A(199),B(7),AR(2)
AREA=0.0
COMP=0.0
IREP=1
97 DL=0.1
C BEGIN FIRST CYCLE AND CHOOSE SUITABLE DL VALUE
IYER=1
103 J=0
RAMP1=0.0
102 J=J+1
IF(J-199) 0,100,100
IF (J-1) 102,102,0
L=(J-1)*DL
CALL FUN(VAL,V1,V2,V3,L)
IF( ABS(VAL)- ABS(RAMP1)) 0,0,99
RAMP1=VAL
99 A(J)=VAL
IF(J-3) 102,0,0
IF(A(J)*A(J-1)) 101,101,0
IF(A(J)) 0,101,104
IF(A(J)-A(J-1)) 102,102,105
104 IF(A(J)-A(J-1)) 106,102,102
100 CONTINUE
C COMPLETED 199 EVALUATIONS TURN POINT NOT REACHED
DL=2.0*DL
DO 107 I=1,100,1
A(I)=A(2*I-1)
107 CONTINUE
J=100
GO TO 102
105 CONTINUE
C FUNCTION NEG HAVE REACHED TURN POINT
IF(J-150) 0,108,108
DL=J*DL/150.0
GO TO 103
106 CONTINUE
C FUNCTION POS HAVE REACHED TURN POINT
IF(J-150) 0,108,108
DL=J*DL/150.0
GO TO 103
101 CONTINUE
C INITIAL SIZE OF DL TOO LARGE
DL=J*DL/200.0
GO TO 103
108 CONTINUE

```

Fig.34.

...continued

```

C      CAN NOW PROCEED WITH INTEGRATION OVER FIRST CYCLE WITH MORE THAN
C      ONE HUNDRED AND FIFTY POINTS OF THE SAME SIGN UP TO THE TURN
      A(1)=0.0
      ICOUNT=2
      TOT=0.0
      K=0
110    K=K+1
      IF((6*K+1)-J) 0,0,109
      SUM=A(6*K-5)+5.0*A(6*K-4)+A(6*K-3)+6.0*A(6*K-2)+A(6*K-1)+5.0*A(6*K
1) +A(6*K+1)
      TOT=TOT+0.1*DL*SUM
      GO TO 110
109    K=K-1
      I=0
112    I=I+1
      IF(I-7) 0,0,113
      IF(6*K+I-J) 0,0,111
      B(I)=A(6*K+I)
      GO TO 112
111    J=J+1
      L=L+DL
      CALL FUN(VA1,V1,V2,V3,L)
      B(I)=VA1
      IF(B(I)) 0,116,0
      IF(B(I)*B(I-1)) 114,114,112
113    CONTINUE
C      WEDDLE INTEGRATION FORMULA CAN NOW BE USED
      SUM=B(1)+5.0*B(2)+B(3)+6.0*B(4)+B(5)+5.0*B(6)+B(7)
      TOT=TOT+0.1*DL*SUM
      B(1)=B(7)
123    I=1
      ICOUNT=ICOUNT+1
115    I=I+1
      IF(I-7) 0,0,113
      J=J+I-1
      L=L+DL
      CALL FUN(VA1,V1,V2,V3,L)
      IF(IREP-2) 98,0,98
      IF(ABS(VA1)-ABS(RAMP2)) 0,0,98
      RAMP2=VA1
      IF(ABS(RAMP2)-ABS(RAMP1)) 98,98,0
      AREA=AR(1)
C      NOW MAKE SECOND CYCLE THE FIRST AND REPEAT DETERMINATION OF DL
      IREP=3
      GO TO 97
98    B(I)=VA1
      IF(B(I)) 0,116,0
      IF(B(I)*B(I-1)) 114,114,115
116    IF(I-7) 114,113,114
114    CONTINUE
      IF(ICOUNT-1) 0,0,128
C      SIGN CHANGE OCCURE IN LESS THAN SEVEN POINTS, EDUCE VALUE OF DL
      L=L-(I-1)*DL
      J=J-I
      DL=DL*I/20.0
      ICOUNT=2
      GO TO 123

```

Fig.34.

... continued

```

C      LAST FUNCTION VALUE ZERO OR CHANGED SIGN, PERFORM SEPARATE INTEGRA
C      -TION OF AVAILABLE INTERVALS WITH I POINTS (I LESS THAN SEVEN)
128    ICOUNT=0
      IF(I-2) 0,0,117
      SUM=0.5*DL*(B(1)+B(2))
      GO TO 118
117    IF(I-3) 0,0,119
      SUM=0.5*DL*(B(1)+2.0*B(2)+B(3))
      GO TO 118
119    IF(I-4) 0,0,120
      SUM=DL*((B(1)+4.0*B(2)+B(3))/3.0 + 0.5*(B(3)+B(4)))
      GO TO 118
120    IF(I-5) 0,0,121
      SUM=DL*((B(1)+4.0*B(2)+B(3))/3.0+0.5*(B(3)+2.0*B(4)+B(5)))
      GO TO 118
121    CONTINUE
      SUM=DL*((B(1)+4.0*(B(2)+B(4))+2.0*B(3)+B(5))/3.0+0.5*(B(5)+B(6)))
118    TOT=TOT+SUM
C      END OF CYCLE
      B(1)=B(I)
      AR(ITER)=TOT
      IF(ITER-2) 0,122,122
      ITER=2
      JI1=J
      RJI1=J*DL
      ICOUNT=0
      RAMP2=0.0
      IREP=IREP+1
      GO TO 123
122    CONTINUE
C      HAVE NOW EVALUATED TWO SUCESSIVE CYCLES
      RJI2=(J-JI1)*DL
      DELAR=AR(1)+AR(2)
      IF(DELAR) 0,125,0
      COMP=COMP+DELAR
      AREA=AREA+DELAR
      IF(ABS(COMP)*0.005 - ABS(DELAR)) 125,0,0
C      REQUIRED ACCURACY ACHIEVED
      GO TO 127
125    CONTINUE
C      MUST UPDATE VALUE OF DL FOR NEXT TWO CYCLES
      ITER=1
      DL=0.05*(RJI2**3)/(RJI1**2)
      J=0
      TOT=0.0
      ICOUNT=0
      GO TO 123
127    RETURN
      END

```

Fig.35.

FUN(V₁, V₂, V₃, L)

D₁ = 80.0 , K_F = 5000.0
(i.e. K₁, K₂)

Other data as Table I.

- | | |
|---|----------------|
| 1 | t = 5.0 mins. |
| 2 | t = 10.0 mins. |
| 3 | t = 15.0 |
| 4 | t = 20.0 |
| 5 | t = 25.0 |
| 6 | t = 30.0 mins. |
| 7 | t = 35.0 mins. |

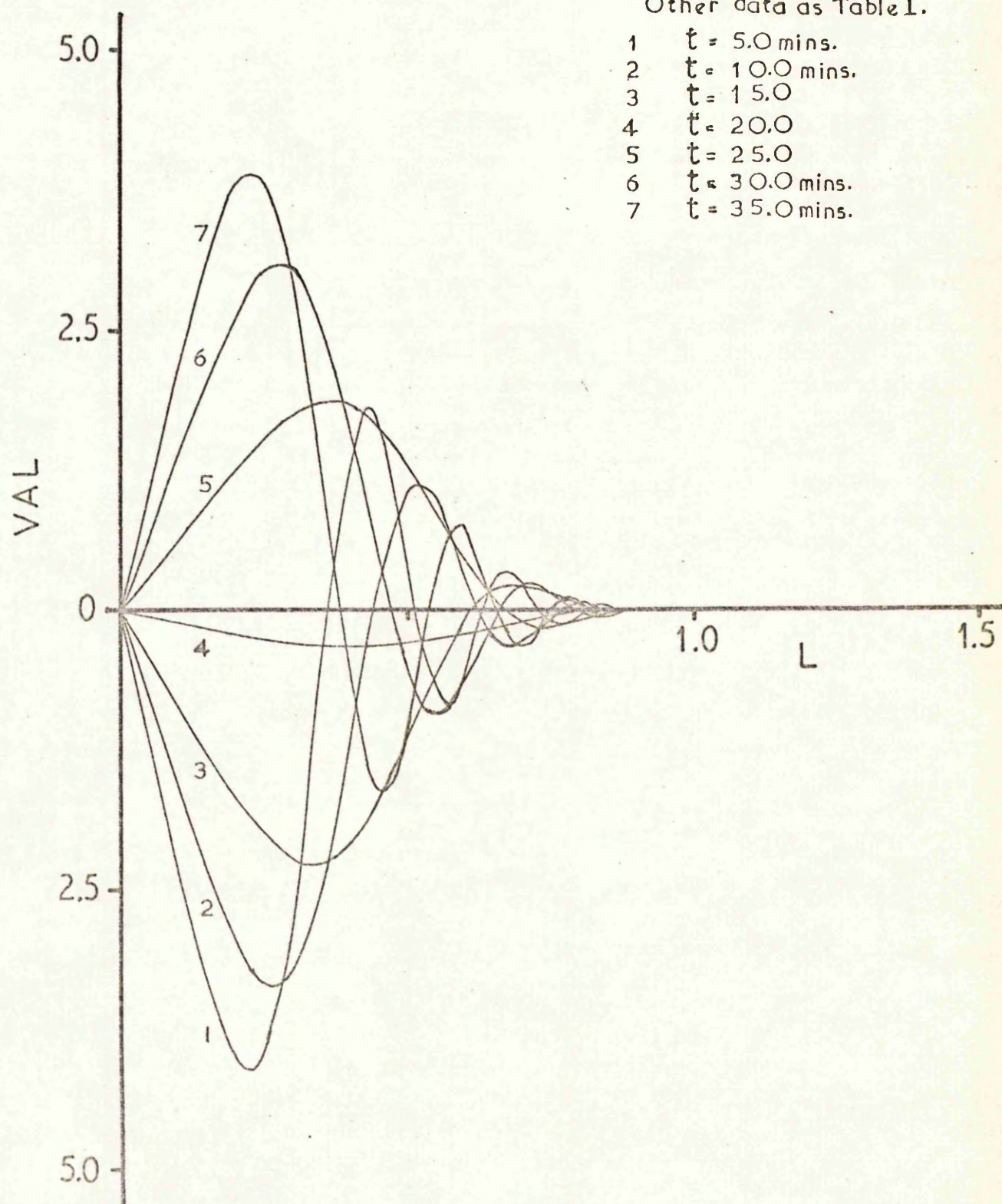


Fig.36. CASE / 8

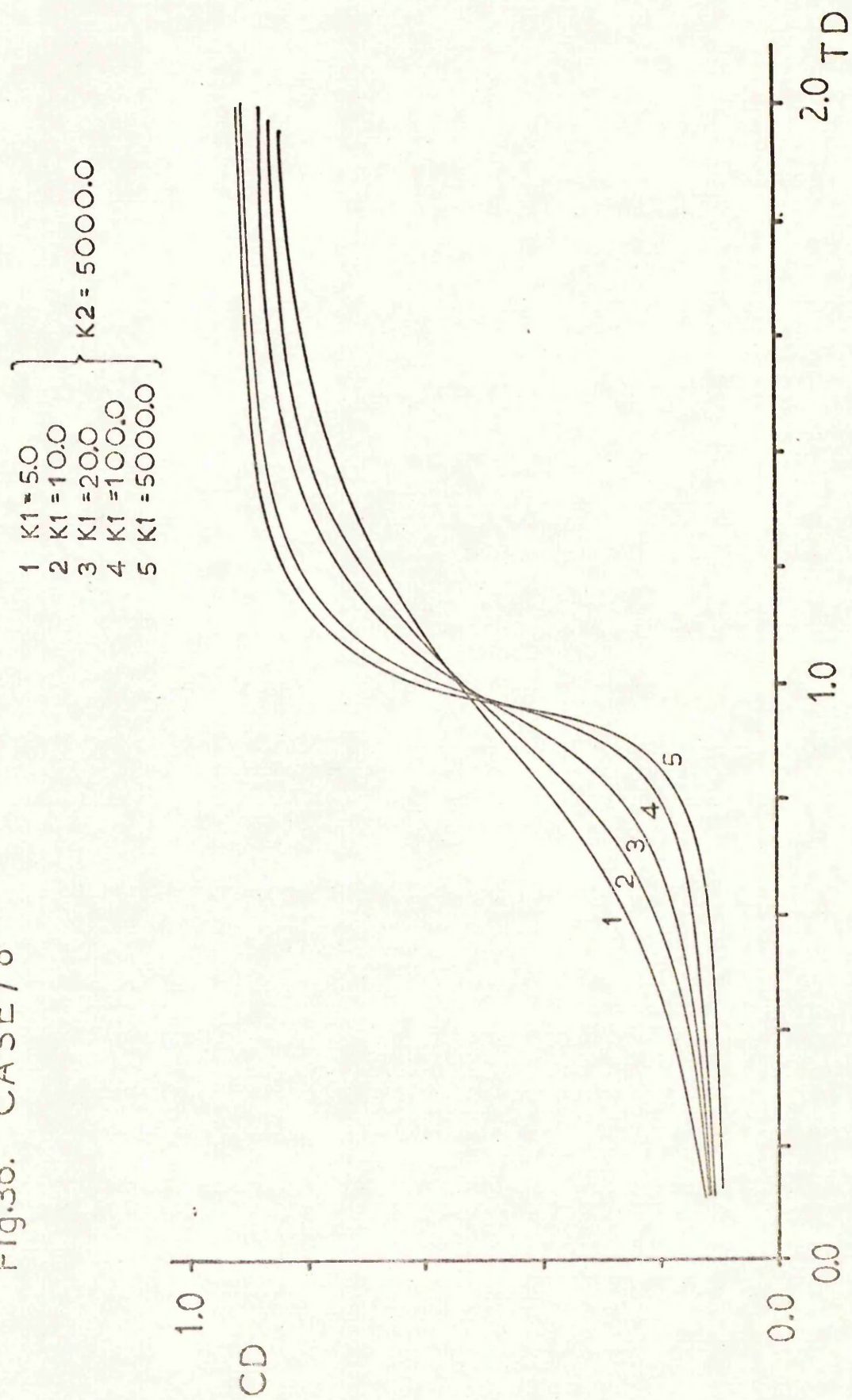


Fig.37. CASE/8

1	K2 = 100.0	} K1 = 80.0
2	K2 = 200.0	
3	K2 = 500.0	
4	K2 = 1000.0	
5	K2 = 50000.0	

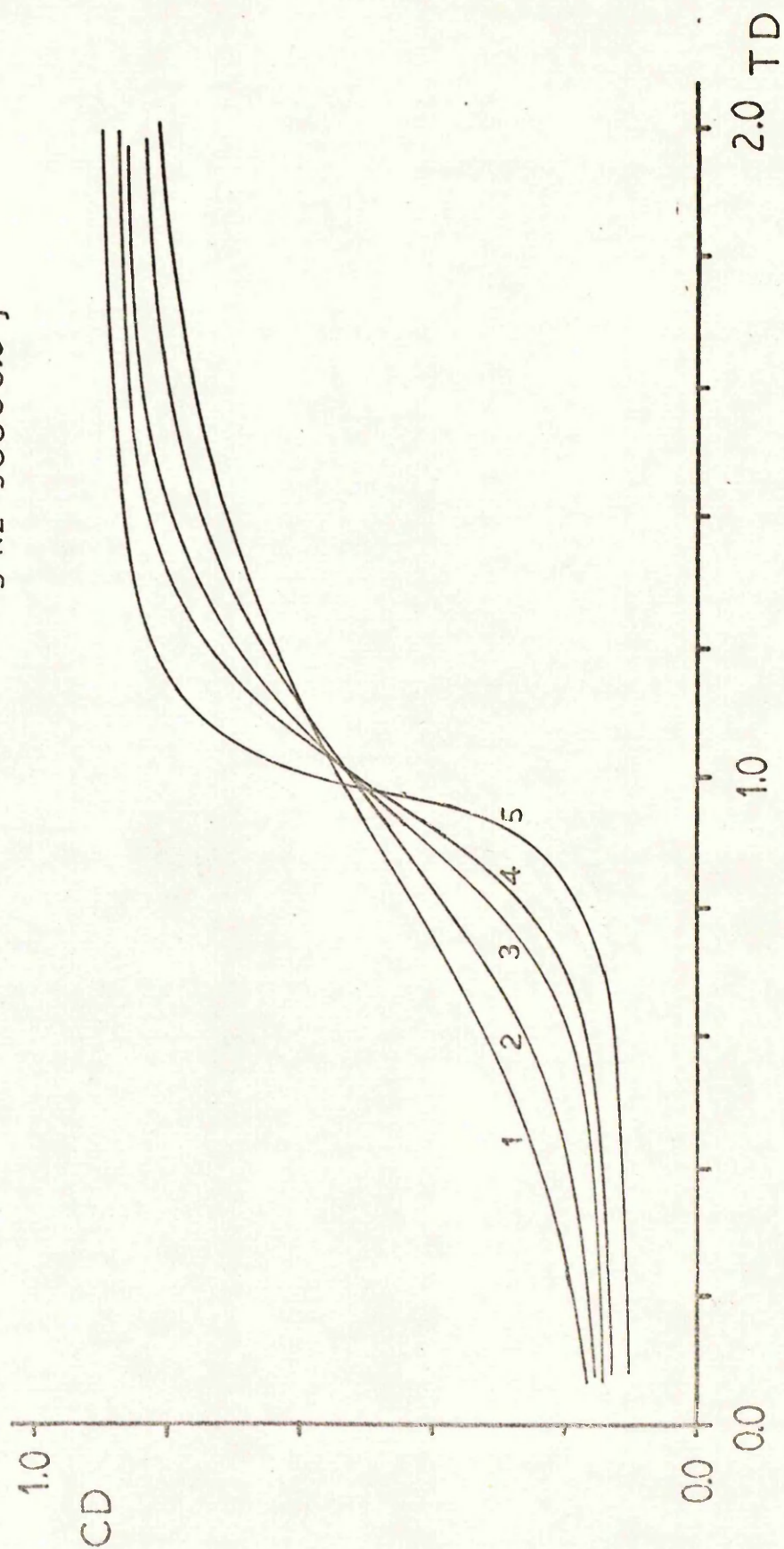


Fig. 38.

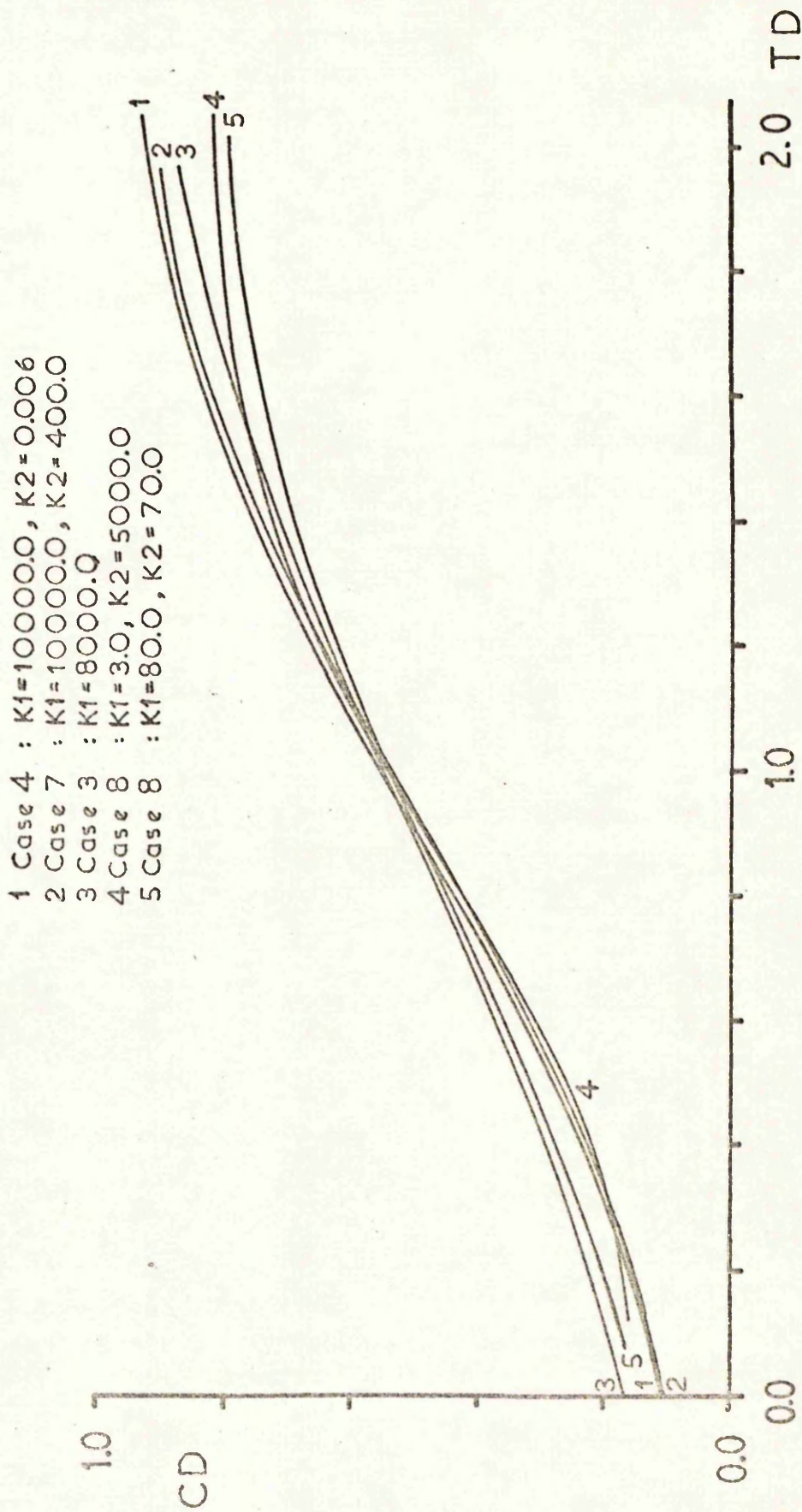


Fig.39.

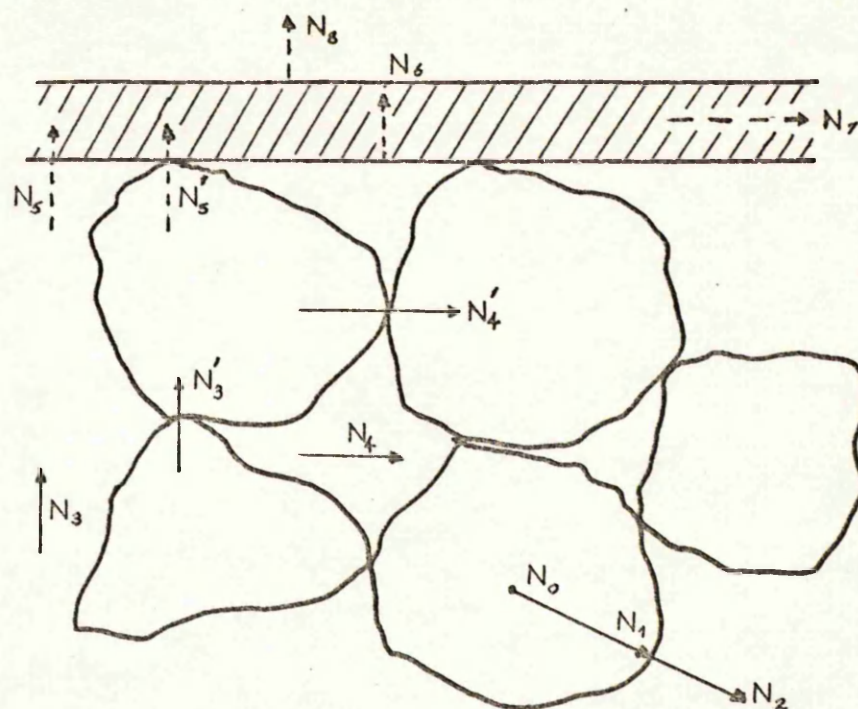


Fig.40.

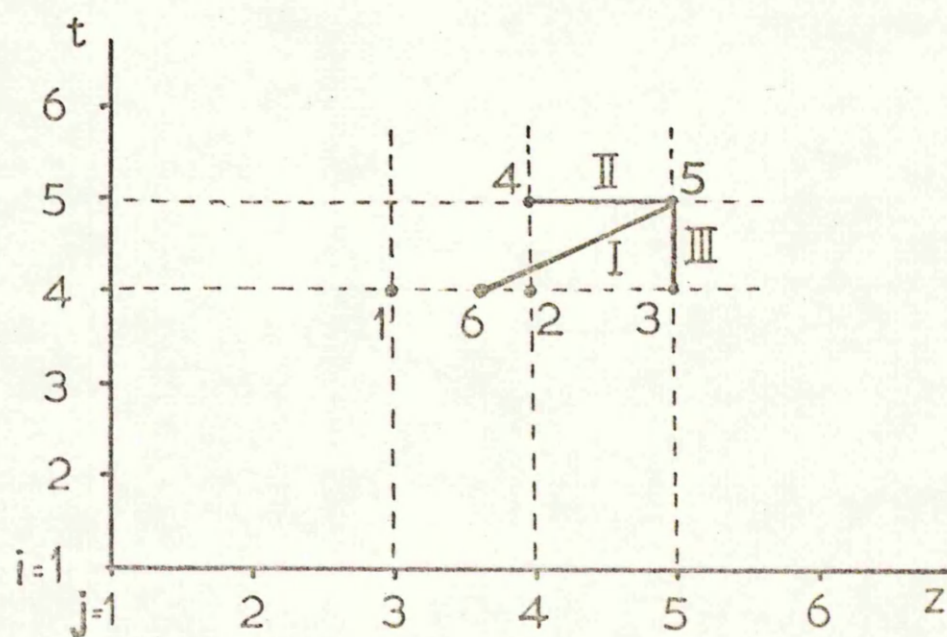


Fig. 41.

```

READ FROM(CR/S1900)
MASTER HAMAN
DIMENSION Y(4),T(2,22),TW(2,22),TP(2,22),Q(2,22),C(2,22)
DIMENSION VE(22)
REAL KM,KH,KW,KU,MU1,MU2,MUP,MUV,MUW,MASS
READ(1,50) TST,TWST,TPST,QST,CST,VO,TO,CO
READ(1,51) H,TIME
READ(1,52) KM,KH,KW,KU,MU1,MU2,MUP,MUV,MUW,MASS
READ(1,52) HEAT,DI,DO,A,AL,GA,ROHP,ROHB,TOUT
WRITE(2,57)
57  FORMAT(11H INPUT DATA)
WRITE(2,50) TST,TWST,TPST,QST,CST,VO,TO,CO
WRITE(2,51) H,TIME
WRITE(2,52) KM,KH,KW,KU,MU1,MU2,MUP,MUV,MUW,MASS
WRITE(2,52) HEAT,DI,DO,A,AL,GA,ROHP,ROHB,TOUT
M=21
DZ=H/(M-1)
DT=DZ/VO
WRITE(2,60)
60  FORMAT(24H DIFFERENTIAL INCREMENTS)
WRITE(2,100) DZ,DT
ROHIN=0.1356385614-0.000223826*TO
ROHIN=ROHIN* 0.016018
CONST=VO*ROHIN
DO 1 J=1,M+1,1
DO 23 I=1,2,1
T(I,J)=TST
TW(I,J)=TWST
TP(I,J)=TPST
Q(I,J)=QST
C(I,J)=CST
23  CONTINUE
1   CONTINUE
DO 2 I=1,2,1
T(I,1)=TO
C(I,1)=CO
2   CONTINUE
VE(1)=VO
WRITE(2,59)
59  FORMAT(26H INITIAL CONDITIOND IN BED)
J=1
DO 70 I=1,M+1,1
WRITE(2,54) T(J,I),TW(J,I),TP(J,I),Q(J,I),C(J,I)
70  CONTINUE
WRITE(2,58)
58  FORMAT(1H1)
INT=1
I=1
J=1
J=J+1
IF(J-(M+1)) 0,0,4
IF(1-M) 0,0,10
C FRONT WITHIN BED
IF(J-(I+1)) 24,24,0
C REMAINING NODES UNCHANGED
TP(2,J-1)=TP(1,J-1)
TW(2,J-1)=TW(1,J-1)
Q(2,J-1)=Q(1,J-1)
DO 22 K=J,M+1,1

```


Fig.41.continued

```

C(2,K)=C(1,K)
T(2,K)=T(1,K)
TP(2,K)=TP(1,K)
TW(2,K)=TW(1,K)
Q(2,K)=Q(1,K)
22 CONTINUE
GO TO 4
24 CONTINUE
CINT=C(1,J-1)
TINT=T(1,J-1)
TPIT=TP(1,J-1)
TWIT=TW(1,J-1)
V=VO
ROHC=0.016018*(0.1356385614 - 0.000223826*TINT)
ROHT=ROHC+CINT
IF(Q(1,J-1)) 0,0,11
CS=0.0
GO TO 25
11 CALL ISOT(Q(1,J-1),TPIT,CS,ROHC)
25 CONTINUE
C(2,J)=CINT+DT*(-A*KM*(CINT-CS)/ROHT)+0.5*((DT*A*KM/ROHT)**2)*
1(CINT-CS)
Q(2,J-1)=Q(1,J-1)+AL*(C(1,J-1)-C(2,J))/ROHB
IF(Q(2,J-1)) 0,32,32
Q(2,J-1)=0.0
C(2,J)=C(1,J-1)+ROHB*Q(1,J-1)/AL
32 CONTINUE
FUN=(-A*KH*(TINT-TPIT)/AL)-(4.0*KW*(TINT-TWIT)/(DI*AL))-A*KM*
1(CINT-CS)*MU1*(TPIT-TINT)/(ROHT*AL)/(CINT*MU1+ROHC*MU2)
T(2,J)=TINT+FUN*DT+0.5*(DT**2)*FUN*(-A*KH/AL-4.0*KW/(DI*AL))-A*KM*
1(CINT-CS)*MU1/(ROHT*AL)/(CINT*MU1+ROHC*MU2)
IF(Q(1,J-1)) 0,0,19
CS=0.0
GO TO 20
19 CALL ISOT(Q(1,J-1),TP(1,J-1),CS,ROHC)
20 TP(2,J-1)=TP(1,J-1)+(ROHP*HEAT*(Q(2,J-1)-Q(1,J-1))-KH*A*DT*
1(ROHP/ROHB)*(TP(1,
2J-1)-T(1,J-1)))/(GA*MU1*CS+ROHP*(MUP+Q(1,J-1)*MUV))
FUN=4.0*ATAN(1.0)*(KW*DI*(T(1,J-1)-TW(1,J-1))-KU*DO*(TW(1,J-1)-
1TOUT))/(MASS*MUW)
TW(2,J-1)=TW(1,J-1)+DT*FUN+0.5*(DT**2)*FUN*(-4.0*ATAN(1.0)*(KW*
1DI+KU*DO)/(MASS*MUW))
V=CONST/(0.1356385614-0.000223826*T(2,J))
VE(J)=V/0.016018
GO TO 6
10 CONTINUE
C BED FULL OF FLUID ALL PROFILES CONTINUOUS
IF(J-2) 24,24,0
Z=(J-1)*DZ-VE(J-1)*DT
X=(Z-(J-2)*DZ)/DZ
IF(CT=1)
IF(J-(M+1)) 31,0,0
IF(CT=-1)
X=X+1.0
IF(CT=J)
J=IFACT-1
31 CONTINUE
C INTERPOLATE TO FIND BASE POINT OF CHARACTERISTIC 1
DEN2=0.1356385614-0.000223826*T(1,J-2)
DEN2=DEN2*0.016018

```

Fig. 41. continued

```

DEN3=0.1356385614-0.000223826*T(1,J-1)
DEN3=DEN3*0.016018
DEN4=0.1356385614-0.000223826*T(1,J)
DEN4=DEN4*0.016018
IF(Q(1,J)) 0,0,13
Y(4)=0.0
GO TO 14
13 CALL ISOT(Q(1,J),TP(1,J),Y(4),DEN4)
14 IF(Q(1,J-1)) 0,0,15
Y(3)=0.0
GO TO 16
15 CALL ISOT(Q(1,J-1),TP(1,J-1),Y(3),DEN3)
16 IF(Q(1,J-2)) 0,0,17
Y(2)=0.0
GO TO 18
17 CALL ISOT(Q(1,J-2),TP(1,J-2),Y(2),DEN2)
18 CONTINUE
CALL TERP(X,CS,Y)
IF(CS) 0,33,33
CS=0.0
33 CONTINUE
Y(2)=C(1,J-2)+DEN2
Y(3)=C(1,J-1)+DEN3
Y(4)=C(1,J)+DEN4
CALL TERP(X,ROHI,Y)
Y(2)=T(1,J-2)
Y(3)=T(1,J-1)
Y(4)=T(1,J)
CALL TERP(X,TINT,Y)
ROHC=0.1356385614-0.000223826*TINT
ROHC=ROHC*0.016018
Y(2)=TP(1,J-2)
Y(3)=TP(1,J-1)
Y(4)=TP(1,J)
CALL TERP(X,TPIT,Y)
Y(2)=TW(1,J-2)
Y(3)=TW(1,J-1)
Y(4)=TW(1,J)
CALL TERP(X,TWIT,Y)
Y(2)=C(1,J-2)
Y(3)=C(1,J-1)
Y(4)=C(1,J)
CALL TERP(X,CINT,Y)
IF(IFICT) 0,0,25
J=1FACT
GO TO 25
4 CONTINUE
C END OF BED REACHED,HAVE EVALUATED C AND T AT M+1 SO THAT OTHER
C PARAMETER COULD BE DETERMINED AT M, THE EXIT FACE.
TIM=I*DT
IF(TIM=INT*0.01) 110,0,0
INT=INT+1
CD=C(2,M+1)/CO
WRITE(2,53) TIM,CD,T(2,M+1)
DO 21 K=1,M,1
XRC(IE(2,54) T(2,K),TW(2,K),TP(2,K),Q(2,K),C(2,K)
21 CONTINUE
110 DO 6 J=1,M+1,1
C(1,J)=C(2,J)
T(1,J)=T(2,J)

```

Fig. 41. continued

```

      TP(1,J)=TP(2,J)
      TW(1,J)=TW(2,J)
      Q(1,J)=Q(2,J)
8      CONTINUE
      I=I+1
      IF(I*DT=TIME) 9,9,0
C      ADSORPTION TIME COMPLETED
50     FORMAT(4F13.6)
51     FORMAT(2F13.6)
52     FORMAT(5F13.8)
53     FORMAT(F13.6,10X,F13.6,10X,F13.6)
54     FORMAT(5(F16.11,5X))
100    FORMAT(12H DIST INT = ,F8.5,12H TIME INT = ,F13.10)
      STOP
      END

```

```

SUBROUTINE ISOT(CAT,TEMP,CONC,DEN)
DIMENSION B(3)
B(1)=-0.00054593+TEMP*((0.371158E-04)-(0.726235E-07)*TEMP)
B(2)=EXP(-9.59158+1926.66/TEMP)
B(3)=-0.0541883+TEMP*(0.000305437-TEMP*(0.444061E-06))
CAP=CAT/16.0
DUM=(CAP-B(1))**2-4.0*(CAP**2)*B(3)/B(2)
PRES=(-(CAP-B(1))-SQRT(DUM))/(2.0*CAP*B(3))
CONC=PRES*16.0*DEN/(4.0*(99.2-PRES))
RETURN
END

```

```

SUBROUTINE TERP(VAR,PROD,TER)
DIMENSION TER(4)
A1=TER(3)
A2=0.5*(TER(4)-TER(2))
A3=0.5*(TER(4)+TER(2))-TER(3)
PROD=A1+VAR*A2+A3*(VAR**2)
RETURN
END

```


Fig. 42.

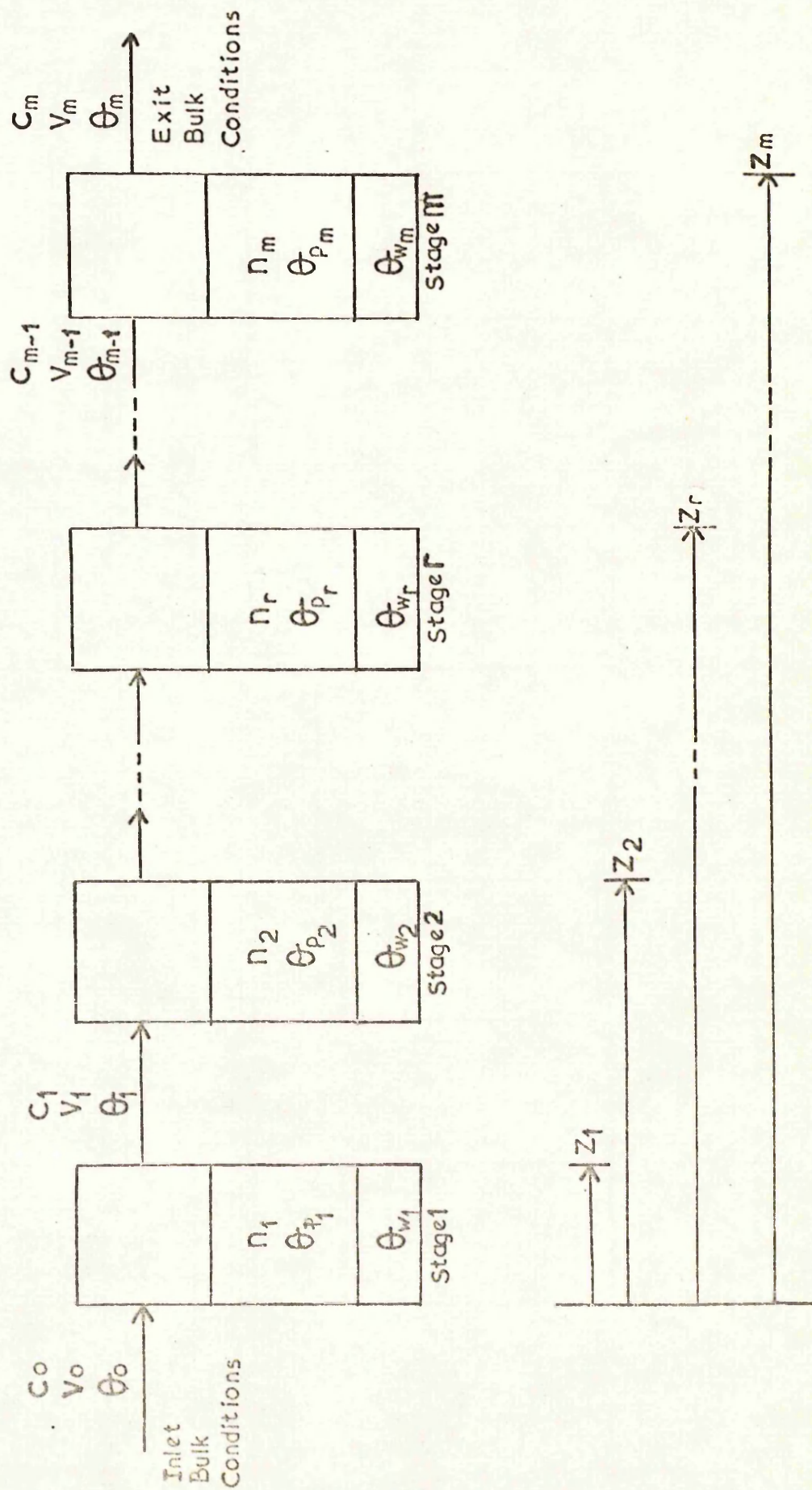


Fig. 43.

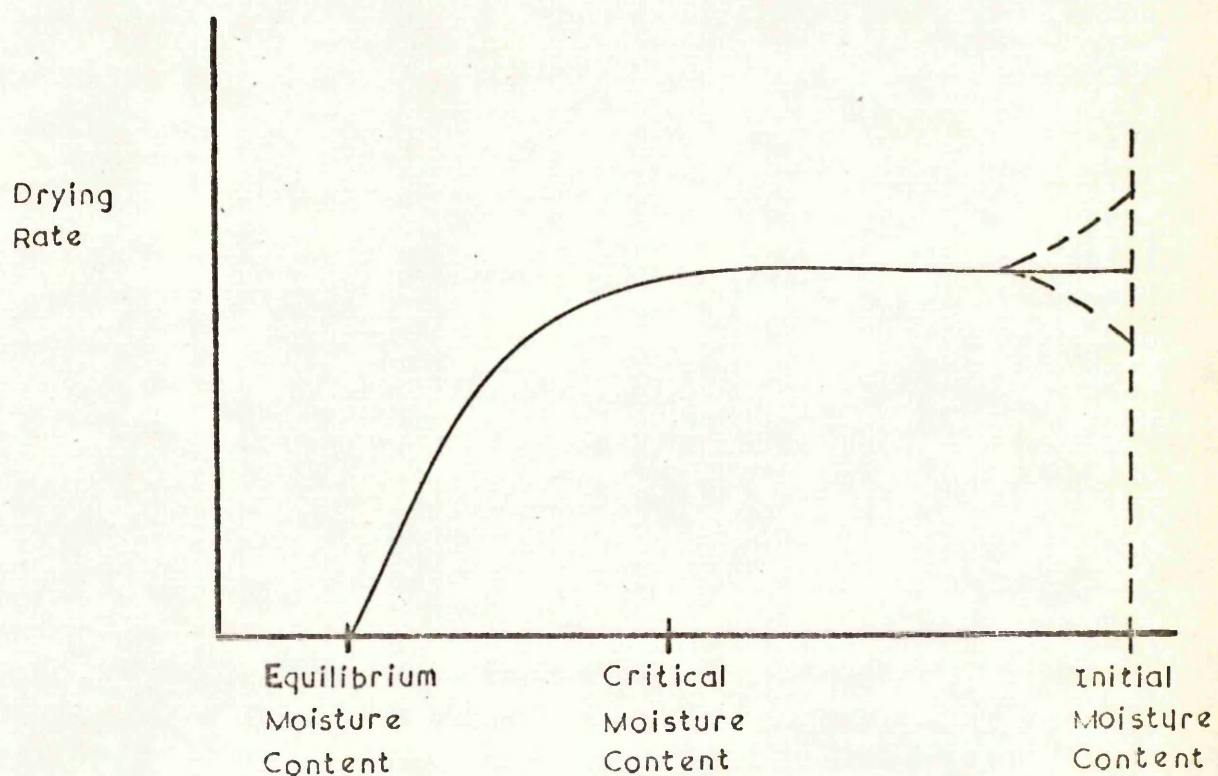


Fig. 44.

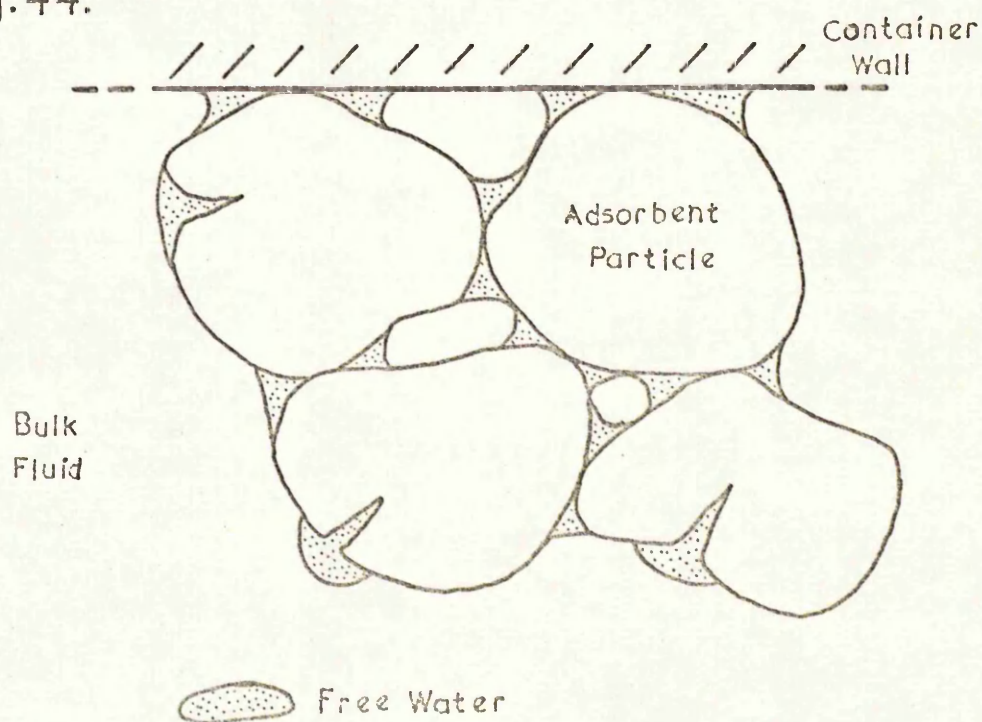


Fig. 45.

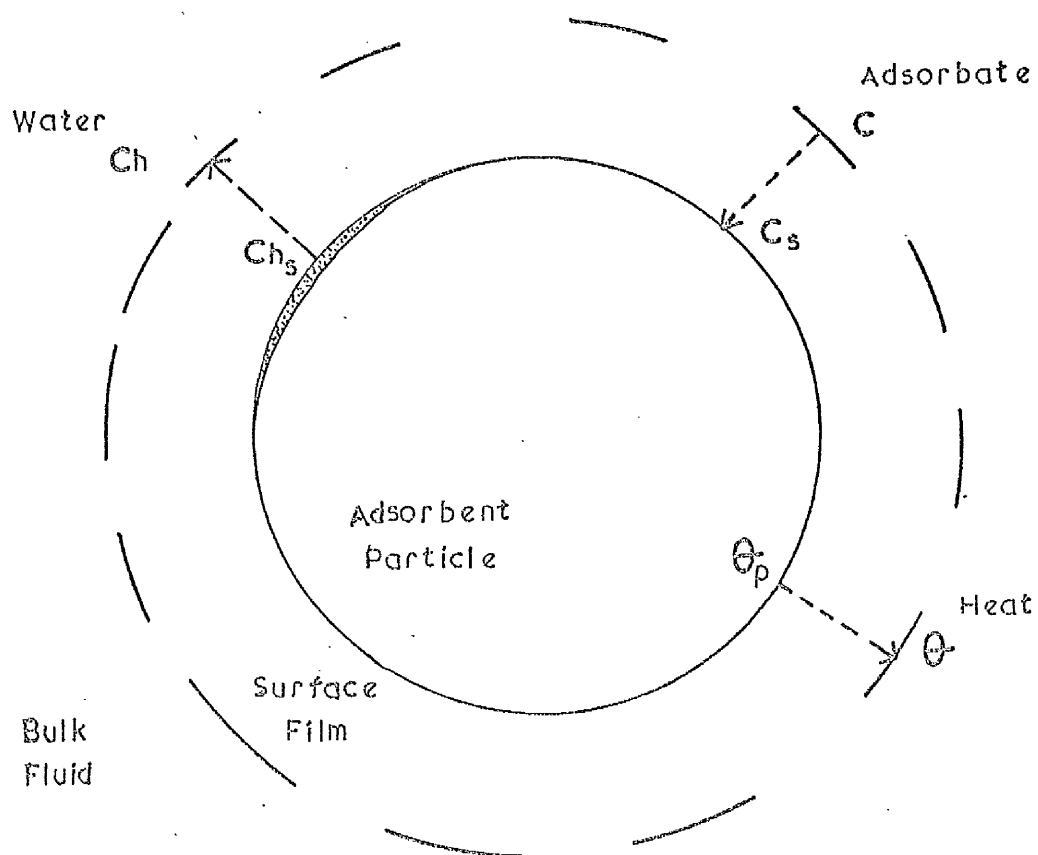


Fig.46.

```

SUBROUTINE FIBS(DINT,CIN)
  DIMENSION FIB(9)
  FIB(1)=1.0
  FIB(2)=2.0
  DO 6 I=3,9,1
    FIB(I)=FIB(I-1)+FIB(I-2)
6  CONTINUE
  DEN=CIN
  DE=0.0
  ACC=0.000001
  I=9
  D1=DE+FIB(I-2)*(DEN+DE)/FIB(I)
  D2=DE+FIB(I-1)*(DEN+DE)/FIB(I)
7  CALL DEL(D1,FD1,CIN)
  CALL DEL(D2,FD2,CIN)
  I=I-1
  IF (I-2) 8,8,0
    IF (FD1-FD2) 9,0,0
  DE=D1
  D1=D2
  D2=DE+FIB(I-1)*(DEN+DE)/FIB(I)
  GO TO 7
9  DEN=D2
  D2=D1
  D1=DE+FIB(I-2)*(DEN+DE)/FIB(I)
  GO TO 7
8  IF (FD1-FD2) 10,0,0
  DE=D1
  DM=D2
  GO TO 11
10 DEN=D2
  DM=D1
11 CALL DEL(DE,FDE,CIN)
  CALL DEL(DM,FDM,CIN)
  CALL DEL(DEN,FDEN,CIN)
  DINT=((DM+DEN)*(DM+DEN)*FDE)+((DEN+DE)*(DEN+DE)*FDM)
  DINT=0.5*(DINT+(DE+DM)*(DE+DM)*FDEN)
  DINT=DINT/((DM+DEN)*FDE+(DEN+DE)*FDM+(DE+DM)*FDEN)
  CALL DEL(DINT,FDINT,CIN)
  IF (FDINT=ACC) 12,12,0
  IF (FDE=FDEN) 0,0,13
  IF (DINT=DM) 0,0,14
  DEN=DM
  DM=DINT
  GO TO 11
14 DEN=DINT
  GO TO 11
13 IF (DINT=DM) 0,0,15
  DE=DINT
  GO TO 11
15 DE=DM
  DM=DINT
  GO TO 11
12 CONTINUE
0  REQUIRED ACCURACY ACHIEVED
  RETURN
  END

```


Fig.47.

Mod.3.

```
SUBROUTINE DEL(VAR,FUN,CIN)
COMMON V1,V2,CO
FUN=(CIN-VAR)/CO-V1*(1.0-EXP(-V2*VAR))
FUN=FUN**2
RETURN
END
```

Mod.4.

```
SUBROUTINE DEL(VAR,FUN,CIN)
COMMON V1,V2,V3,V4,V5,CO
FUN=(CIN-VAR)/CO-V4*((VAR*V1+V2-V5)/(VAR*V2+V3))*(1.0-EXP
1(-V2*VAR-V3))
FUN=FUN**2
RETURN
END
```

Mod.7.

```
SUBROUTINE DEL(VAR,FUN,CIN)
COMMON V1,V2,V3,V4,V5,CO
DUM=V2*VAR/(V4*VAR+V3)
FUN=(CIN-VAR)/CO*(V1/CO)*(DUM-V5)*(1.0-EXP(-V4*VAR+V3))
FUN=FUN**2
RETURN
END
```

Fig. 48.

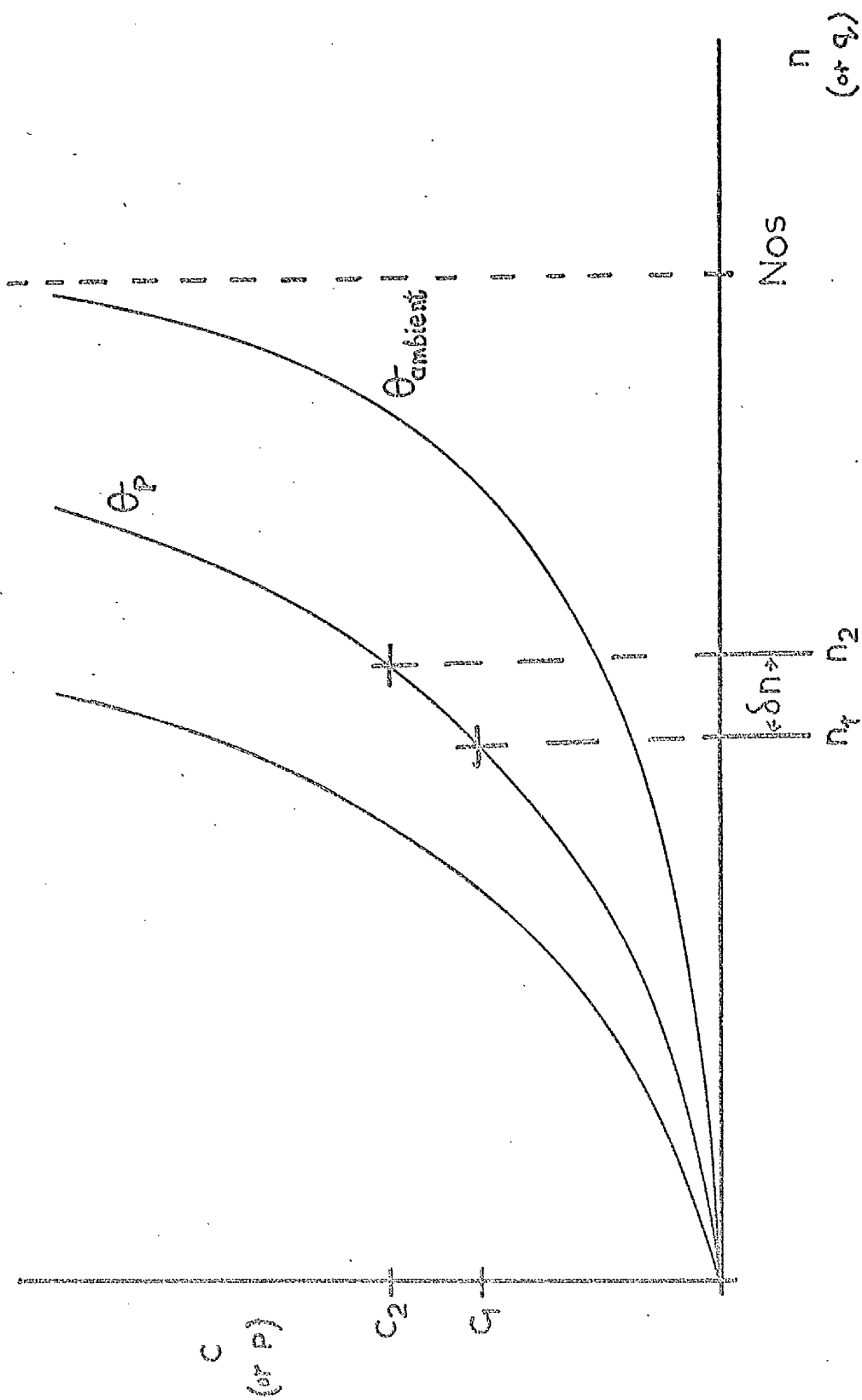


Fig. 49.

```

READ FROM(CR/S1900)
MASTER MOD/1
REAL K1,INO,NOS,N(40),NO(40)
DIMENSION C(40),Z(40)
READ (1,50) CO,INO,NOS,AL,V
READ(1,53) H
READ(1,54) TM
READ(1,55) L
99  CONTINUE
    READ(1,56) K1
    IF(K1) 100,100,0
    WRITE(2,56) K1
    TOS=(NOS*H)/(CO*AL*V)
    DO 1 I=1,40,1
    NO(I)=INO
    Z(I)=I*0.025*H
1    CONTINUE
    T=0.0
    INT=0
C    EVALUATE FIRST SECTION OF MODEL
12   DT=TM/L
    TIM=DT
    IF(INT-1) 13,0,0
    C(1)=CO
    N(1)=NOS
    GO TO 5
13   C(1)=CO/(1.0+K1*Z(1)/V)
    IF(CO-C(1)-CO/L) 17,17,0
C    REDUCE Z-DISTANCES WITHIN THIS BED INCREMENT
    KUT=1
18   KUT=KUT+1
    DO 20 KOUNT=1,KUT,1
    IF(KOUNT-1) 0,0,19
    CIN=CO
19   CUT=CIN/(1.0+K1*Z(1)/(V*KUT))
    IF(CIN-CUT-CO/L) 0,0,18
    CIN=CUT
20   CONTINUE
    C(1)=CUT
17   N(1)=NO(1)+V*AL*(CO-C(1))*DT/Z(1)
    IF (N(1)-NOS) 2,3,0
C    ADSORBENT CAPACITY ABOVE SATURATION, REDUCE TIME INTERVAL
C    CONCENTRATION PROFILE INDEPENDANT OF DT
    TIM=(Z(1)*(NOS-NO(1)))/(V*AL*(CO-C(1)))
    GO TO 3
2    IF(N(1)/NOS-0.999) 0,3,3
    NO(1)=N(1)
    IF(C(1)/CO-0.005) 0,5,5
    I=1
    GO TO 16
3    N(1)=NOS
    NO(1)=N(1)
    INT=1
    DT=TIM
C    NEW VALUE OF DT USED FOR REMAINING SECTIONS UNSATURATED
5    DO 6 I=2,40,1
    IF(I-INT) 0,0,7
    C(I)=CO
    N(I)=NOS

```

Fig. 49.continued

```

      GO TO 6
7      C(I)=C(I-1)/(1.0+K1*(Z(I)-Z(I-1))/V)
      IF(C(I-1)-C(I)-C0/L) 21,21,0
C      REDUCE Z-DISTANCES WITHIN THIS BED INCREMENT
      KUT=1
22     KUT=KUT+1
      DO 23 KOUNT=1,KUT,1
      IF(KOUNT-1) 0,0,24
      CIN=C(I-1)
24     CUT=CIN/(1.0+K1*(Z(I)-Z(I-1))/(V*KUT))
      IF(CIN-CUT-C0/L) 0,0,22
      CIN=CUT
23     CONTINUE
      C(I)=CUT
21     N(I)=NO(I)+V*AL*(C(I-1)-C(I))*DT/(Z(I)-Z(I-1))
      IF (N(I)-NOS) 8,9,0
      TIM=((Z(I)-Z(I-1))*(NOS-NO(I)))/(V*AL*(C(I-1)-C(I)))
      GO TO 9
8      IF(N(I)/NOS-0.999) 0,9,9
      NO(I)=N(I)
      IF(C(I)/C0-0.005) 0,6,6
16     SUMN=C(I)*AL*V*DT
      DEP=H-Z(I)
      DO 14 J=I+1,40,1
      C(J)=0.0
      N(J)=NO(J)+(Z(J)-Z(J-1))*SUMN/DEP
      NO(J)=N(J)
14     CONTINUE
      GO TO 15
9      N(I)=NOS
      NO(I)=N(I)
      INT=I
      DT=TIM
6      CONTINUE
15     T=T+DT
      TD=T/TOS
      WRITE (2,51) TD
      I=40
      C(I)=C(I)/C0
      WRITE (2,52) Z(I),N(I),C(I)
      IF(T-TM) 12,12,99
100    CONTINUE
50     FORMAT (5F12.6)
51     FORMAT(1H0/F8.4)
52     FORMAT (10X,F6.2,10X,F10.6,10X,F12.9)
53     FORMAT(F10.4)
54     FORMAT(F10.4)
55     FORMAT(I4)
56     FORMAT(F13.6)
      STOP
      END

```

1a Case 1 } $K_1 = 10000.0$
 1b Mod 1 }
 2a Case 1 } $K_1 = 20000.0$
 2b Mod 1 }

Fig. 50.

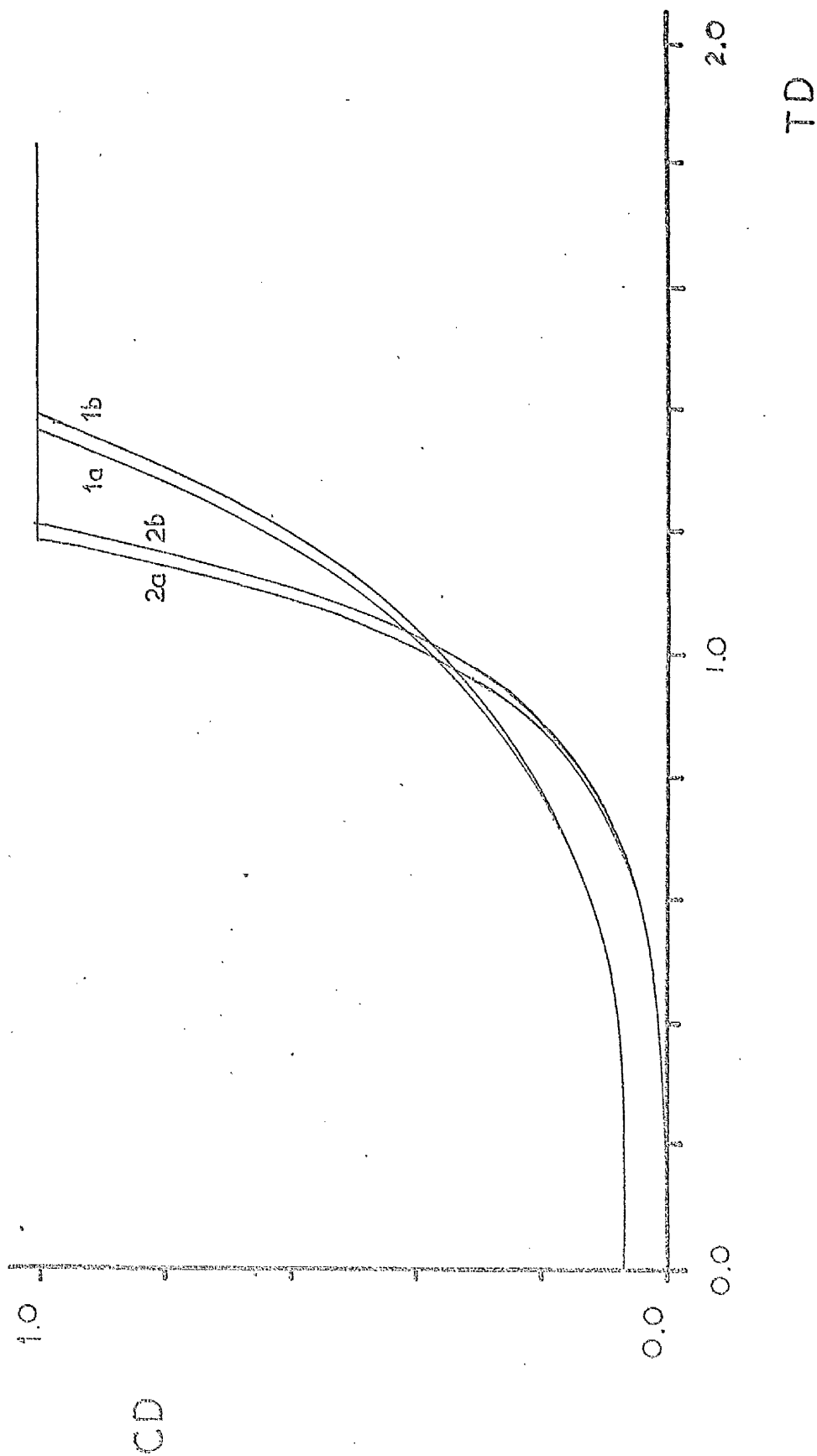


Fig. 51.

```

READ FROM(CR/S1900)
MASTER MOD/2
REAL K1,INO,NOS,N(40),NO(40),K2
DIMENSION C(40),Z(40)
READ(1,50) CC,INO,NOS,AL,V
READ(1,53) H
READ(1,54) TM
READ(1,55) L
TOS=(NOS*H)/(CO*AL*V)
9 CONTINUE
READ(1,56) K1
IF(K1) 2,2,0
K2=K1*CO/NOS
WRITE(2,57) K1 ,K2
DO 1 I=1,40,1
NO(I)=INO
Z(I)=I*0.025*H
1 CONTINUE
DT=TM/L
T=0.0
5 T=T+DT
IF(T-TM) 0,0,9
TD=T/TOS
WRITE (2,51) TD
C EVALUATE FIRST SECTION OF BED
V1=Z(1)/(V*AL*DT)
C(1)=(CO +NO(1)*V1*(1.0*EXP(-K2*AL*DT)))/(K1*V1/K2*(1.0*EXP(
1-K2*AL*DT))+1,0)
IF(CO=C(1)=CC/40,0) 100,100,0
C REDUCE Z-DISTANCES WITHIN THIS BED INCREMENT
KUT=1
18 KUT=KUT+1
DO 20 KOUNT =1,KUT,1
IF(KOUNT=1) 0,0,19
CIN=CO
19 V1=Z(1)/(V*AL*DT*KUT)
CUT=(CIN +NO(1)*V1*(1.0*EXP(-K2*AL*DT)))/(K1*V1/K2*(1.0*EXP(
1-K2*AL*DT))+1,0)
IF(CIN=CUT=CC/40,0) 0,0,18
CIN=CUT
20 CONTINUE
C(1)=CUT
100 N(1)=NO(1)+V*AL*(CO=C(1))*DT/Z(1)
NO(1)=N(1)
IF(C(1)/CO=0.005) 0,6,6
I=1
GO TO 104
C REMAINING SECTIONS NOW EVALUATED
6 DO 3 I=2,40,1
V1=(Z(I)-Z(I-1))/(V*AL*DT)
C(I)=(C(I-1)+NO(I)*V1*(1.0*EXP(-K2*AL*DT)))/(K1*V1/K2*(1.0*EXP(
1-K2*AL*DT))+1,0)
IF(C(I-1)=C(I)=CO/40,0) 105,105,0
C REDUCE Z-DISTANCES WITHIN THIS BED INCREMENT
KUT=1
22 KUT=KUT+1

```

Fig. 51.continued

```

DO 23 KOUNT = 1, KUT, 1
IF (KOUNT-1) 0, 0, 24
CIN = C(I-1)
24  V1 = (Z(I) - Z(I-1)) / (V * AL * DT * KUT)
    CUT = (CIN * NU(I) * V1 * (1.0 - EXP(-K2 * AL * DT))) / (K1 * V1 / K2 * (1.0 - EXP(
1 = K2 * AL * DT)) + 1, 0)
    IF (CIN - CUT = 60/40, 0) 0, 0, 22
    CIN = CUT
23  CONTINUE
    C(I) = CUT
105  N(I) = NU(I) * V * AL * (C(I-1) - C(I)) * DT / (Z(I) - Z(I-1))
    NO(I) = N(I)
    IF (C(I) / 60 = 0, 005) 0, 3, 3
104  SUMN = C(I) * AL * V * DT
    DEP = H = Z(I)
    IF (I = 40) 0, 7, 7
    DO 7 J = I + 1, 40, 1
    C(J) = 0, 0
    N(J) = NU(J) + (Z(J) - Z(J-1)) * SUMN / DEP
    NO(J) = N(J)
7    CONTINUE
    GO TO 5
3    CONTINUE
8    I = 40
    C(I) = C(I) / 60
    WRITE (2, 22) Z(I), N(I), C(I)
    GO TO 2
2    CONTINUE
50   FORMAT (5F12, 6)
51   FORMAT (1H0 / F8, 4)
52   FORMAT (10X, F6, 2, 10X, F10, 6, 10X, F12, 9)
53   FORMAT (F10, 4)
54   FORMAT (F10, 4)
55   FORMAT (I4)
56   FORMAT (F13, 6)
57   FORMAT (F13, 6, 10X, F13, 6)
    STOP
    END

```


1a Case 2 } $K1=1000.0, K2=0.365854$
 1b Mod 2
 2a Case 2 } $K1=3500.0, K2=1.280488$
 2b Mod 2

Fig. 52.

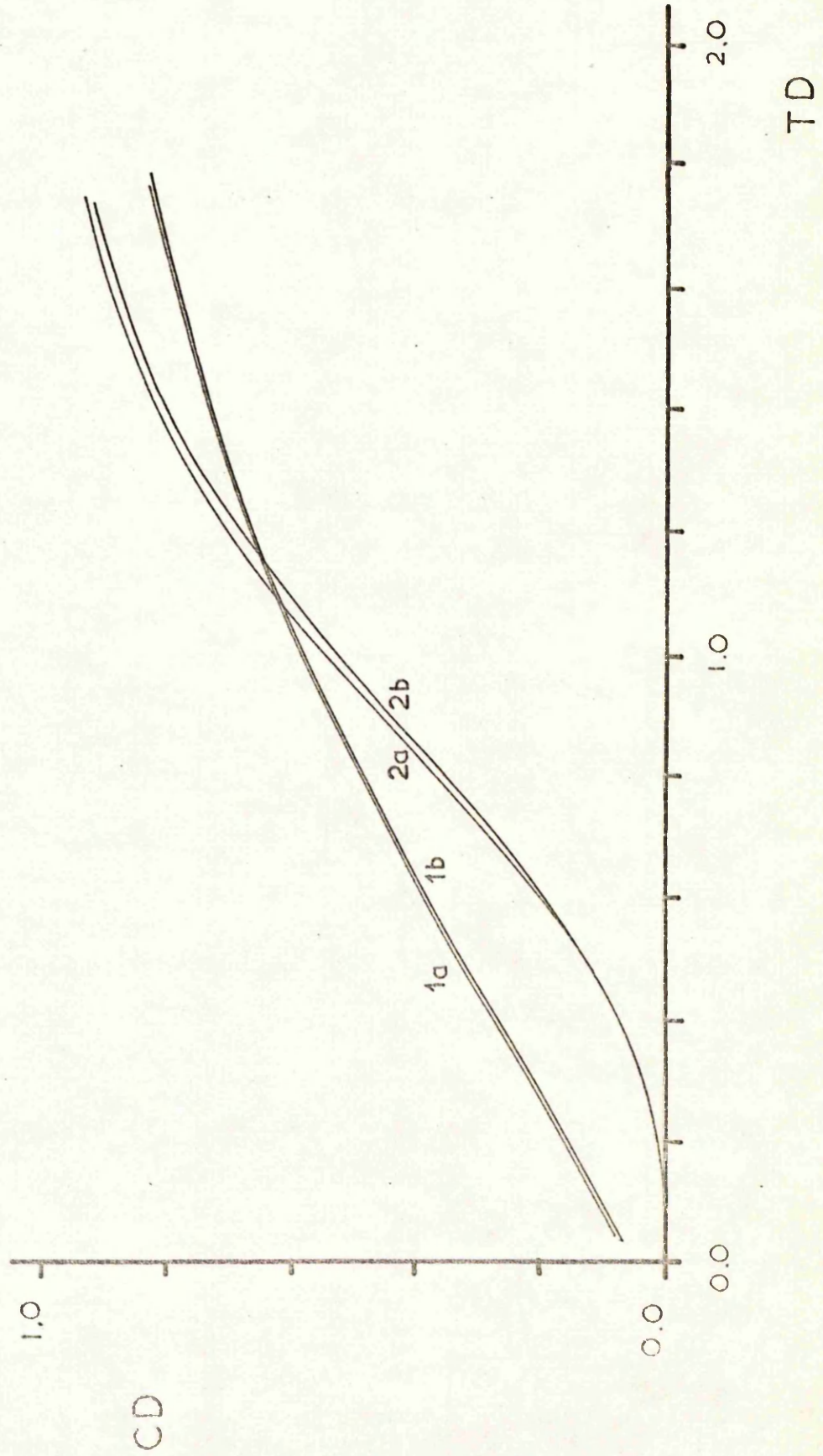


Fig. 53.

```

      READ FROM(CR/$1900)
      MASTER MOD/3
      EXTERNAL DEL,FIBS
      REAL K1,INO,NOS,N(40),NO(40)
      DIMENSION C(40),Z(40)
      COMMON V1,V2,C0
      READ(1,50) CC,INO,NCS,AL,V
      READ(1,53) H
      READ(1,54) TM
      READ(1,55) L
9      CONTINUE
      READ(1,56) K1
      IF(K1) 2,2,0
      WRITE(2,57) K1
      TOS=(NOS*H)/(C0*AL*V)
      DO 1 I=1,40,1
      NO(I)=INO
      Z(I)=I*0.025*H
1      CONTINUE
      DT=TM/L
      V2=K1*AL*DT
      T=0.0
5      T=T+DT
      IF(T-TM) 0,0,9
      TD=T/TOS
      WRITE(2,54) TD
      C EVALUATE FIRST SECTION OF MODEL
      V1=(NOS-NO(1))*Z(1)/(V*AL*DT*C0)
      CIN=C0
      CALL FIBS(COUT,CIN)
      C(1)=COUT
      IF(C0-C(1)=C0/40.0) 100,100,0
      C REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
      KUT=1
101      KUT=KUT+1
      V1=(NOS-NO(1))*Z(1)/(V*AL*DT*C0*KUT)
      DO 102 KOUNT=1,KUT,1
      IF(KOUNT-1) 0,0,103
      CIN=C0
103      CALL FIBS(COUT,CIN)
      IF(CIN-COUT=C0/40.0) 0,0,101
      CIN=COUT
102      CONTINUE
      C(1)=COUT
100      N(1)=NO(1)+V*AL*(C0-C(1))*DT/Z(1)
      NO(1)=N(1)
      IF(C(1)/C0=0.005) 0,6,6
      I=1
      GO TO 104
      C REMAINING SECTIONS NOW EVALUATED
      DO 3 I=2,40,1
      V1=(NOS-NO(1))*(Z(I)-Z(I-1))/(V*AL*DT*C0)
      CIN=C(I-1)
      CALL FIBS(COUT,CIN)
      C(1)=COUT
      IF(C(I-1)-C(1)=C0/40.0) 105,105,0
      C REDUCE Z-DISTANCES WITHIN THE BED INCREMENT

```

Fig. 53.continued

```

      KUT=1
106  KUT=KUT+1
      V1=(NOS-NO(I))*(Z(I)-Z(I+1))/(V*AL*DT*CO*KUT)
      DO 107 KOUNT=1,KUT,1
      IF(KOUNT=1) 0,0,108
      CIN=C(I-1)
108  CALL FIBS(COUT,CIN)
      IF(CIN=COUT=CO/40,0) 0,0,106
      CIN=COUT
107  CONTINUE
      C(I)=COUT
105  N(I)=NO(I)+V*AL*(C(I-1)-C(I))*DT/(Z(I)-Z(I+1))
      NO(I)=N(I)
      IF(C(I)/CO=0,005) 0,3,3
104  SUMN=C(I)*AL*V*DT
      DEP=H-Z(I)
      IF(I=40) 0,7,7
      DO 7 J=I+1,40,1
      C(J)=0,0
      N(J)=NO(J)+(Z(J)-Z(J+1))*SUMN/DEP
      NO(J)=N(J)
7    CONTINUE
      GO TO 8
3    CONTINUE
8    I=40
      C(I)=C(I)/CO
      WRITE (2,52) Z(I),N(I),C(I)
      GO TO 5
2    CONTINUE
50   FORMAT (5F12,6)
51   FORMAT (1H0/F8,4)
52   FORMAT (10X,F6,2,10X,F10,6,10X,F12,9)
53   FORMAT (F10,4)
54   FORMAT (F10,4)
55   FORMAT (I4)
56   FORMAT (2F13,6)
57   FORMAT (F13,6)
      STOP
      END

```

Fig. 54.

1a Case3 } $K1=150000.0$
 1b Mod3 }
 2a Case3 } $K1=300000.0$
 2b Mod3 }

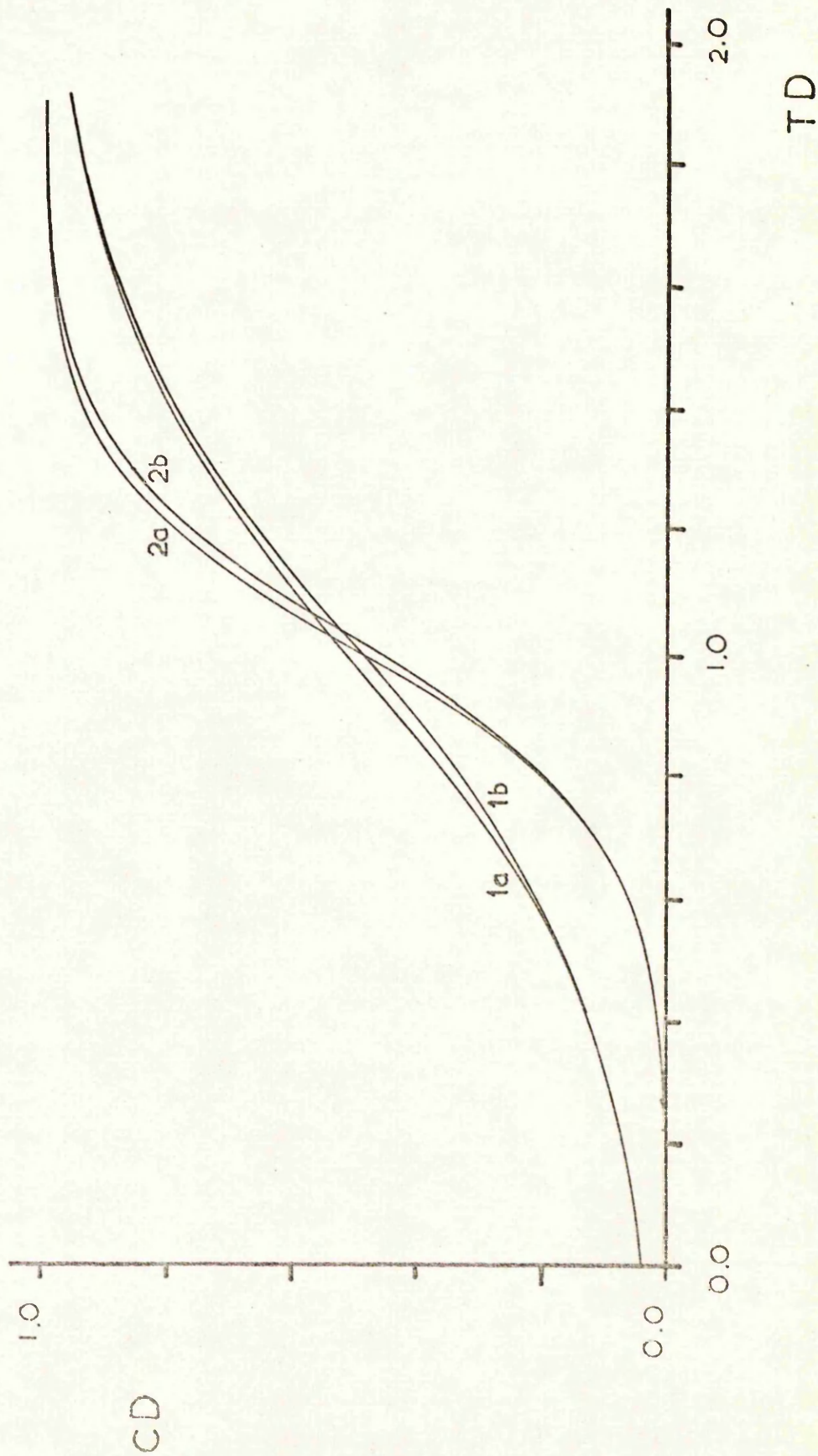


Fig. 55.

```

READ FROM(CCR/S1900)
MASTER MOD/4
EXTERNAL DEL,FIBS
REAL K1,INO,NOS,N(40),NO(40),K2
DIMENSION C(40),Z(40)
COMMON V1,V2,V3,V4,V5,CO
READ(1,50) CO,INO,NOS,AL,V
READ(1,53) H
READ(1,54) TM
READ(1,55) L
9  CONTINUE
   READ(1,56) K1,K2
   IF(K1) Z,Z,0
   WRITE(2,57) K1,K2
   TOS=(NOS*N)/(CO*AL*V)
   DO 1 I=1,40,1
   NO(I)=INO
   Z(I)=I*0.025*H
1  CONTINUE
   DT=TM/L
   V2=K1*AL*DT
   V3=K2*AL*DT
   T=0,0
5  T=T+DT
   IF(T-TM) 0,0,9
   TD=T/TOS
   WRITE(2,59) TD
C  EVALUATE FIRST SECTION OF MODEL
   V1=NOS-NO(1)
   V5=V3*NO(1)
   V4=Z(1)/(V*AL*DT*CO)
   CIN=CO
   CALL FIBS(COUT,CIN)
   C(1)=COUT
   IF(CO=C(1)-CO/40,0) 100,100,0
C  REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
   KUT=1
101 KUT=KUT+1
   V4=Z(1)/(V*AL*DT*CO*KUT)
   DO 102 KOUNT=1,KUT,1
   IF(KOUNT=1) 0,0,103
   CIN=CO
103 CALL FIBS(COUT,CIN)
   IF(CIN=COUT-CO/40,0) 0,0,101
   CIN=COUT
102 CONTINUE
   C(1)=COUT
100 N(1)=NO(1)+V*AL*(CO-C(1))*DT/Z(1)
   NO(1)=N(1)
   IF(C(1)/CO=0,005) 0,6,6
   I=1
   GO TO 104
C  REMAINING SECTIONS NOW EVALUATED

```

Fig.55.continued

```

6      DO 3 I=2,40,1
          V1=NOS*NO(I)
          V5=V3*NO(I)
          V4=(Z(I)-Z(I-1))/(V*AL*DT*CO)
          CIN=C(I-1)
          CALL FIBS(COUT,CIN)
          C(I)=COUT
          IF(C(I-1)-C(I)-CO/40.0) 105,103,0
C      REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
          KUT=1
106     KUT=KUT+1
          V4=(Z(I)-Z(I-1))/(V*AL*DT*CO*KUT)
          DO 107 KOUNT=1,KUT,1
          IF(KOUNT=1) 0,0,108
          CIN=C(I-1)
108     CALL FIBS(COUT,CIN)
          IF(CIN-COUT-CO/40.0) 0,0,106
          CIN=COUT
107     CONTINUE
          C(I)=COUT
105     N(I)=NO(I)*V*AL*(C(I-1)-C(I))*DT/(Z(I)-Z(I-1))
          NO(I)=N(I)
          IF(C(I)/CO=0.005) 0,3,3
104     SUMN=C(I)*AL*V*DT
          DEP=H-Z(I)
          IF(I=40) 0,3,3
          DO 7 J=I+1,40,1
          C(J)=0.0
          N(J)=NO(J)+(Z(J)-Z(J-1))*SUMN/DEP
          NO(J)=N(J)
7      CONTINUE
          GO TO 8
3      CONTINUE
8      I=40
          C(I)=C(I)/CO
          WRITE (2,52) Z(I),N(I),C(I)
4      CONTINUE
          GO TO 2
2      CONTINUE
50     FORMAT(5F12.6)
51     FORMAT(1H0/F8.4)
52     FORMAT (10X,F6.2,10X,F10.6,10X,F12.9)
53     FORMAT(F10.4)
54     FORMAT(F10.4)
55     FORMAT(I4)
56     FORMAT(2F13.6)
57     FORMAT(2F13.6)
          STOP
          END

```

1a Case 4 } $K1=15000.0, K2=0.368182$
 1b Mod 4 }
 2a Case 4 } $K1=25000.0, K2=0.250$
 2b Mod 4 }
 3a Case 4 } $K1=35000.0, K2=0.0055263$
 3b Mod 4 }

Fig. 56.

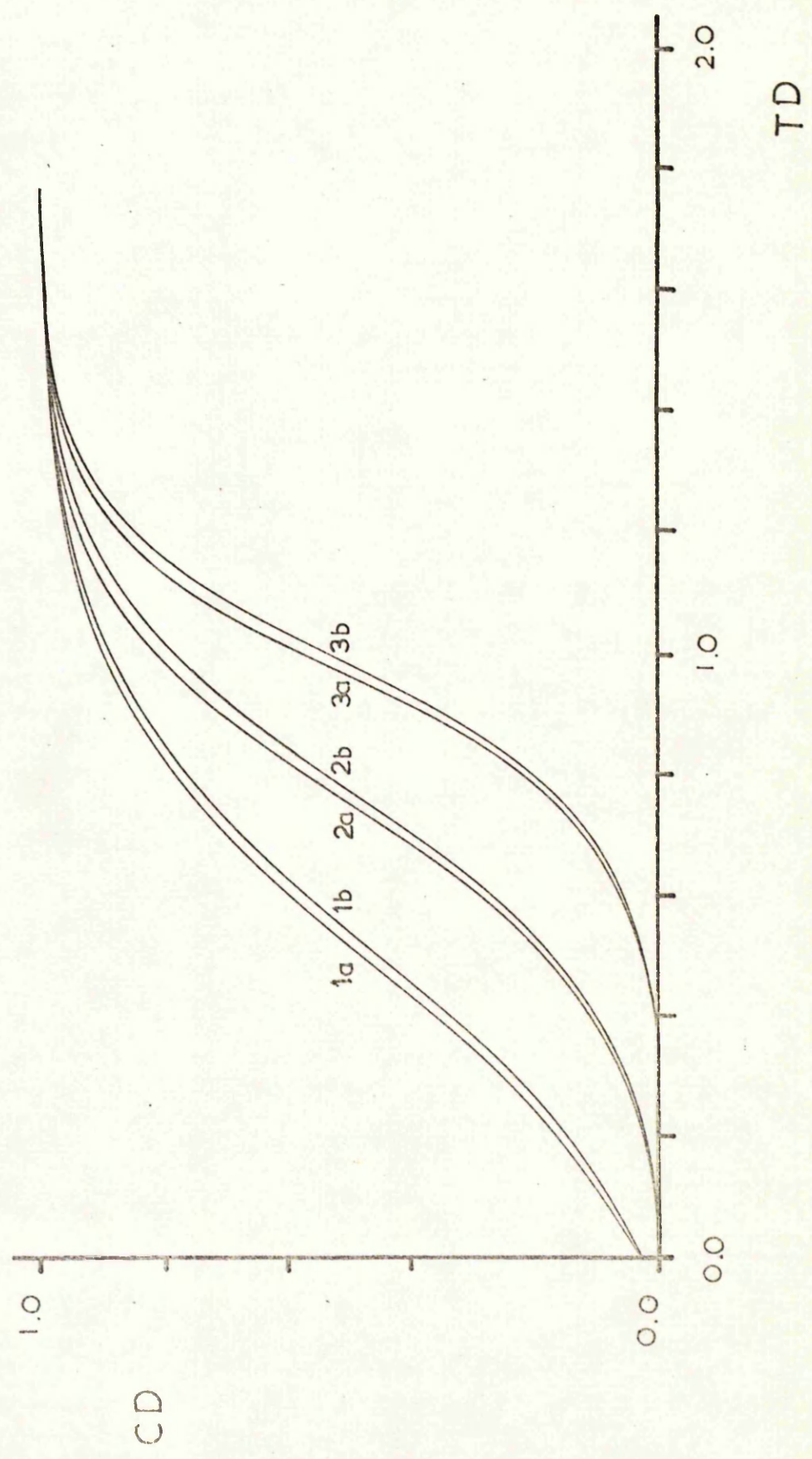


Fig. 57.

```

READ FROM(CR/S1900)
MASTER MOD/5
REAL K1,INO,NOS,N(40),NO(40)
DIMENSION C(40),Z(40)
READ(1,50) CO,INO,NOS,AL,V
READ(1,53) H
READ(1,54) TM
READ(1,55) L
90 CONTINUE
READ(1,56) K1
IF(K1) 2,2,0
WRITE(2,57) K1
YOS=(NOS*N)/(CO*AL*V)
DO 1 I=1,40,1
NO(I)=INO
Z(I)=1*0.025*H
1 CONTINUE
DT=TM/L
T=0,0
5 T=T+DT
IF(T-TM) 0,0,90
TD=T/YOS
WRITE(2,51) TD
C EVALUATE FIRST SECTION OF BED
V1=Z(1)*(NOS-NO(1))/(V*AL*DT)
C(1)=CO-V1*(1,0-EXP(-K1*AL*DT))
IF(C(1)) 0,0,9
C NEGATIVE CONCENTRATION WITHIN FIRST SECTION
C(1)=0,0
9 IF(CO-C(1)-CO/40,0) 100,100,0
C REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
KUT=1
101 KUT=KUT+1
V1=Z(1)*(NOS-NO(1))/(V*AL*DT*KUT)
DO 102 KOUNT=1,KUT,1
IF(KOUNT-1) 0,0,103
CIN=CO
103 COUT=CIN-V1*(1,0-EXP(-K1*AL*DT))
IF(COUT) 0,0,10
C(1)=0,0
GO TO 100
10 IF(CIN-COUT-CO/40,0) 0,0,101
CIN=COUT
102 CONTINUE
C(1)=COUT
100 N(1)=NO(1)+V*AL*(CO-C(1))*DT/Z(1)
NO(1)=N(1)
IF(C(1)/CO-0,005) 0,6,6
I=1
GO TO 104
C REMAINING SECTIONS NOW EVALUATED
6 DO 3 I=2,40,1
V1=(Z(I)-Z(I-1))*(NOS-NO(1))/(V*AL*DT)
C(I)=C(I-1)-V1*(1,0-EXP(-K1*AL*DT))
IF(C(I)) 0,12,12
C NEGATIVE CONCENTRATION OCCURS WITHIN STAGE I
C(I)=0,0
12 IF(C(I-1)-C(I)-CO/40,0) 105,105,0
C REDUCE Z-DISTANCES WITHIN THE BED INCREMENT

```

Fig. 57.continued

```

      KUT=1
106  KUT=KUT+1
      V1=(Z(I)-Z(I-1))*(NOS-NO(I))/(V*AL*DT*KUT)
      DO 107 KOUNT=1,KUT,1
      IF(KOUNT=1) 0,0,108
      CIN=C(I-1)
108  COUT=CIN+V1*(1.0-EXP(-K1*AL*DT))
      IF (COUT) 0,0,13
      COUT=0.0
      GO TO 14
13  IF(CIN-COUT=CO/40.0) 0,0,106.
      CIN=COUT
107  CONTINUE
14  C(I)=COUT
105  N(I)=NO(I)+V*AL*(C(I-1)-C(I))*DT/(Z(I)-Z(I-1))
      NO(I)=N(I)
      IF(C(I)/CO=0.005) 0,3,3
104  SUMN=C(I)*AL*V*DT
      DEP=H-Z(I)
      IF(I=40) 0,3,3
      DO 7 J=I+1,40,1
      C(J)=0.0
      N(J)=NO(J)*(Z(J)-Z(J-1))*SUMN/DEP
      NO(J)=N(J)
7   CONTINUE
      GO TO 8
3   CONTINUE
8   I=40
      C(I)=C(I)/CO
      WRITE(2,52) Z(I),N(I),C(I)
4   CONTINUE
      GO TO 5
2   CONTINUE
50  FORMAT(5F12.6)
51  FORMAT(1H0/F8.4)
52  FORMAT(10X,F6.2,10X,F10.6,10X,F12.9)
53  FORMAT(F10.4)
54  FORMAT(F10.4)
55  FORMAT(I4)
56  FORMAT(F13.6)
57  FORMAT(F13.6)
      STOP
      END

```


1a	Case5	} $K1 = 0.15$
1b	Mod5	
2a	Case5	} $K1 = 0.30$
2b	Mod5	
3a	Case5	} $K1 = 0.60$
3b	Mod5	

Fig. 58.

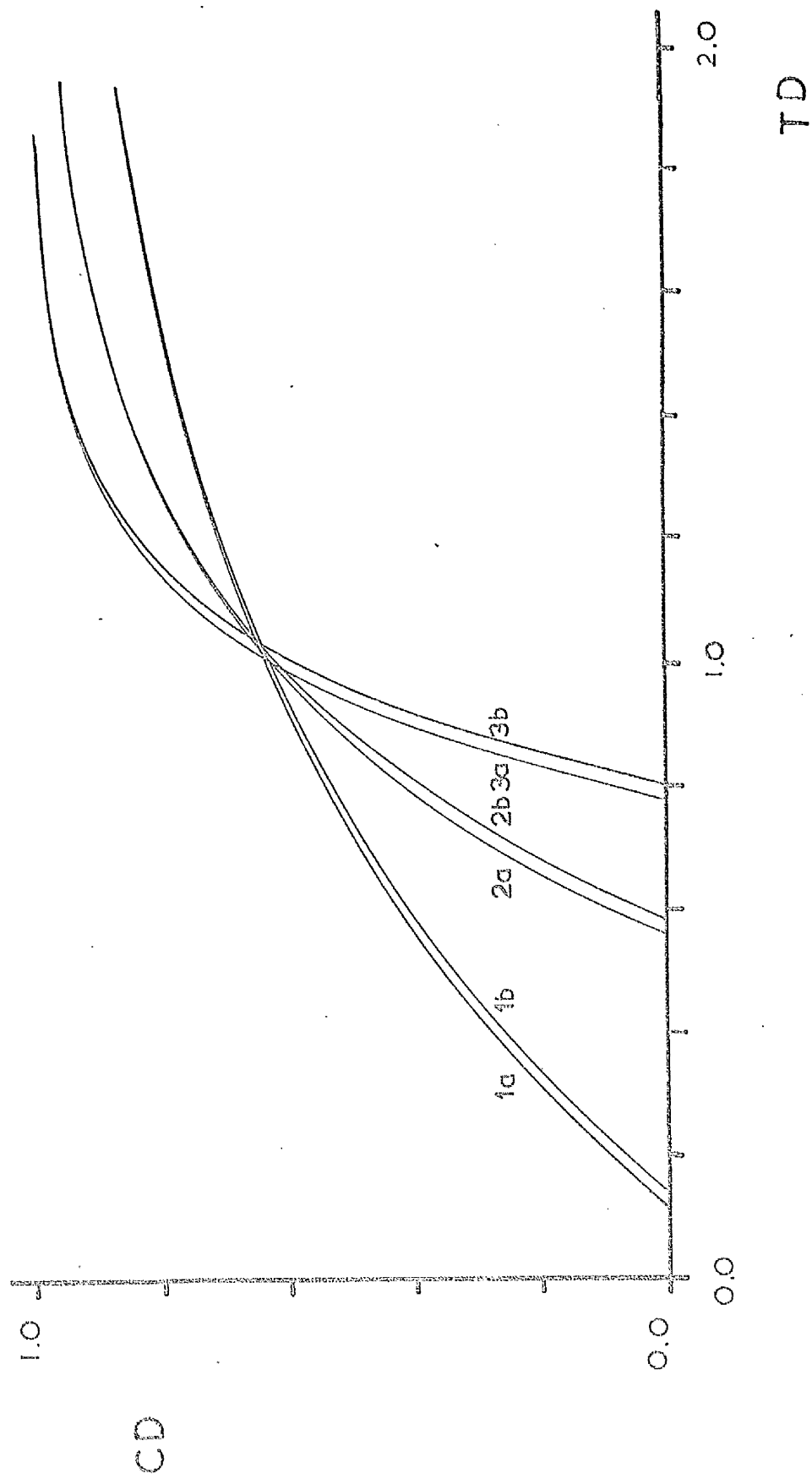


Fig. 59.

```

READ FROM(CR/S1900)
MASTER MOD/6
REAL K1,INO,NOS,N(40),NO(40)
DIMENSION C(40),Z(40)
READ(1,50) CO,INO,NOS,AL,V
READ(1,53) H
READ(1,54) TM
READ(1,55) L
90  CONTINUE
    READ(1,56) K1
    IF(K1) 2,2,0
    WRITE(2,57) K1
    TOS=(NOS*H)/(CO*AL*V)
    DO 1 I=1,40,1
    NO(I)=INO
    Z(I)=I*0.025*H
1    CONTINUE
    DT=TM/L
    T=0.0
5    T=T+DT
    IF(T-TM) 0,0,90
    TD=T/TOS
    WRITE(2,51) TD
C    EVALUATE FIRST SECTION OF BED
    V1=Z(1)/(V*AL*DT)
    C(1)=CO-V1*(-NO(1)+SQRT(NO(1)**2+(NOS-NO(1))*(NOS+NO(1))*(1.0-EXP
1(-K1*AL*DT))))
    IF(C(1)) 0,0,9
C    NEGATIVE CONCENTRATION OCCURS WITHIN STAGE 1
    C(1)=0.0
9    IF(CO-C(1)-CO/40.0) 100,100,0
C    REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
    KUT=1
101  KUT=KUT+1
    V1=Z(1)/(V*AL*DT*KUT)
    DO 102 KOUNT=1,KUT,1
    IF(KOUNT-1) 0,0,103
    CIN=CO
103  COUT=CIN-V1*(-NO(1)+SQRT(NO(1)**2+(NOS-NO(1))*(NOS+NO(1))*(1.0-
1EXP(-K1*AL*DT))))
    IF(COUT) 0,0,10
    C(1)=0.0
    GO TO 100
10  IF(CIN-COUT-CO/40.0) 0,0,101
    CIN=COUT
102  CONTINUE
    C(1)=COUT
100  N(1)=NO(1)+V*AL*(CO-C(1))*DT/Z(1)
    NO(1)=N(1)
    IF(C(1)/CO-0.005) 0,6,6
    I=1
    GO TO 104
C    REMAINING SECTIONS NOW EVALUATED
6    DO 3 I=2,40,1
    V1=(Z(I)-Z(I-1))/(V*AL*DT)
    C(I)=C(I-1)-V1*(-NO(I)+SQRT(NO(I)**2+(NOS-NO(I))*(NOS+NO(I))*(1.0
1-EXP(-K1*AL*DT))))
    IF(C(I)) 0,12,12
C    NEGATIVE CONCENTRATION OCCURS WITHIN STAGE I

```

Fig. 59.continued

```

C(I)=0.0
12 IF(C(I-1)-C(I)-CO/40.0) 105,105,0
C REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
KUT=1
106 KUT=KUT+1
V1=(Z(I)-Z(I-1))/(V*AL*DT*KUT)
DO 107 KOUNT=1,KUT,1
IF(KOUNT-1) 0,0,108
CIN=C(I-1)
108 COUT=CIN-V1*(-NO(I)+SQRT(NO(I)**2+(NOS-NO(I))*(NOS+NO(I))*(1.0-
1 EXP(-K1*AL*DT))))
IF (COUT) 0,0,13
COUT=0.0
GO TO 14
13 IF(CIN-COUT-CO/40.0) 0,0,106
CIN=COUT
107 CONTINUE
14 C(I)=COUT
105 N(I)=NO(I)+V*AL*(C(I-1)-C(I))*DT/(Z(I)-Z(I-1))
NO(I)=N(I)
IF(C(I)/CO-0.005) 0,3,3
104 SUMN=C(I)*AL*V*DT
DEP=H-Z(I)
IF(I-40) 0,3,3
DO 7 J=I+1,40,1
C(J)=0.0
N(J)=NO(J)+(Z(J)-Z(J-1))*SUMN/DEP
NO(J)=N(J)
7 CONTINUE
GO TO 8
3 CONTINUE
8 I=40
C(I)=C(I)/CO
WRITE(2,52) Z(I),N(I),C(I)
GO TO 5
2 CONTINUE
50 FORMAT(5F12.6)
51 FORMAT(1H0/F8.4)
52 FORMAT(10X,F6.2,10X,F10.6,10X,F12.9)
53 FORMAT(F10.4)
54 FORMAT(F10.4)
55 FORMAT(I4)
56 FORMAT(F13.6)
57 FORMAT(F13.6)
STOP
END

```

1a	Case 6	} $K1 = 0.003257, \eta_0 = 0.001$
1b	Mod 6	
2	Mod 6	} $\eta_0 = 0.00$
3	Mod 6	
4	Mod 6	

Fig. 60.

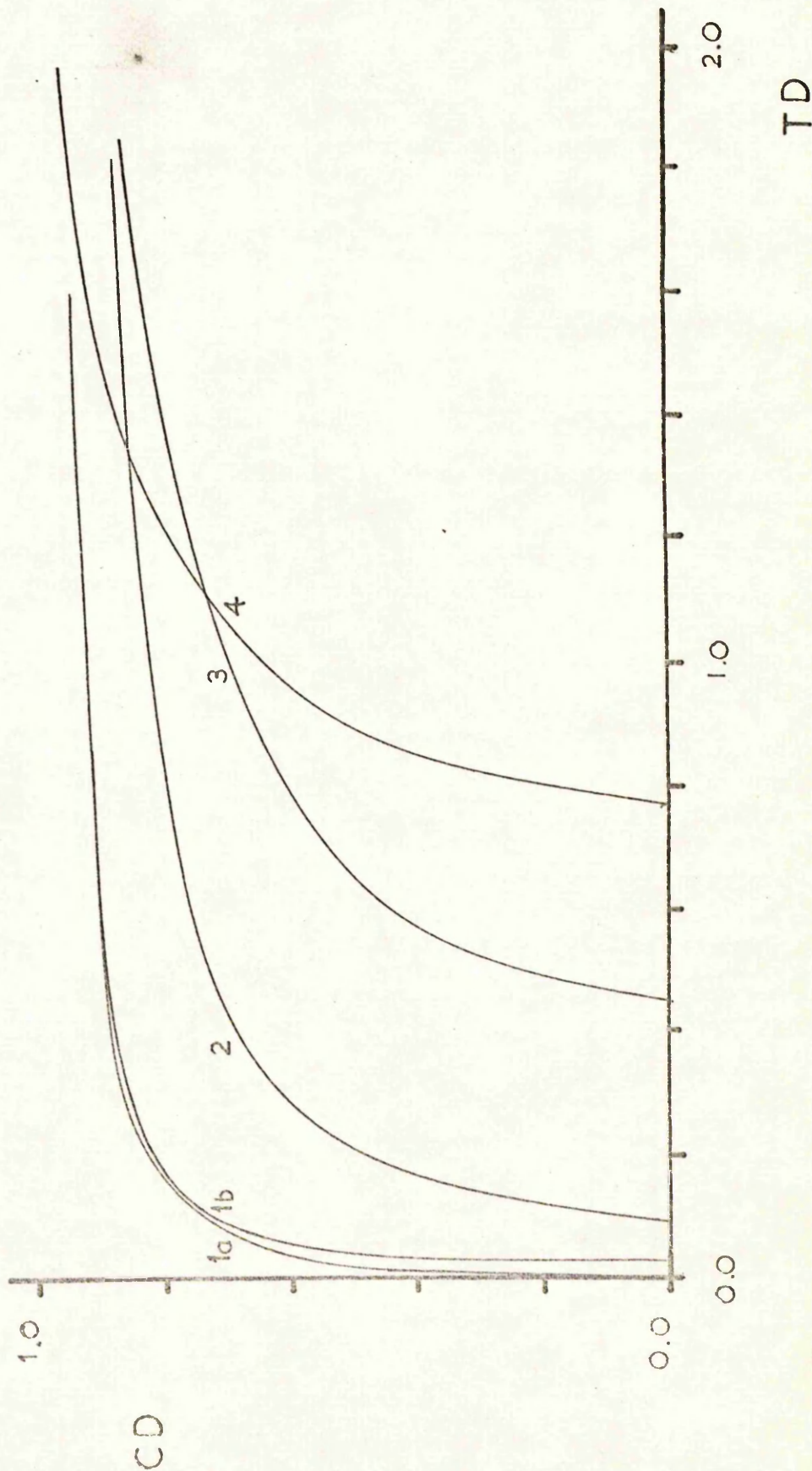


Fig. 61.

```

      READ FROM(CR/S1900)
      MASTER MOD/7
      EXTERNAL DEL,FIBS
      REAL K1,INO,NOS,N(40),NO(40),K2
      DIMENSION C(40),Z(40)
      COMMON V1,V2,V3,V4,V5,C0
      READ(1,50) C0,INO,NOS,AL,V
      READ(1,53) H
      READ(1,54) TM
      READ(1,55) L
9      CONTINUE
      READ(1,56) K1,K2
      IF(K1) 2,2,0
      WRITE(2,57) K1,K2
      TOS=(NOS*H)/(C0*AL*V)
      DO 1 I=1,40,1
      NO(I)=INO
      Z(I)=I*0.025*H
1      CONTINUE
      DT=TM/L
      V2=K1*NOS*AL*DT
      V3=K2*AL*C0*DT
      V4=(K1-K2)*AL*DT
      T=0.0
5      T=T+DT
      IF(T-TM) 0,0,9
      TD=T/TOS
      WRITE(2,51) TD
C      EVALUATE FIRST SECTION OF BED
      VS=NO(1)
      CIN=C0
      V1=Z(1)/(V*AL*DT)
      CALL FIBS(COUT,CIN)
      C(1)=COUT
      IF(C0-C(1)=C0/40.0) 100,100,0
C      REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
      KUT=1
101      KUT=KUT+1
      V1=Z(1)/(V*AL*DT*KUT)
      DO 102 KOUNT=1,KUT,1
      IF(KOUNT=1) 0,0,103
      CIN=C0
103      CALL FIBS(COUT,CIN)
      IF(CIN-COUT=C0/40.0) 0,0,101
      CIN=COUT
102      CONTINUE
      C(1)=COUT
100      N(1)=NO(1)+V*AL*(C0-C(1))*DT/Z(1)
      NO(1)=N(1)
      IF(C(1)/C0=0.005) 0,6,6
      I=1
      GO TO 104
C      REMAINING SECTIONS NOW EVALUATED
6      DO 3 I=2,40,1
      VS=NO(I)
      V1=(Z(I)-Z(I-1))/(V*AL*DT)
      CIN=C(I-1)
      CALL FIBS(COUT,CIN)

```


Fig. 61.continued

```

      C(I)=COUT
      IF(C(I-1)=C(I)=CO/40,0) 105,105,0
C      REDUCE Z-DISTANCES WITHIN THE BED INCREMENT
      KUT=1
106     KUT=KUT+1
      V1=(Z(I)-Z(I-1))/(V*AL*DT*KUT)
      DO 107 KOUNT=1,KUT,1
      IF(KOUNT=1) 0,0,108
      CIN=C(I-1)
108     CALL FIBS(COUT,CIN)
      IF(CIN-COUT=CO/40,0) 0,0,106
      CIN=COUT
107     CONTINUE
      C(I)=COUT
105     N(I)=NU(I)+V*AL*(C(I-1)-C(I))*DT/(Z(I)-Z(I-1))
      NO(I)=N(I)
      IF(C(I)/CO=0,005) 0,3,3
104     SUMN=C(I)*AL*V*DT
      DEP=H-Z(I)
      IF(I=40) 0,3,3
      DO 7 J=I+1,40,1
      C(J)=0,0
      N(J)=NU(J)+(Z(J)-Z(J-1))*SUMN/DEP
      NO(J)=N(J)
7      CONTINUE
      GO TO 4
3      CONTINUE
8      I=40
      C(I)=C(I)/CO
      WRITE(4,54) Z(I),N(I),C(I)
      GO TO 3
2      CONTINUE
50     FORMAT(5F12.6)
51     FORMAT(1H0/F8.4)
52     FORMAT(10X,F6.2,10X,F10.6,10X,F12.9)
53     FORMAT(F10.4)
54     FORMAT(F10.4)
55     FORMAT(I4)
56     FORMAT(2F13.6)
57     FORMAT(2F13.6)
      STOP
      END

```

1a	Case7	}	K1=15000.0, K2=60000.0
1b	Mod7		
2a	Case7	}	K1=25000.0, K2=20000.0
2b	Mod7		
3a	Case7	}	K1=35000.0, K2=10000.0
3b	Mod7		

Fig. 62.

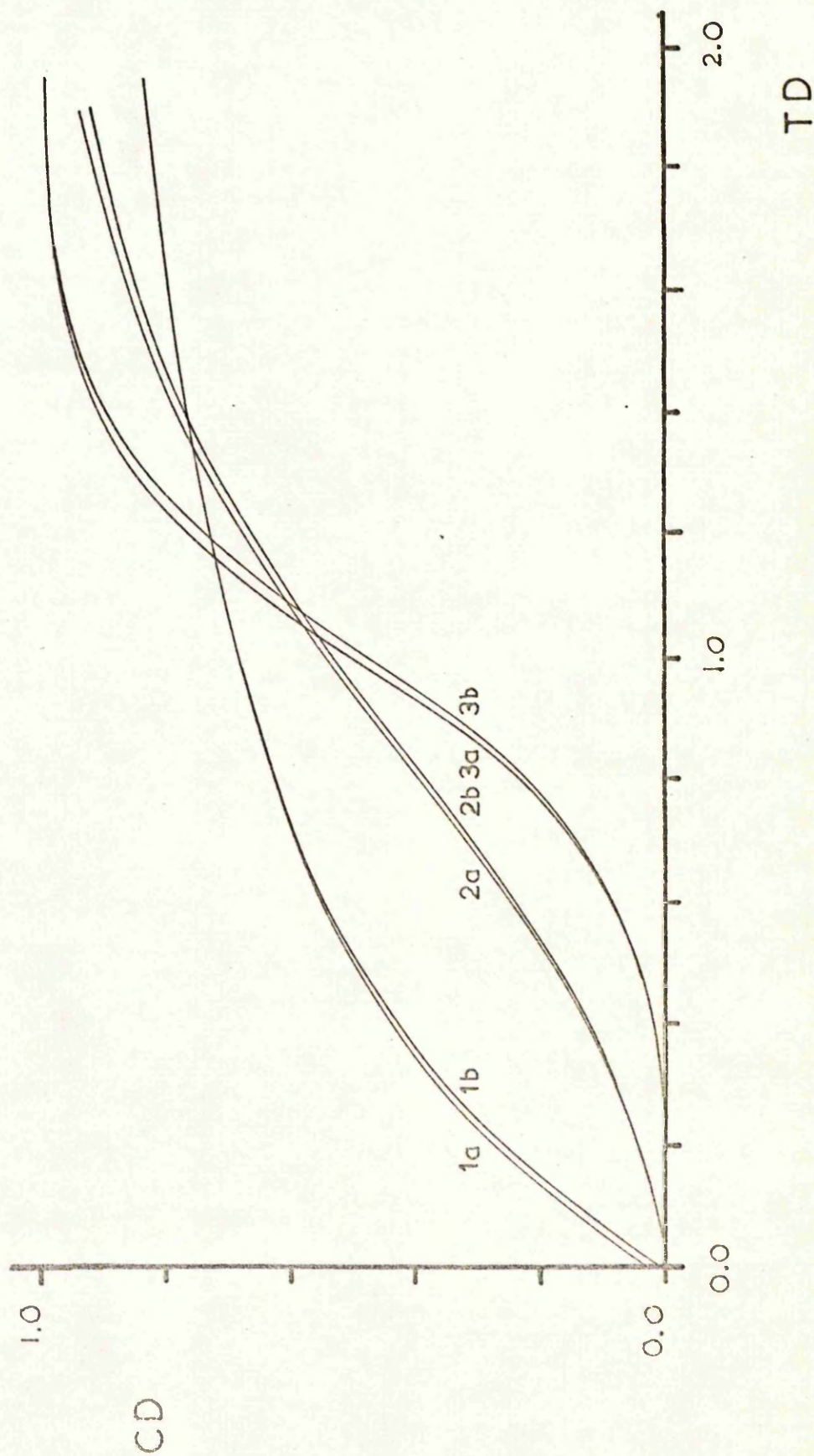


Fig.63.

```

READ FROM(CR/S1900)
MASTER GENHAM
REAL KM,KH,KW,KU,MASS,MU1,MU2,MU3,MUW,MUP,NOS,NST,N(40),FN(40)
DIMENSION C(41),T(41),TP(40),TW(40),Z(41),FTP(40),FTW(40)
READ(1,50)TWST,TPST,NST,VO,TO,CO
READ(1,51) H,DT,TIME
READ(1,52) KM,KH,KW,KU,MU1,MU2,MU3,MUW,MUP,MASS
READ(1,52) AL,GA,A,DI,DO,TOUT,ROHP,ROHB,NOS,HEAT
WRITE(2,57)
57  FORMAT(11H INPUT DATA)
WRITE(2,50) TWST,TPST,NST,VO,TO,CO
WRITE(2,51) H,DT,TIME
WRITE(2,52) KM,KH,KW,KU,MU1,MU2,MU3,MUW,MUP,MASS
WRITE(2,52) AL,GA,A,DI,DO,TOUT,ROHP,ROHB,NOS,HEAT
WRITE(2,58)
58  FORMAT(11H)
100  CONTINUE
READ(1,60) KM
60  FORMAT(F13,6)
IF(KM) 99,99,0
DO 1 I=1,40,1
IF(I=1) 0,0,2
C(I)=CO
Z(I)=0.0
2  N(I)=NST
T(I)=TO
TW(I)=TWST
TP(I)=TPST
C(I+1)=0.0
Z(I+1)=0.025*H*I
1  CONTINUE
DTT=DT
TCOUNT=1.0
INT=5
CONST=VO*(0.1356385614+0.000223826*VO)*0.016018
DELN=0.025*NOS
TIM=0.0
5  CONTINUE
IF(DT=DTT) 14,14,0
DT=DTT
14  CONTINUE
TIM=TIM+DT
IF(TIM=TIME) 0,0,3
IPORT=1
IPART=1
ROHC=CONST/VO
ROHY=ROHC+CO
V=VO
IND=1
I=0
4  I=I+1
IF(I=40) 0,0,6
IF(IND) 34,0,0
CAP1=N(I)/(16.0*ROHB)
CAP2=(N(I)+DELN)/(16.0*ROHB)
IF(CAP1) 0,0,7
C1=0.0
GO TO 3
7  CALL ISOT(CAP1,TP(I),C1,ROHC)
8  IF(CAP2) 0,0,9

```


Fig.63.

....continued

```

C2=0.0
GO TO 10
9 CALL ISOT(CAP2,TP(I),C2,ROHC)
10 A2=(C2-C1)/DELN
A1=C1=N(I)*A2
V2=A*KH*AL*A2/ROHT
KUT=0
22 KUT=KUT+1
DO 20 KOUNT=1,KUT,1
V1=(Z(I+1)-Z(I))/(V*AL*DT*A2*KUT)
DUM=V1*(1.0-EXP(-V2*DT))
IF(KOUNT=1) 0,0,21
CIN=C(I)
21 COUT=(CIN+DUM*(A1+A2*N(I)))/(1.0+DUM)
IF(CIN=COUT-0.025*C0) 0,0,22
CIN=COUT
20 CONTINUE
IF(COUT=0.000000001) 0,0,33
IND=-1
34 COUT=0.0
33 CONTINUE
C(I+1)=COUT
DN=(C(I)-C(I+1))*V*AL*DT/(Z(I+1)-Z(I))
DTP=(HEAT*DN+MU1*DN*(T(I)-TP(I))-KH*A* 1.0 *(TP(I)-T(I))*DT)/
1 (ROHB*MUP+(N(I)+0.5*DN)*MU3)
IF((DTP**2)=4.0) 11,11,0
TIM=TIM-DT
DT=DT*2.0*0.8/(SQRT(DTP**2))
GO TO 5
11 CONTINUE
IF(DTP**2=0.25) 0,28,28
IPART=-1
GO TO 27
28 CONTINUE
IPORT=0
27 CONTINUE
DTB=(-DN*MU1*(T(I)-TP(I)-0.5*DTP)+KH*A*(TP(I)+0.5*DTP-T(I))*DT
1=4.0*KW*(T(I)-TW(I))*DT/DI)/(AL*(C(I+1)*MU1+ROHC*MU2)*V*DT
2/(Z(I+1)-Z(I)))
DTW=(4.0*ATAN(1.0)*DT*(KW*DI*(T(I)+0.5*DTB-TW(I))-KH*DO*(TW(I)-
1TOUT)))/(MASS*MIW)
FN(I)=N(I)+DN
FTP(I)=TP(I)+DTP
FTW(I)=TW(I)+DTW
T(I+1)=T(I)+DTB
C UPDATE C(I+1) ON VOLUME BASIS
CFA=C(I+1)/ROHC
ROHC=0.1356385614=0.000223826 *T(I+1)
ROHC=ROHC+0.016018
C(I+1)=CFA*ROHC
ROHT=ROHC+C(I+1)
V=CONST/ROHC
GO TO 4
6 CONTINUE
C HAVE COMPLETED ONCE THROUGH CALCULATION
IF(IPART*IPORT) 0,38,38
DT=DT*2.0
38 CONTINUE
IF(TIM=(TCOUNT=0.001)) 23,23,0
CD=C(41)*CONST/(CO*VO*ROHC)
WRITE(2,53) TIM,CD,T(41)
TCOUNT=TCOUNT+1.0

```

Fig. 63.continued

```

23  CONTINUE
    DO 13 I=1,40,1
      N(I)=FN(I)
      TP(I)=FTP(I)
      TW(I)=FTW(I)
      IF(TIM=INT*1.0) 13,0,0
      K=I
      WRITE(2,54) N(K),TP(K),TW(K),T(K),C(K)
13  CONTINUE
      IF(TIM=INT*1.0) 5,0,0
      INT=INT+5
      GO TO 5
3    CONTINUE
C    END OF ADSORPTION PERIOD
      GO TO 100
99  CONTINUE
50  FORMAT(6F12.6)
51  FORMAT(3F13.6)
52  FORMAT(5F13.6)
53  FORMAT(F13.6,10X,F13.6,10X,F13.6)
54  FORMAT(5(F15.10,5X))
      STOP
      END

```

Standard Isotherm Subroutine

```

SUBROUTINE ISOT(CAP,TEMP,CONC,DEN)
  B1  =0.54593E+03+TEMP*(0.371158E+04+TEMP*0.726236E+07)
  B1=B1*10.0
  B1=B1/(EXP(((TEMP-300.0)/16.0)-1.0))
  B2  =EXP(=9.89158+1926.66/TEMP)
  B3  =0.541883E+01+TEMP*(0.305437E+03+TEMP*0.444061E+06)
  DUM=(CAP=B1)**2+4.0*(CAP**2)*B3/B2
  PRES=(=(CAP=B1)+SQRT(DUM))/(2.0*CAP*B3)
  PRES=PRES*(0.01+(TEMP-300.0)/800.0)
  CONC=16.0*PRES*DEN/(99.2*4.0+PRES*4.0)
  RETURN
  END

```

Fig. 64.

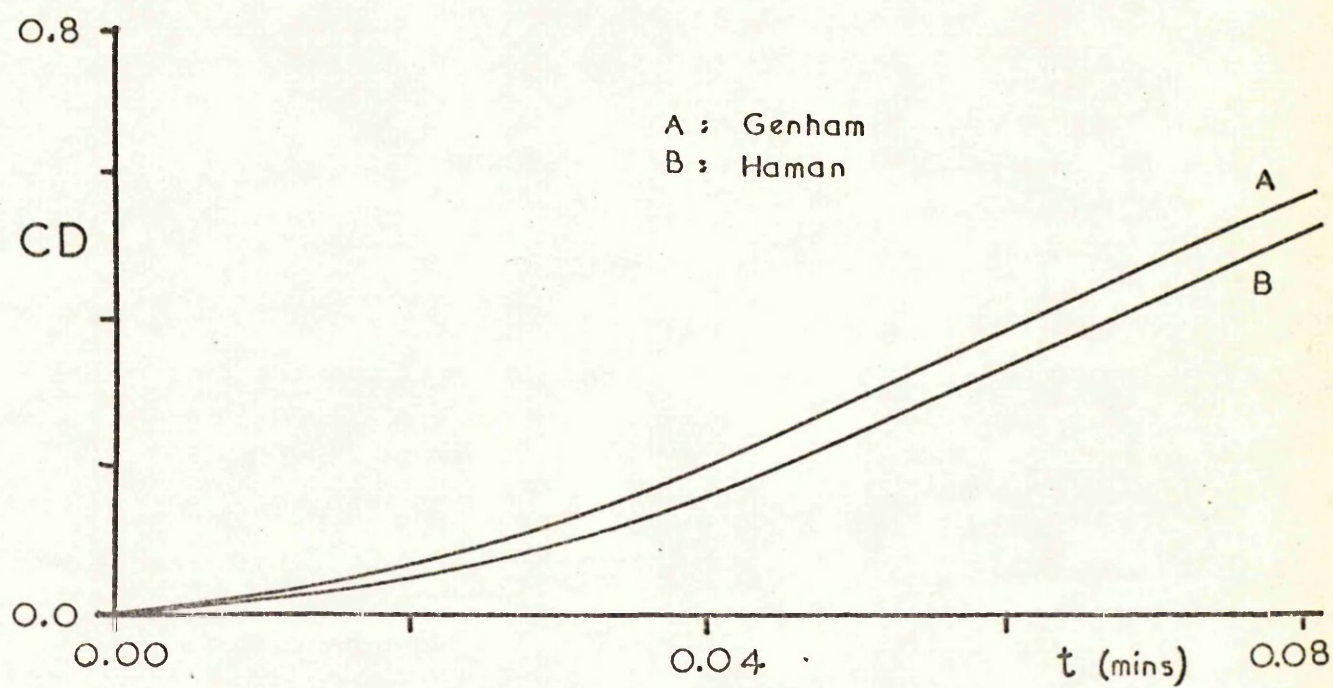


Fig. 65.

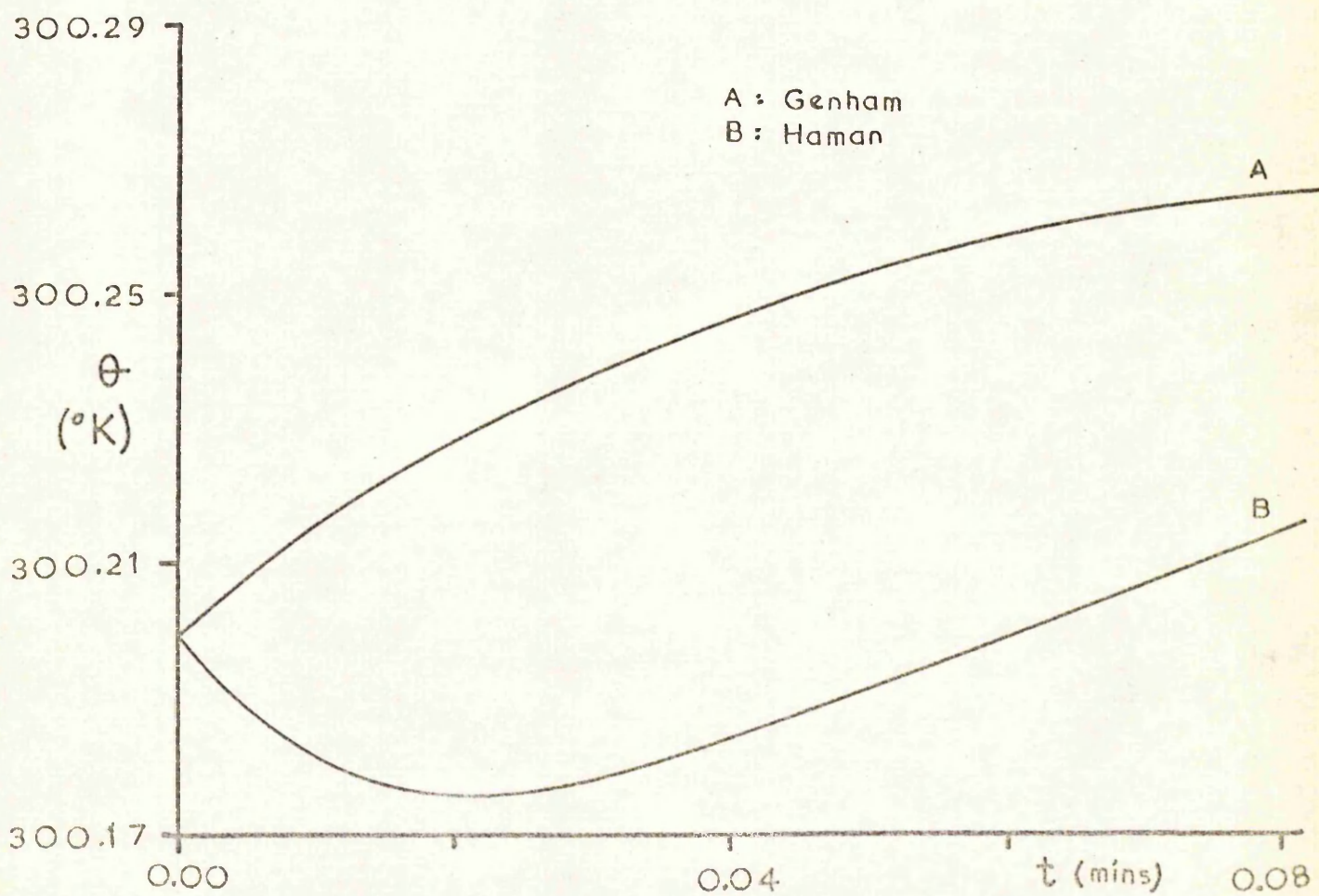


Fig. 66.

A : GENHAM
B : HAMAN

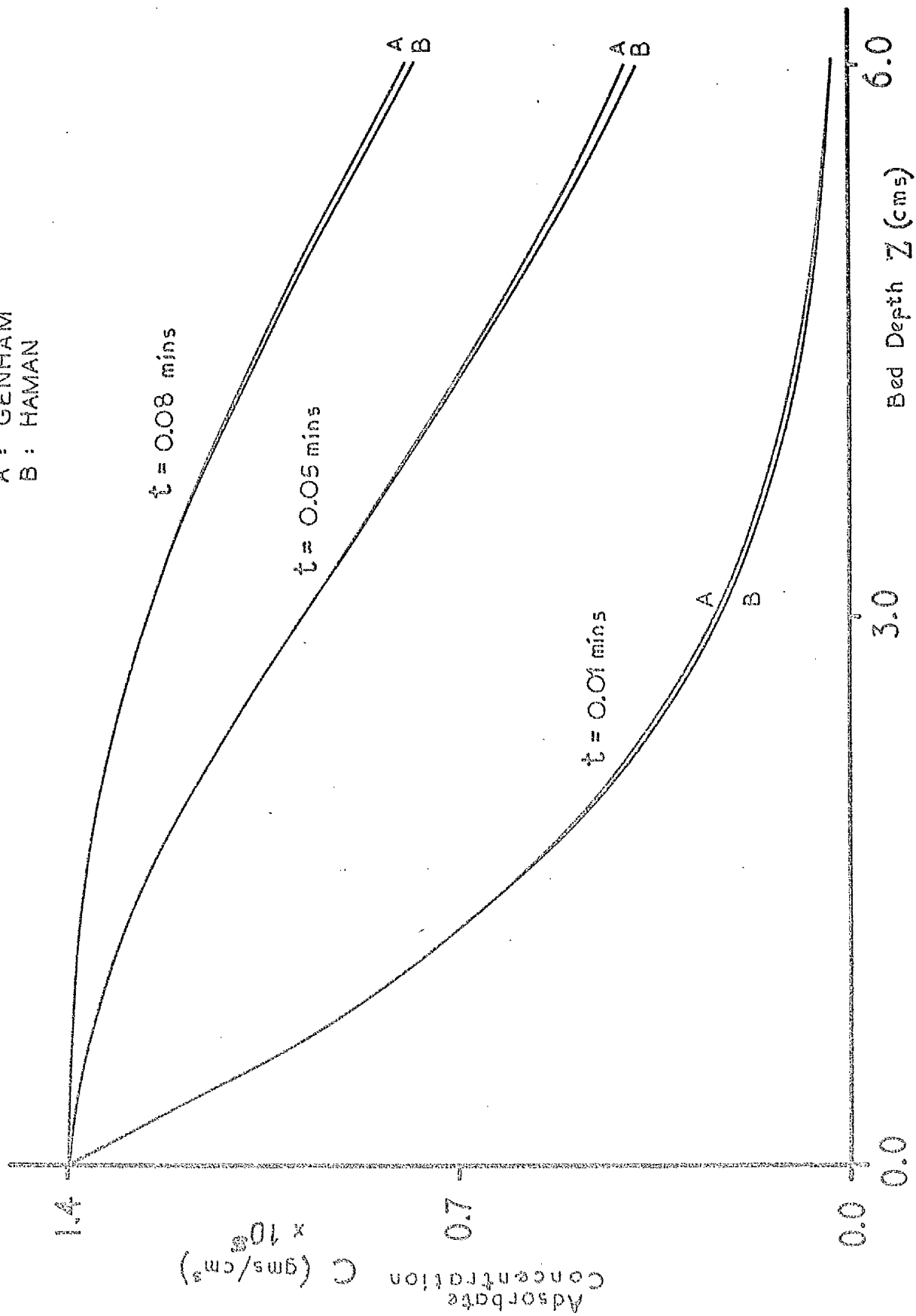


Fig. 67.

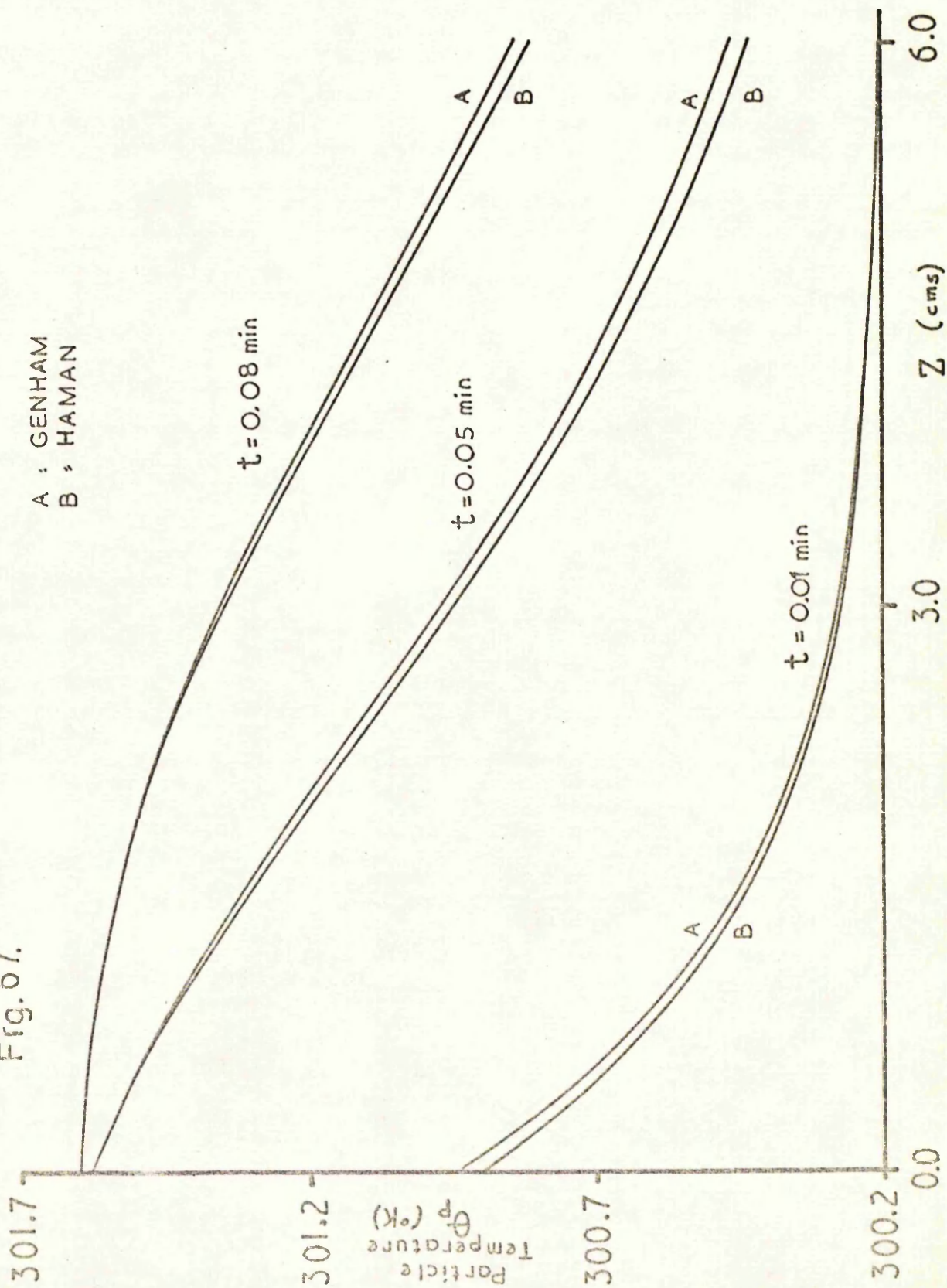


Fig. 68.

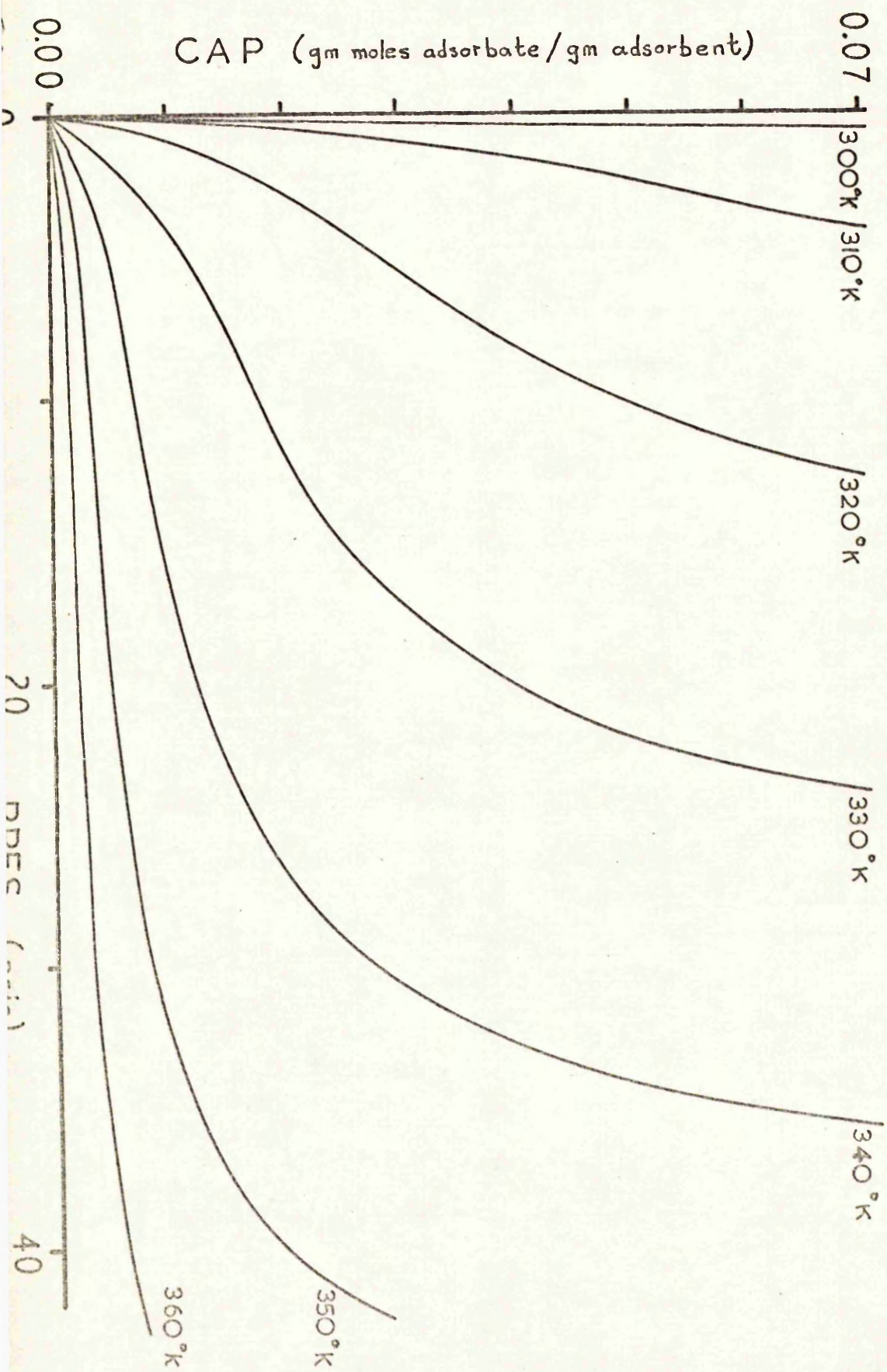


Fig. 69.

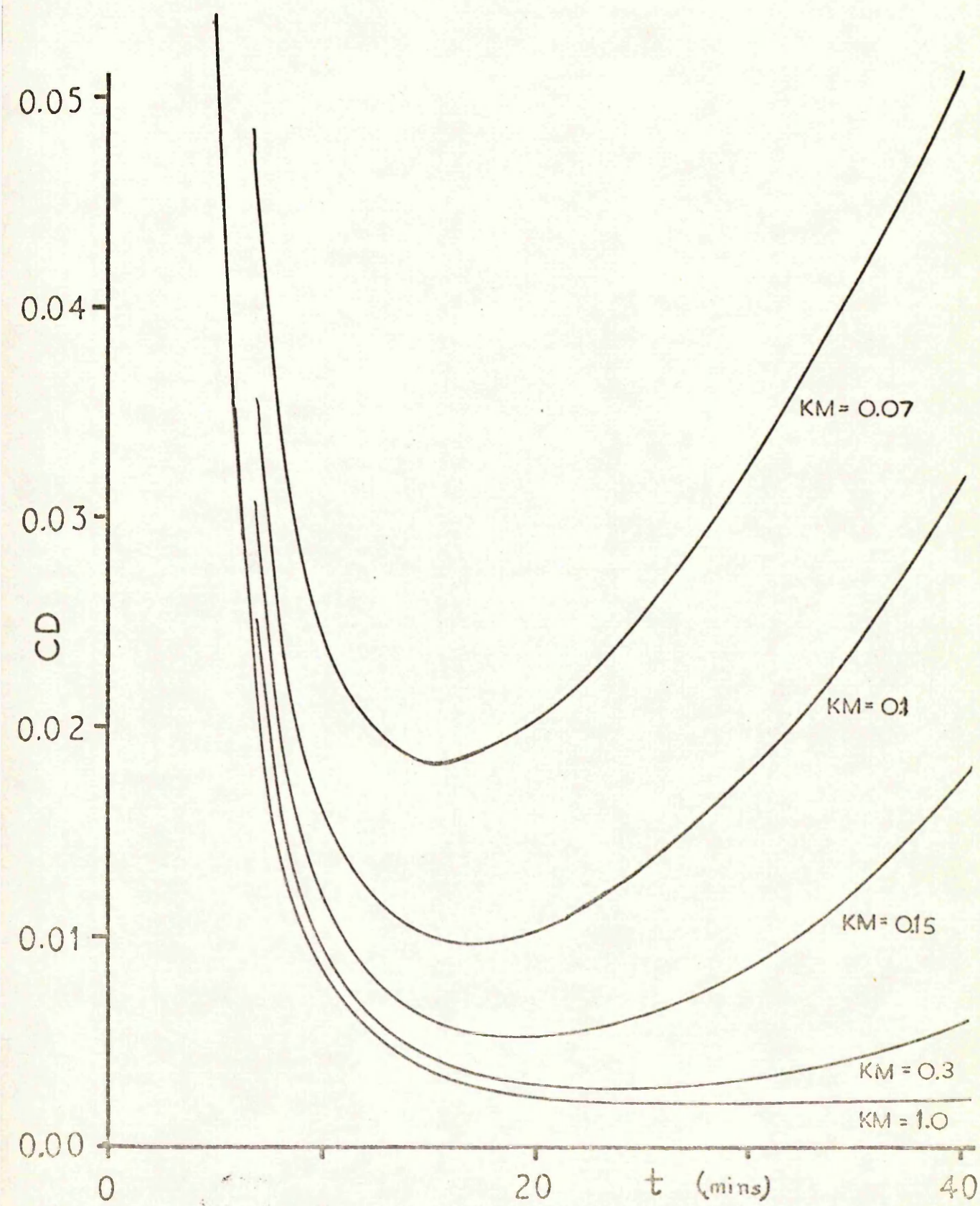


Fig.70.

```

READ FROM(CR/S1900)
MASTER WETBED
REAL KM,KH,KW,KU,MASS,MU1,MU2,MU3,MUW,MUP,NOS,NST,N(40) ,FN(40)
REAL NH(40),FNH(40),KF,MU4,MU5,NHST
DIMENSION C(41),T(41),TP(40),TW(40),Z(41),FTP(40),FTW(40),CH(41)
READ(1,50)TWST,TPST,NST,VO,TO,CO
READ(1,51) H,DT,TIME
READ(1,52) KM,KH,KW,KU,MU1,MU2,MU3,MUW,MUP,MASS
READ(1,52) AL,GA,A,DI,DO,TOUT,ROHP,ROHB,NOS,HEAT
READ(1,59) KF,HVAP,MU4,MU5,CHO,NHST
WRITE(2,57)
57 FORMAT(11H INPUT DATA)
WRITE(2,50) TWST,TPST,NST,VO,TO,CO
WRITE(2,51) H,DT,TIME
WRITE(2,52) KM,KH,KW,KU,MU1,MU2,MU3,MUW,MUP,MASS
WRITE(2,52) AL,GA,A,DI,DO,TOUT,ROHP,ROHB,NOS,HEAT
WRITE(2,59) KF,HVAP,MU4,MU5,CHO,NHST
WRITE(2,58)
58 FORMAT(1H1)
DO 1 I=1,40,1
IF(I-1) 0,0,2
C(I)=CO
CH(I)=CHO
Z(I)=0.0
2 N(I)=NST
NH(I)=NHST
T(I)=TO
TW(I)=TWST
TP(I)=TPST
C(I+1)=0.0
Z(I+1)=0.025*H*I
1 CONTINUE
DTT=DT
TCOUNT=1.0
INT=5
CONST=VO*(0.1356385614-0.000223826*TO)*0.016018
DELN=0.025*NOS
TIM=0.0
5 CONTINUE
IF(DT-DTT) 14,14,0
DT=DTT
14 CONTINUE
TIM=TIM+DT
WRITE (2,55) TIM,DT
IF(TIM-TIME) 0,0,3
DTPMAX=0.5
ROHC=CONST/VO
ROHT=ROHC*CO+CHO
V=VO
IND=1
I=0
4 I=I+1
IF(I-40) 0,0,6
IT=0
IF(IND) 34,0,0

```


Fig. 70.

...continued

```

CAP1=N(I)/(16.0*RONB)
CAP2=(N(I)*DELN)/(16.0*RONB)
IF(CAP1) 0,0,7
C1=0.0
GO TO 8
7 CALL ISOT(CAP1,TP(I),C1,RONC,NHST,NH(I))
8 IF(CAP2) 0,0,9
C2=0.0
GO TO 10
9 CALL ISOT(CAP2,TP(I),C2,RONC,NHST,NH(I))
10 A2=(C2-C1)/DELN
A1=C1-N(I)*A2
V2=A*KM*AL*A2/ROHT
KUT=0
22 KUT=KUT+1
DO 20 KOUNT=1,KUT,1
V1=(Z(I+1)-Z(I))/(V*AL*DT*A2*KUT)
DUM=V1*(1.0-EXP(-V2*DT))
IF(KOUNT=1) 0,0,21
CIN=C(I)
21 COUT=(CIN+DUM*(A1+A2*N(I)))/(1.0+DUM)
IF(CIN-COUT=0.025*CO) 0,0,22
CIN=COUT
20 CONTINUE
IF(COUT=0.000000001) 0,0,33
IND=-1
34 COUT=0.0
33 CONTINUE
C(I+1)=COUT
DN=(C(I)-C(I+1))*V*AL*DT/(Z(I+1)-Z(I))
CALL HUMID(CHOS,T(I))
IF(CHOS=CH(I)) 30,30,0
CALL HUMID(CHS,TP(I))
IF(CHS) 0,31,31
IT=1
GO TO 27
31 CONTINUE
DCH=KF*A*(CHS-CH(I))*DT/ROHT
DNH=DCH*V*AL*DT/(Z(I+1)-Z(I))
IF(NH(I)-DNH) 0,23,23
27 CONTINUE
DNH=NH(I)
DCH=DNH*(Z(I+1)-Z(I))/(V*AL*DT)
23 CONTINUE
CH(I+1)=CH(I)+DCH
IF(CH(I+1)) 0,29,29
DCH=-CH(I)
CH(I+1)=0.0
DNH=DCH*V*AL*DT/(Z(I+1)-Z(I))
GO TO 32
29 CONTINUE
IF(CH(I+1)-CHOS) 32,32,0
30 CH(I+1)=CHOS
DCH=CHOS-CH(I)
DNH=DCH*V*AL*DT/(Z(I+1)-Z(I))
32 CONTINUE
DTP=(HEAT*DN-HVAP*DNH*(DN*MU1+DNH*MU5))*(T(I)-TP(I))-KH*A*(TP(I)-
T(I))*DT/(RONB*MUP*(N(I)+0.5*DN)+MU3+(NH(I)+0.5*DNH)*MU4)

```

Fig. 70. continued

```

IF(DTP**2=4.0) 11,11,0
IF(IT) 0,0,12
TIM=TIM-DT
DT=DT*2.0*0.8/(SQRT(DTP**2))
GO TO 5
12 IF(DTP**2=25.0) 11,11,0
DNH=DNH*4.0/(SQRT(DTP**2))
DCH=DNH*(Z(I+1)-Z(I))/(V*AL*DT)
GO TO 23
11 CONTINUE
DTB=(-(DN*MU1-DNH*MU5)*(T(I)-TP(I)-0.5*DTP)+KH*A*(TP(I)+0.5*DTP
1-T(I))*DT=4.0*KW*(T(I)-TW(I))*DT/DI)/(V*AL*DT*(C(I+1)*MU1+ROHC
2*MU2+CH(I+1)*MU5)/(Z(I+1)-Z(I)))
DTW=(4.0*ATAN(1.0)*DT*(KW*DI*(T(I)+0.5*DTB-TW(I))-KU*DO*(TW(I)-
1TOUT)))/(MASS*MUW)
FN(I)=N(I)+DN
FNH(I)=NH(I)+DNH
FTP(I)=TP(I)+DTP
FTW(I)=TW(I)+DTW
T(I+1)=T(I)+DTB
IF(IT) 0,0,28
IF(DTP**2=DTPMAX**2) 28,28,0
DTPMAX=SQRT(DTP**2)
28 CONTINUE
C UPDATE C(I+1) AND CH(I+1) ON VOLUME BASIS
CFA=C(I+1)/ROHC
CHFA=CH(I+1)/ROHC
ROHC=0.1356385614-0.000223826 *T(I+1)
ROHC=ROHC*0.016018
C(I+1)=CFA*ROHC
CH(I+1)=CHFA*ROHC
ROHT=ROHC+C(I+1)+CH(I+1)
V=CONST/ROHC
GO TO 4
6 CONTINUE
C HAVE COMPLETED ONCE THROUGH CALCULATION
IF(DTPMAX=0.5) 0,0,38
DT=DT*1.5
38 CONTINUE
IF(TIM-(TCOUNT-0.001)) 24,24,0
CD=C(41)*CONST/(CO*VO*ROHC)
WRITE(2,53) TIM,CD,T(41),CH(41)
TCOUNT=TCOUNT+1.0
24 CONTINUE
DO 13 I=1,40,1
N(I)=FN(I)
NH(I)=FNH(I)
TP(I)=FTP(I)
TW(I)=FTW(I)
IF(TIM-INT*1.0) 13,0,0
K=I
WRITE(2,54) N(K),TP(K),TW(K),T(K),C(K),CH(K),NH(K)
13 CONTINUE
IF(TIM-INT*1.0) 5,0,0
INT=INT+5
GO TO 5

```

Fig. 70. continued

```

3      CONTINUE
C      END OF ADSORPTION PERIOD
50     FORMAT(6F12.6)
51     FORMAT(3F13.6)
52     FORMAT(5F13.8)
53     FORMAT(F13.6,10X,F13.6,10X,F13.6,10X,F13.6)
54     FORMAT (7(F15.10,2X))
55     FORMAT(2F13.9)
59     FORMAT(6F13.6)
      STOP
      END

```

Standard Isotherm Subroutine

```

      SUBROUTINE HUMID(HUM,THETA)
      DENC=0.1356385614+0.000223826*THETA
      DENC=DENC*0.016018
      PZERO=EXP(13.64146496-5089.94836672/THETA)
      IF(1.015-PZERO) 0,0,99
      HUM=-100.0
      GO TO 98
99     CONTINUE
      HUM=PZERO*DENC*18.0/((1.015-PZERO)*4.0)
98     CONTINUE
      RETURN
      END

```

Fig. 70 (d). Blocked Isotherm Subroutine

```

      SUBROUTINE ISOT(CAP,TEMP,CONC,DEN,HUMIN,HUMP)
      B1 =-0.54593E-03+TEMP*(0.371158E-04+TEMP*0.726235E-07)
      B1=B1*10.0*(HUMIN+0.95*HUMP)/HUMIN
      B1=B1/(EXP(((TEMP-300.0)/16.0)-1.0))
      B2 =EXP(-9.89158+1926.66/TEMP)
      B3 =-0.541883E-01+TEMP*(0.305437E-03+TEMP*0.464061E-06)
      DUM=(CAP-B1)**2-4.0*(CAP**2)*B3/B2
      PRES=(-(CAP-B1)-SQRT(DUM))/(2.0*CAP*B3)
      PRES=PRES*(0.01+(TEMP-300.0)/800.0)
      CONC=16.0*PRES*DEN/(99.2*4.0-PRES*4.0)
      RETURN
      END

```


Fig. 71.

- 1 GENHAM
- 2 WETBED: (Unblocked): $KF = 0.0001$
- 3 WETBED: (Unblocked) } $KF = 0.00001$
- 4 WETBED: (95% Blocked) }

{ $KM = 0.1$ for all curves}

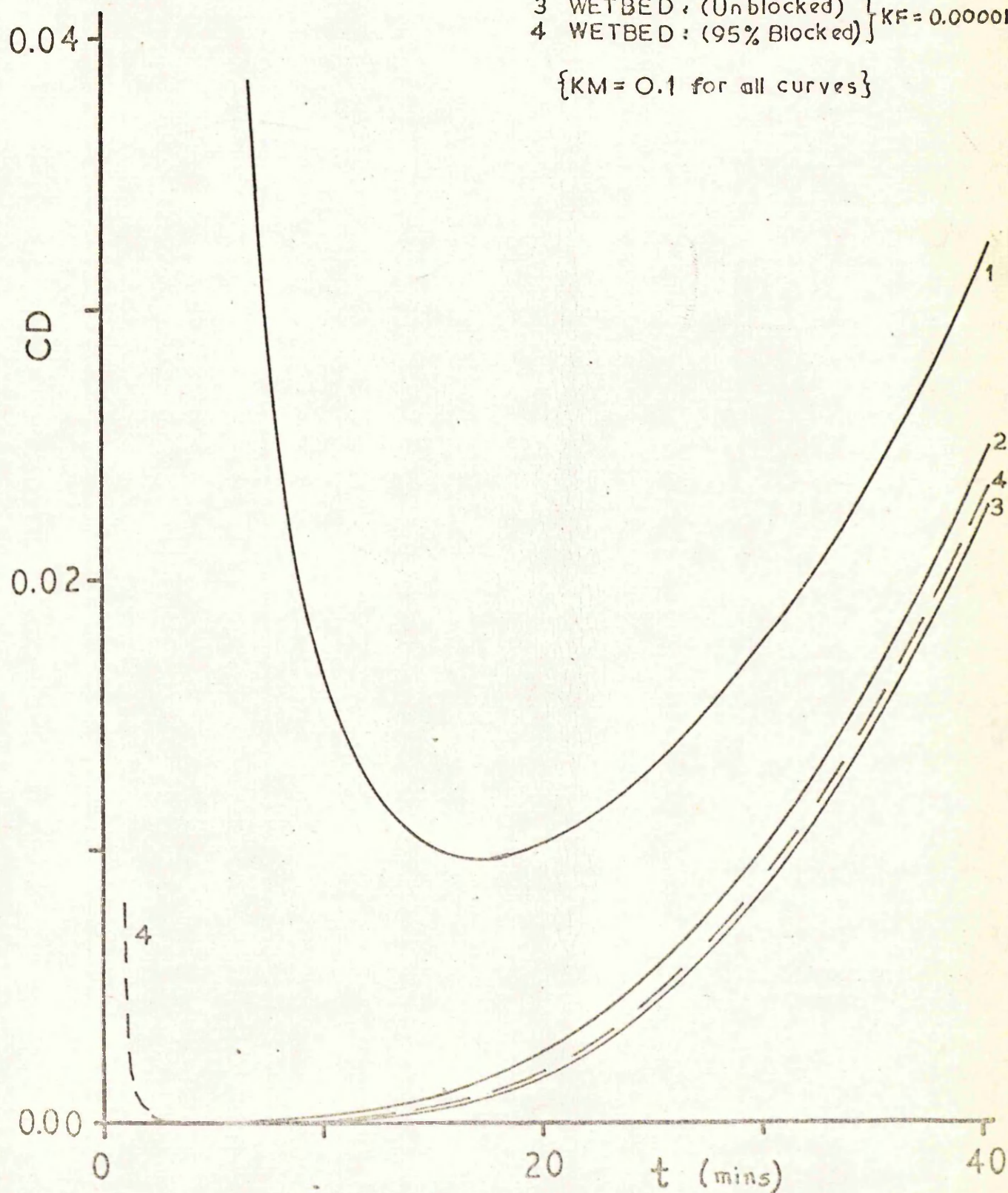


Fig.72.

- 1 GENHAM
- 2 WETBED : $KF = 0.0001$
- 3 WETBED : $KF = 0.00001$

{ $KM = 0.1$ for all curves}

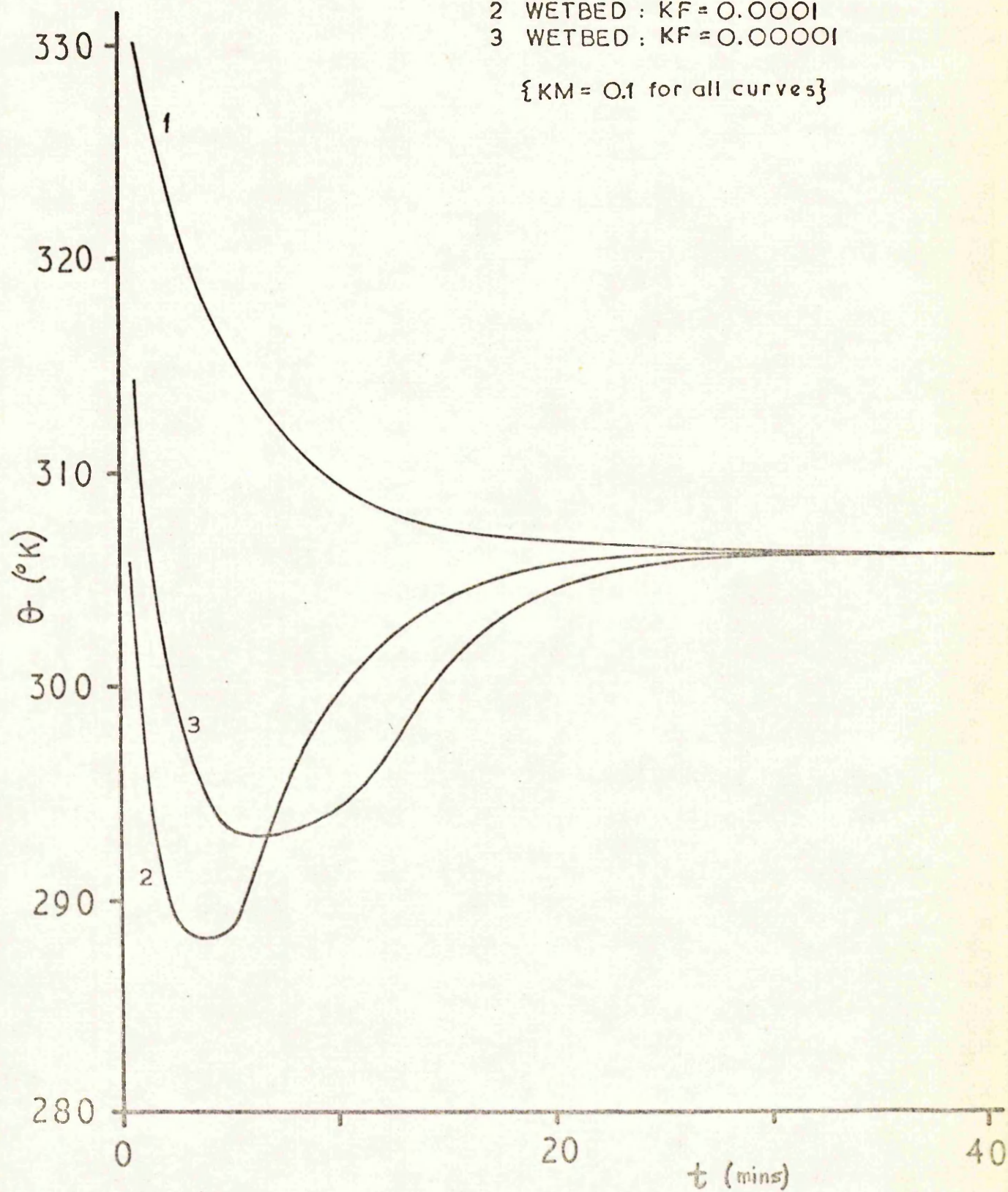


Fig.73.

- 1 GENHAM
- 2 WETBED : $KF = 0.0001$
- 3 WETBED : $KF = 0.000001$

- A : $t = 5 \text{ mins}$
- B : $t = 15 \text{ mins}$
- C : $t = 40 \text{ mins}$

{ $KM = 0.1$ for all curves}

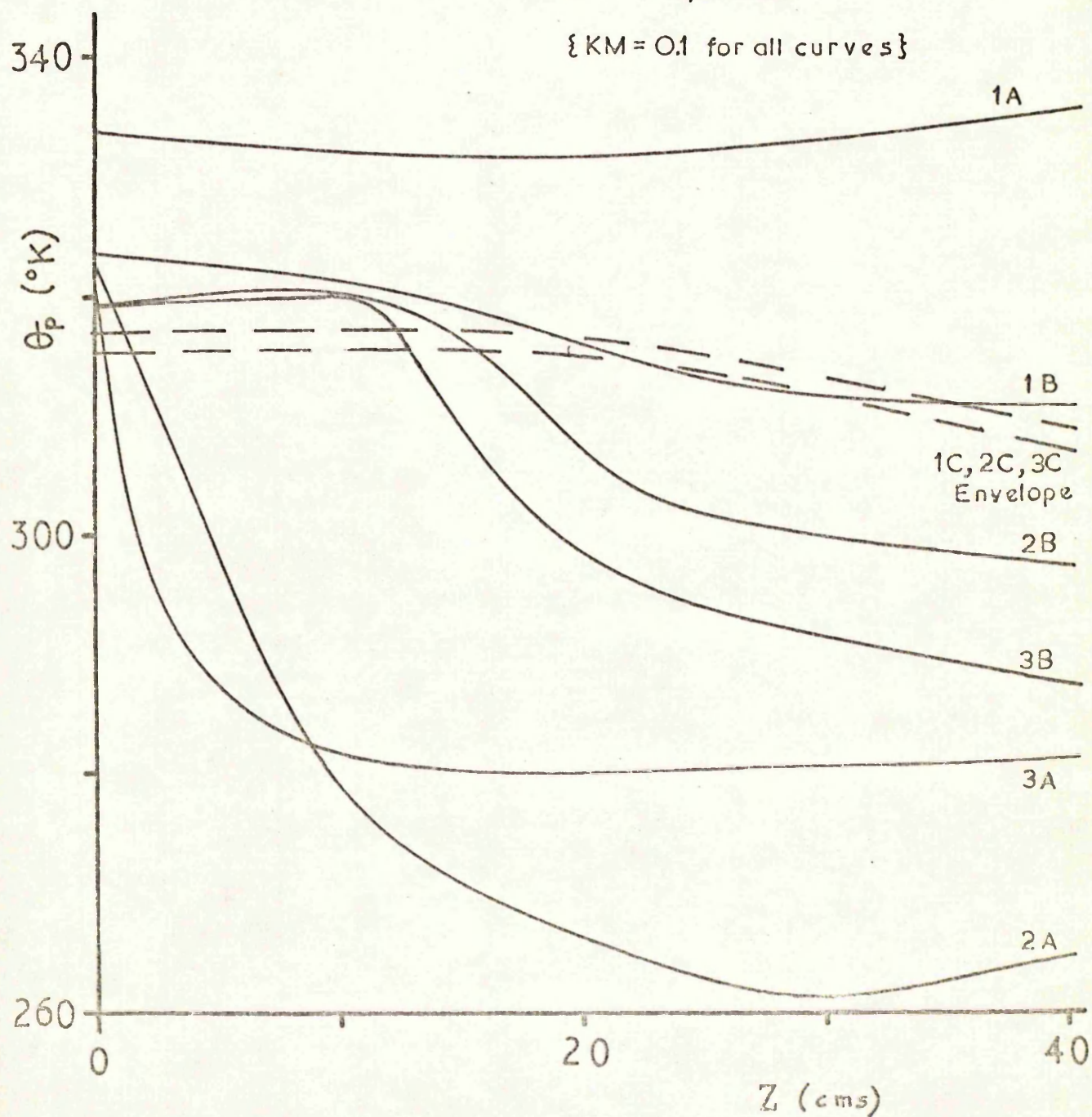


Fig.74.

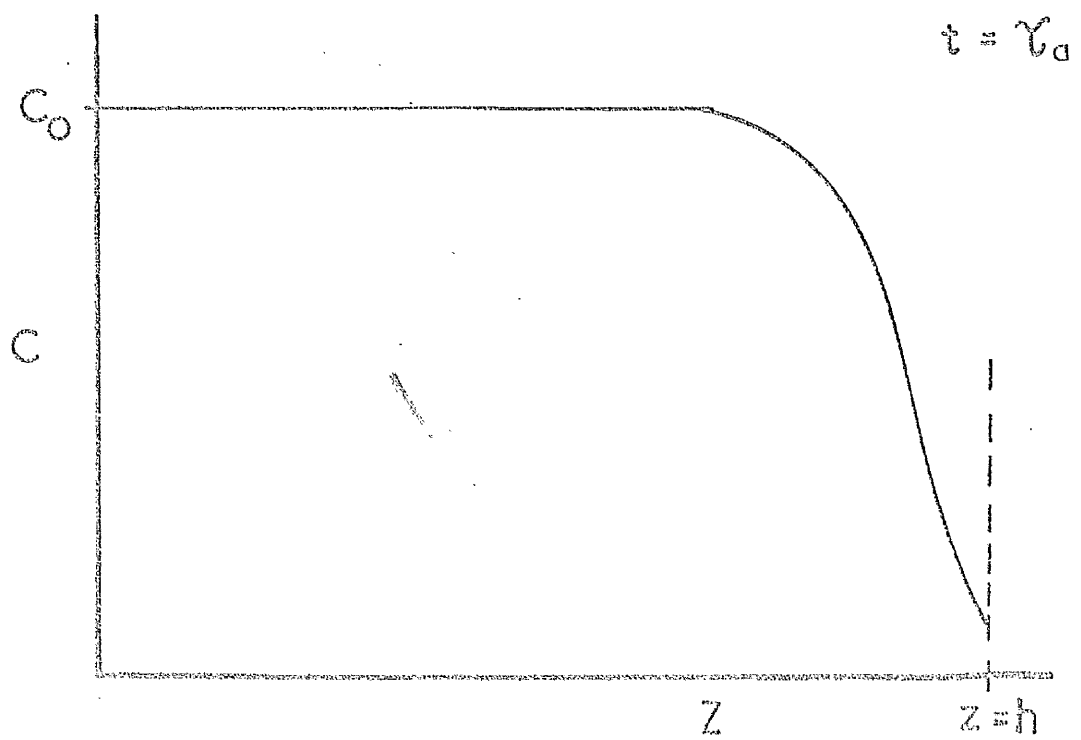
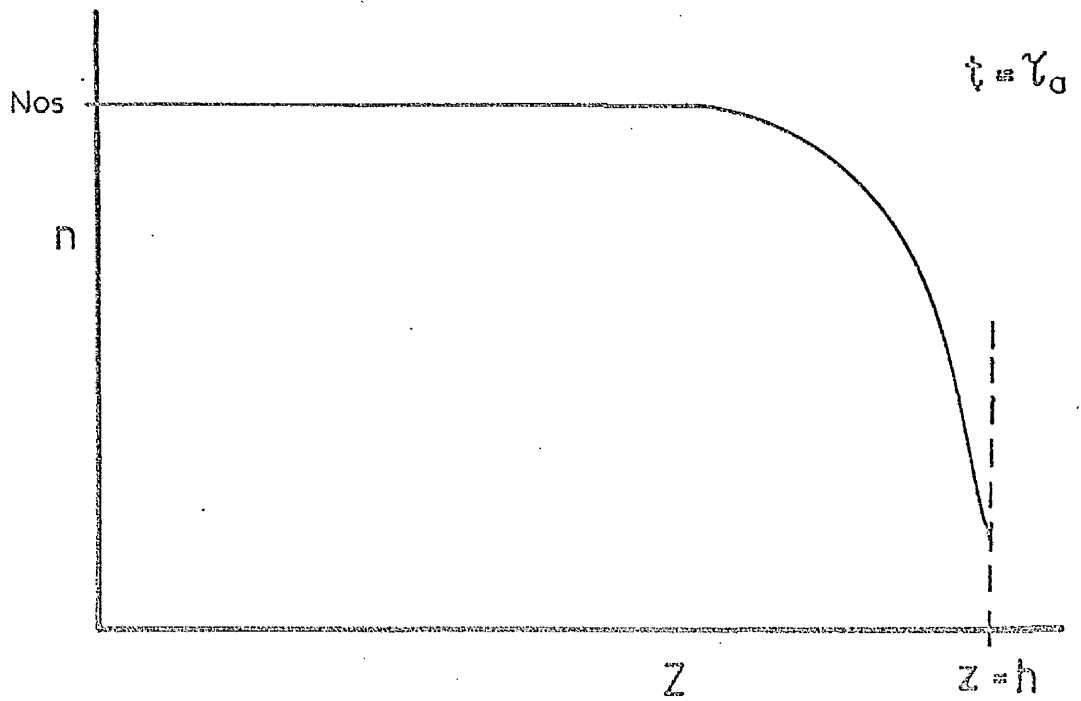


Fig.75 (a).

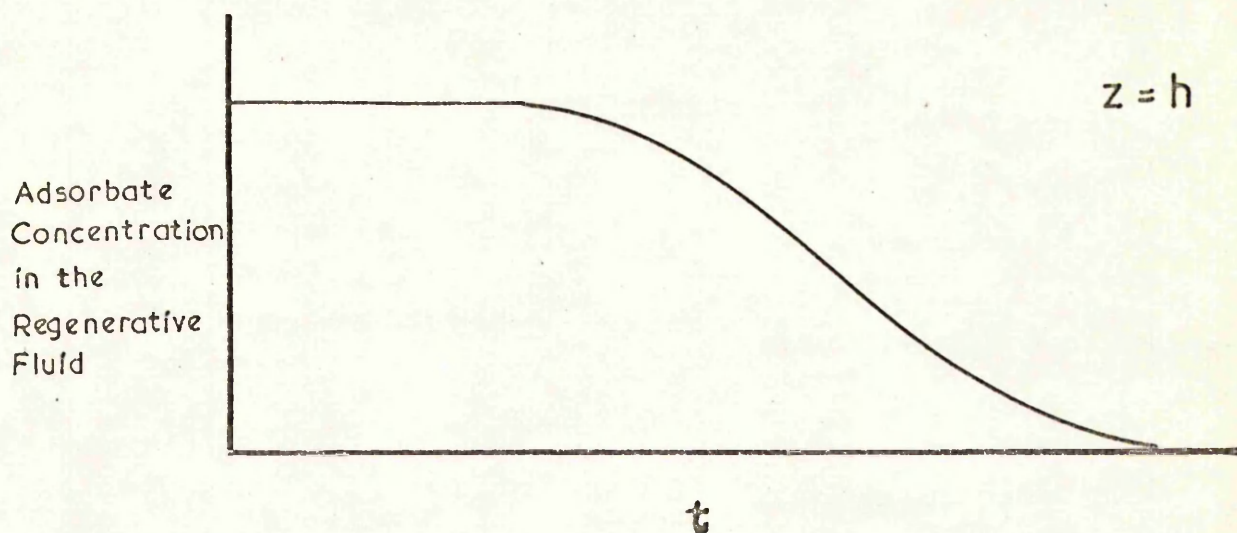


Fig.75 (b).

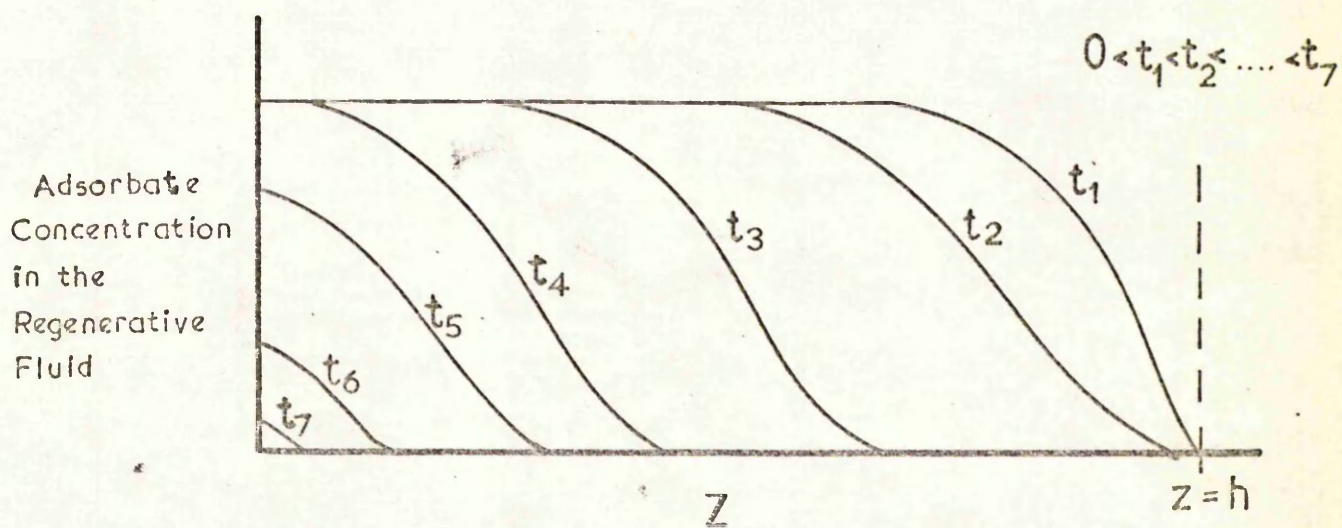


Fig.75 (c).

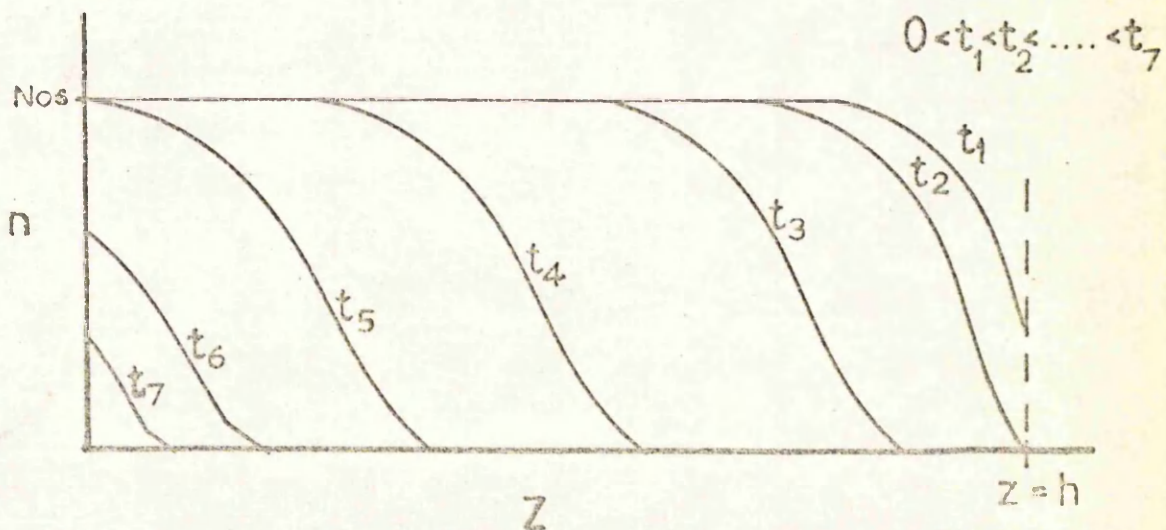


Fig.76.

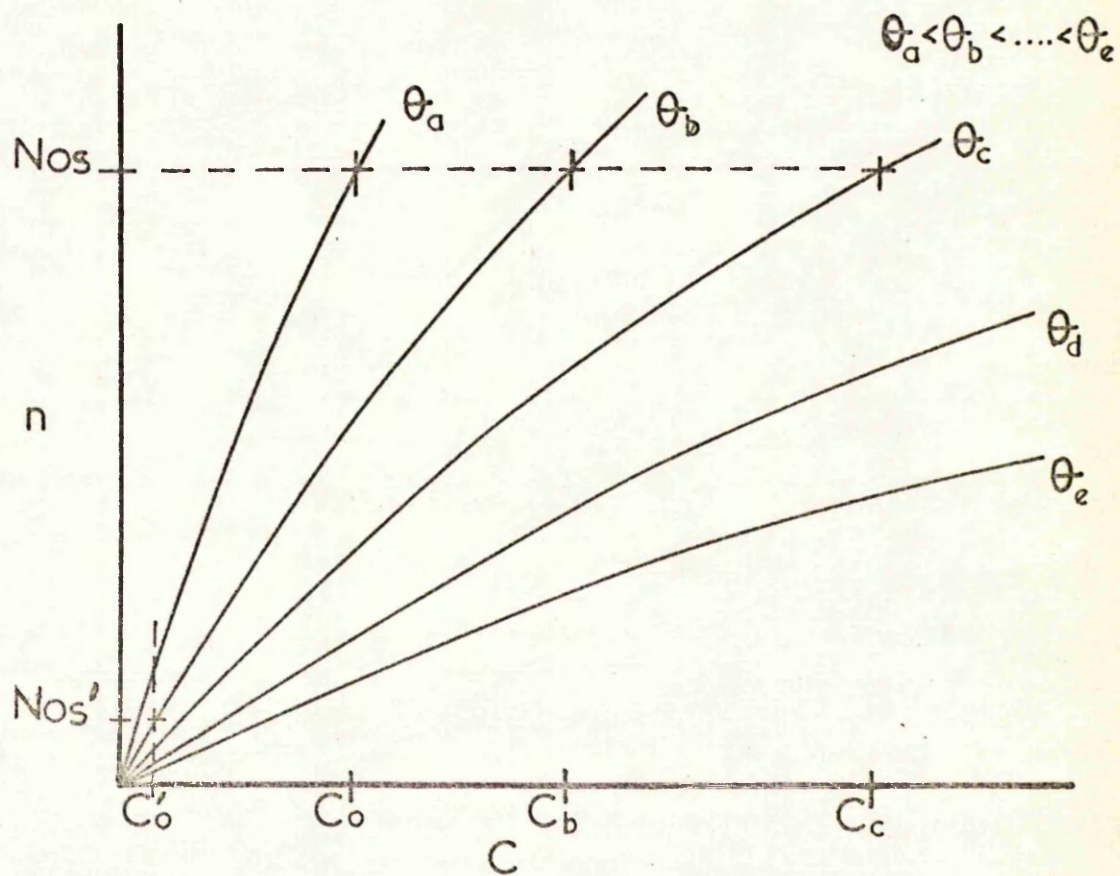


Fig.77(a).

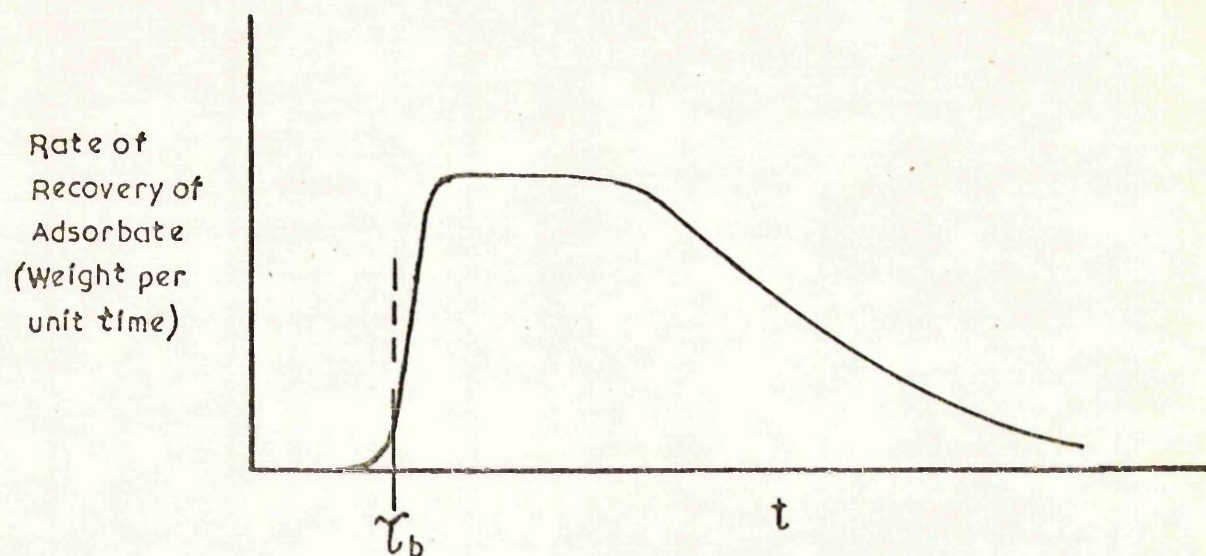


Fig.77(b).

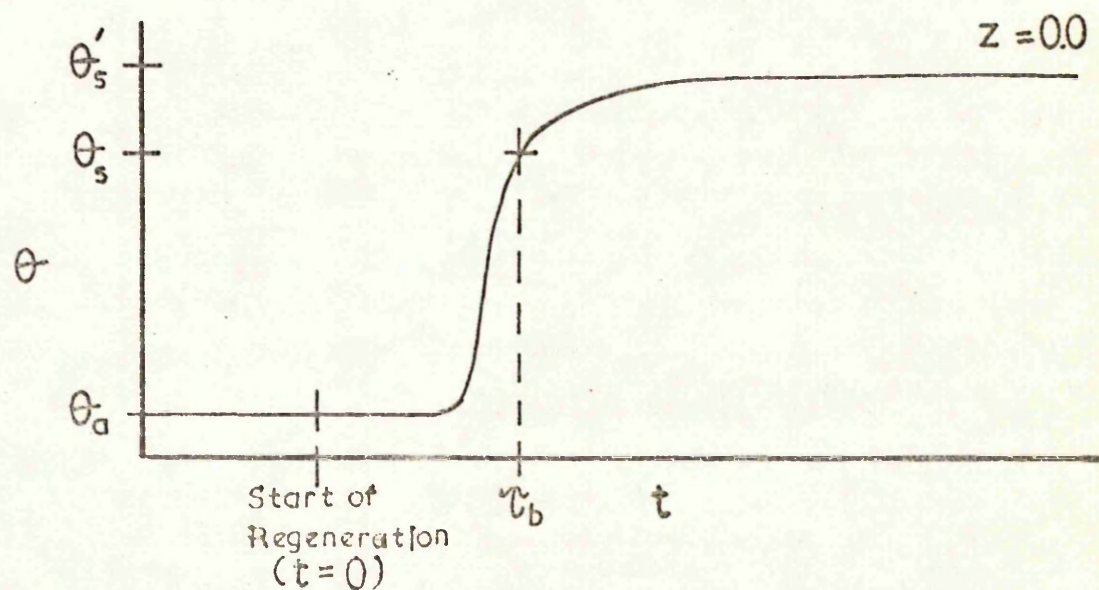


Fig.77(c).

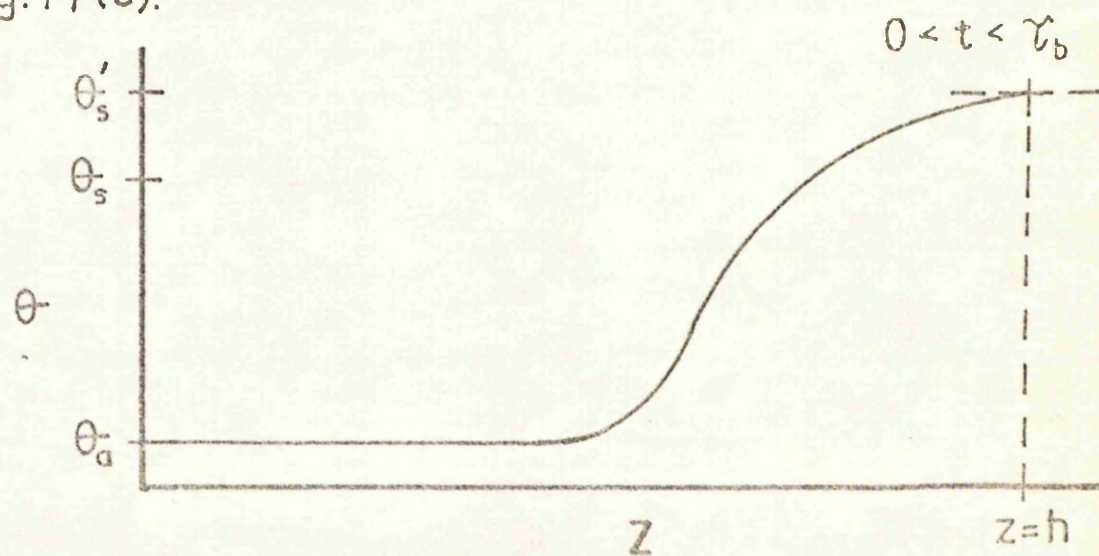


Fig. 78.

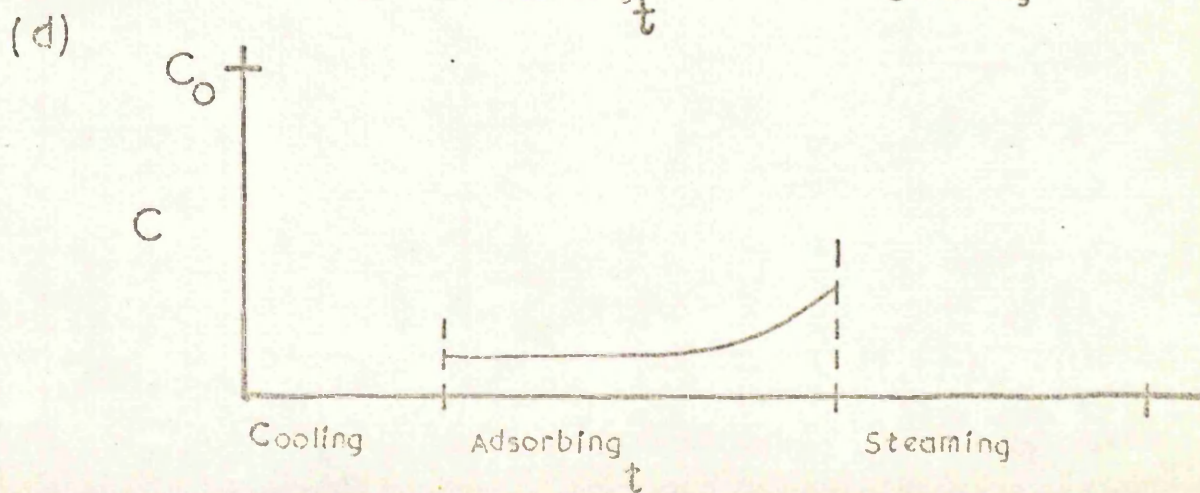
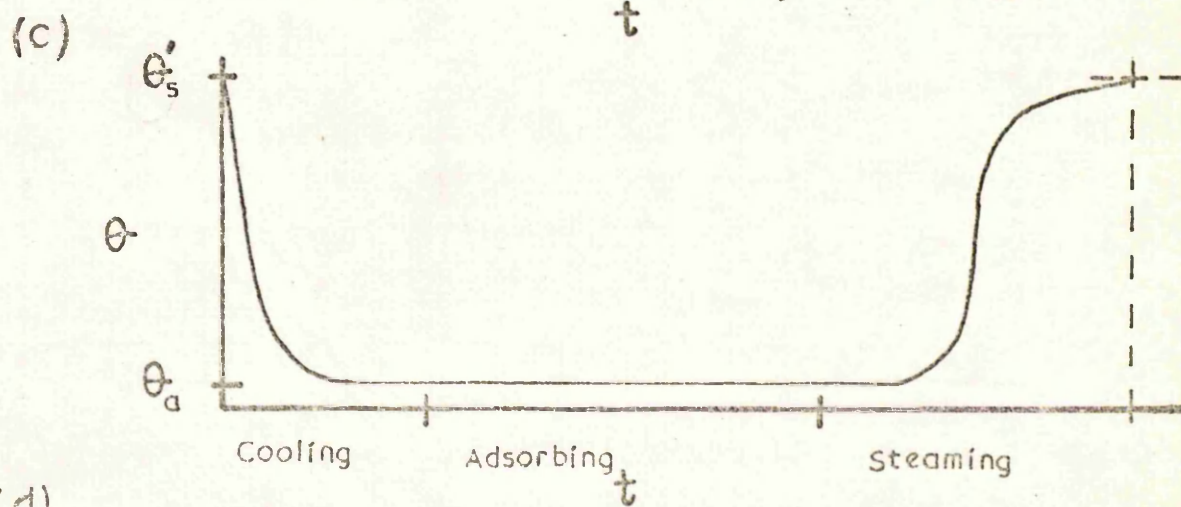
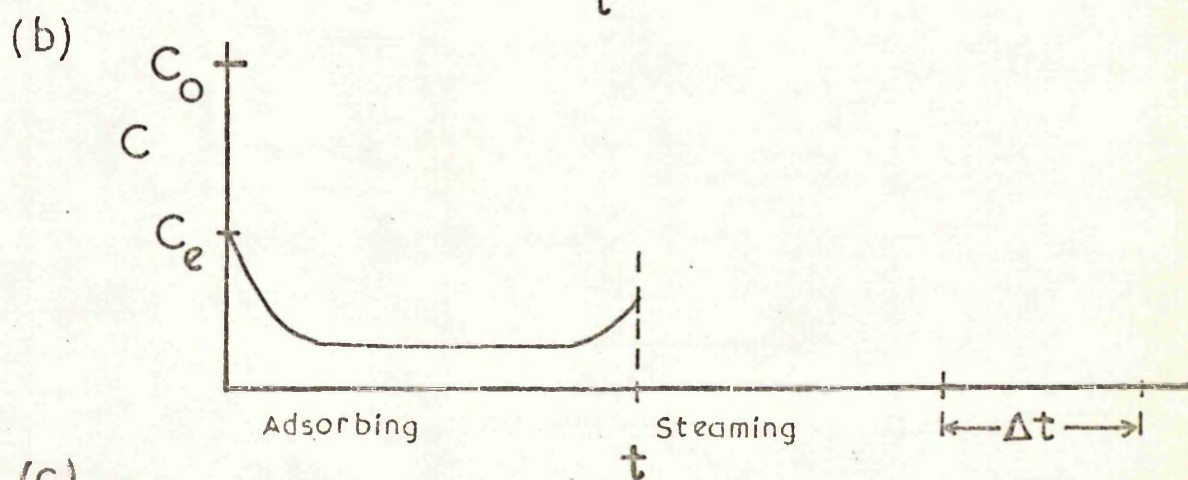
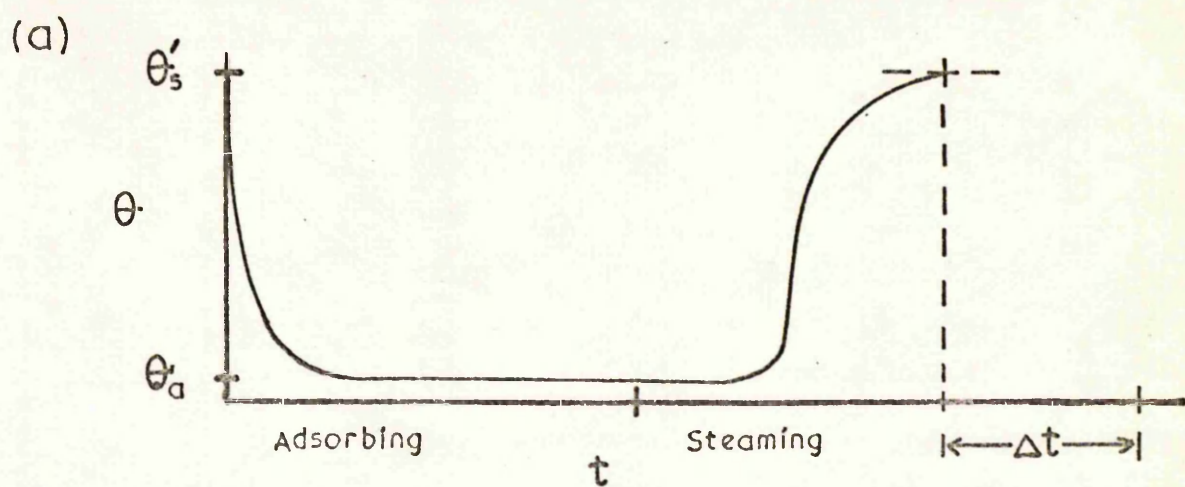
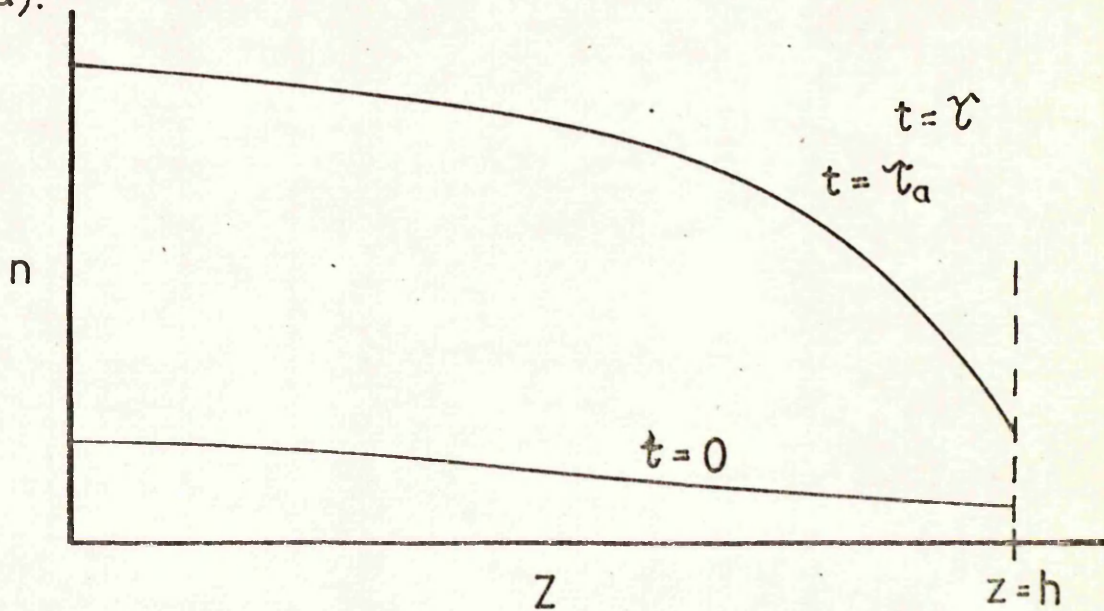
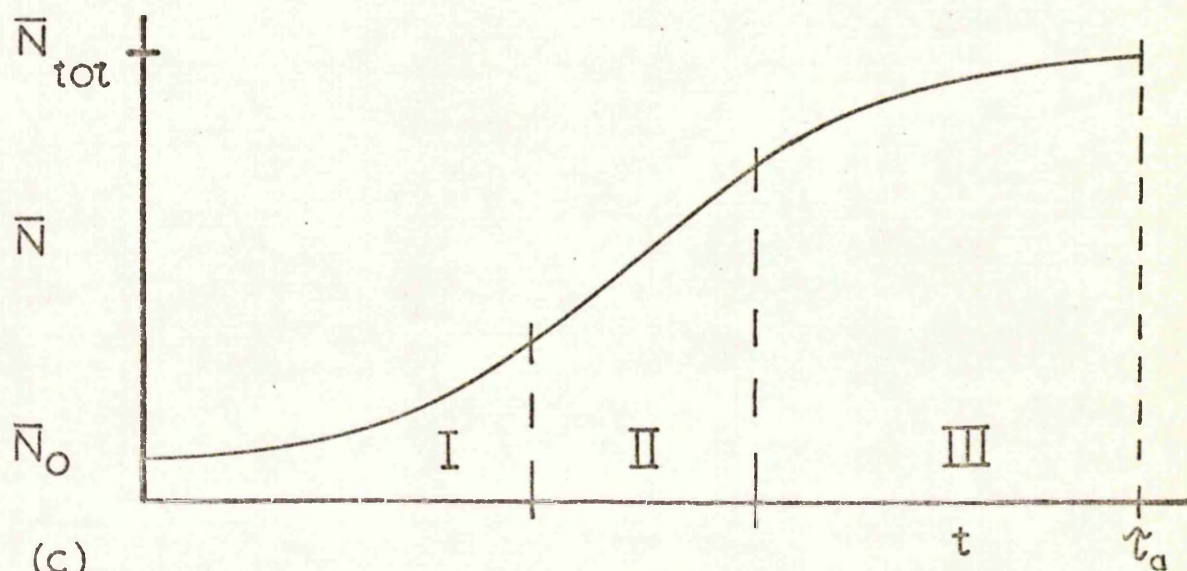


Fig.79.

(a).



(b).



(c).

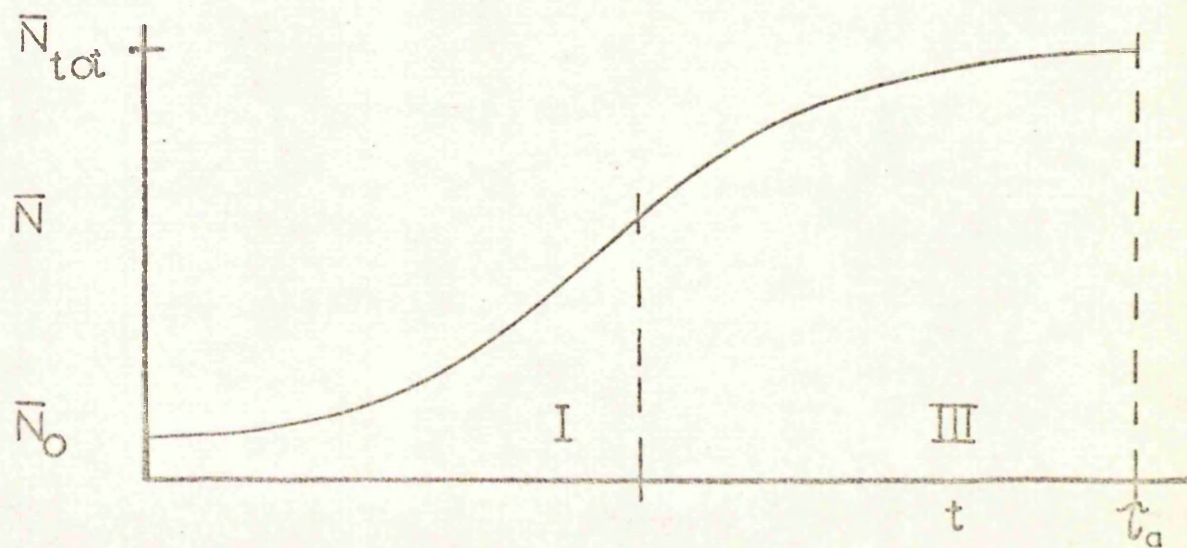


Fig.80.

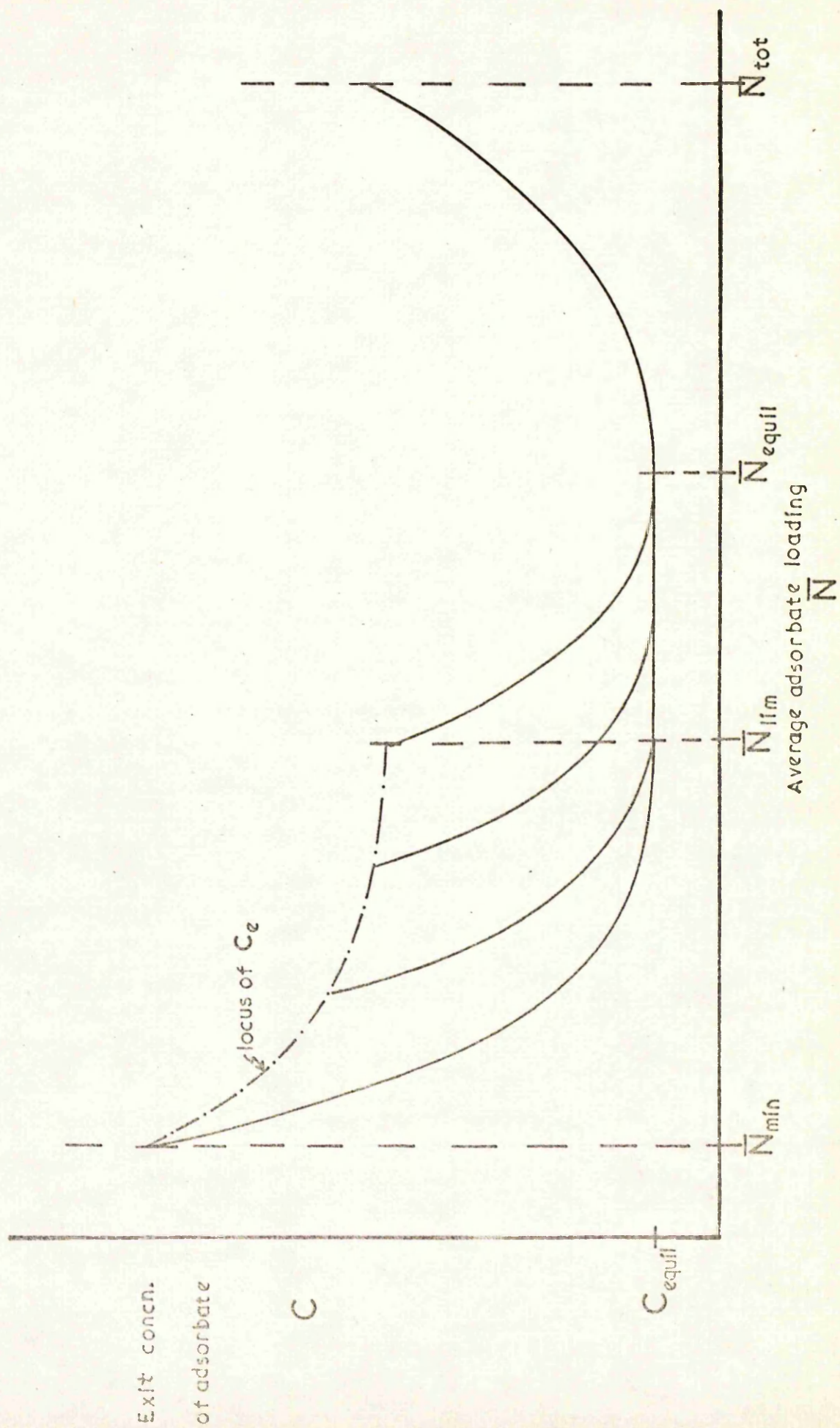


Fig. 81.

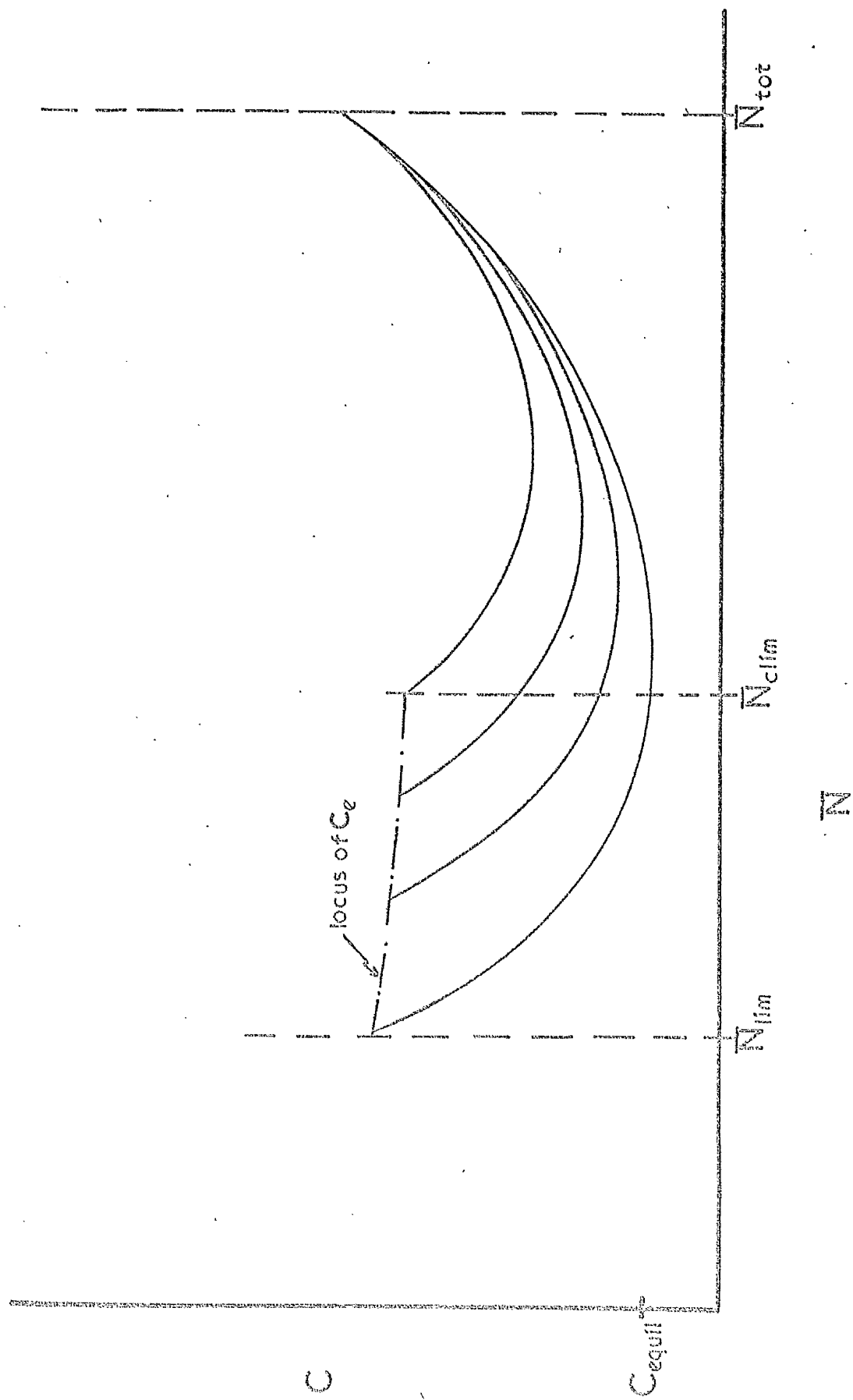


Fig. 82.

Key	
1	Viscose feed tank
2	Viscose filter
3a	Regeneration and coagulation
3b	Hot water wash
3c	Hydroxide treatment
3d	Cool water wash
3e	Bleaching/Washing
3f	Softening
3g	Drying
4a	Film heater
4b	Solvent/coating spray
4c	Spreader
4d	Solvent evaporation
4e	Film moisturising
4f	Film cooling
5	Solvent/coating tank
6	Heat exchanger
7	Recirculation tank

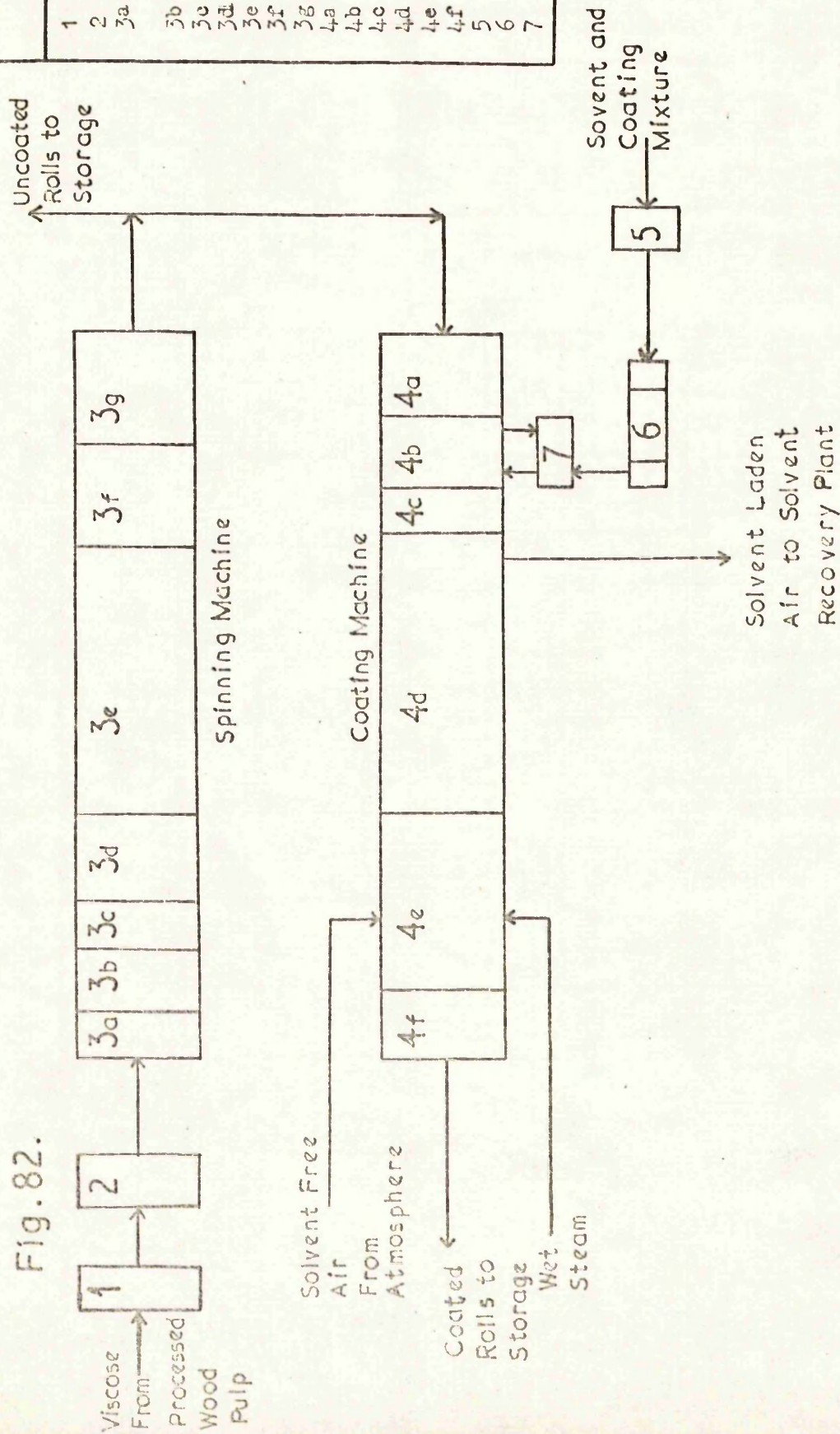


Fig. 83.

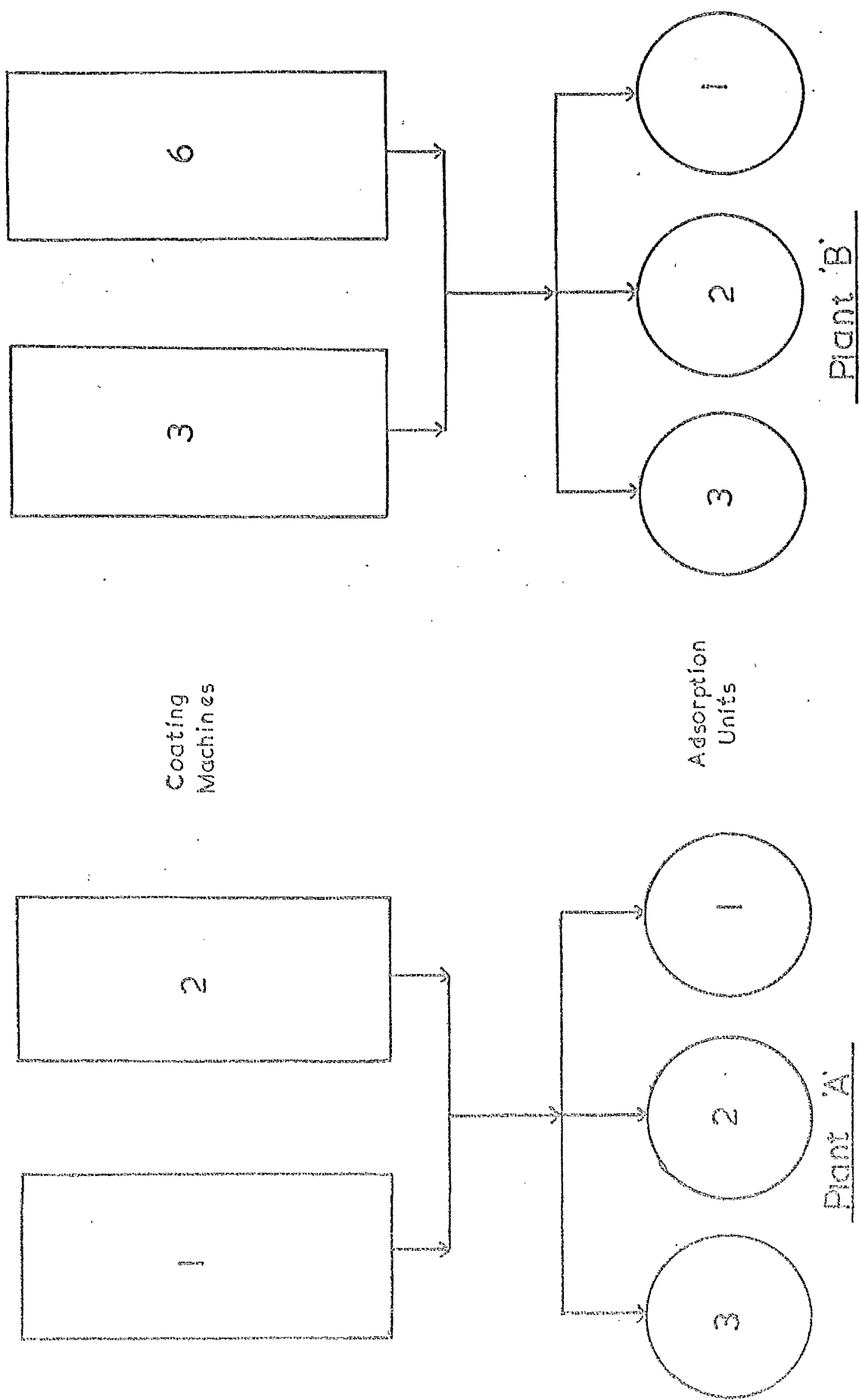


Fig.84.

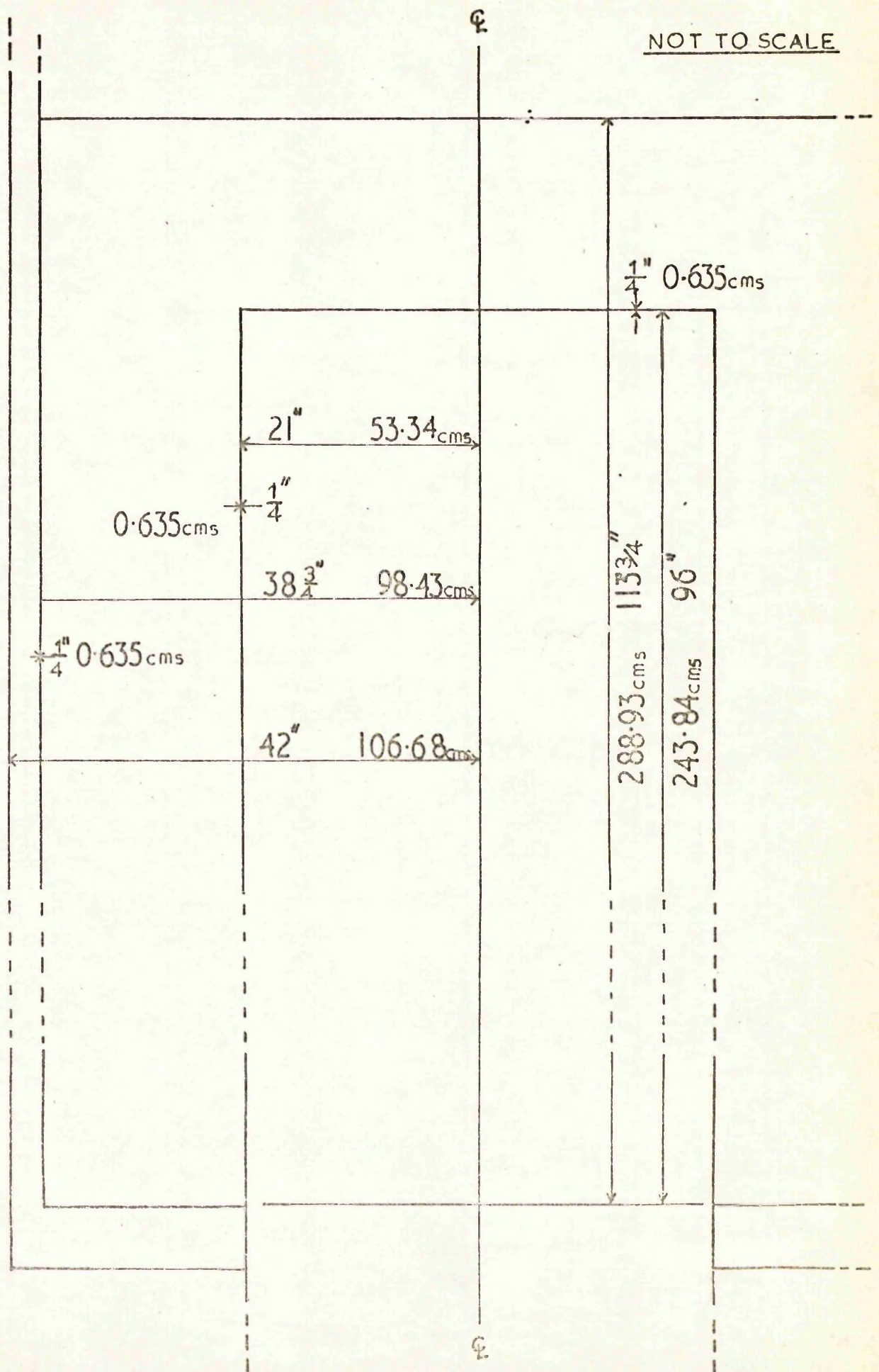


Fig.85.

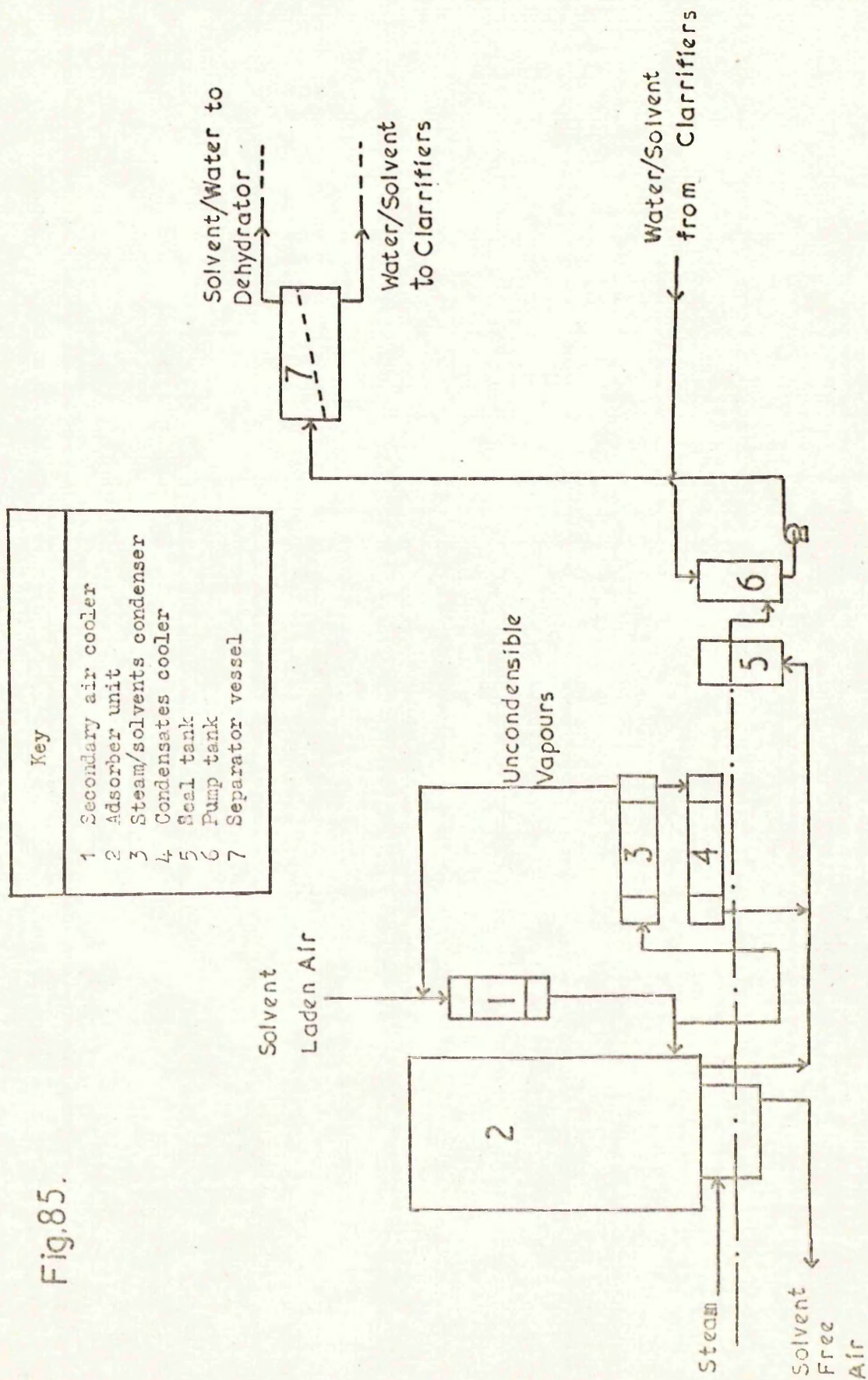


Fig.86.

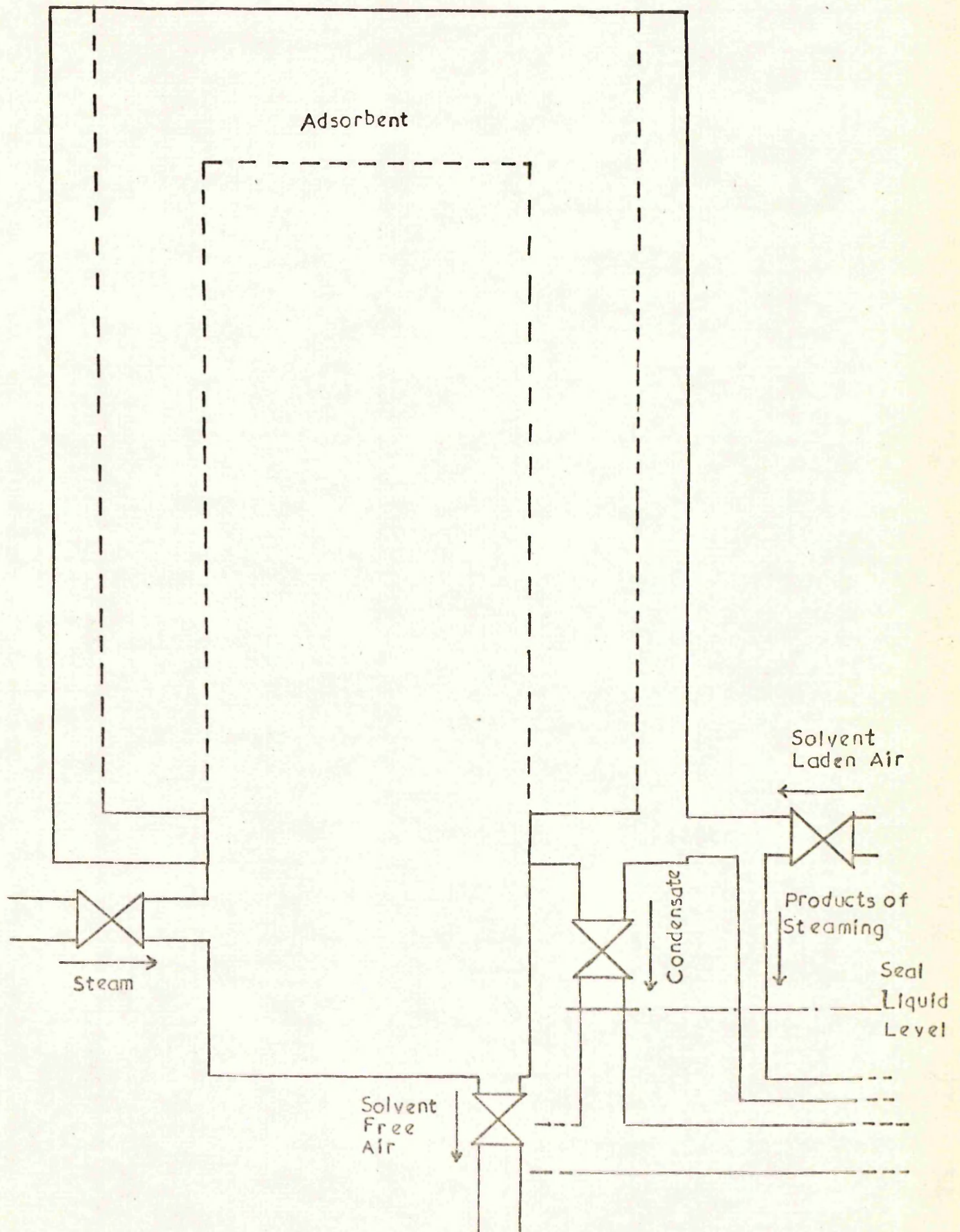


Fig.87.

PlantA Adsorber3

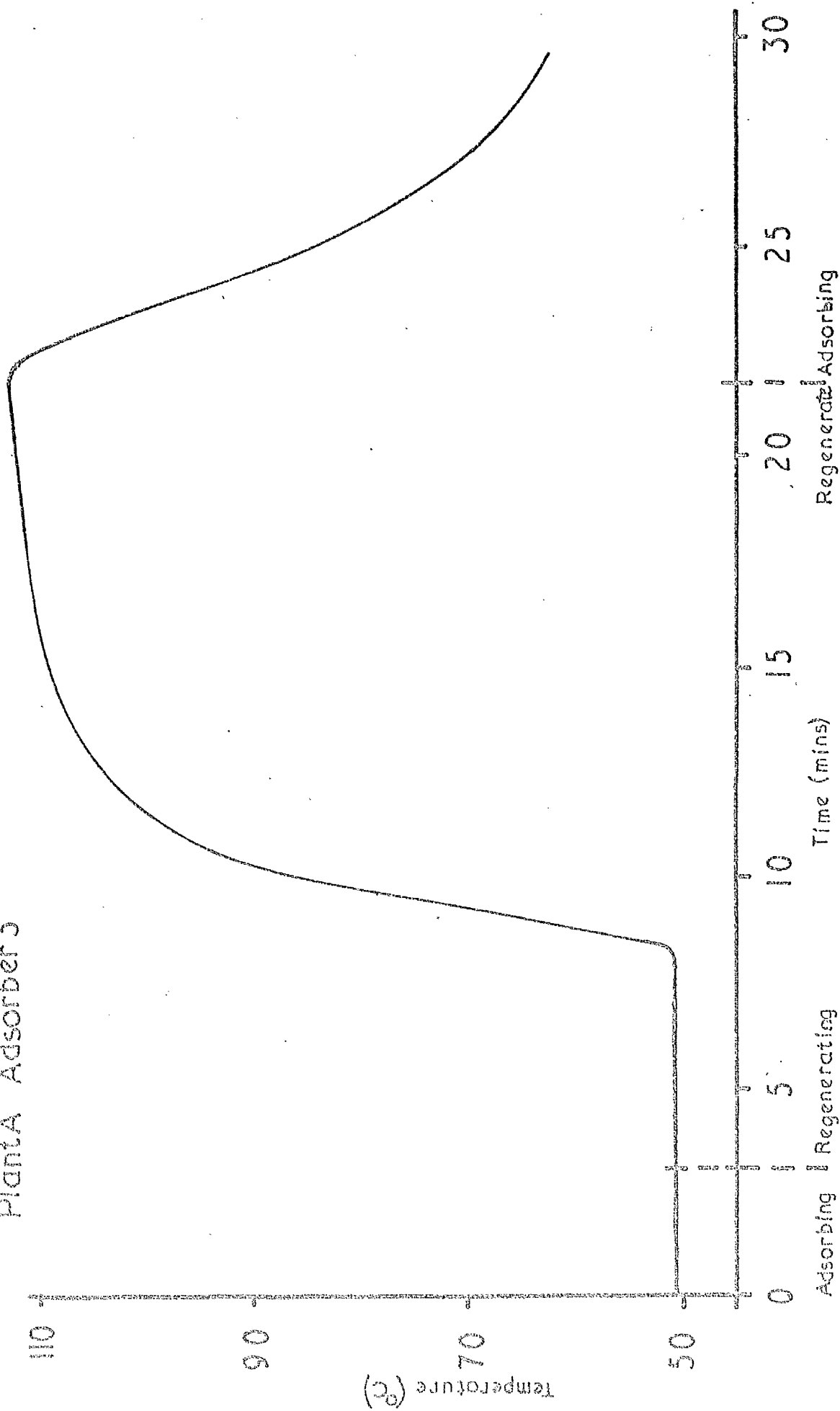


Fig.88.
Plant B Adsorber1

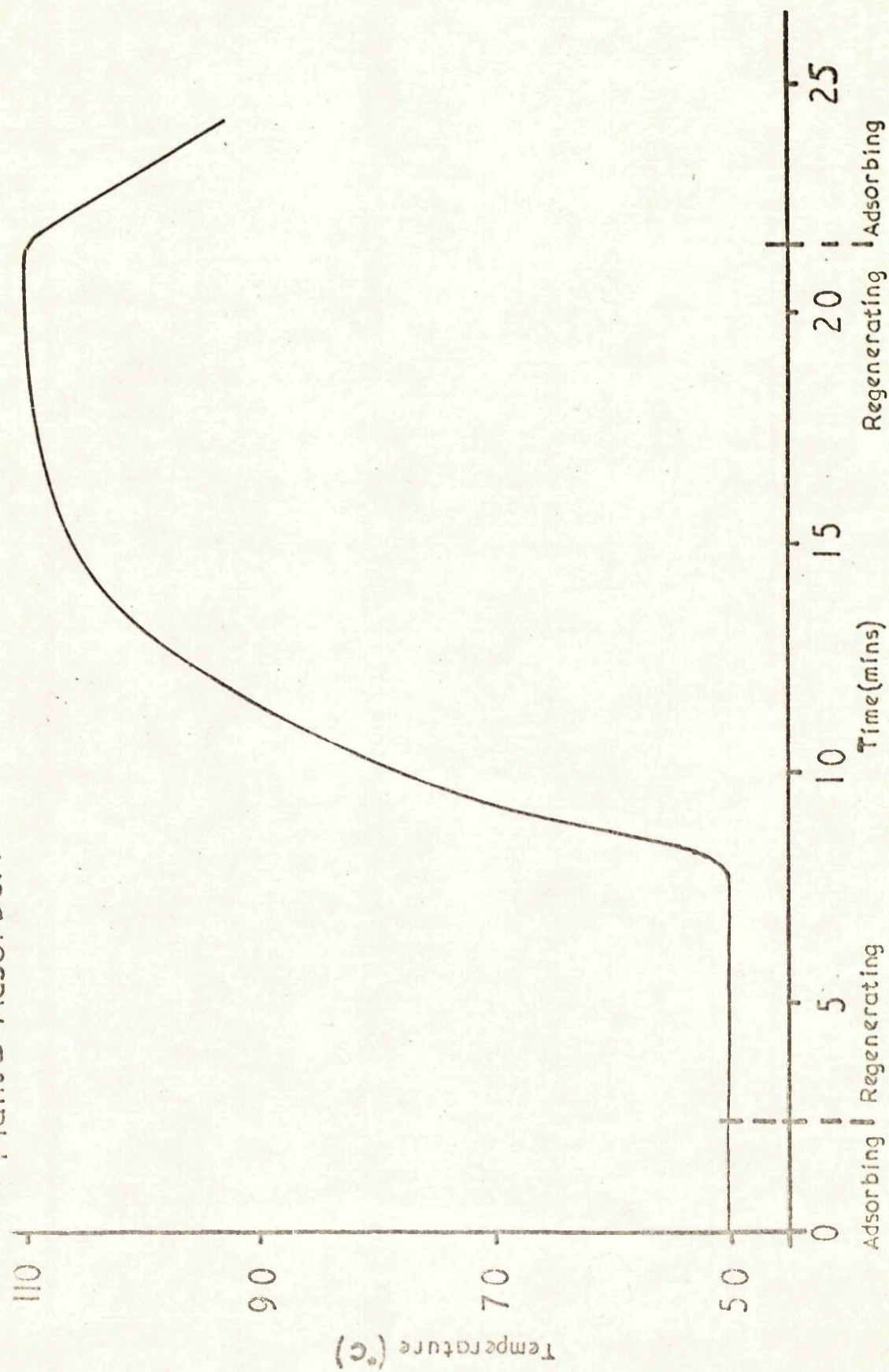
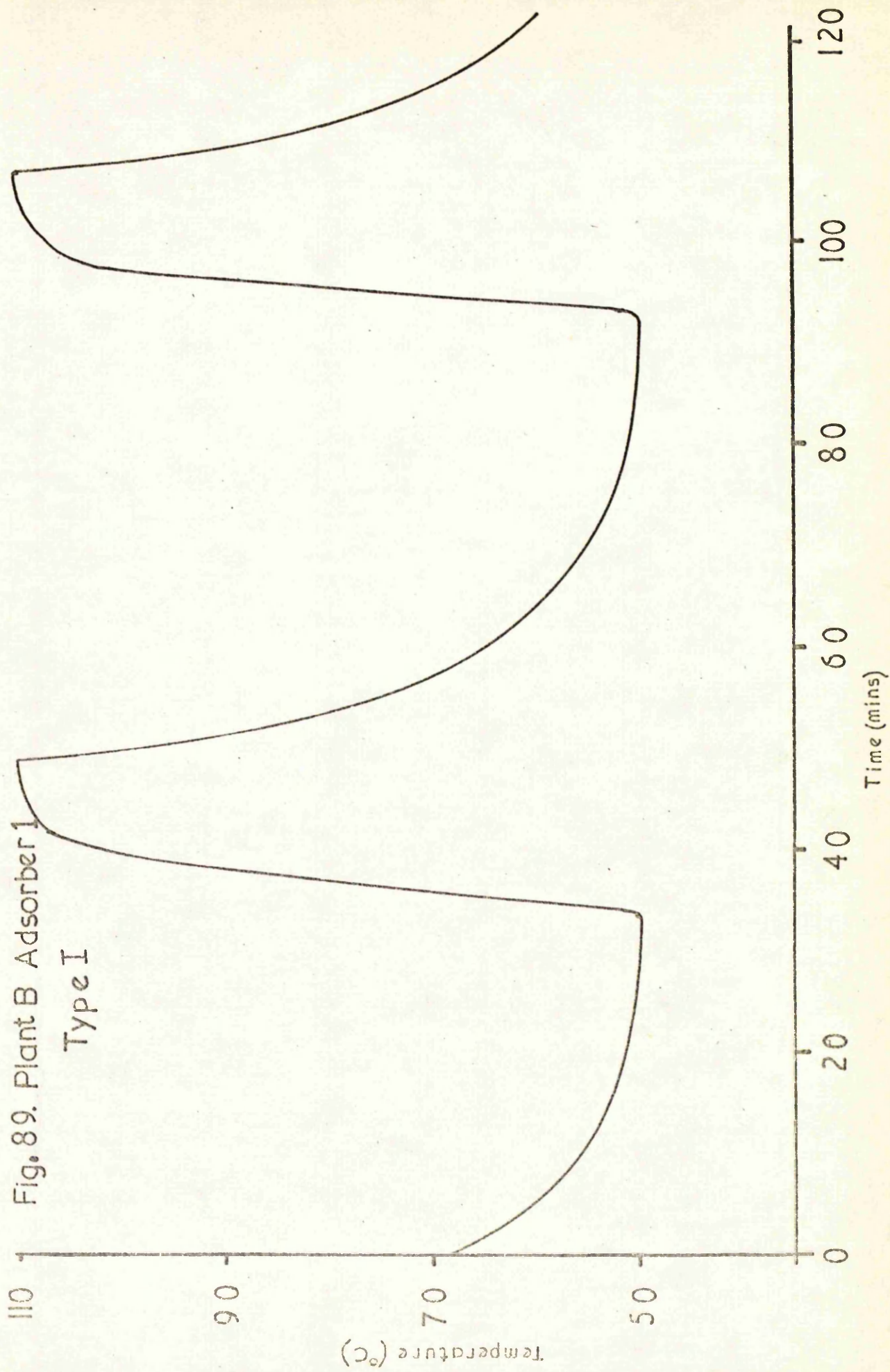


Fig. 89. Plant B Adsorber 1
Type I



110 Fig.90.Plant A. Adsorber 1

Type II

Temperature (°C)

90

70

50

0

20

40

60

80

100

120

Time (mins)

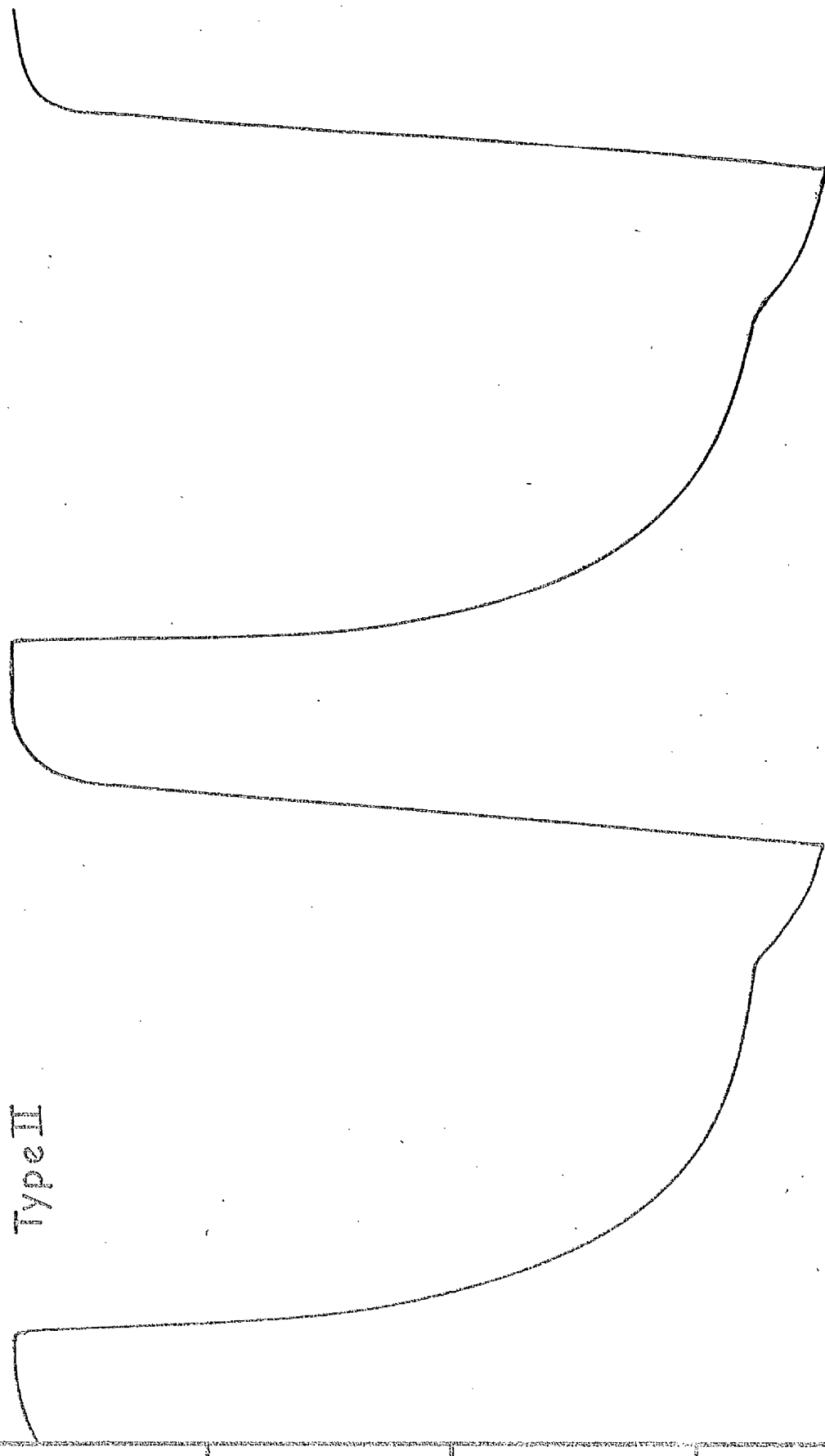


Fig. 91.

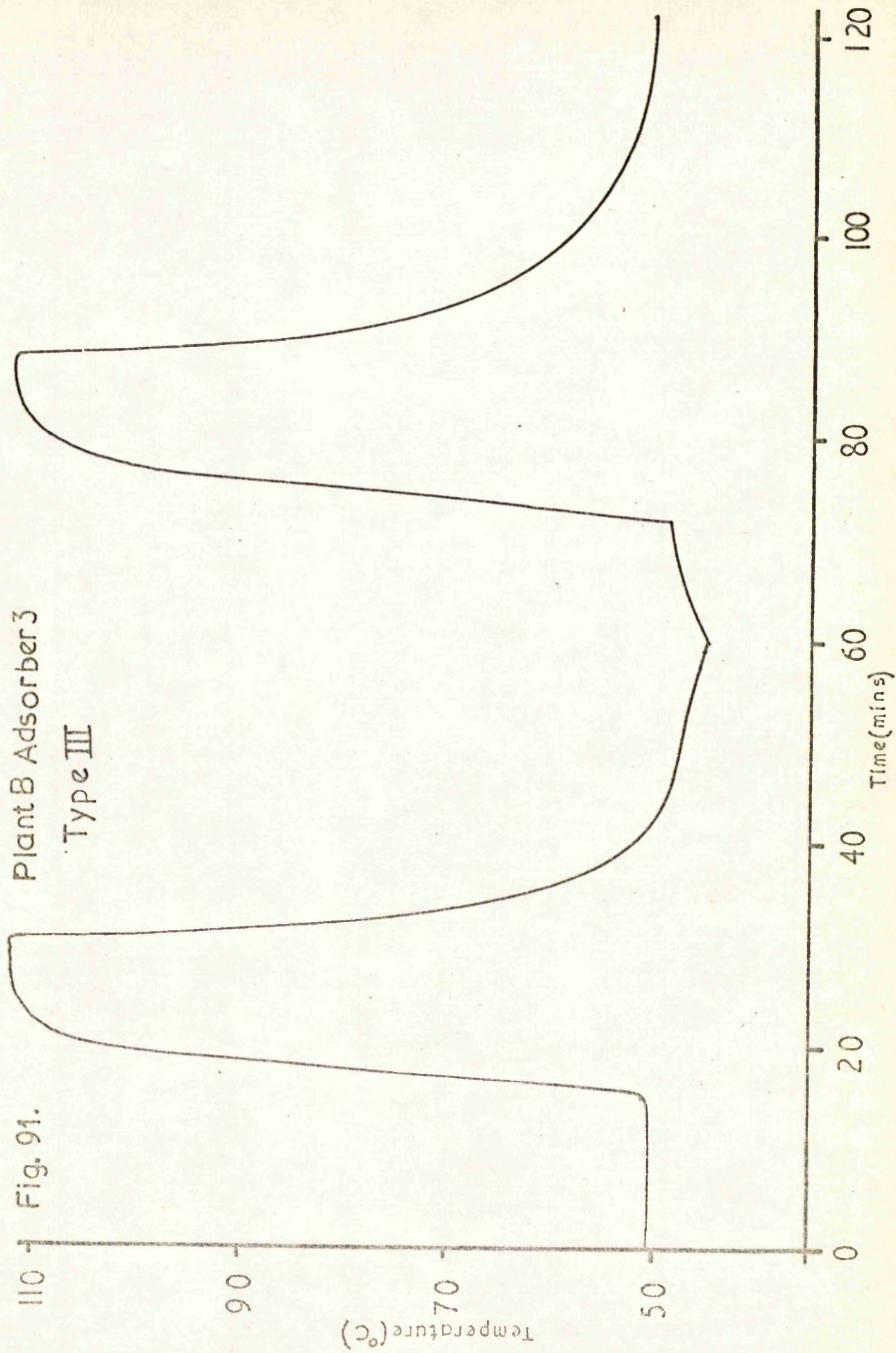
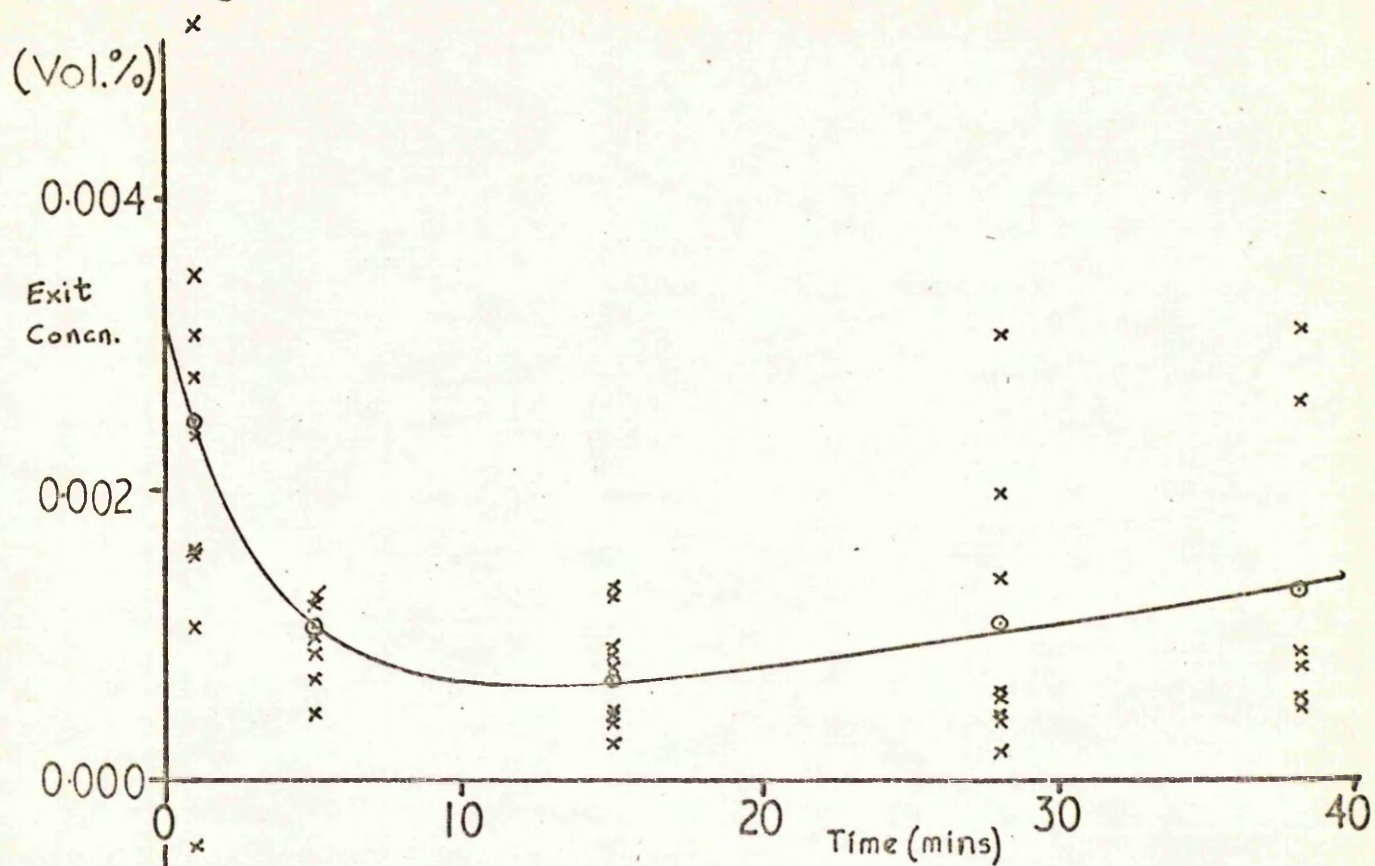


Fig.92. Plant A : Ethyl Acetate



Plant A : Toluene

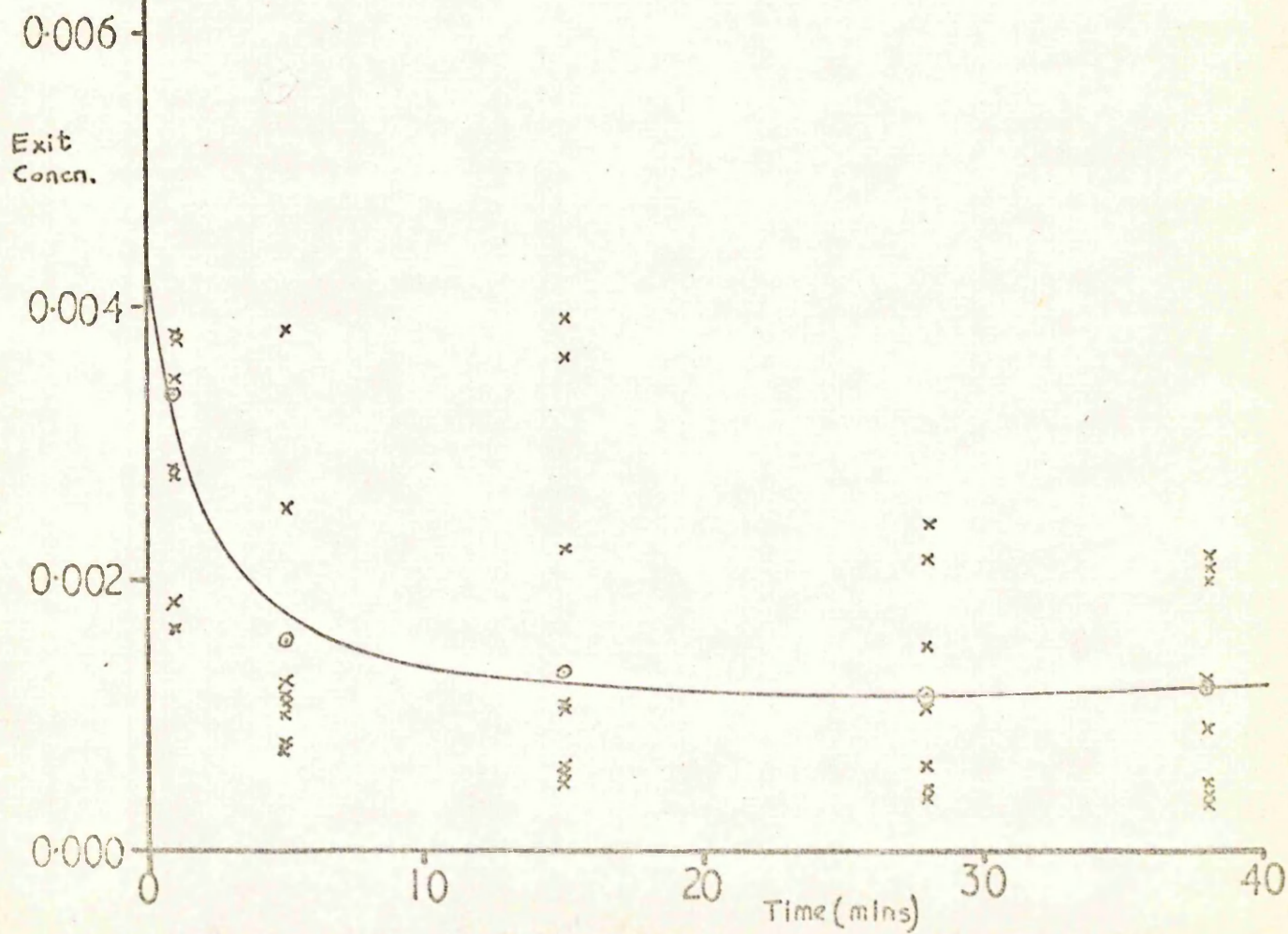
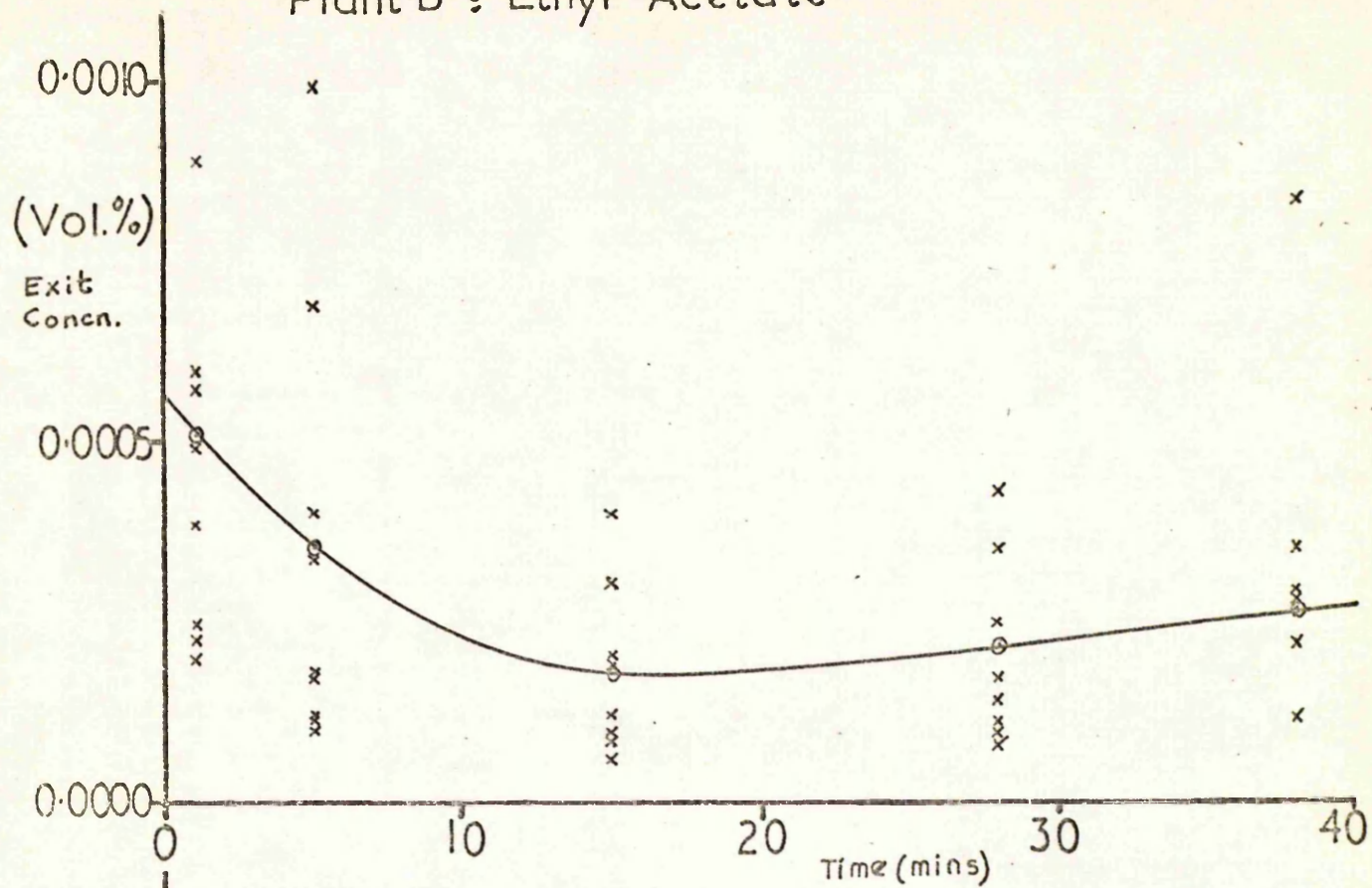


Fig. 93.

Plant B : Ethyl Acetate



Plant B : Toluene

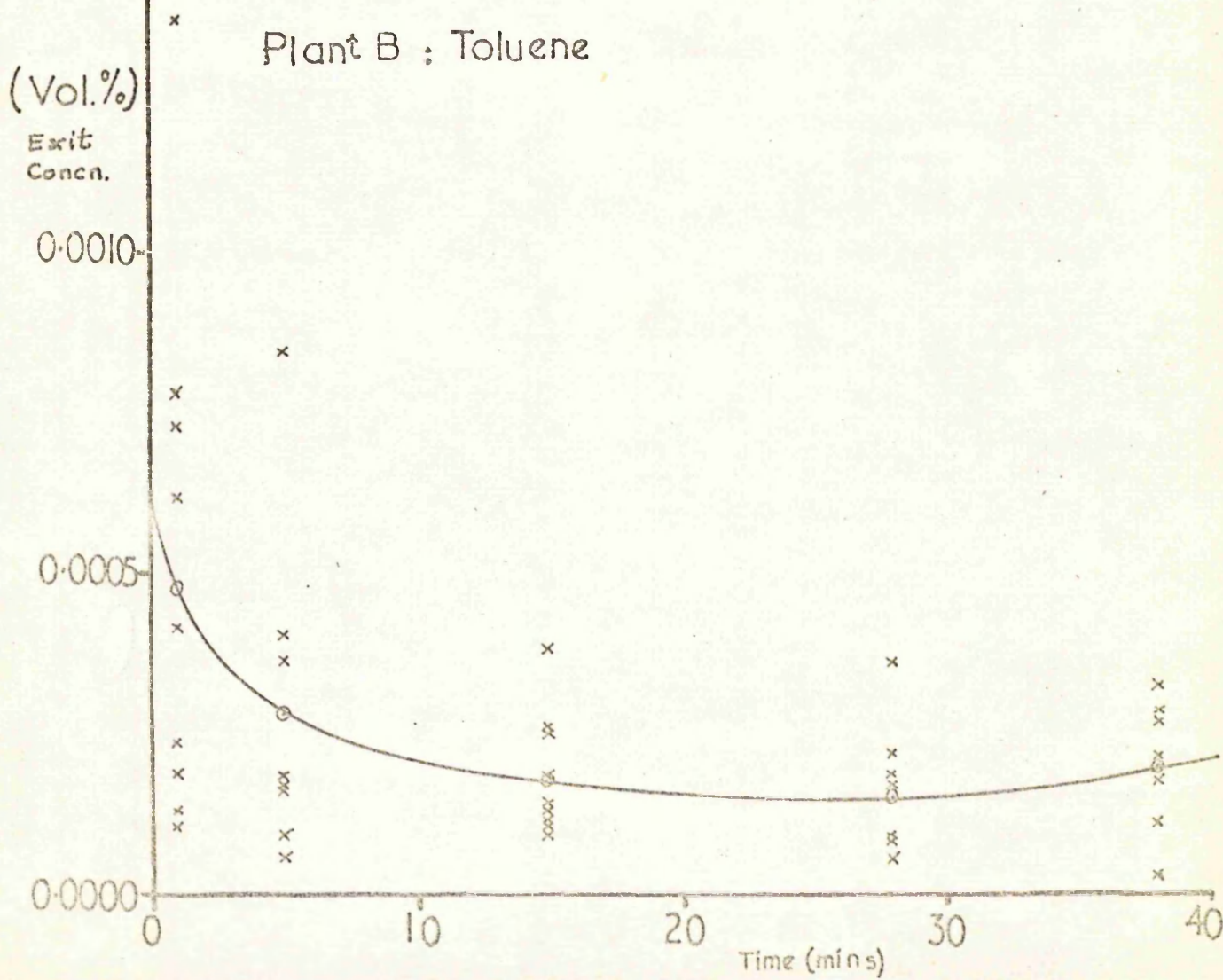
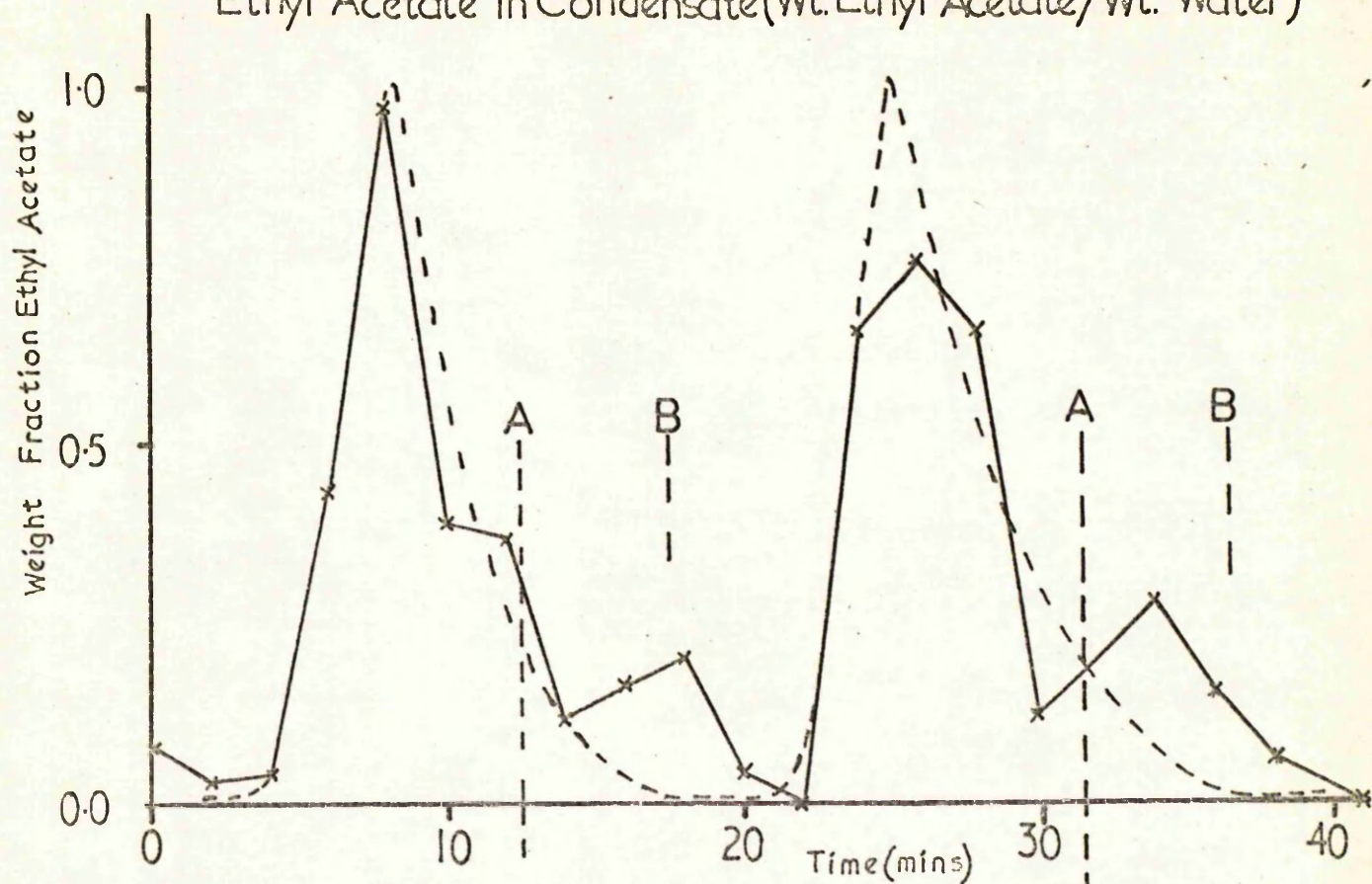


Fig. 94.

Ethyl Acetate In Condensate (Wt. Ethyl Acetate/Wt. Water)



Toluene In Condensate (Wt. Toluene/Wt. Water)

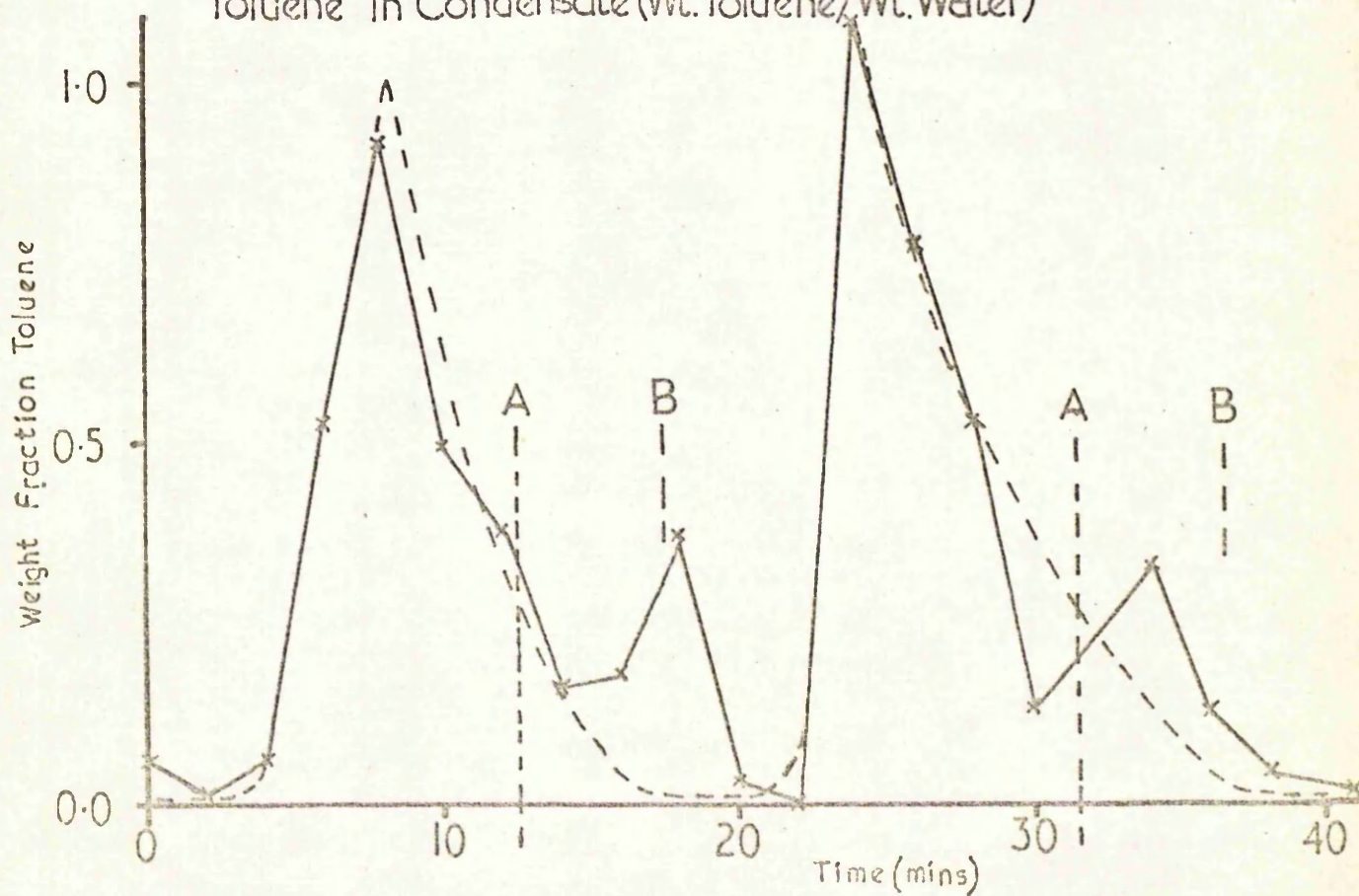


Fig.95.
SLA from Vaporiser

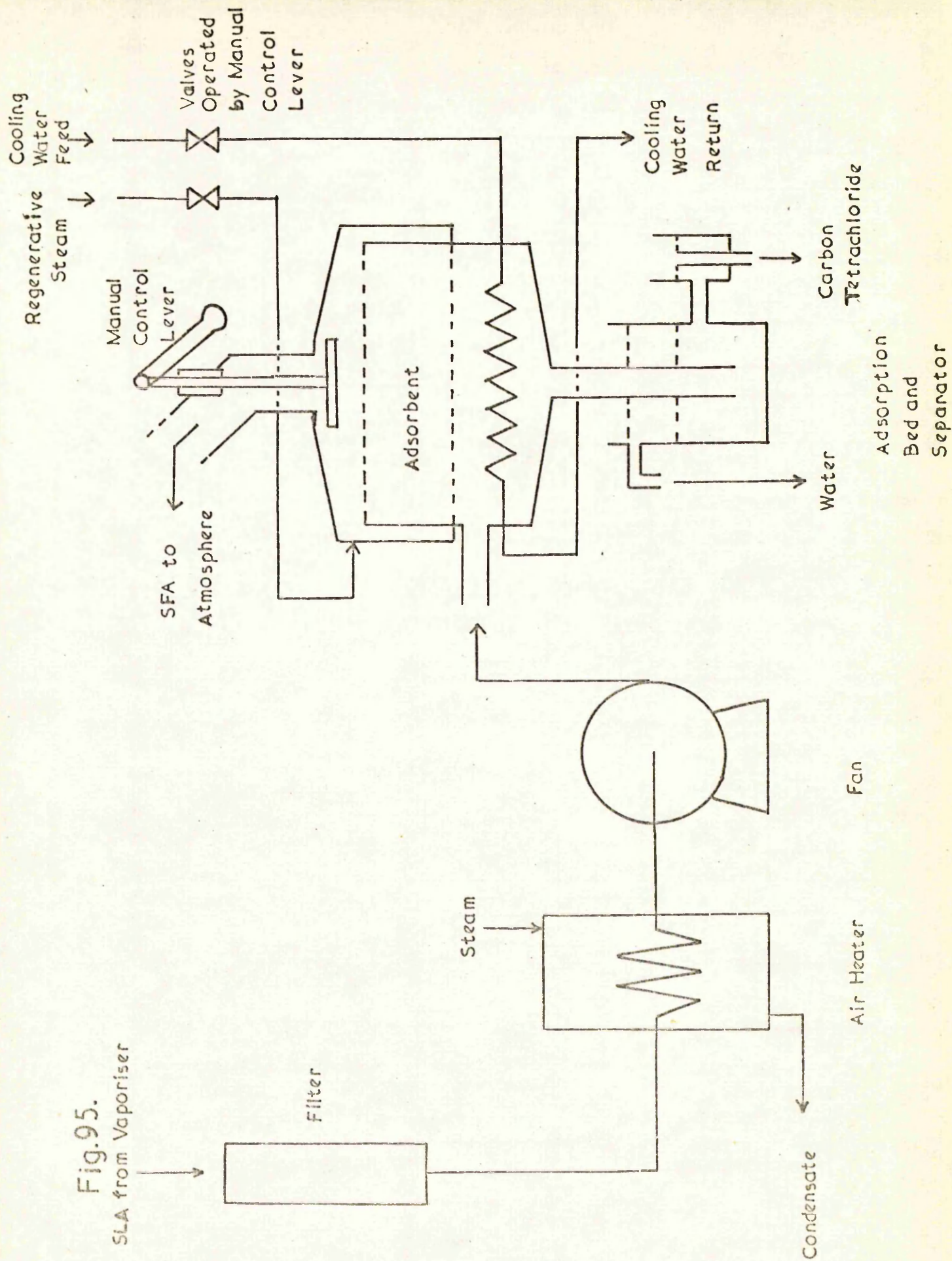


Fig.96.

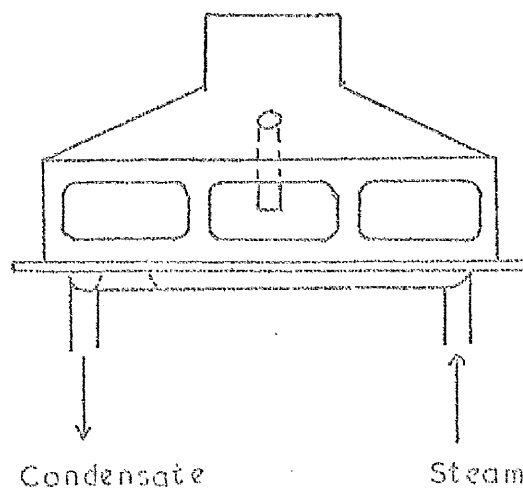
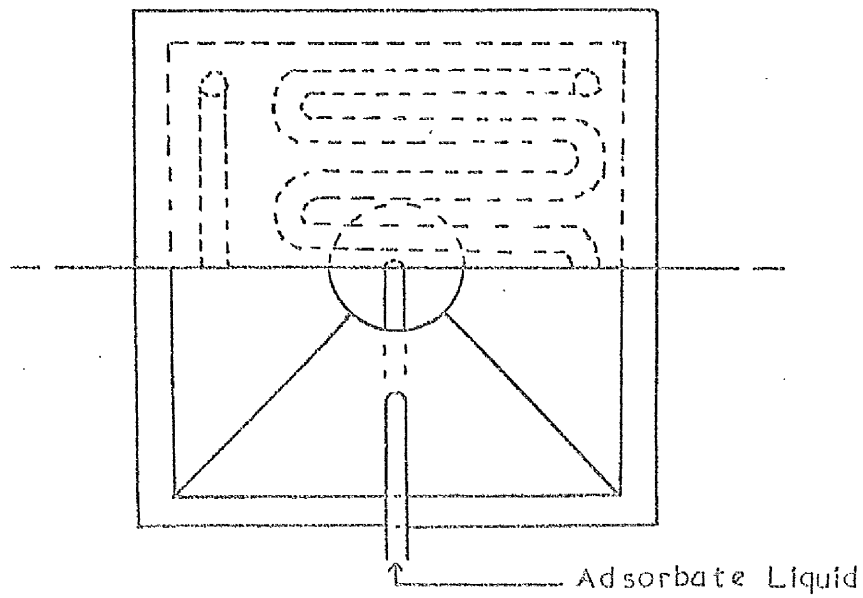
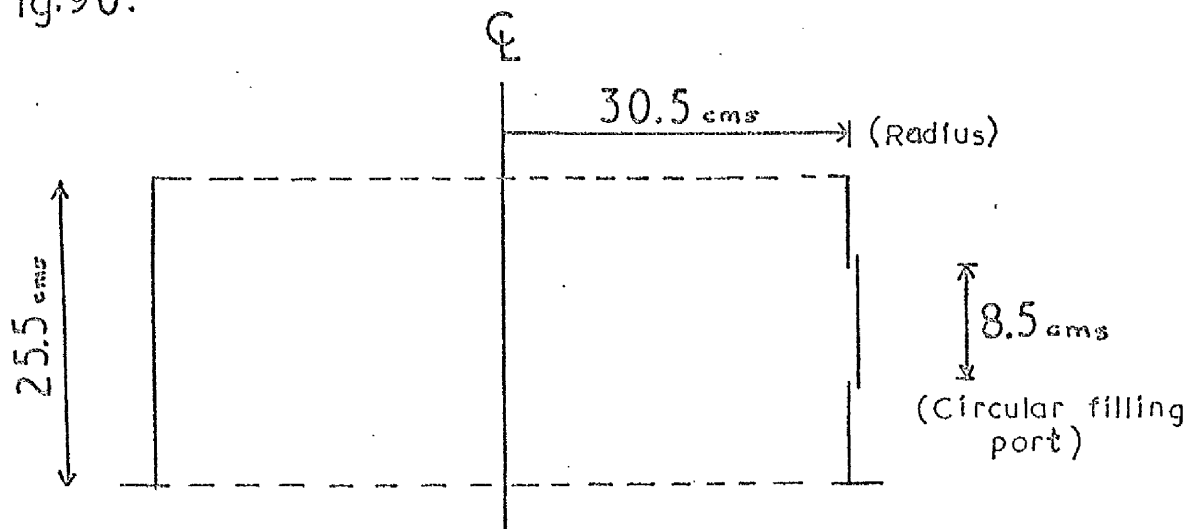


Fig. 97.

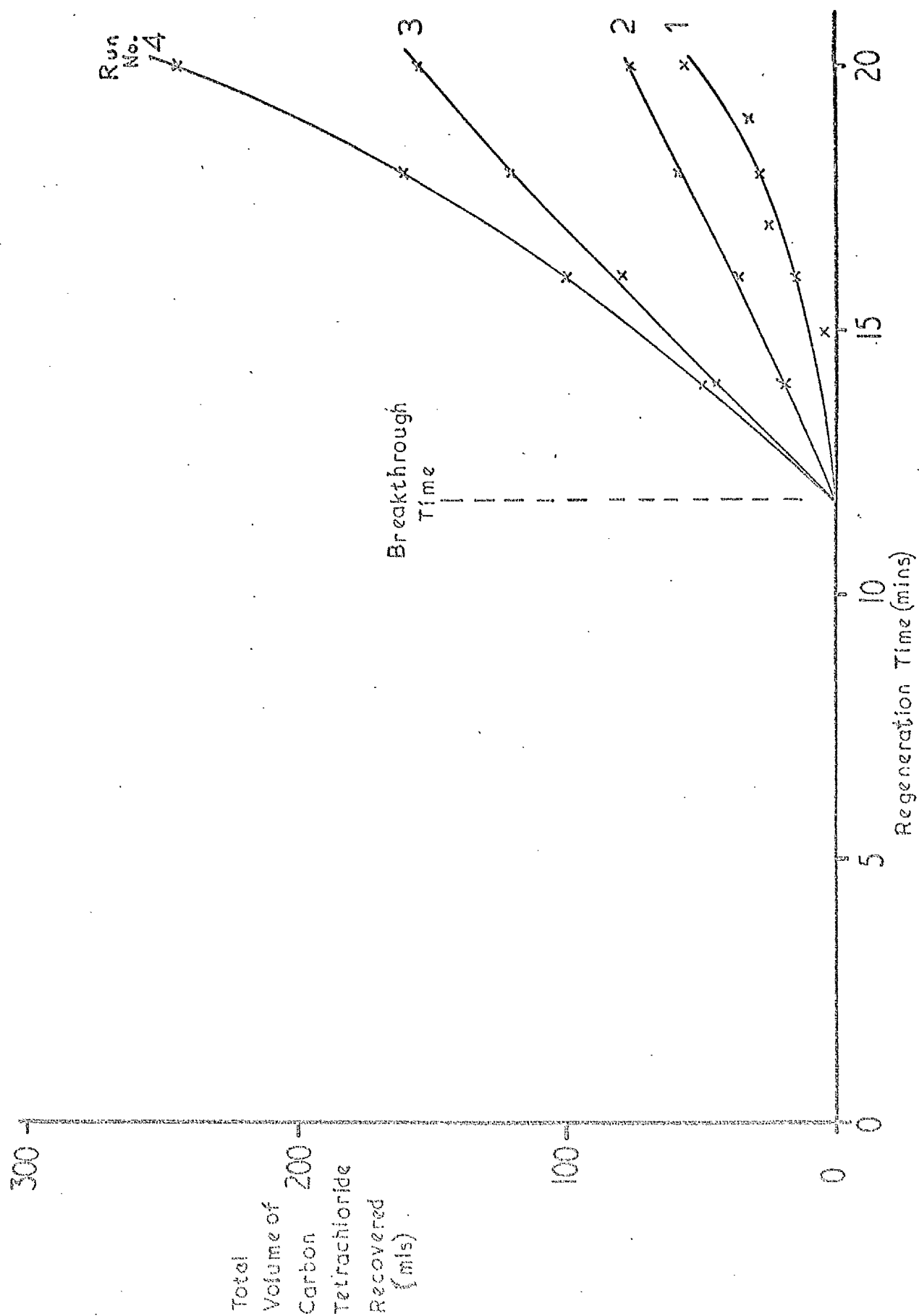


Fig. 98.

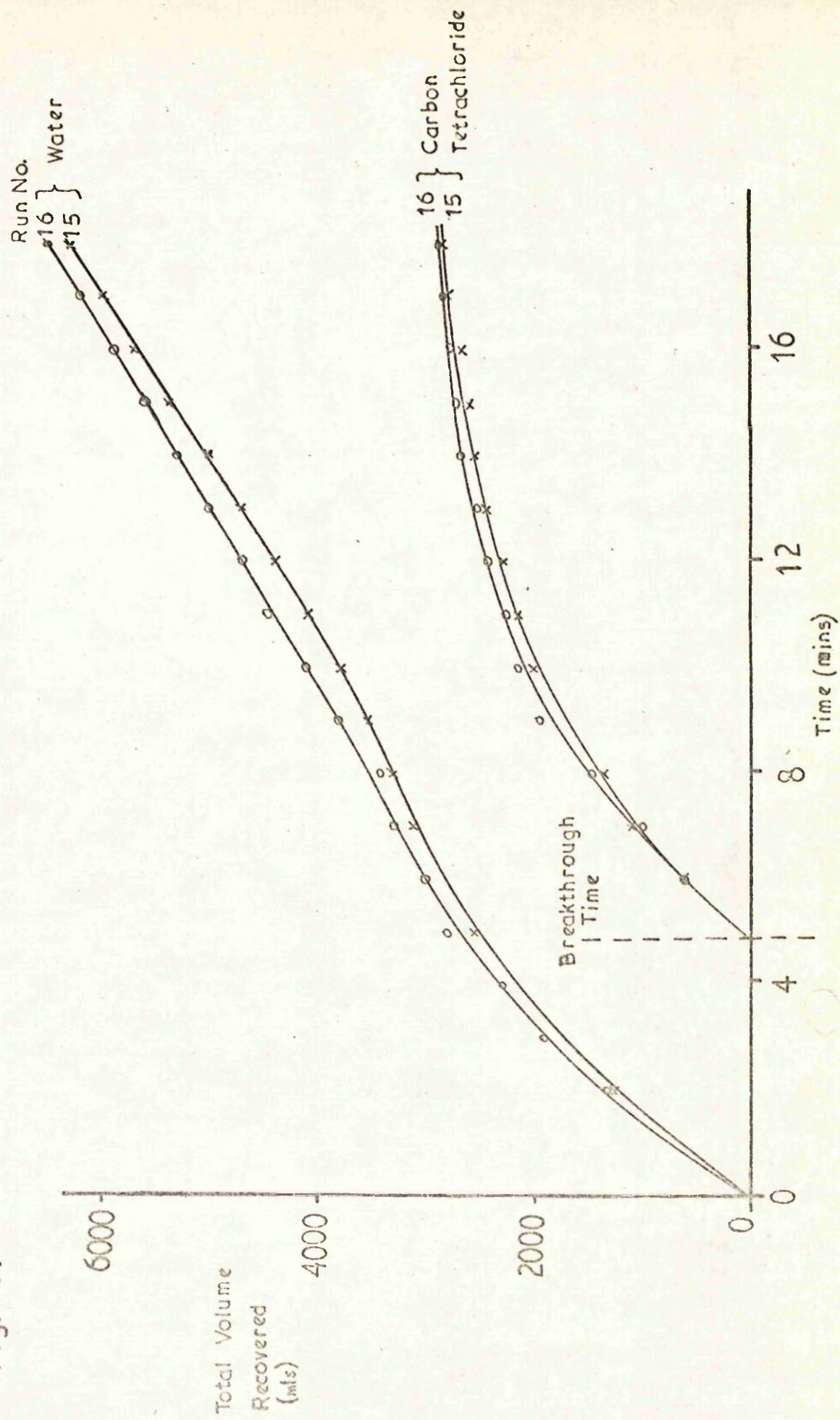


Fig. 99.

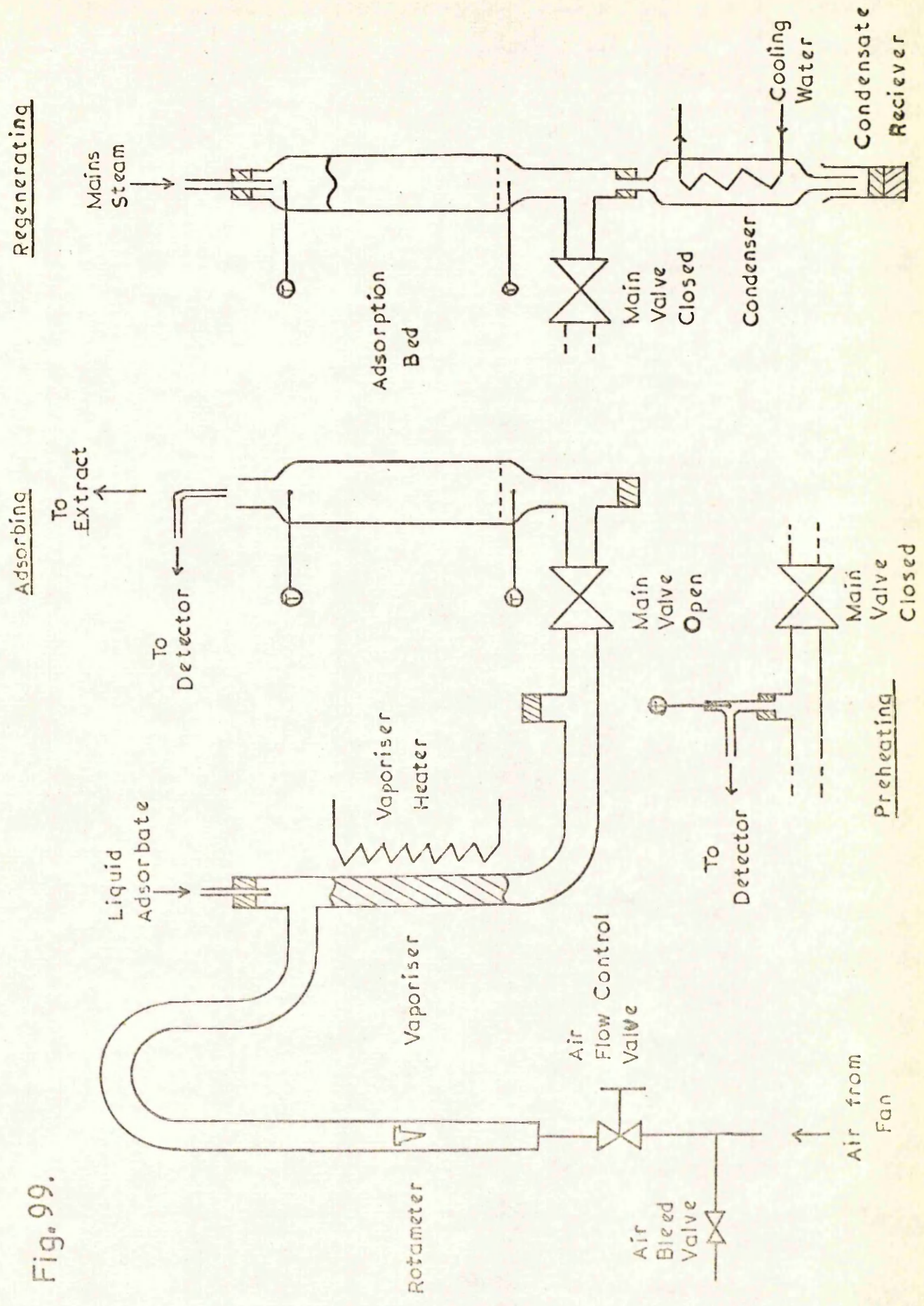
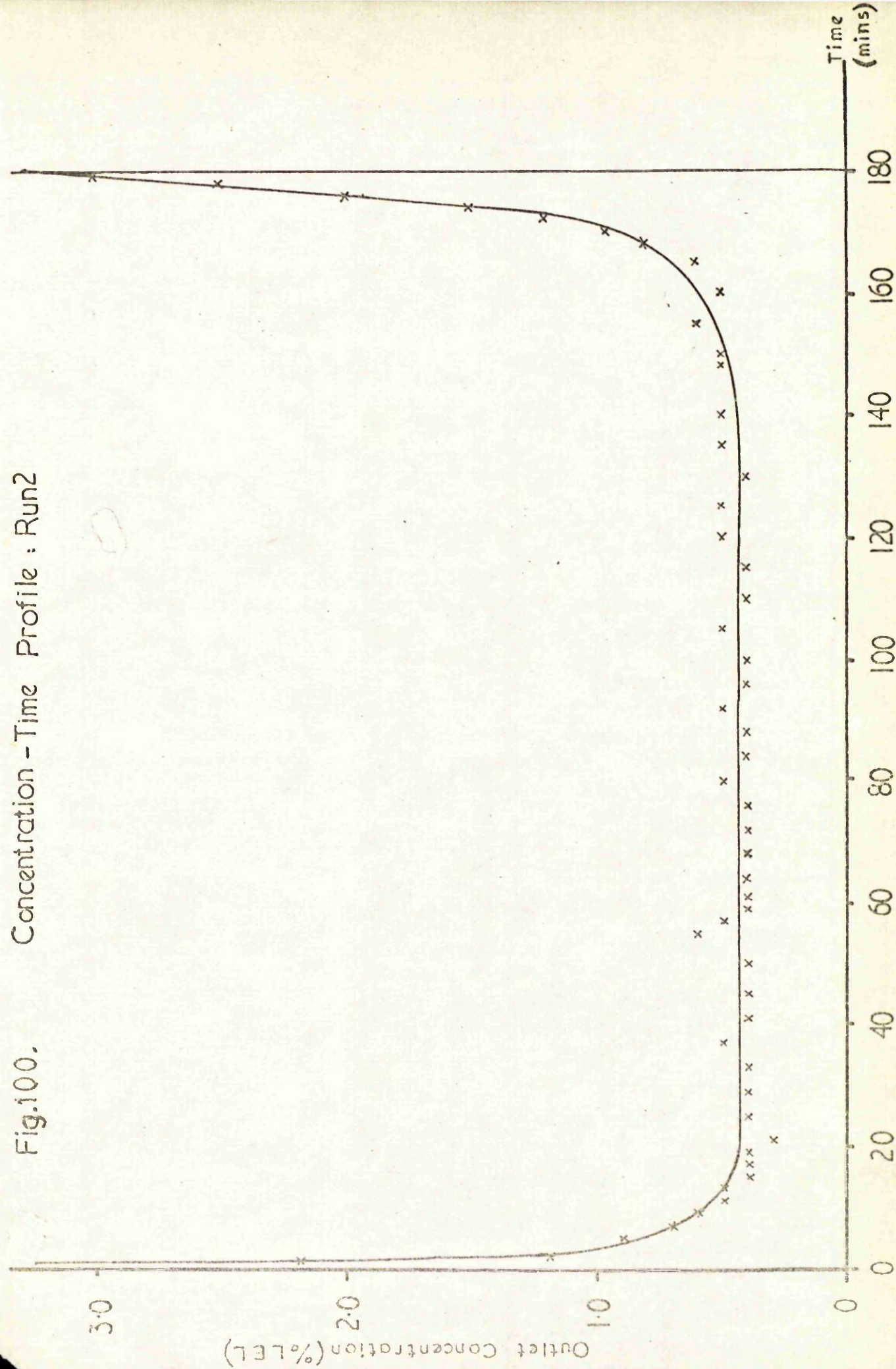


Fig.100. Concentration - Time Profile : Run2



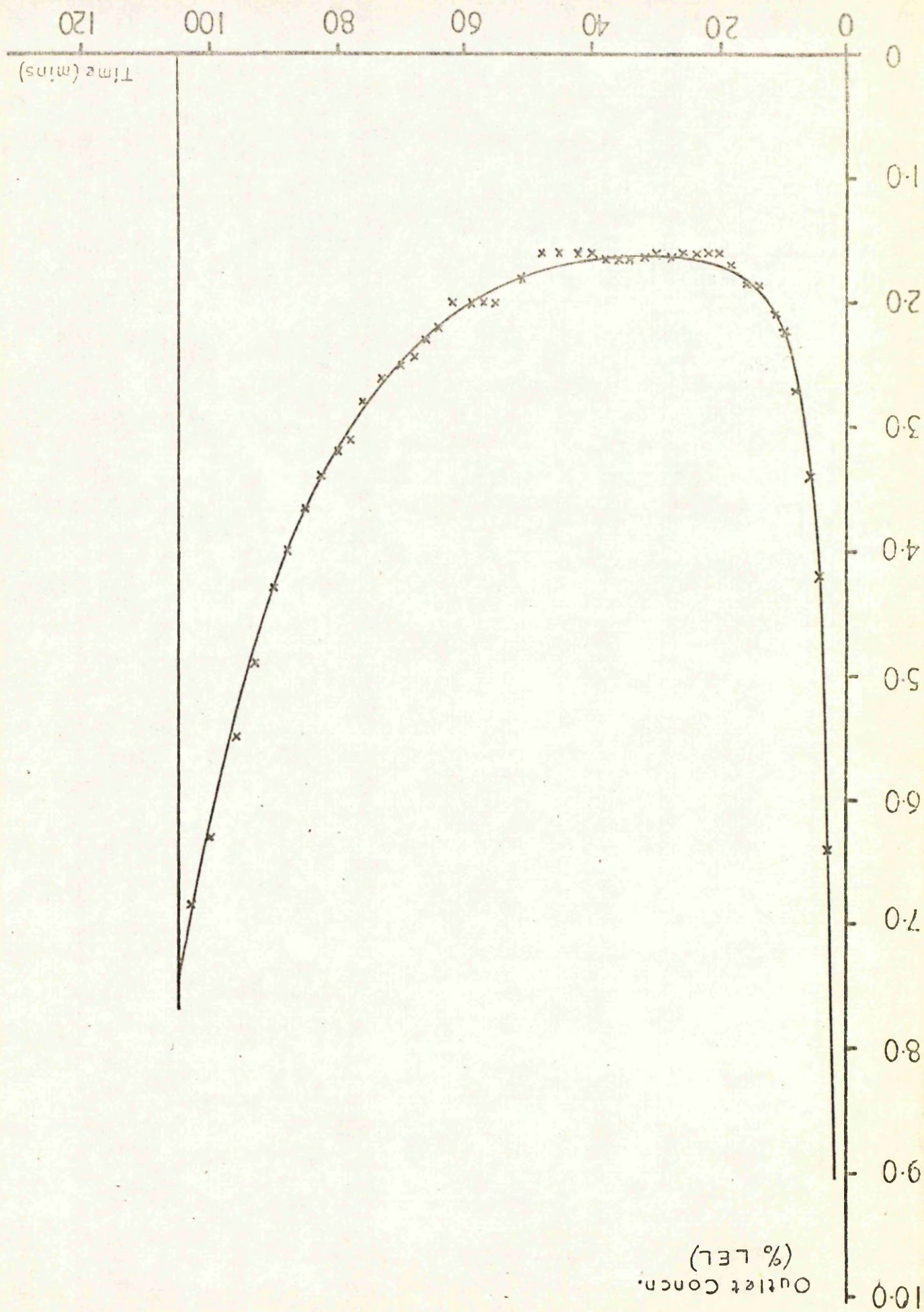


Fig.101. Concentration-Time Profile: Run 4

Fig.102. Concentration-Time Profile: Run6

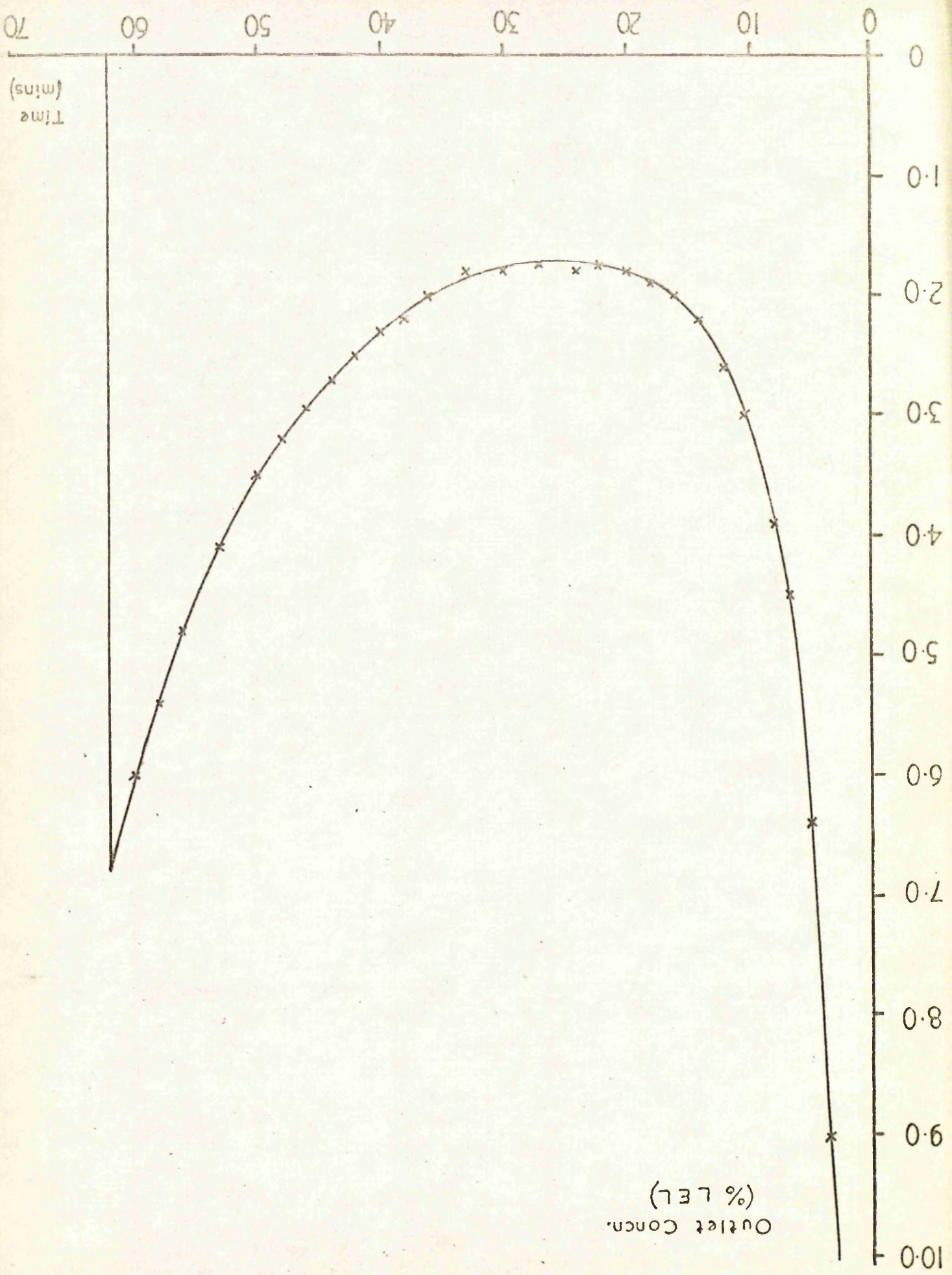
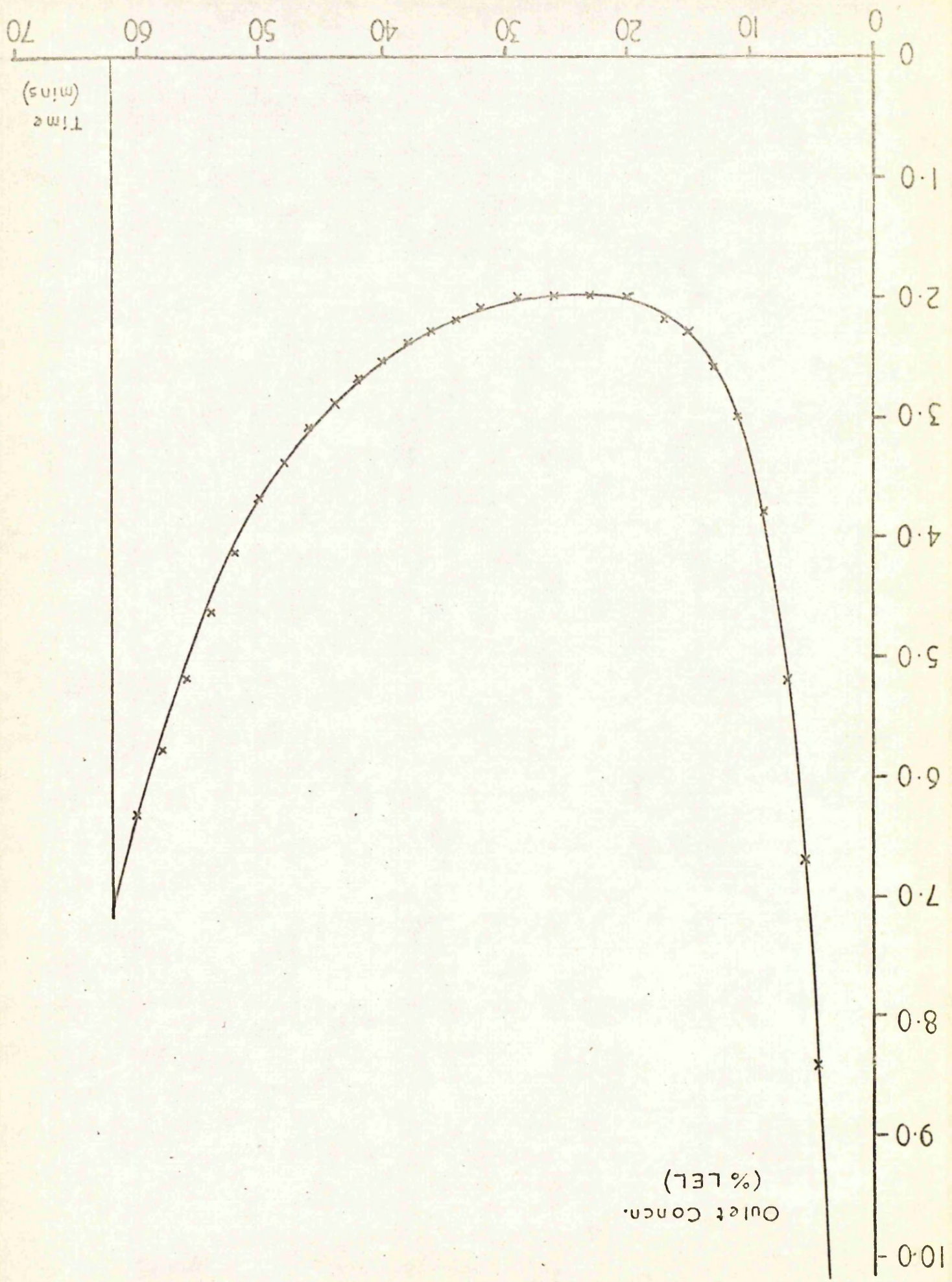


Fig.103. Concentration-Time Profile: Run8



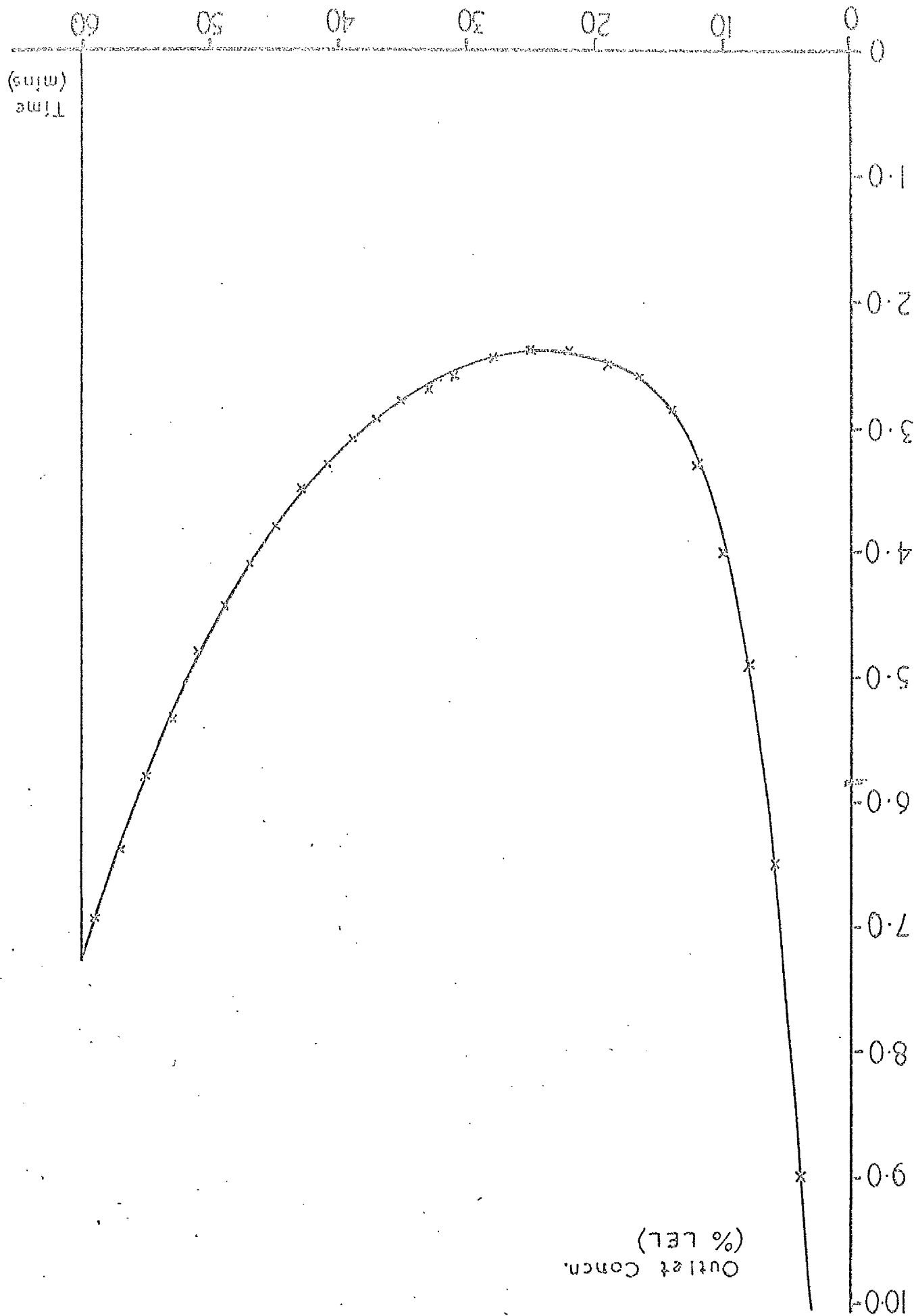
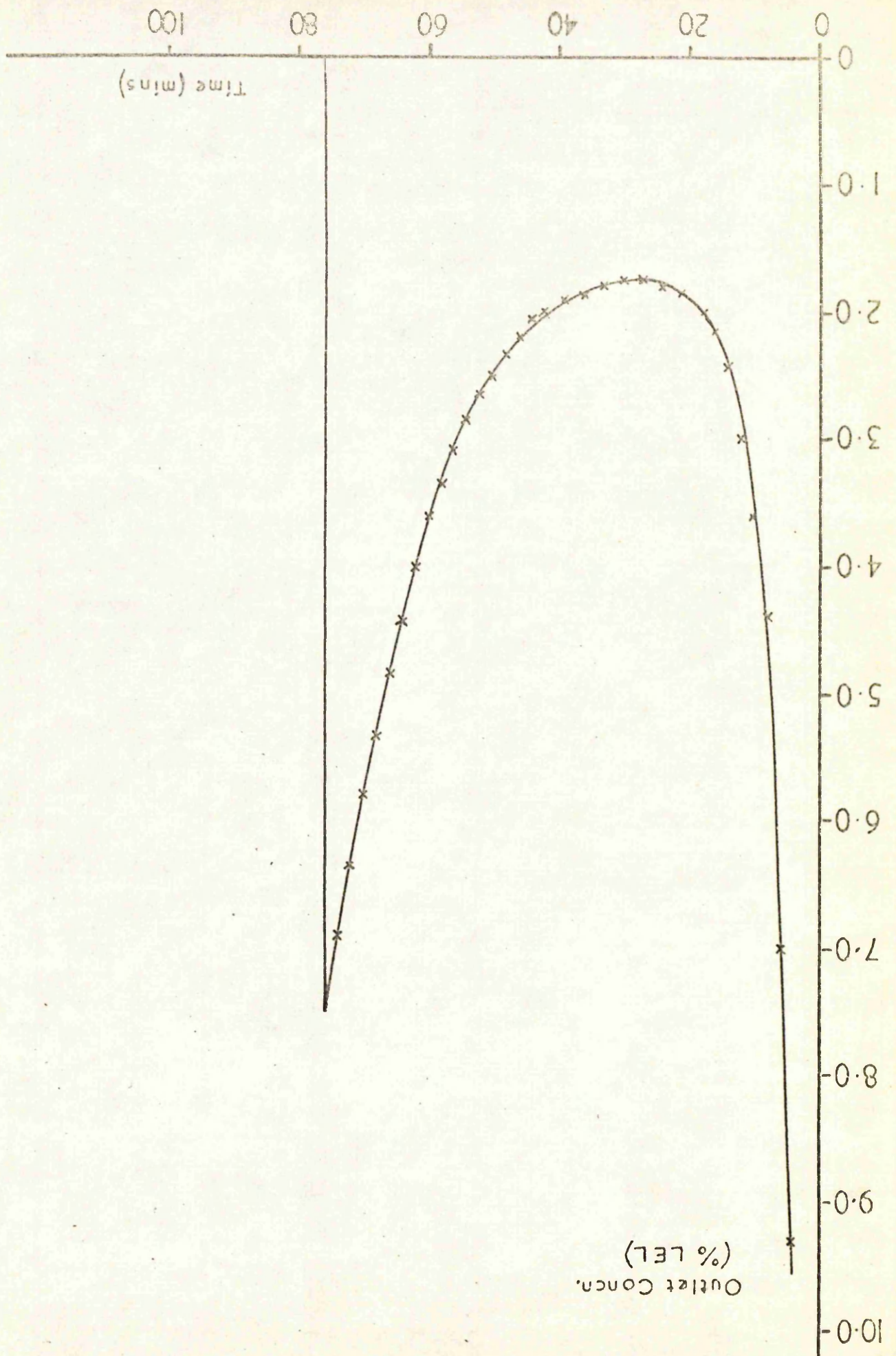


Fig:104. Concentration - Time Profile : Run 10

Fig. 105. Concentration - Time Profile: Run 12



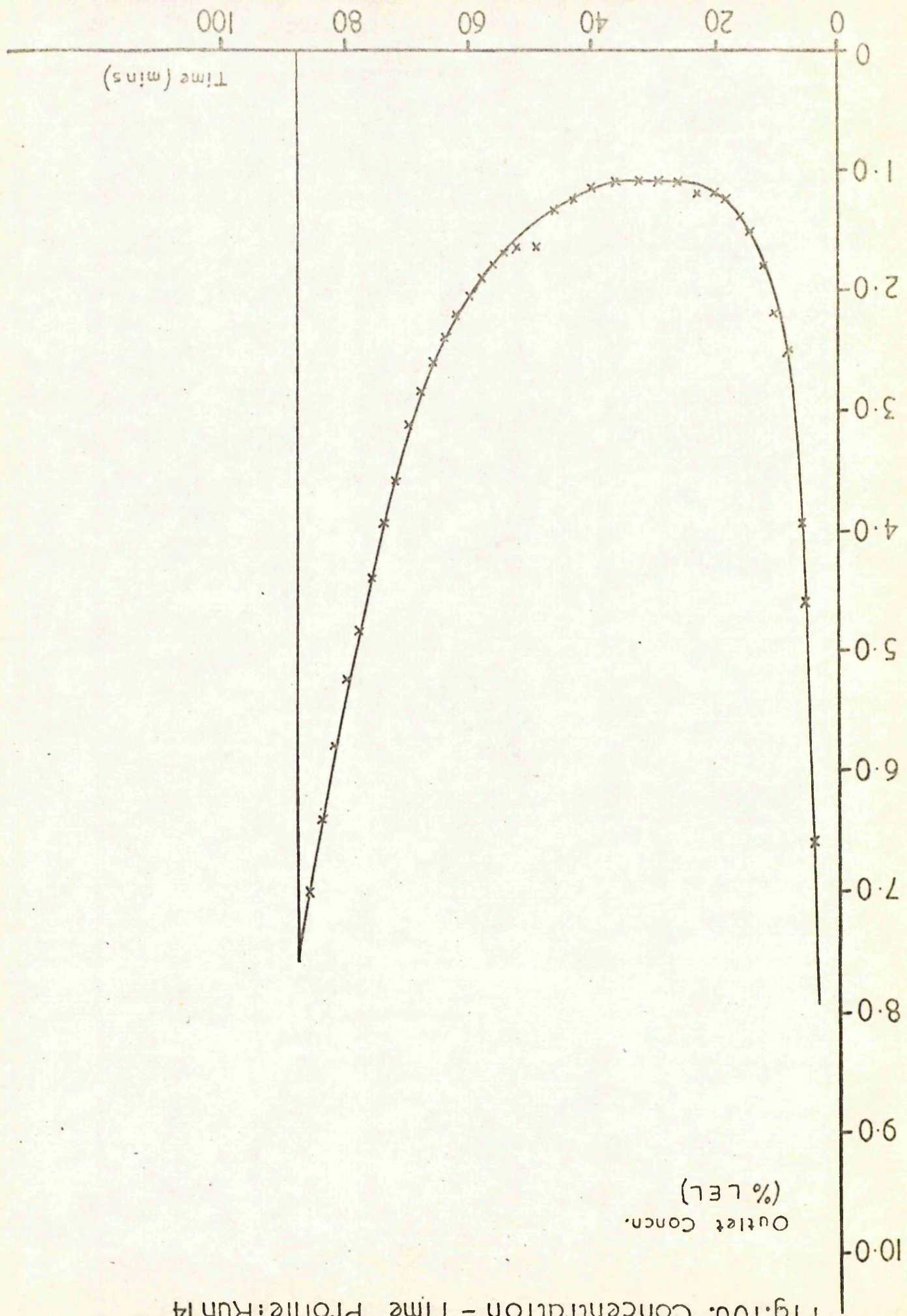


Fig.106. Concentration - Time Profile: Run 14

Fig. 107.

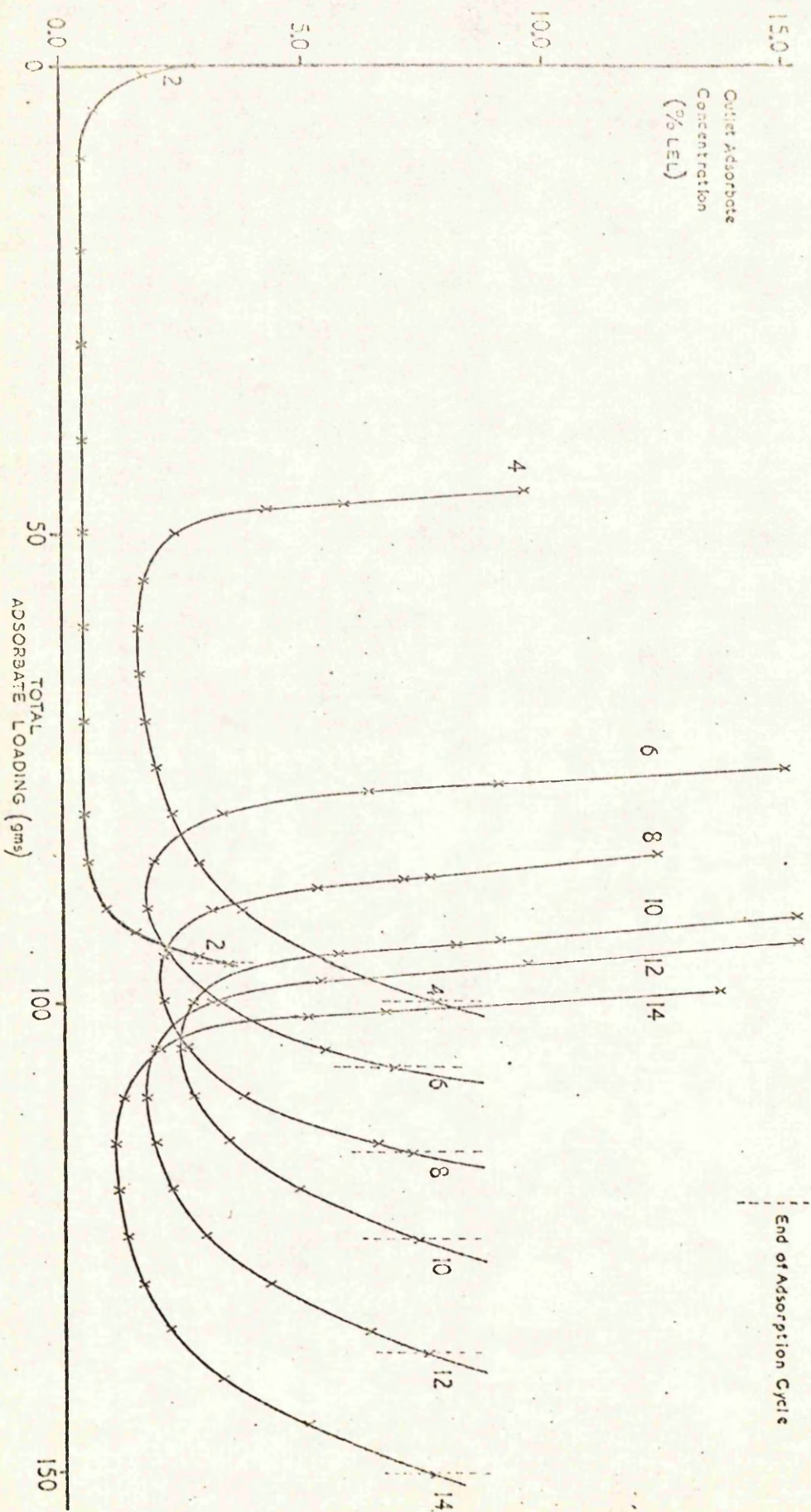


Fig.108.

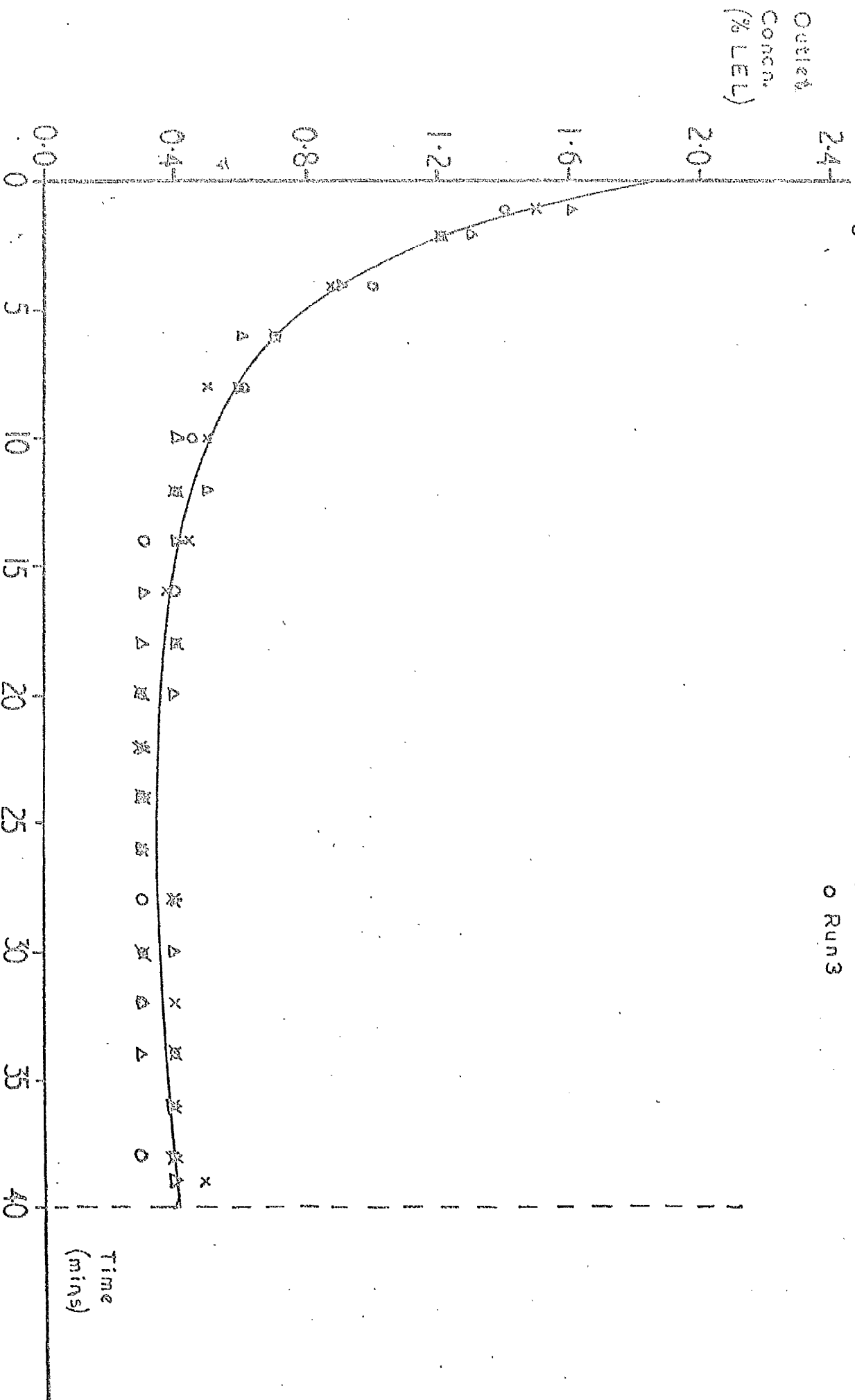


Fig.109.

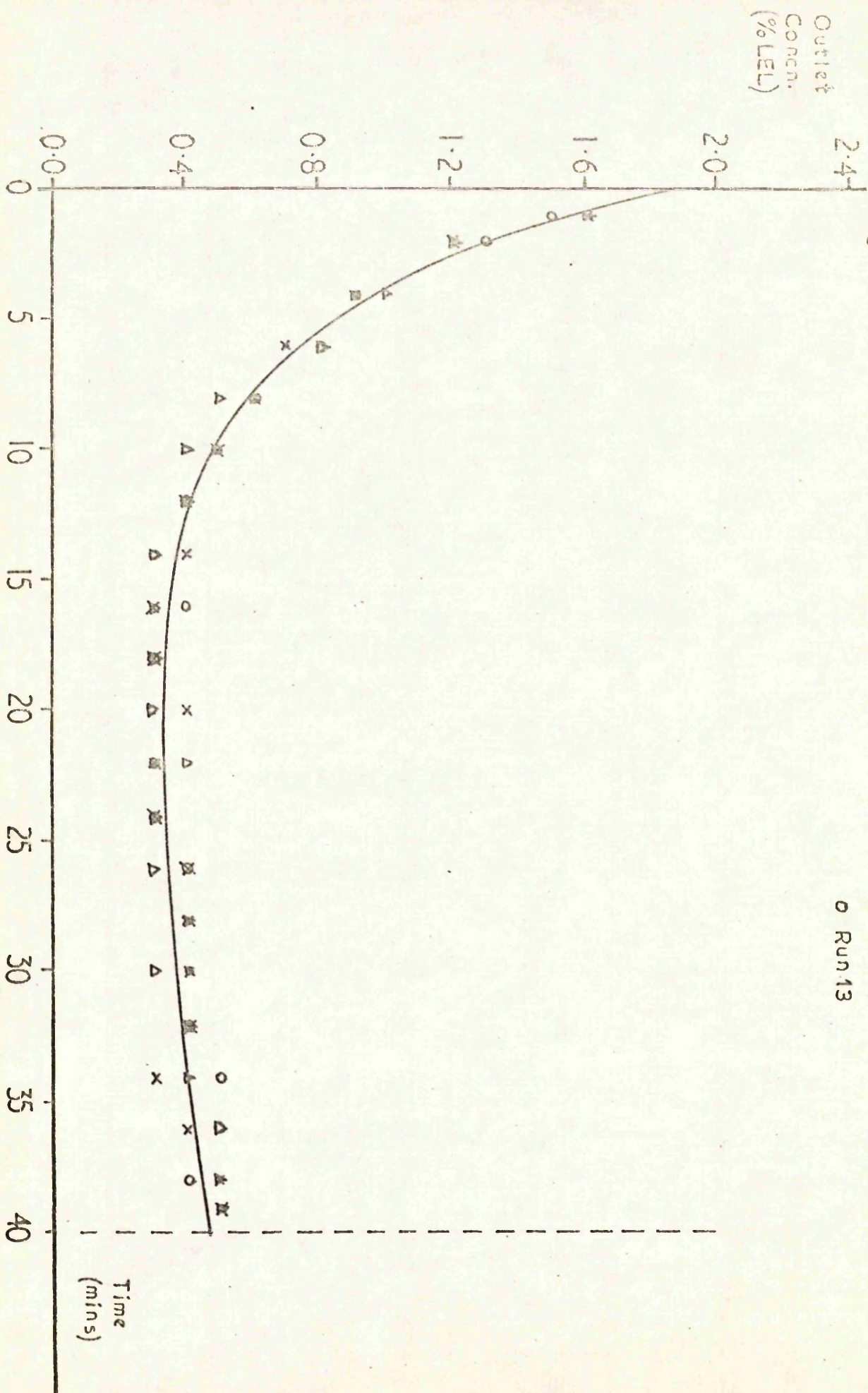


Fig.110.

Outlet
Concn.
(%LED)

x Run 19
Δ Run 21
o Run 23

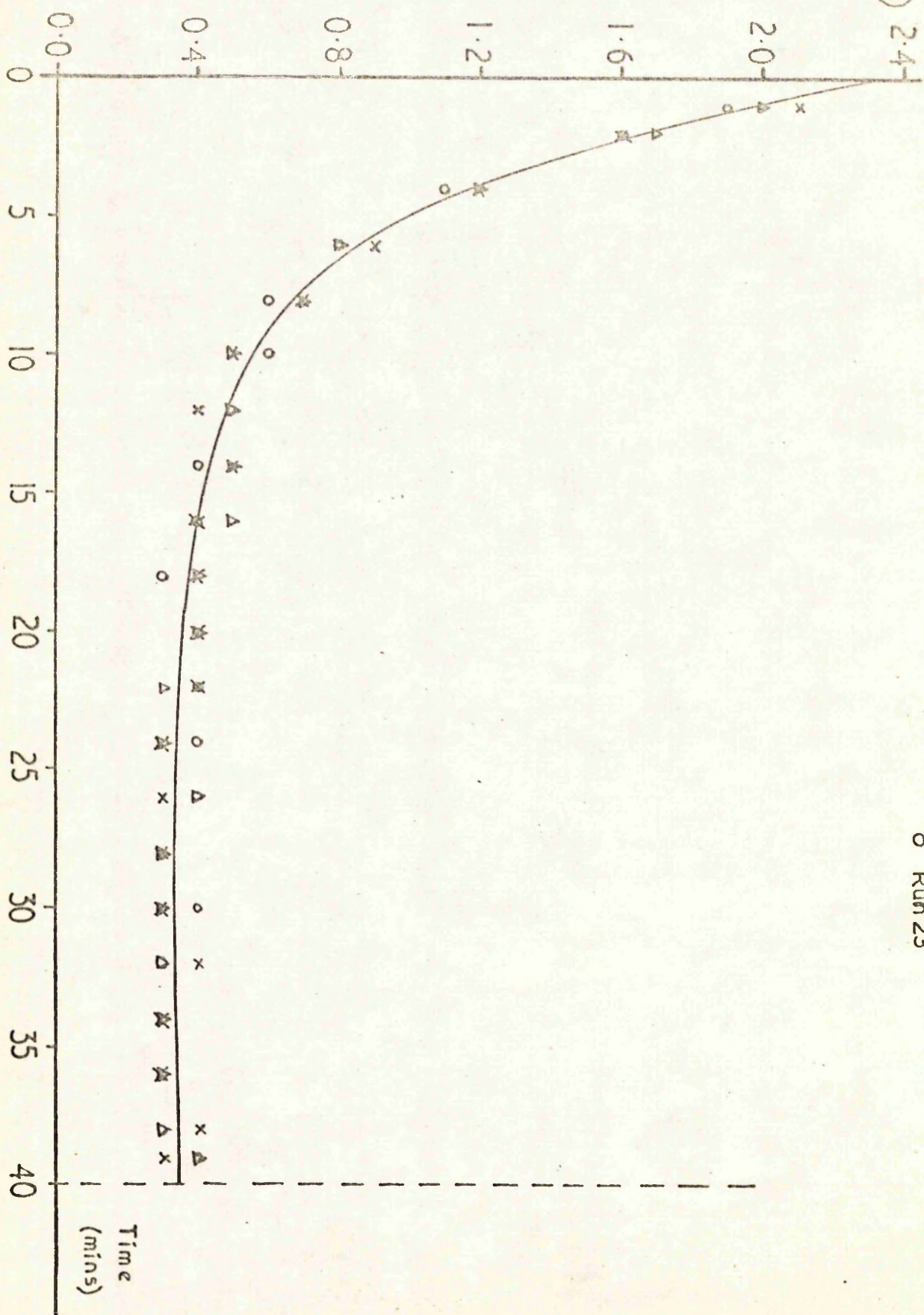


Fig.111.

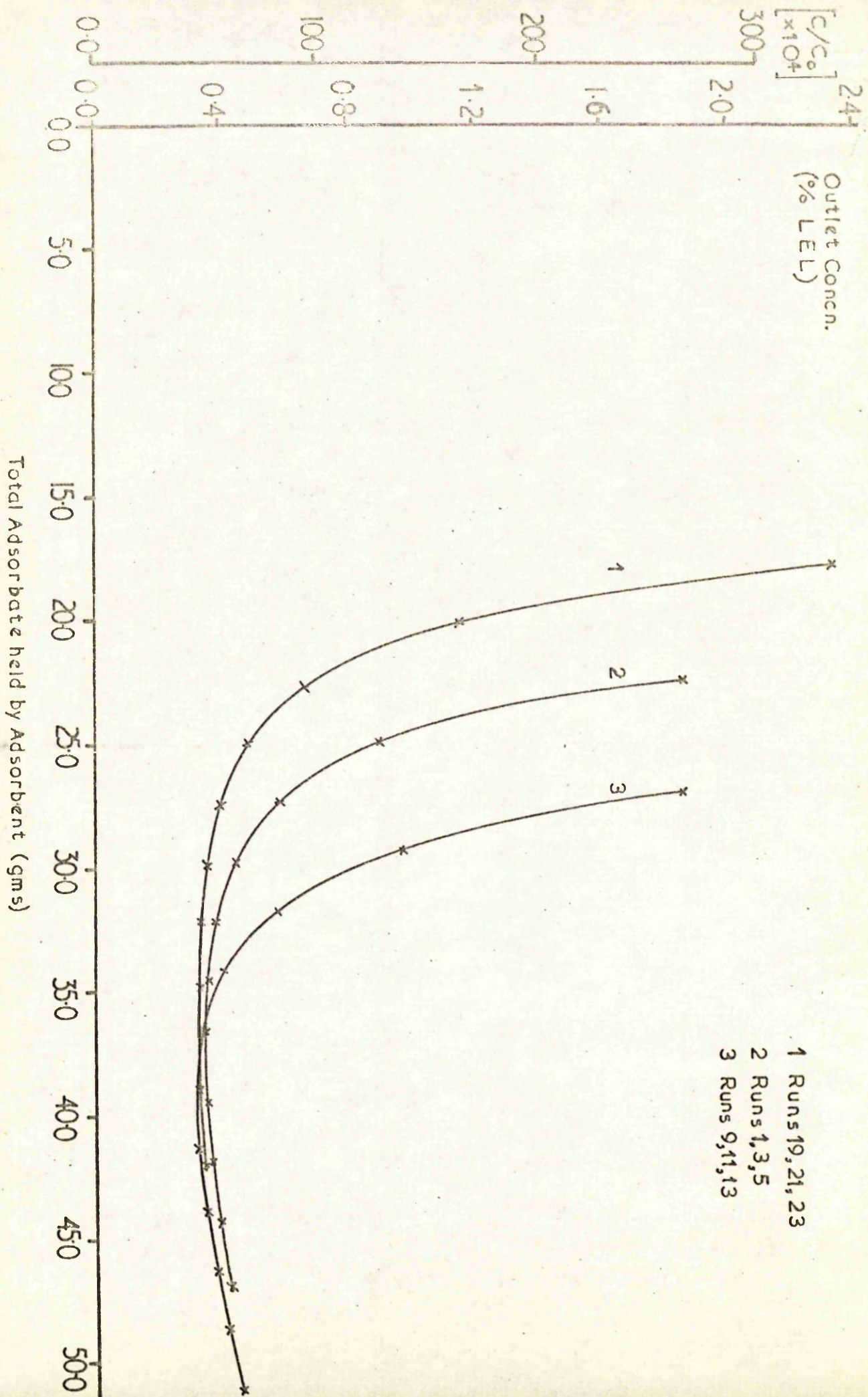
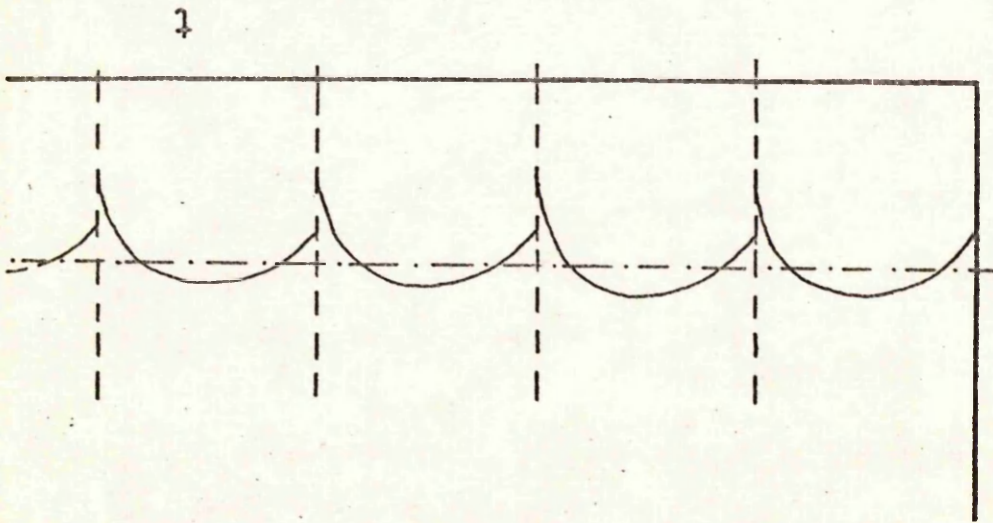


Fig. 112.

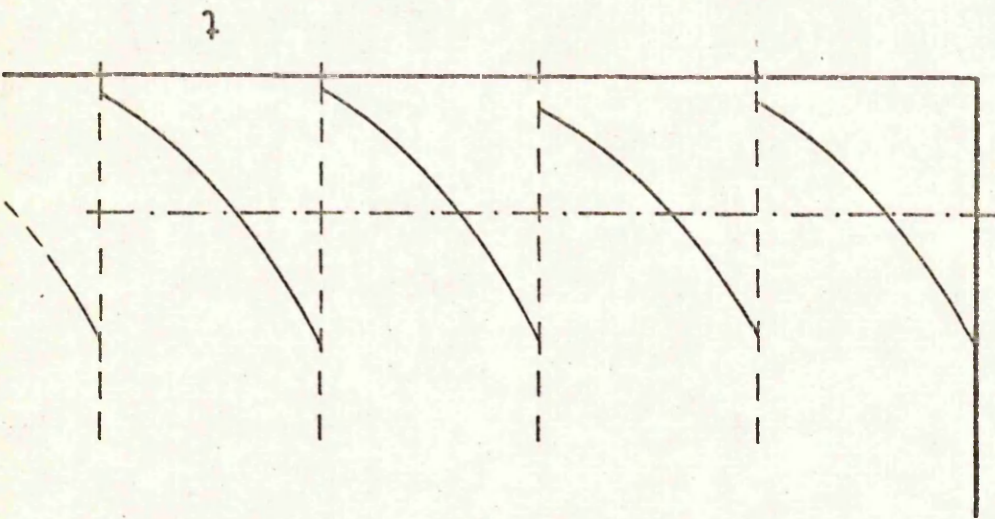
(a)

Absorption
Rate



(b)

Adsorbate
Recovery
Rate



(c)

Total
Adsorbate
Loading
(L)

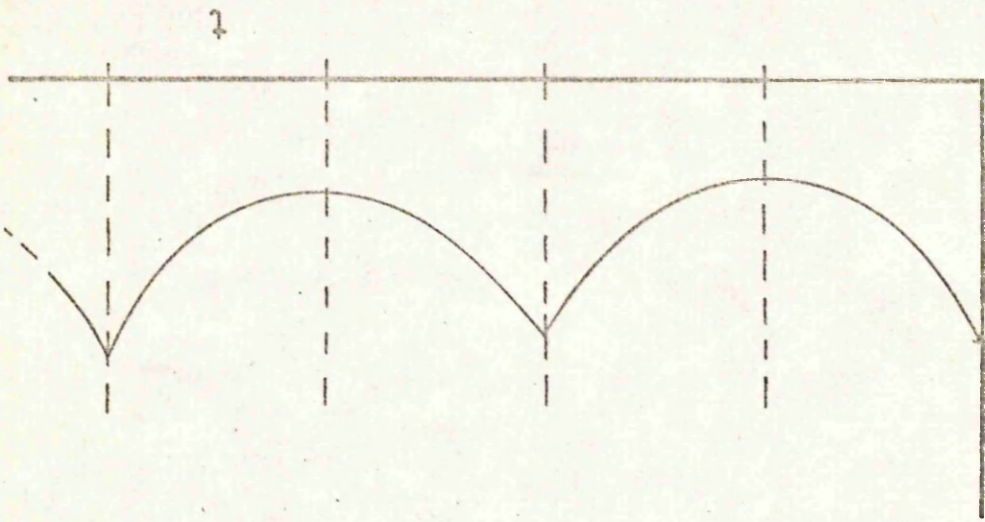


Fig.113.

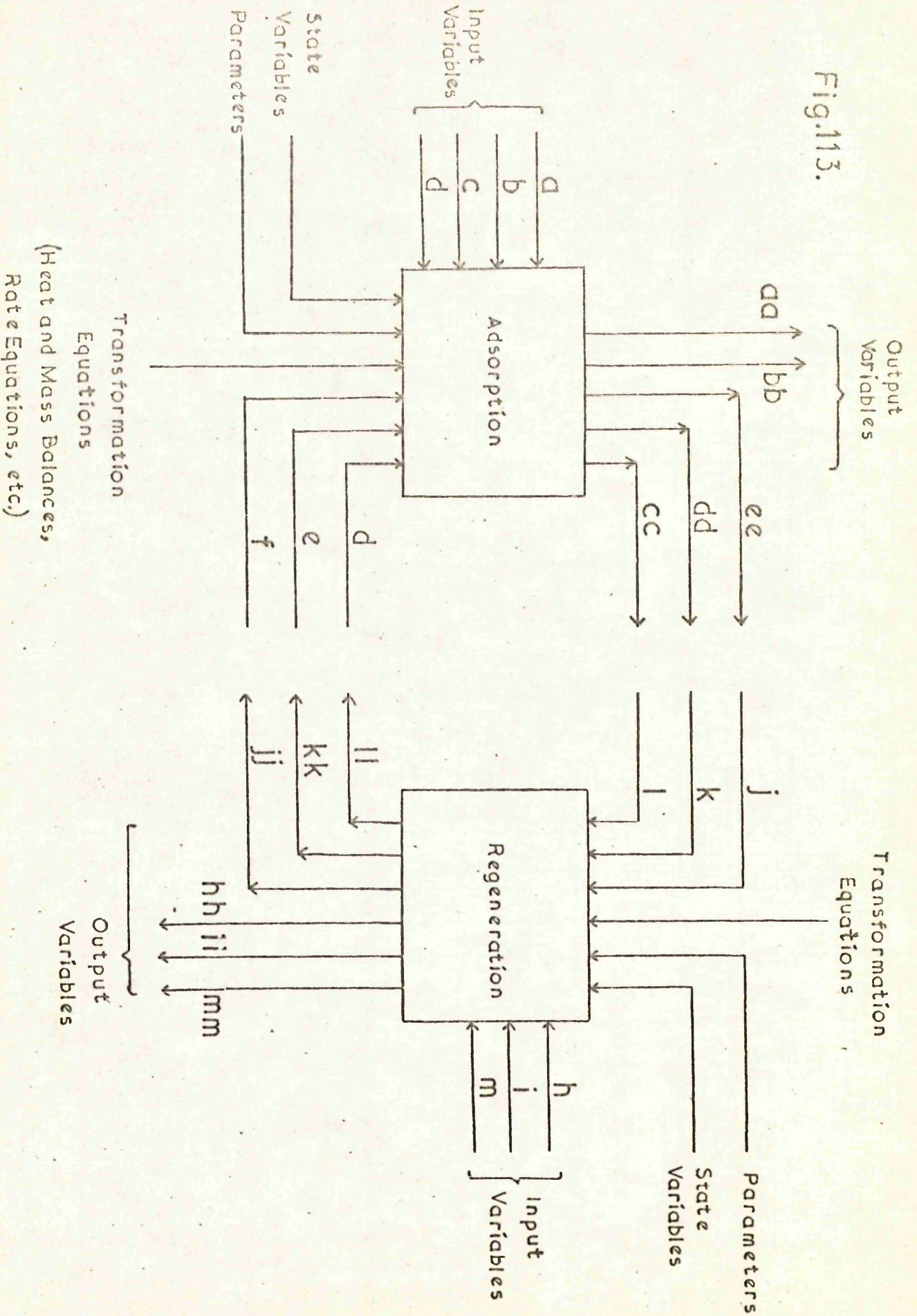


Fig. 114.

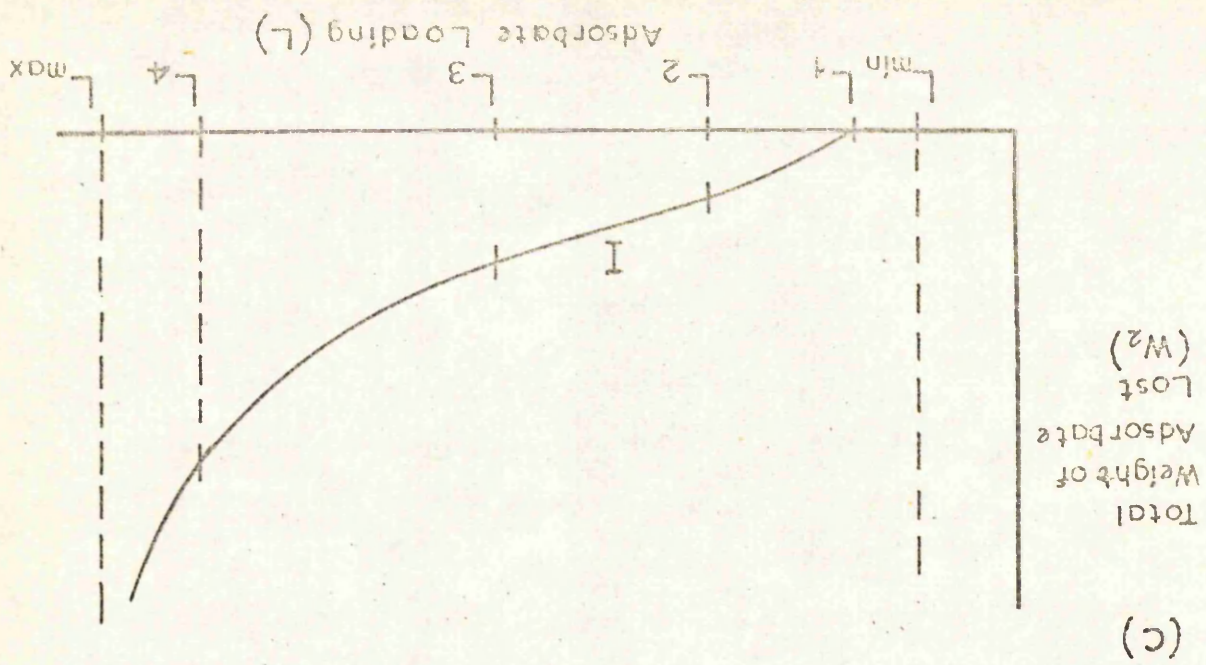
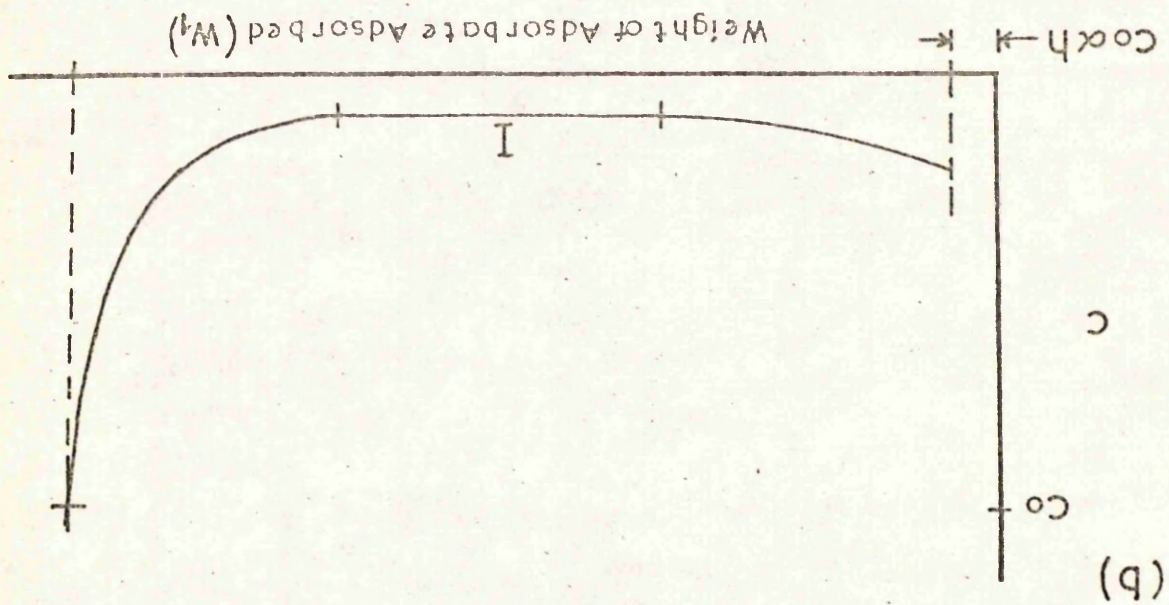
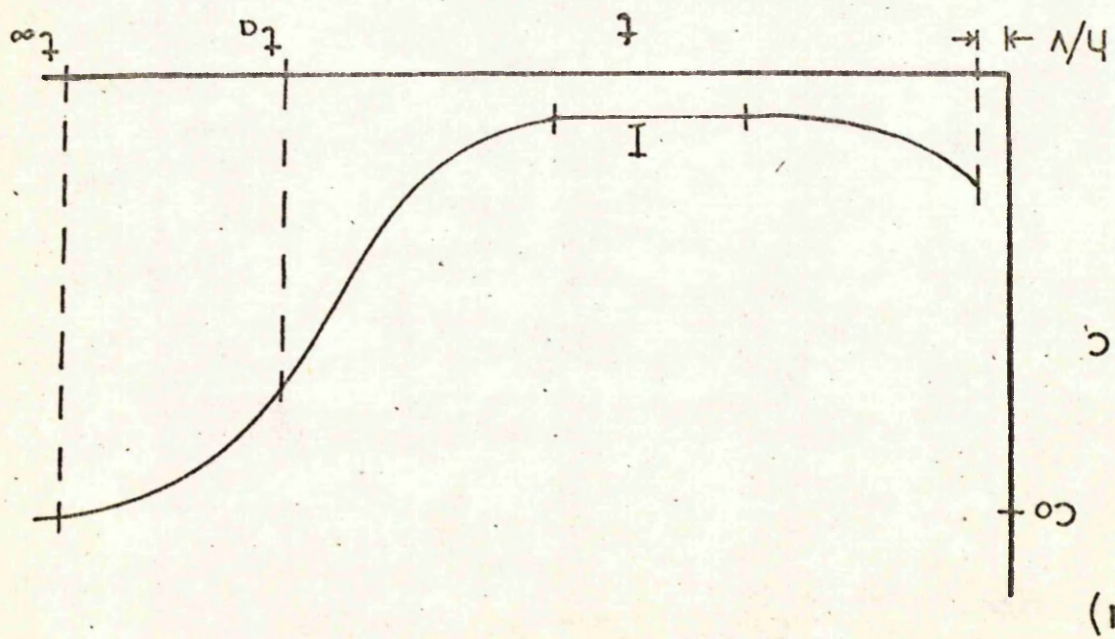


Fig. 11.5.

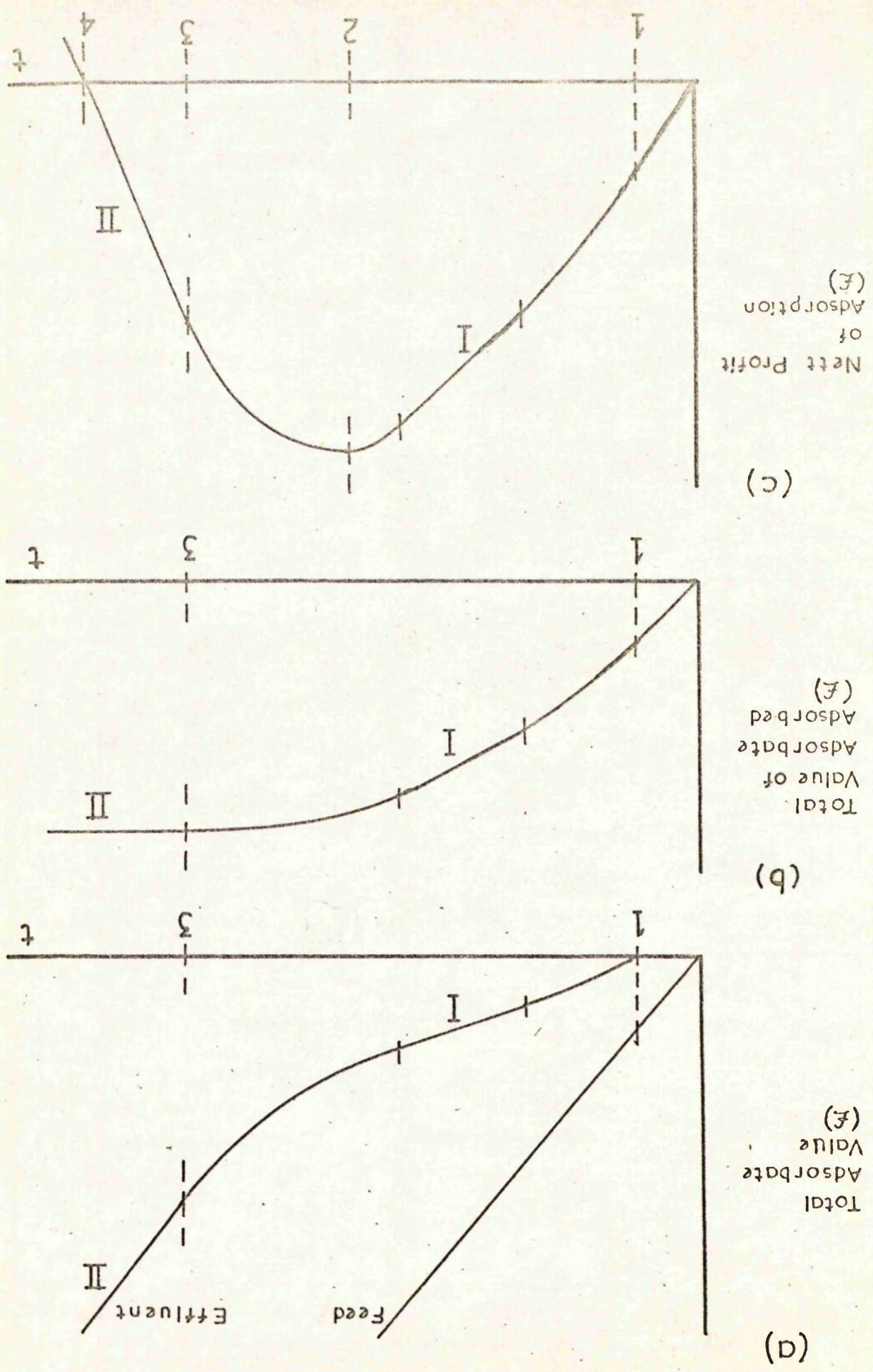


Fig. 116.

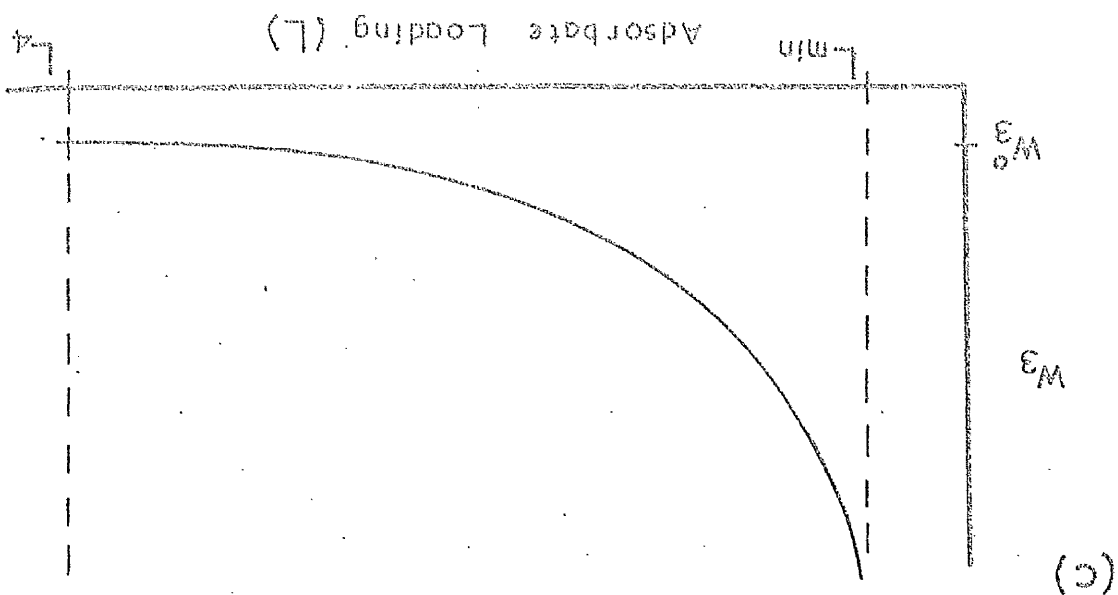
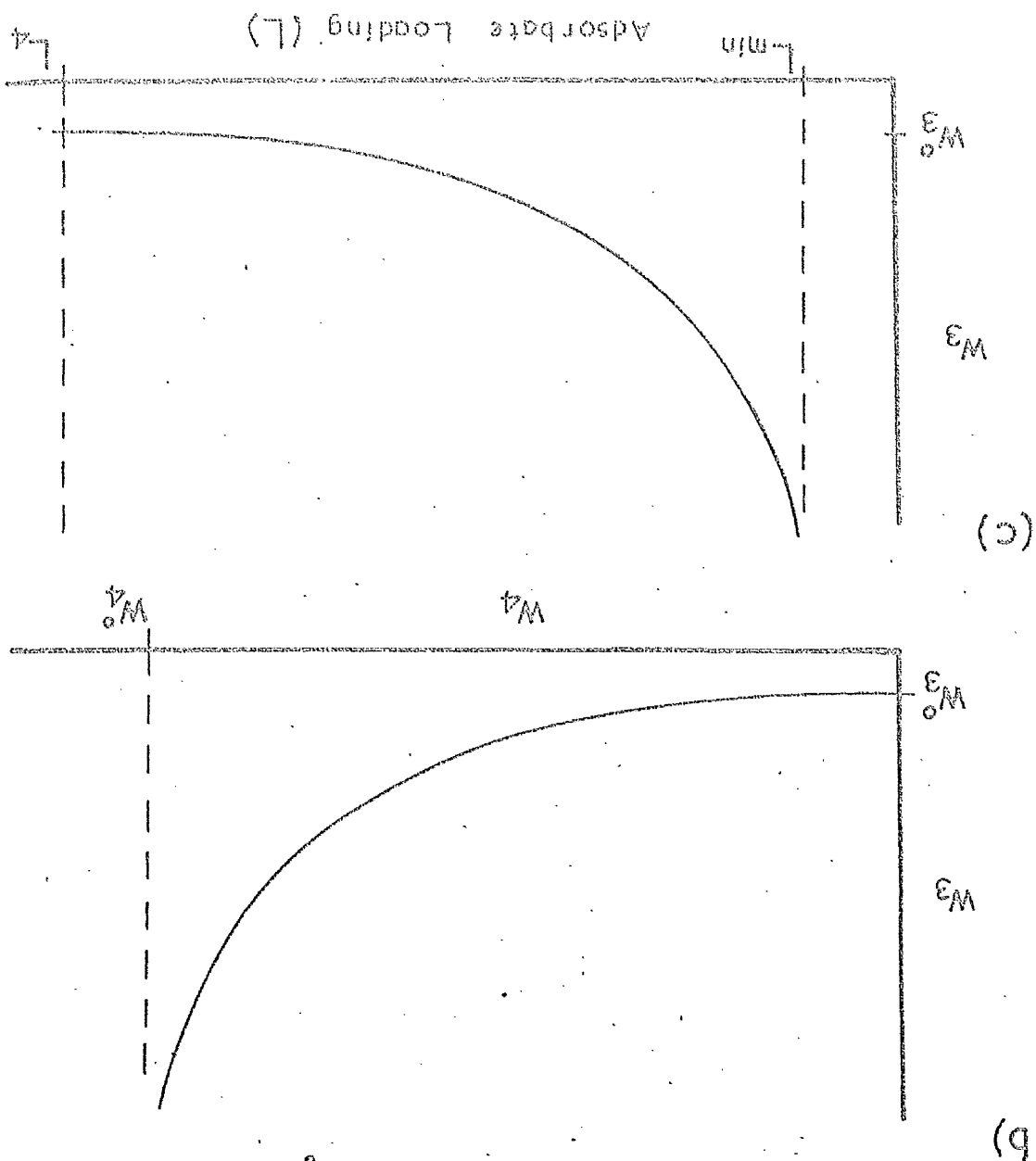
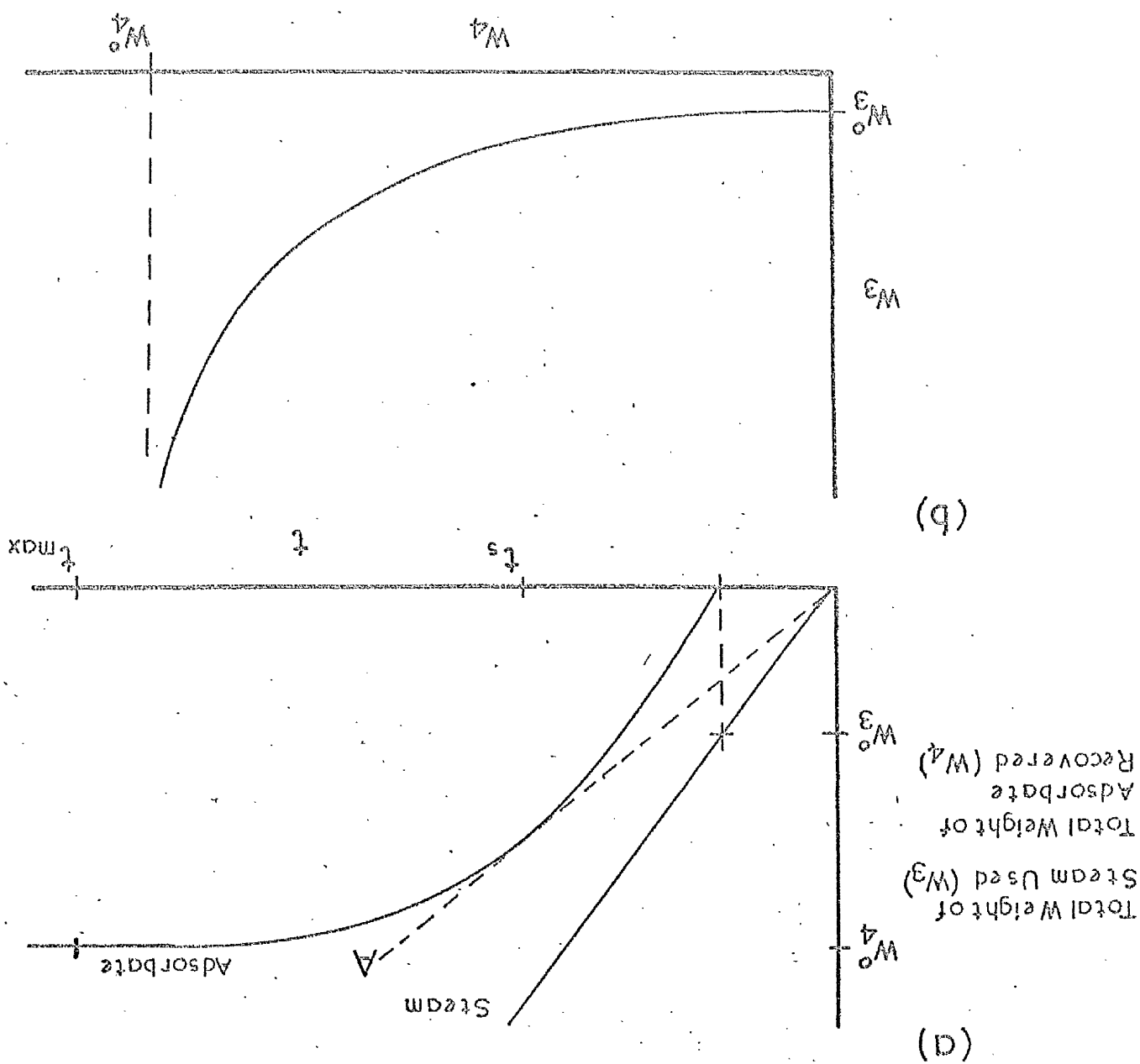


Fig. 117.

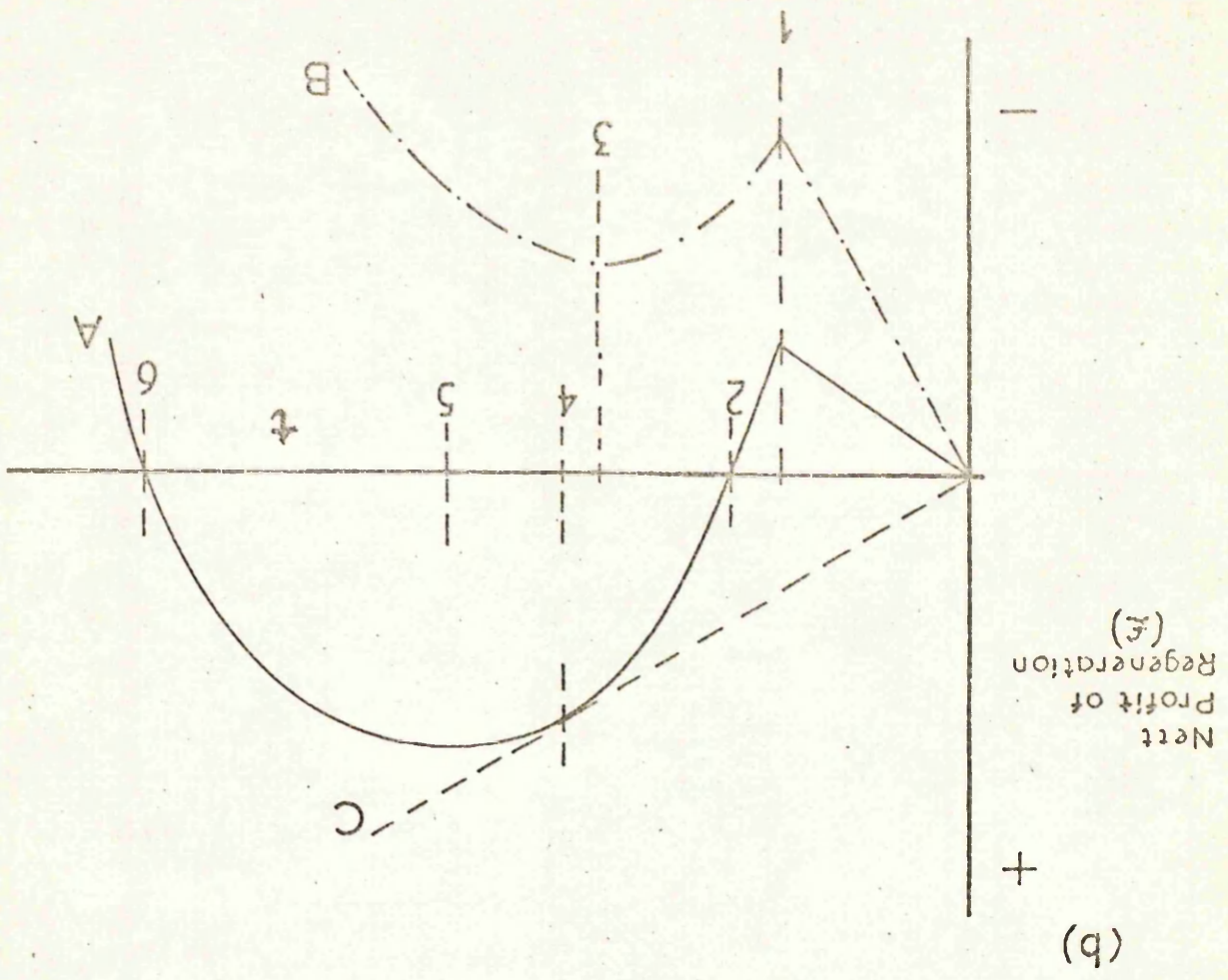
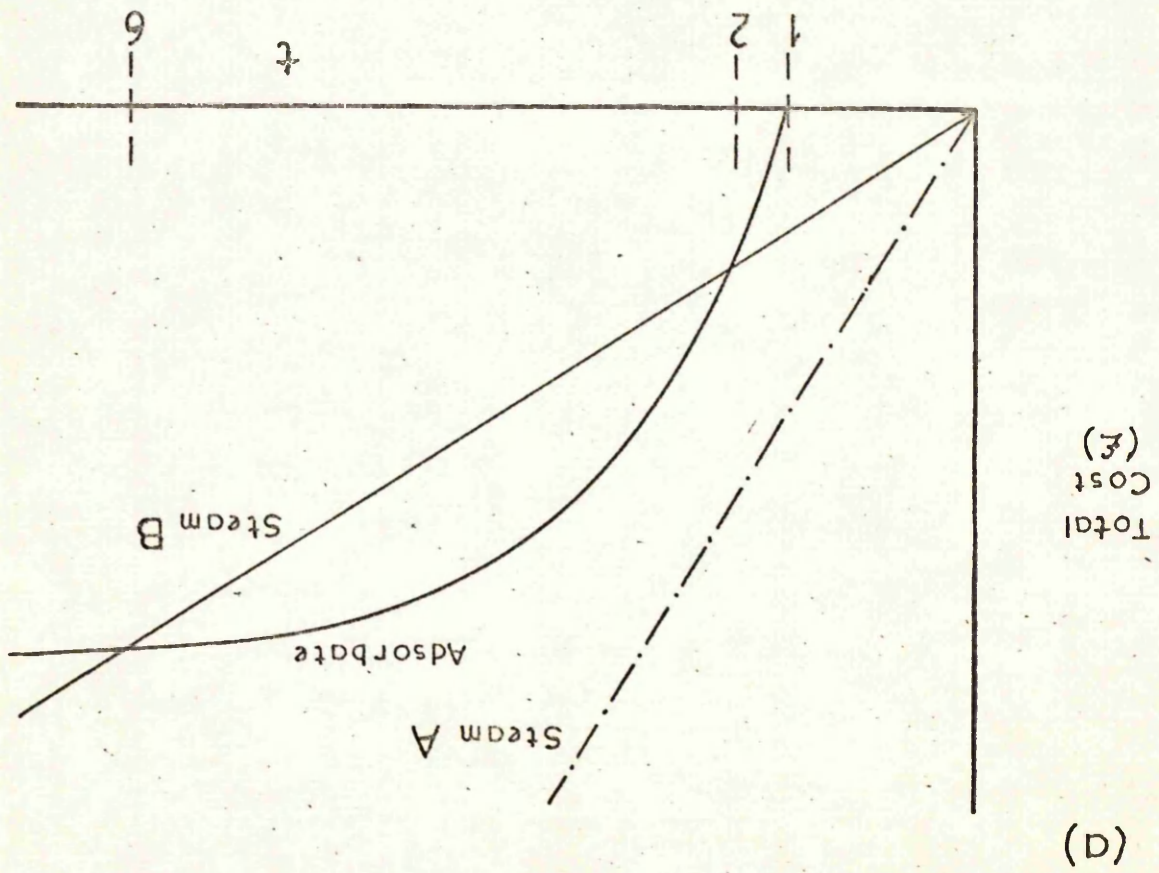


Fig.118.

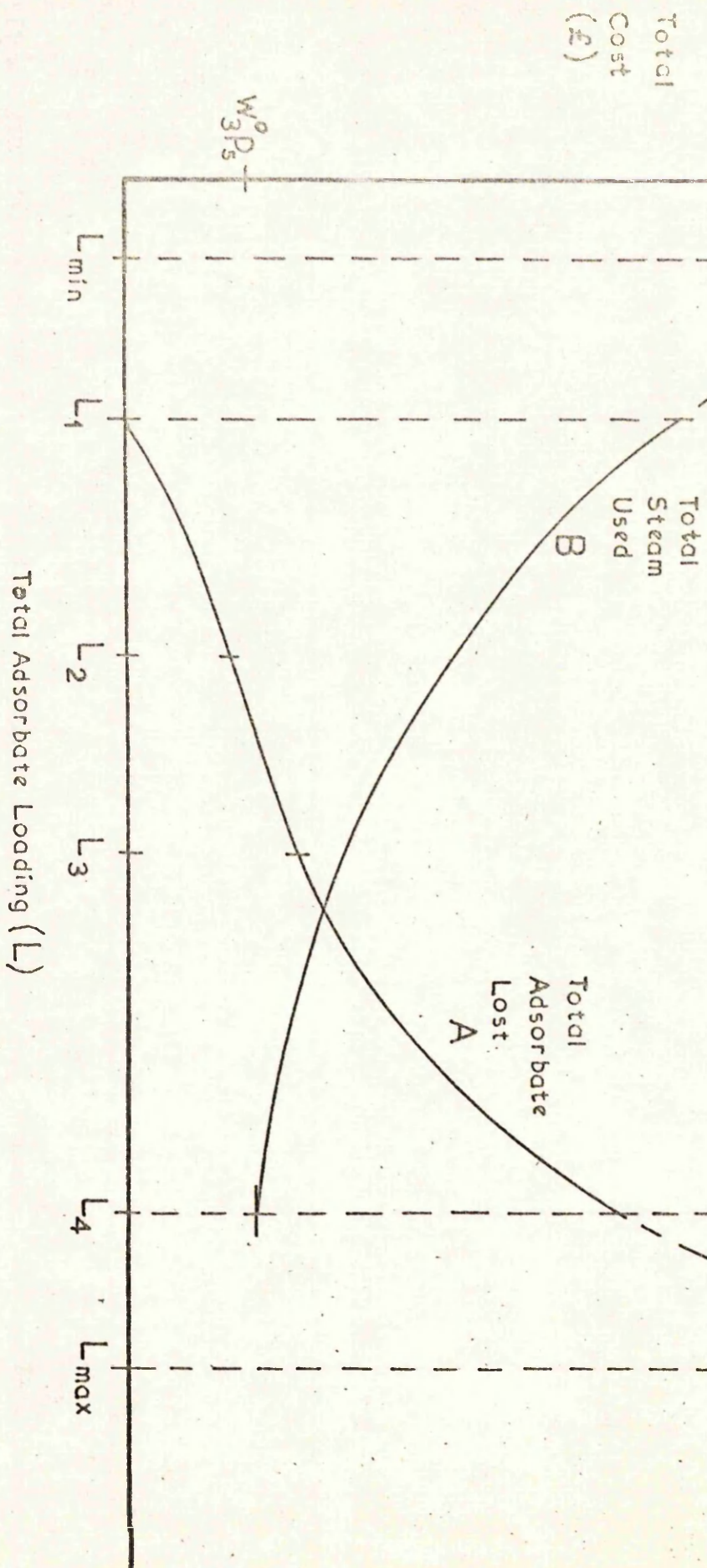
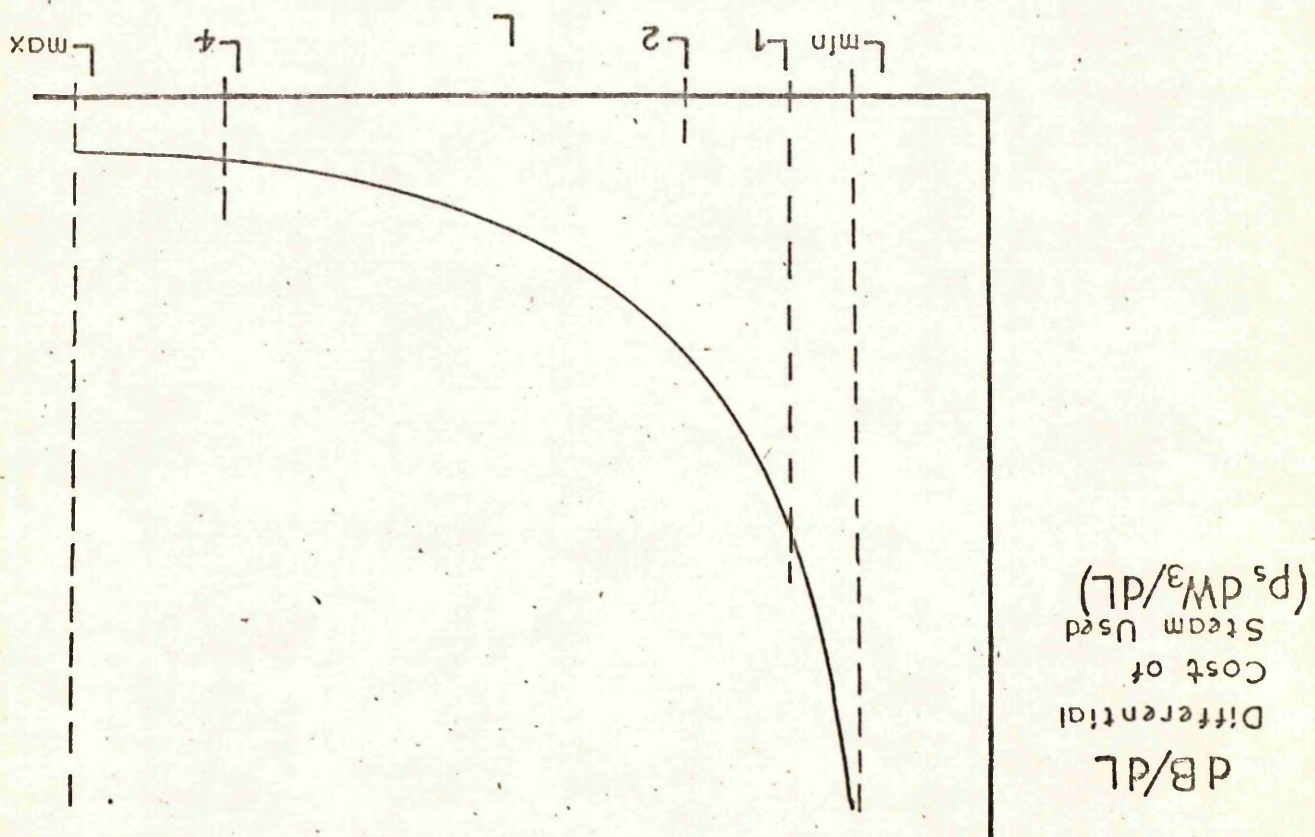


Fig. 119.

(d)



(b)

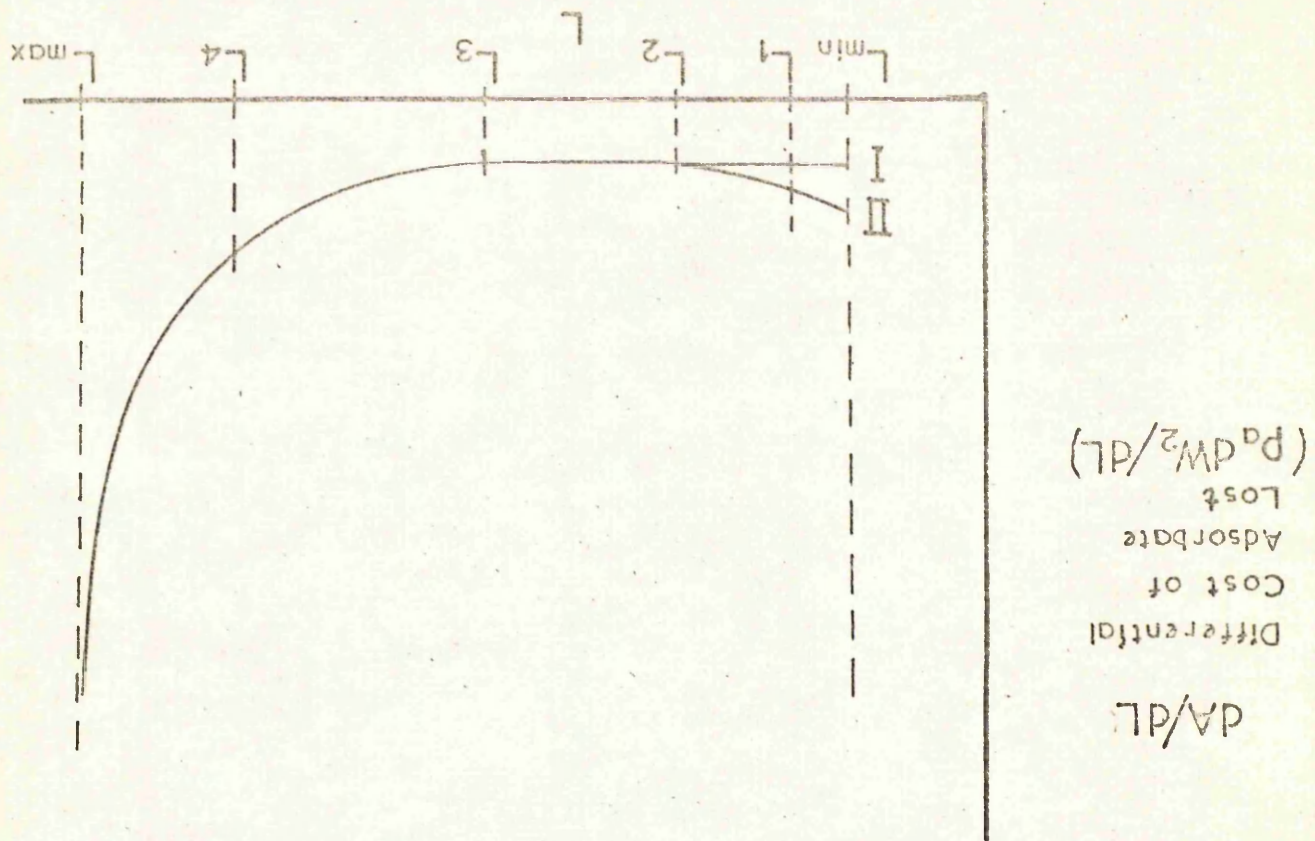
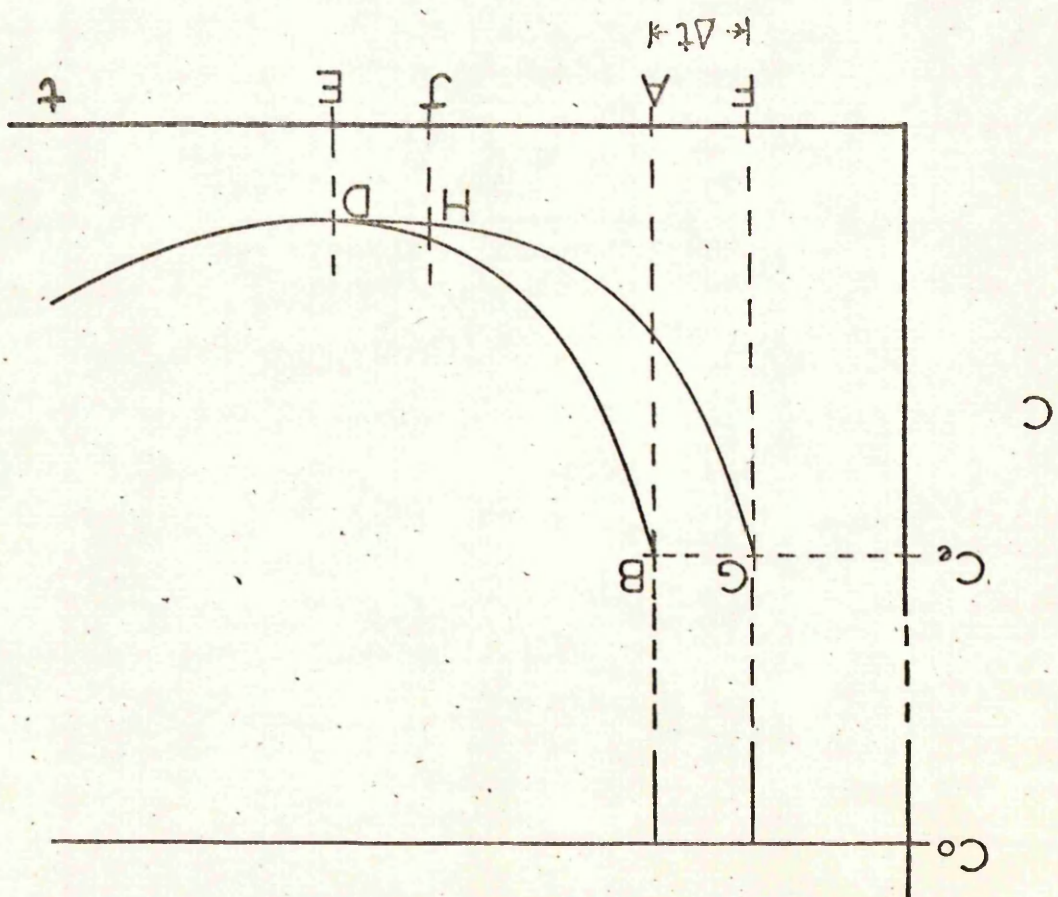


Fig. 120.

(a) Type I



(b) Type II

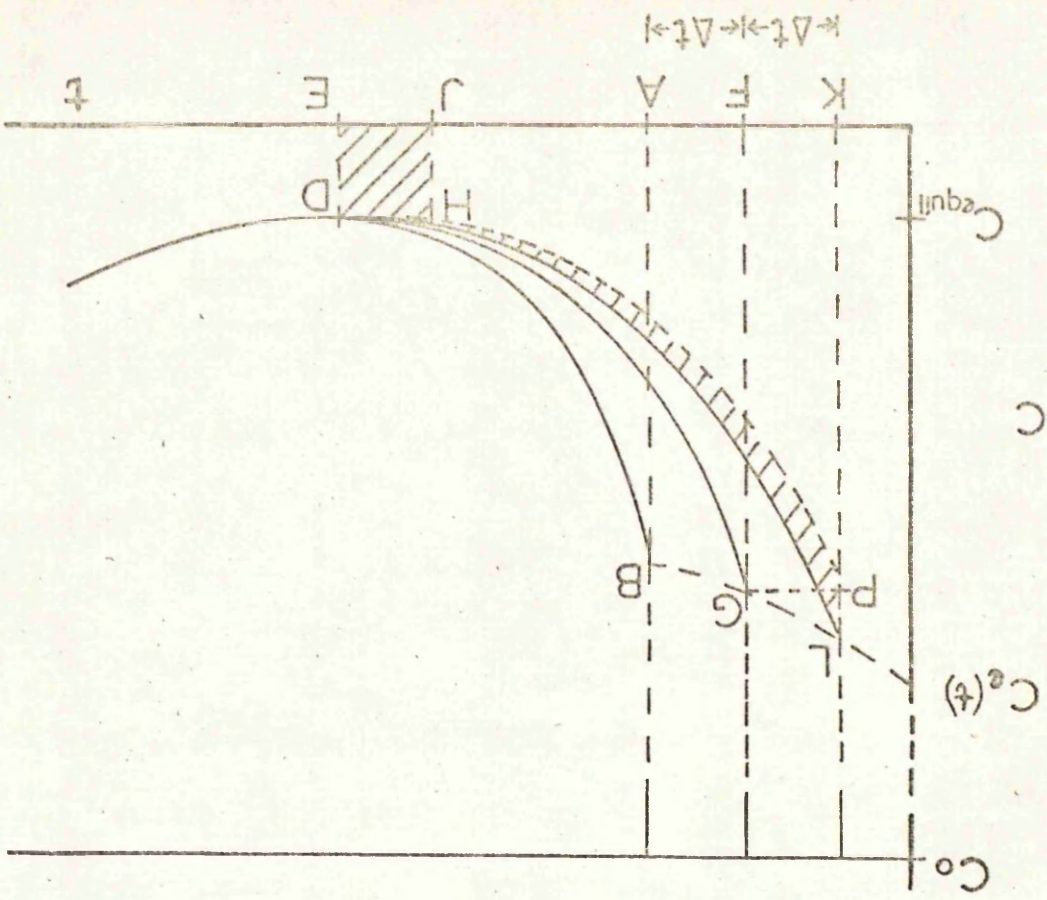
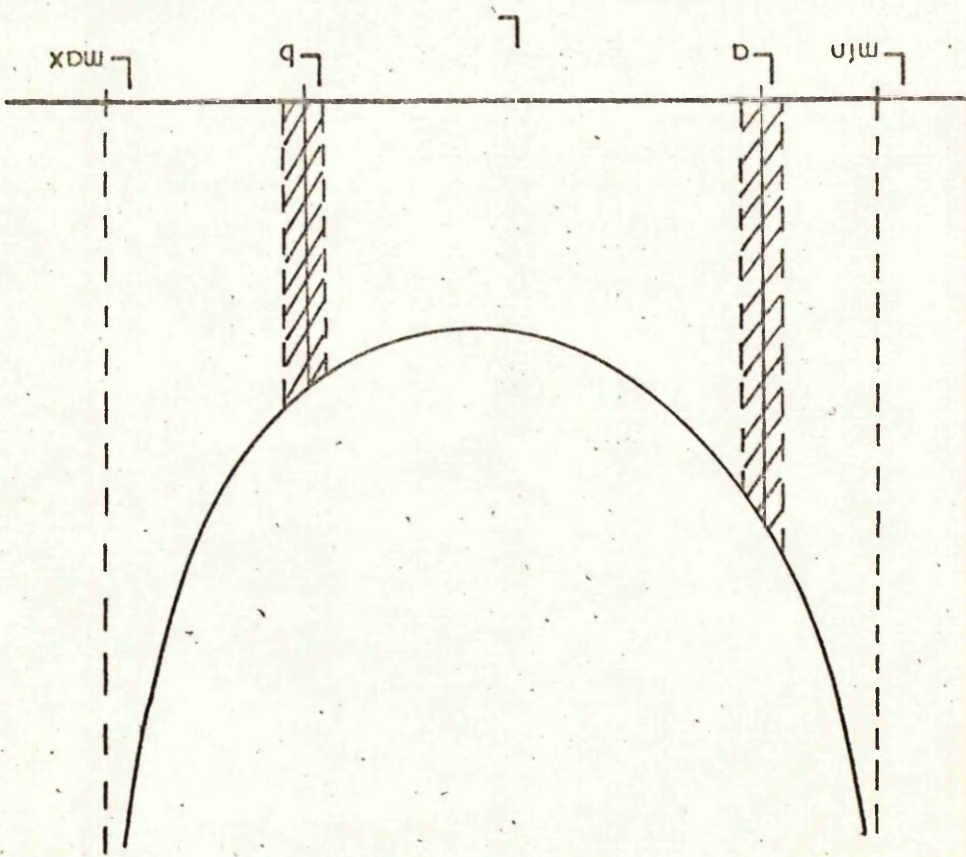


Fig. 121.

(a)

Total
Differential
Cost
(£/lb)



(b)

Cost
per unit
Loading
(£/lb)
Minimum
Cost

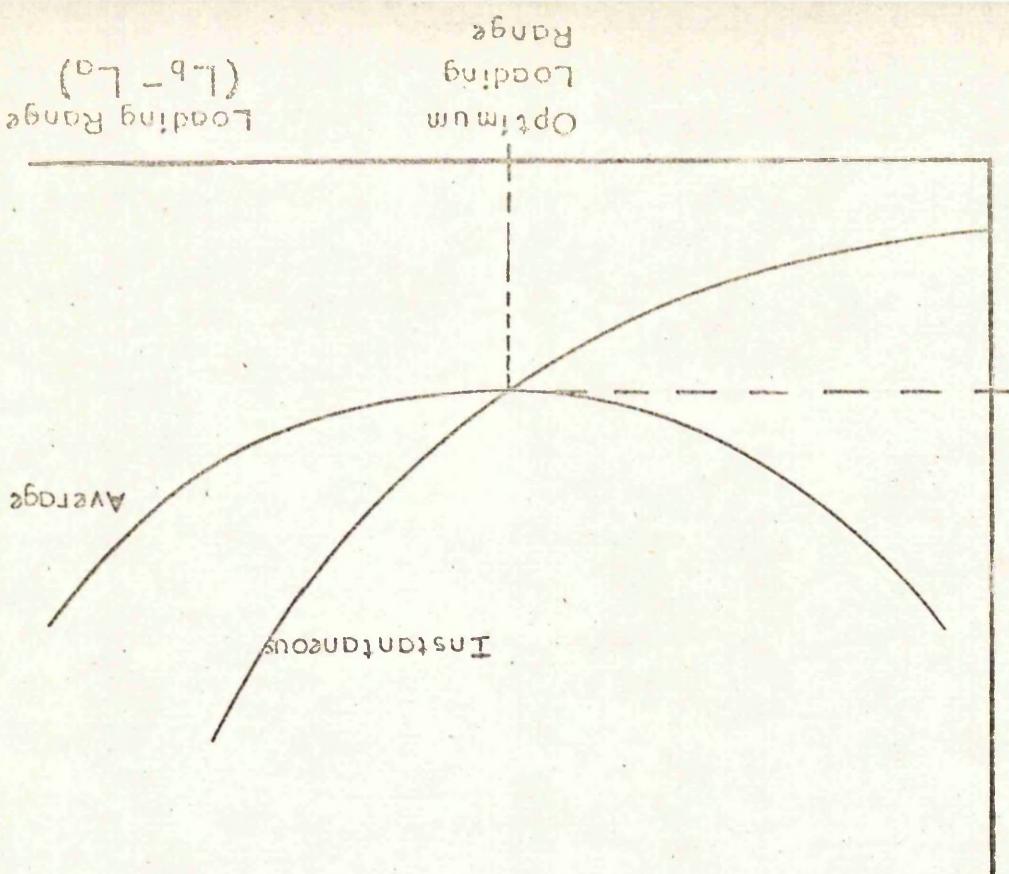
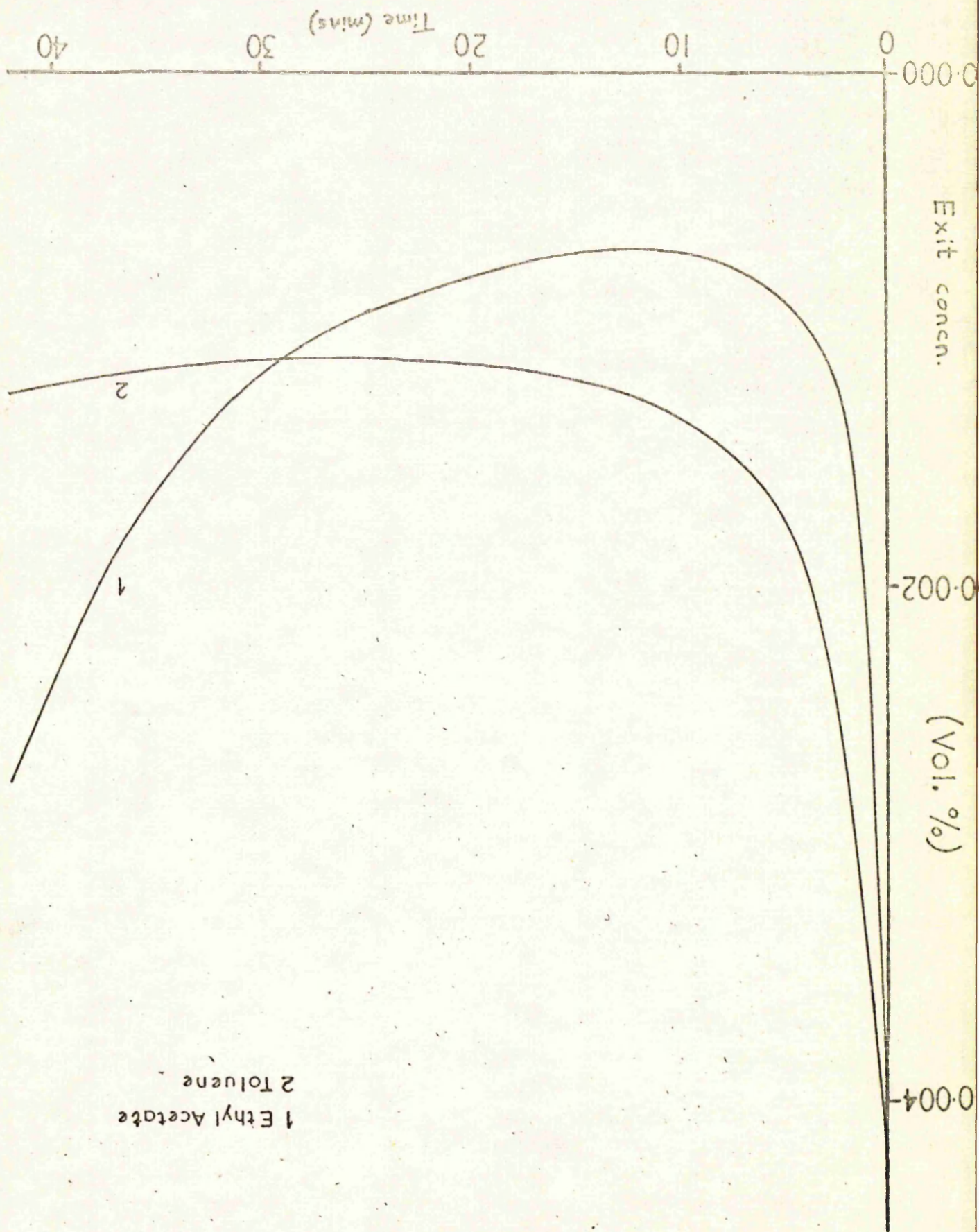


Fig. 122. Plant A



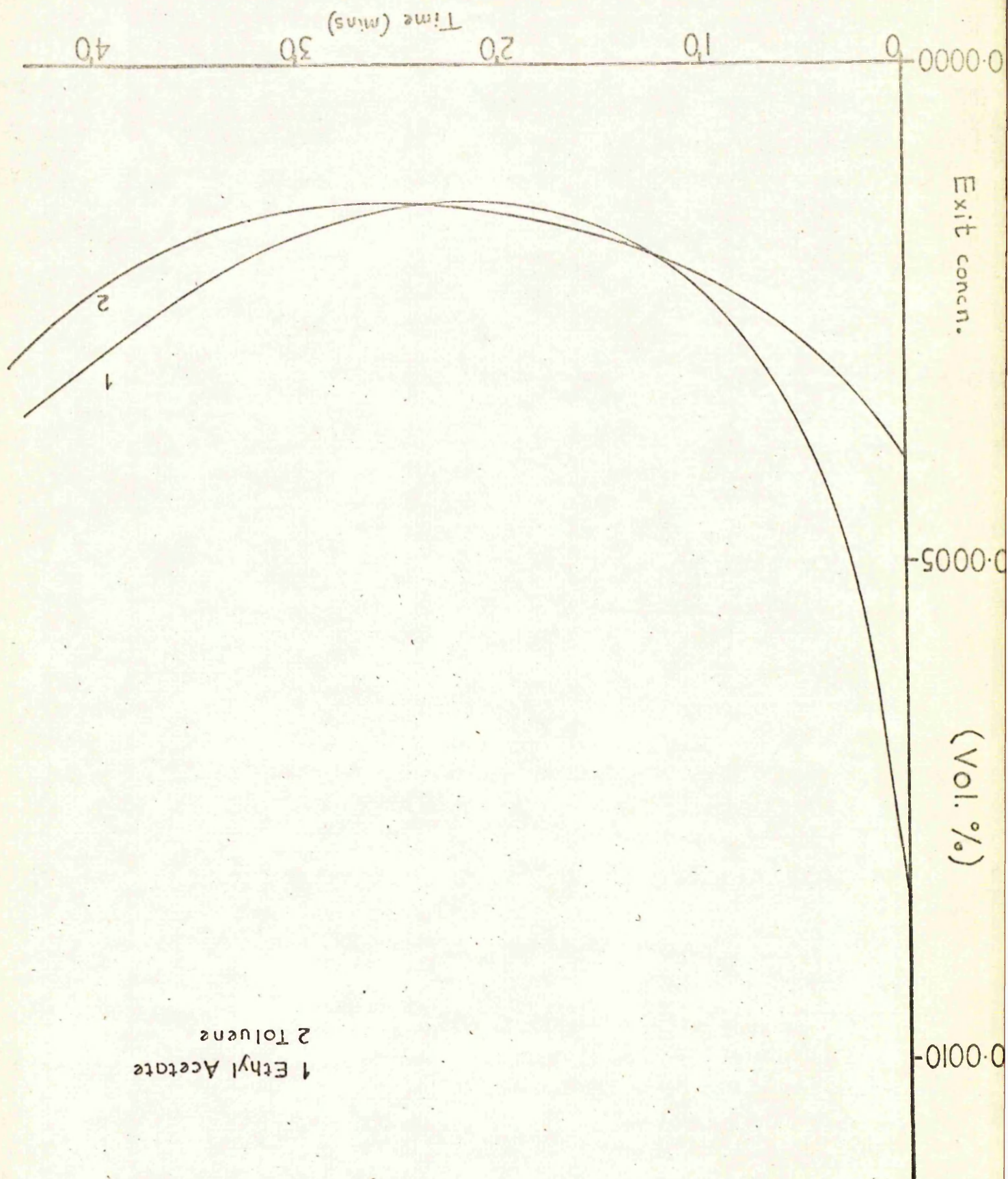


Fig. 123. Plant B

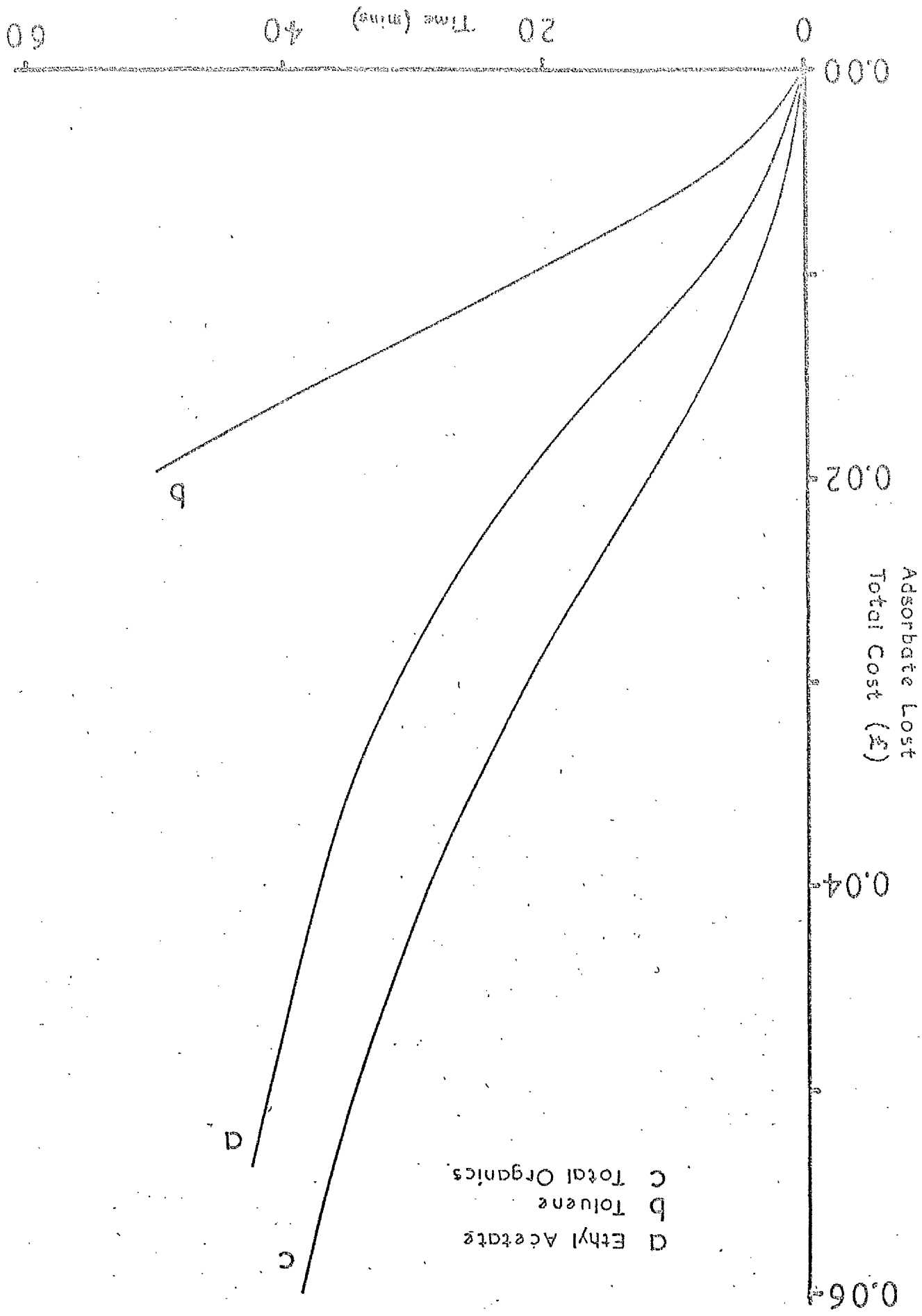


Fig. 124.

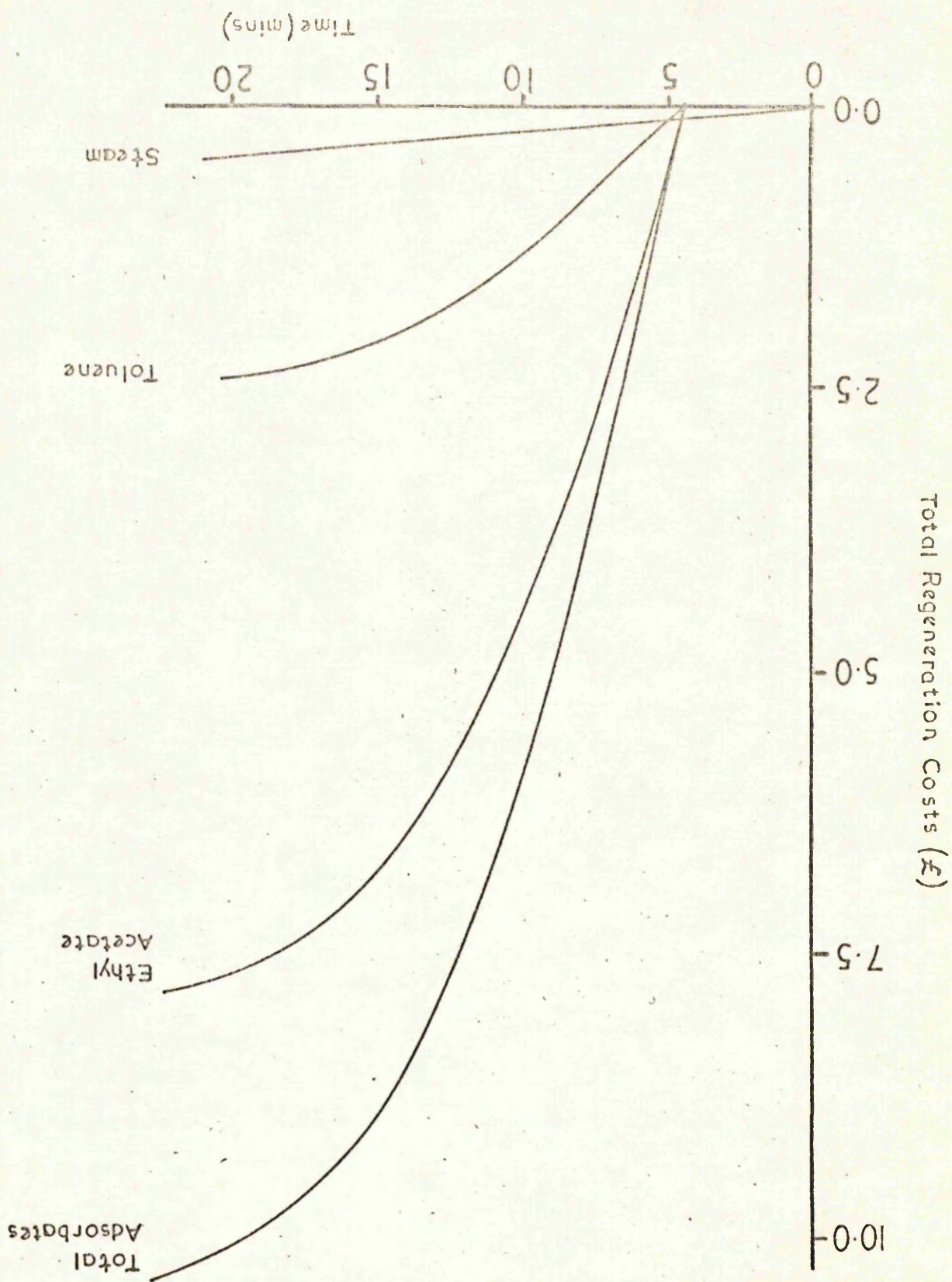


Fig. 125.

Fig.126.

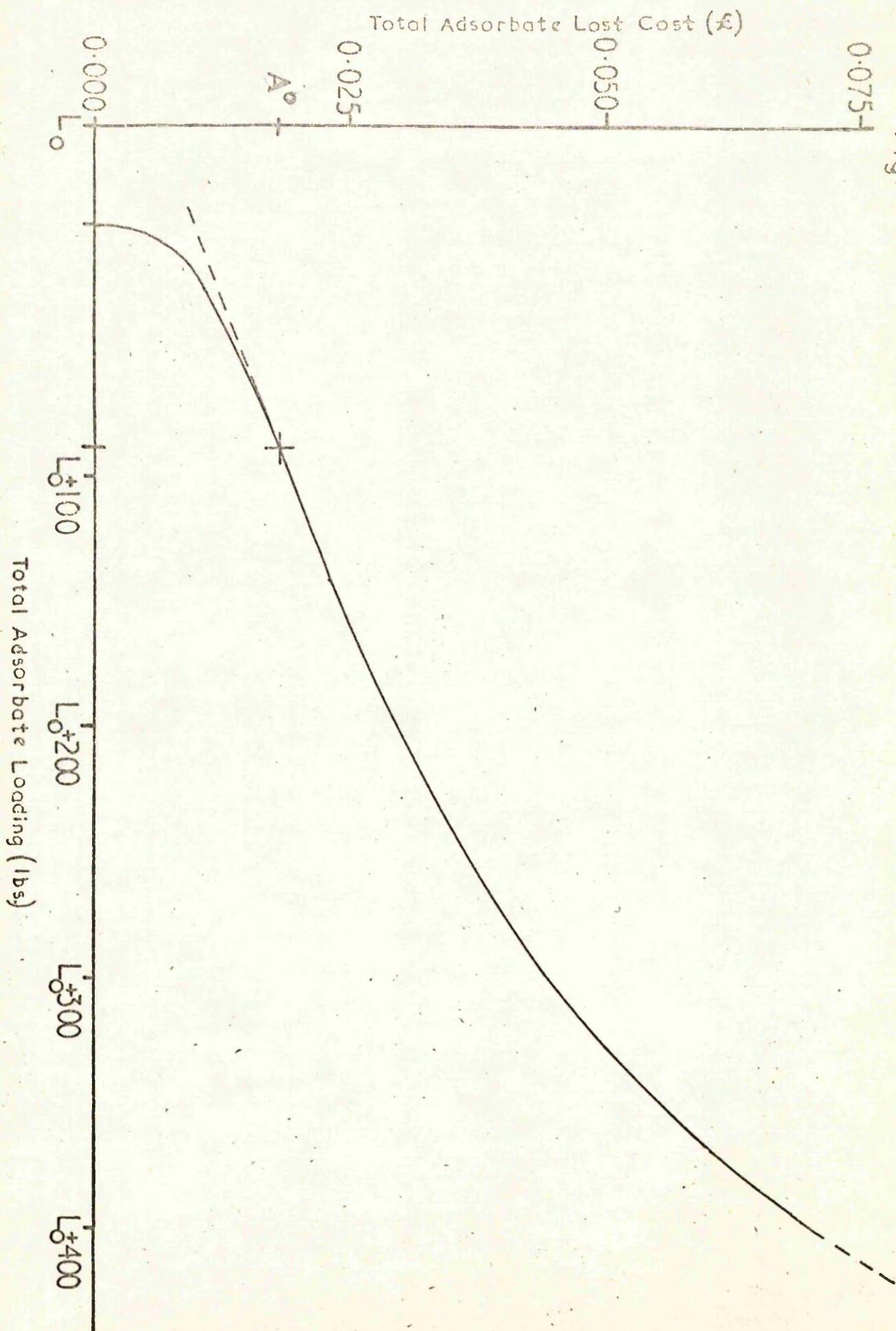
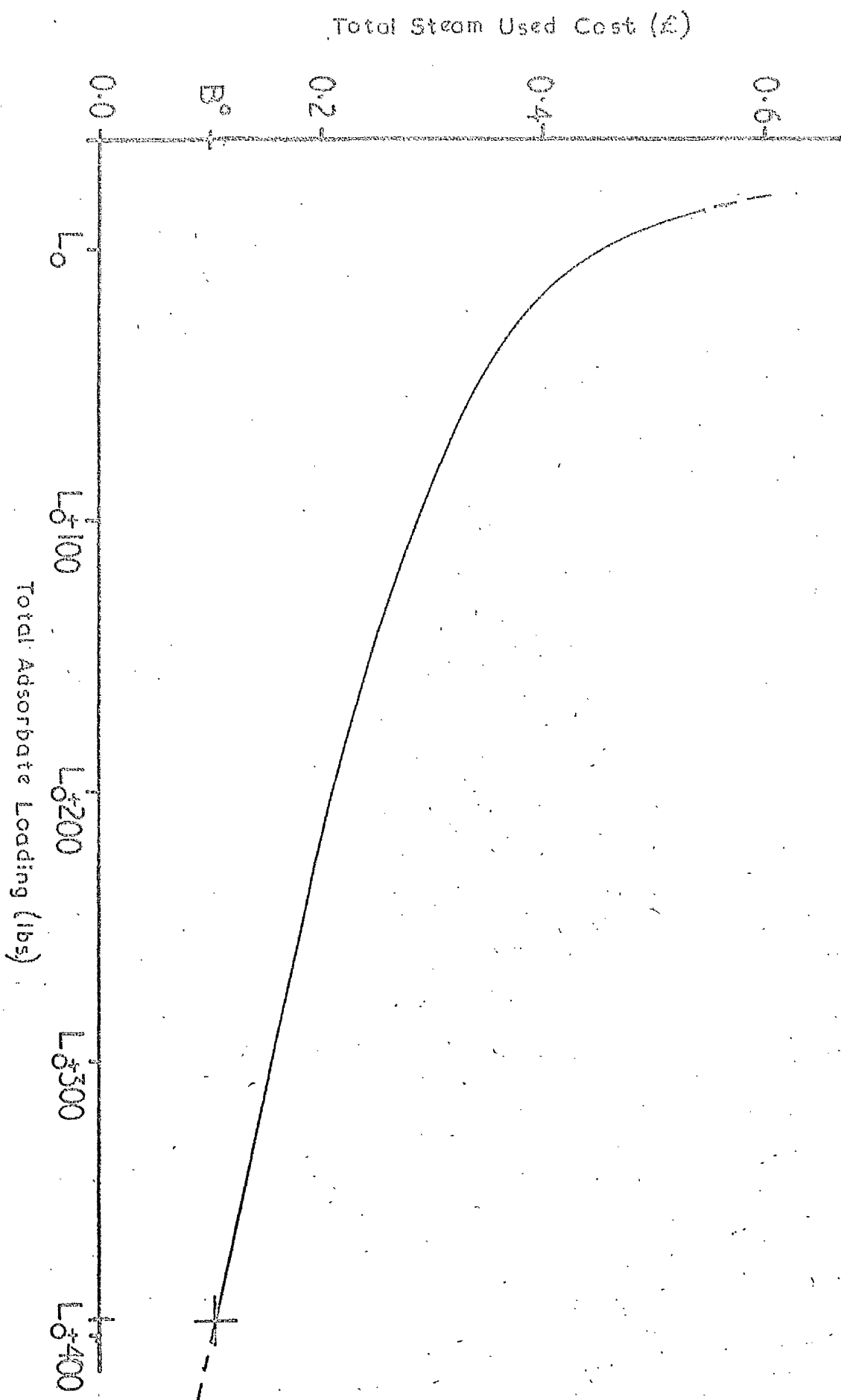


Fig.127.



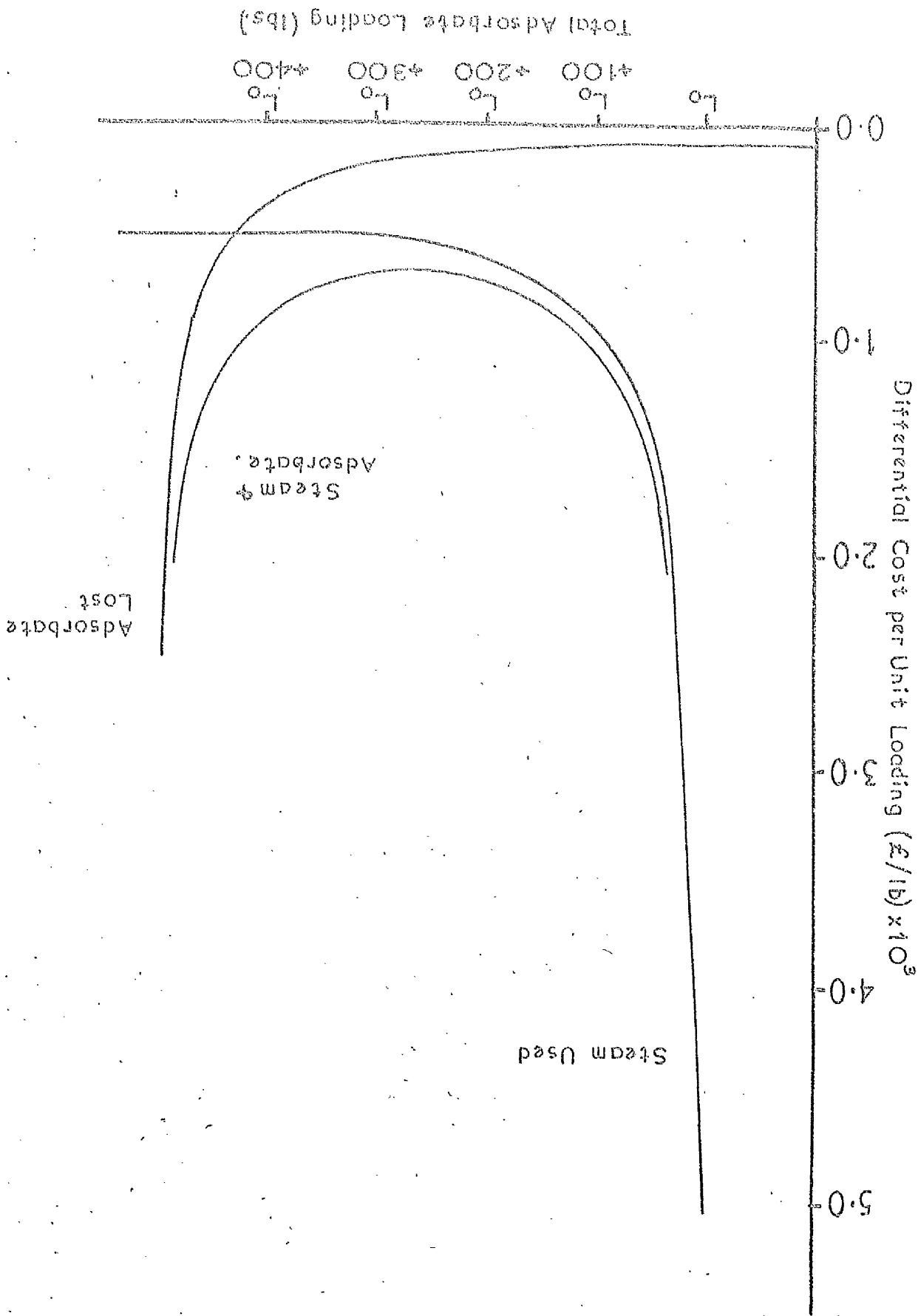


Fig. 128.

Fig. 129.

