

A STUDY ON THE PERFORMANCE OF A
FIXED-BED ADSORBER

Thesis

Submitted for the Degree of
Doctor of Philosophy
in the
Faculty of Engineering
of the
University of London

by

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AUGUST, 1962

ABSTRACT

An experimental study has been made of the adsorption of carbon dioxide from air using a bed of molecular sieve pellets (type 4A), the object being to compare the relative suitability of the various existing analytical solutions describing the dynamic behaviour of fixed-bed adsorbers, and to test the extent to which the simplifying assumptions may be relaxed before significant deviations occur.

Data have been obtained for the concentration history at different bed depths and conclusions are drawn on the rate-determining mechanism of solid diffusion for this system.

A programme for use with the Mercury Digital Computer for the analysis of such data, has been developed.

ACKNOWLEDGEMENTS

I wish to express my gratitude to:

Professors D.M. Newitt, F.R.S., and R.W.H. Sargent, Ph.D., D.I.C., for the supervision and guidance in carrying out the research work described in this thesis.

Mr.L.O.Dworjanyn, my colleague, working in the same field, for the many interesting discussions.

The Director and Staff of the Computer Unit, University of London, and Mr. S. Michaelson and Miss E.R.Fenn of the Mathematics Department of the Imperial College, for the facilities made available for carrying out the Computer work.

The late Mr.A.C.V. Sweeting,

Mr. J.S. Oakley and his workshop staff and in particular Mr. A.R. Barnes and Mr. J.F. Harman, for the help given in setting up the apparatus used for this investigation.

The United Nations Educational, Scientific and Cultural Organisation, Paris, for awarding me a Fellowship for studying in the United Kingdom.

The Government of India and the University of Madras for sponsoring my candidature for the Fellowship.

The British Council, London and in particular, Mr.C.J. Ritchie, Director, and Miss B.I.Hubbard, Programme Organiser, of the Fellowship Department, for making my stay in the United Kingdom

comfortable and educative.

My thanks are due to Mrs. Yamuna Madhavankutty for the help rendered in faircopying the manuscripts and to Miss J. Rogers of The Cranley Typing Office for the final printing.

- K.Chandrasekharan

"Kattradu Kaimannalavu Kalladulagalavenruttra
Kalaimadandai Odugiral"

- A Tamil Poem.

Translation:

"What has been learnt is just a handful;
What remains is large as the world - So
Speaketh the Goddess of Learning"

CONTENTS

	Page
ABSTRACT	2
ACKNOWLEDGEMENTS	3
 Chapter 1 - INTRODUCTION	 8
Chapter 2 - EQUIPMENT	27
Chapter 3 - EXPERIMENTAL	42
Chapter 4 - THEORETICAL	56
Chapter 5 - RESULTS & DISCUSSIONS	73
Chapter 6 - CONCLUSIONS	100
NOMENCLATURE	103
REFERENCES	107
 APPENDIX I	 110
SECTION I.1 Column Characteristics	111
SECTION I.2 Molecular Sieves	112
SECTION I.3 Allowable Gas Velocity	113
SECTION I.4 Temperature Profile	114
SECTION I.5 Isotherm	115
SECTION I.6 Isotherm - Formula	116
 APPENDIX II	 119
SECTION II.1 Breakthrough Data-Series 10	120
SECTION II.2 Breakthrough Data-Series 20	136
SECTION II.3 Breakthrough Data-Series 50	146
SECTION II.4 Calculations - Thomas's Solution	151
SECTION II.5 Calculations - Rosen's Parameters	152
SECTION II.6 Tables - Rosen's Parameters for Experimental Runs	154
SECTION II.7 Results of Curve-matching	176

	Page
APPENDIX III.	178
SECTION III.1 Mass Balance	179
SECTION III.2 Radial Effects	185
SECTION III.3 Pressure Drop Measurements	187
 APPENDIX IV	 189
SECTION IV.1 Crossplot Data	190
SECTION IV.2 Computer Programme	196

Chapter 1

INTRODUCTION

Adsorption has been very widely investigated by the physical chemist. The surface phenomena associated with adsorption have provided an interesting field for extended studies on the molecular behaviour of gases and de Boer⁹ has given a graphic description of the phenomenon of adsorption, annotated from this point of view.

Most of the physico-chemical studies concern themselves with obtaining thermodynamic data as a basis for a satisfactory theoretical explanation of the phenomenon, or with the search for better adsorbents. Chemical literature abounds with reports of such investigations, though very little of it adds up to a comprehensive theory. However, a few stand out as significant contributions towards the better understanding of the phenomenon. Langmuir²³ suggested that adsorption takes place in a monolayer on the surface of the solid and gave a quantitative interpretation to the shape of the isotherm commonly obtained. Freundlich¹³ provided an alternative equation which often better represented the equilibria in real systems. Brunauer, Emmett and Teller⁶ extended the 'Langmuir' model to multilayer adsorption, and their equation is perhaps the best that is available for representing a wide range of adsorption isotherms. Their

equation has also been of value in determining the total surface areas of porous or finely divided solids by an adsorption technique. Polanyi³⁷ introduced the concept of an adsorption potential and this has been useful in the study of multicomponent systems.

Apart from the theoretical studies mentioned above, a good deal of fundamental work has been carried out on the structure and properties of porous materials. The publications of the Second International Congress of Surface Activity⁴⁴ and the Proceedings of the Tenth Symposium of the Colston Research Society³⁸ contain many important articles on this subject. Literature on heterogeneous catalysis, though mainly dealing with the process of chemisorption, also provides useful information on the pore structure and surface properties that should be applicable to physical adsorption as well.

The information provided by such fundamental studies as mentioned above form the background on which the industrial chemist or the chemical engineer makes his choice of the adsorbent for a specific case. For example, a knowledge of the equilibrium capacities of a set of adsorbents for a particular solute which he wishes to remove from a gas stream would enable him to select the most suitable adsorbent, under the circumstances, more or less directly. He would also be aware of the temperature and pressure at which it would be most advantageous to carry out the adsorption. Information on the heats of adsorption, available from the above sources,

would help him in the design of the equipment.

However, more refined design requires information on the rate-behaviour of the system. The term 'rate-behaviour' has a very wide meaning and includes the study of the time-dependence of any of the properties of the system, right from the test tube stage of experimentation to the large scale plant operation. What is implied at this stage, however, is the kinetics of the system examined on a laboratory scale. A useful property that can be determined on this scale would be the diffusion rate of the solute into the adsorbent in the presence of other components expected to be encountered during the plant operation. There have indeed been instances where a reversal in behaviour from that indicated by the equilibrium studies has occurred. A specific example of this behaviour is seen in the report of Habgood¹⁶ who found that although a molecular sieve type 4A normally adsorbs methane from mixtures of nitrogen and methane, it showed a temporary selectivity for nitrogen prior to the time of reaching equilibrium, due to the more rapid nitrogen diffusion rate. In our own laboratory, Dworjany¹⁰ employing radioactive tracer techniques, observed two different rates for the desorption of carbon dioxide from an initially saturated molecular sieve type 4A, the lower one occurring during the later stages of desorption, presumably because the desorption at this stage takes place from the smaller cages contained within the larger ones of the molecular sieves. These instances

stress the importance of a kinetic examination prior to undertaking any major design of equipment for the system. Carman's⁷ monograph on the flow of gases through porous media also presents an interesting study in this connection.

The Unit Operation:

As a unit operation, adsorption has been employed widely in commercial processes for dehydration, solvent recovery and also for the removal of impurities from gases (and liquids). Where alternative methods of recovery exist, adsorption still has the advantage over gas-liquid or liquid-liquid systems in its simplicity of operation, relative insensitivity to moderate changes in temperature, flow rate and pressure and freedom from problems of corrosion, foaming, etc. It has, however, the disadvantages of a relatively high heat requirement (for regeneration), susceptibility to poisoning or break up of the adsorbent material and normally only semi-continuous operation. Mantell²⁸ gives a comprehensive account of adsorption fundamentals, adsorbents and their applications to industry. Kohl and Riesenfeld²² give a good report of the industrial application of adsorption for gas dehydration and gas purification, citing much useful technical data. In a recent paper, Carter⁸ reviews the application of adsorption techniques for process separation purposes and gives an excellent coverage of the relevant literature. Barry⁴ discusses certain aspects of the economics of adsorption in relation to

distillation as a separation process.

The Equipment:

In industry, fluid-solid contacting for purposes of adsorption is normally carried out in fixed-beds. Moving and fluidized beds can also be used, but their applications, so far, have been confined to isolated instances only, perhaps due to the attrition problems and relatively high cost involved in keeping the solids continuously in motion. Multi-component separations have also been successfully carried out in industry using some of the equipment mentioned above, developed more or less on a trial and error basis.

The object of the present research, has been to study the mechanism of the removal of a single component from the gas phase by physical adsorption on to a porous solid adsorbent in a fixed-bed.

The Fixed-Bed:

In a fixed-bed system, the solid adsorbent is held stationary over a suitable false bottom in a column that is usually cylindrical and stands vertical, and the gas to be purified is passed through the bed at a convenient velocity. For gases, the direction of flow is immaterial as long as the velocity is lower than the attrition velocity. Regeneration is usually carried out with gas flow in the reverse direction to that used for adsorption, and normally the practice is to arrange for the largest volumetric gas flow to be downwards.

Since every adsorption cycle is followed by a regeneration cycle for re-activating the bed, the operation of the fixed-bed is semi-continuous. The time cycles are fixed partly to suit convenience, and partly on the basis of economic efficiency, since usually the regeneration procedure involves the heating up of the column followed by a final cooling operation, usually carried out by blowing cool dry carrier gas through the bed in the same direction as during regeneration.

The Adsorption Wave:

During the adsorption cycle, as the gas passes through the bed, the solid adsorbs increasing amounts of the solute, and an unsteady state prevails. It is this condition that distinguishes fixed-bed operations from the other continuous operations encountered in absorption, liquid-liquid extraction etc., and makes design procedures more complicated. In the early stages, the mass transfer takes place essentially over a short length of the bed near the upstream end of the column, and the effluent gas comes out practically free of the solute. With time, this short mass transfer zone approaches saturation while at the same time downstream layers come into action. The movement of the mass transfer zone continues at a velocity which is very much lower than the linear velocity of the gas through the bed, and, after a sufficient length of time, the effluent gas concentration suddenly rises to a substantial value (recognizable analytically) above zero. This point is

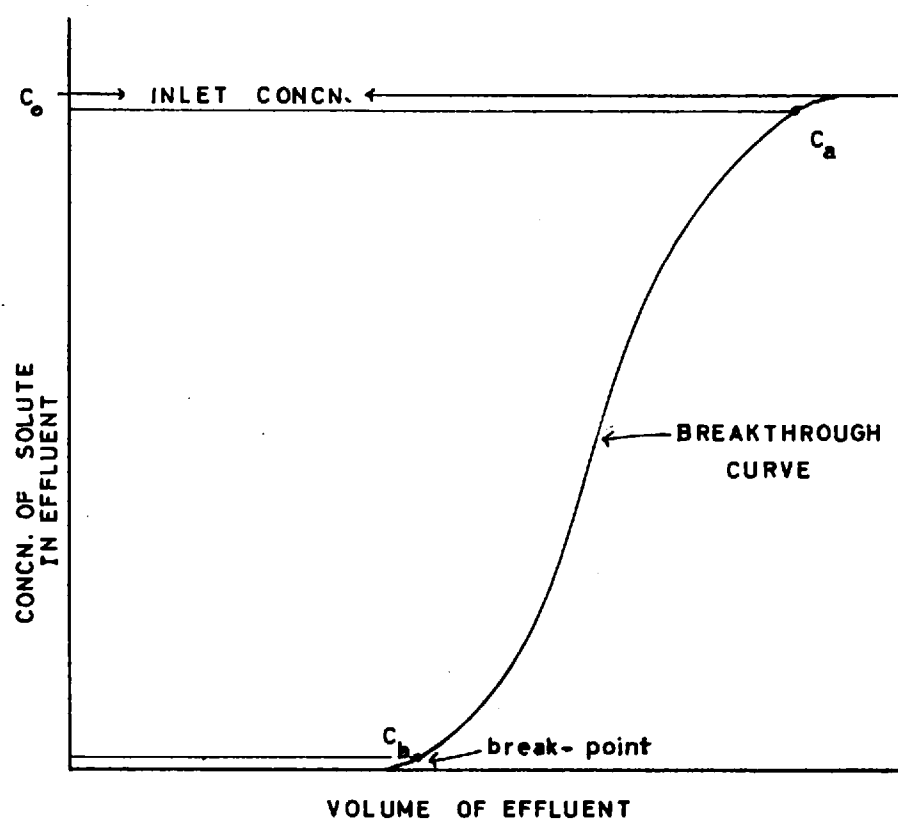


FIG. 1.1.
GENERAL CONCENTRATION HISTORY
CURVE

termed the "break-point". The solute concentration in the effluent gas now rises rapidly as the adsorption zone passes the downstream end of the bed, till it reaches a value approximating the inlet concentration. At this stage the bed may be considered, for all practical purposes to have reached equilibrium with the feed gas. Fig. 1.1 shows the general nature of the concentration-history of the effluent gas usually obtained during a fixed-bed operation. The portion of the effluent concentration curve between the break-point (C_b) and an arbitrary point (C_a) very near where the curve becomes asymptotic to the inlet concentration (horizontal) line, is termed the "breakthrough" curve. The shape of the breakthrough curve is a physical expression of the resultant effect of all the complicated processes that are taking place in the bed. A theoretical analysis of the shape of the breakthrough curve can, therefore, be expected to help in understanding the mechanisms involved in the process. More important, the time taken for the break-point to occur since the first entry of the gas into the column is by itself an important design factor as, in purification processes, it is the freedom of the effluent gas from even traces of the impurity, that determines the adsorption cycle time. The concentration-history beyond the break-point may have direct interest in mixture separation problems, but can also serve as a basis for developing a more fundamental approach to the problem of designing the equipment.

Performance Aspects:

The design of a fixed bed adsorber involves the predicting of the time of occurrence of the break-point and the percentage approach to the saturation of the bed, at the break-point. Both these items are reflected in the shape of the breakthrough curve which under the unsteady-state conditions prevailing in a fixed-bed, taking due account of the many steps involved in the adsorption process, is difficult to predict. Exact analytical solutions have been established only for a few specialised cases where simplifying assumptions are justified. Klotz²¹ has outlined the various steps involved in the transfer of the solute from the gas phase to the interior surface of the adsorbent as consisting of: (1) diffusion of the solute from the bulk of the gas on to the surface of the granule across the boundary layer; (2) diffusion of the molecules of the solute into the large pores of the adsorbing particle (or along the surface); (3) adsorption of the molecules on the interior surface of the granule; and (4) reaction at the surface. Where the rate controlling process is any single one of these steps, it has been possible to obtain, within recognized limits, a complete analytical expression for the adsorption curve, as shown by Klotz.

The analytical solution presented by Hougen and Marshall¹⁸ is one such specialized case and is applicable to adsorption of a dilute gas possessing a linear adsorption isotherm

under conditions where mass transfer across the gas film is controlling. Their equations are similar in form to those developed by Anzelius³ for the analogous problem of heat transfer. They have also presented the solution in the form of charts similar to those given by Schumann⁴³ and Furnas¹⁴ for heat transfer. Where the adsorption isotherm is concave to the solution-concentration axis the length of the adsorption zone remains approximately constant as it travels along the bed, for dilute feed mixtures. Michaels²⁹ has given a simplified treatment for calculation of the length of the adsorption zone. Treybal⁴⁶ has shown how the H.T.U. concept can be extended to such a case and the breakthrough curve plotted by graphical evaluation of the integral for the N.T.U. The success of this analysis, however, would depend upon the constancy of the value of the H.T.U. for the concentrations within the adsorption zone, which, in turn, will depend upon the constancy of the resistance to mass transfer in the fluid and within the pores of the solid. Treybal has illustrated this procedure with an example from the work of Eagleton and Bliss¹¹.

The importance of the effect of diffusion of the solute within the pores of the solid as a rate-determining step has been recognized, and Wicke⁴⁸ has obtained a series expansion of the solution for a bed of spherical particles. Jury and Licht¹⁹ have used a simplification of this series to obtain a

more generalised solution applicable to the alternative cases of diffusion in the granules controlling or mass transfer in the boundary layer around the granule controlling. Magleton and Bliss¹¹ while analysing their own experimental results have taken account of both the gas and the solid resistances, approximating the latter to a solid "film" resistance. They obtained reasonable prediction of their experimental curves on this basis.

The more rigorous treatments of the problem are found in papers which deal essentially with the theoretical aspects of adsorption in fixed beds. Vermeulen⁴⁷ in his comprehensive paper entitled "Separation by Adsorption Methods", presents in considerable detail the numerous theoretical correlations dealing with adsorption in fixed beds. Vermeulen's own treatment is essentially for ion exchange systems but, except for certain cases such as irreversible equilibrium, it is applicable to physical adsorption as well. In his review of the literature Vermeulen has not only given a systematic classification of the various types of adsorption but has also unified the nomenclature.

Goldstein¹⁵ presents a mathematical discussion of exchange processes associated with fixed-beds, from the point of view of the equilibrium theory (which is more applicable to chromatography) as well as the kinetic theory. Amundson² presents generalised solutions for the kinetic case involving

an arbitrary distribution of adsorbate on the bed, and an arbitrary dependence on time of the inlet solute concentration. Kasten, Lapidus and Amundson²⁰ consider the effect of intra-particle diffusion on the rate of adsorption in a fixed-bed. Hiester and Vermeulen¹⁷ present a reaction-kinetic approach based on Thomas's⁴⁵ general solution for the performance of an ion exchange column in which the rate of exchange is governed by a second order reaction-law. Application of this solution involves the use of an equilibrium factor defined in terms of the Langmuir isotherm constant. Hiester and Vermeulen¹⁷ and Opler and Hiester³⁶ have given graphical and tabulated values of the solution for the exit concentration of the solute in terms of the equilibrium factor, the number of transfer units and the throughput ratio, all of which are dimensionless.

Where solid phase diffusion into the interior of the particles in the bed is an important rate-determining step, but the mass-transfer resistance of the gas-film is also significant the combined effect on the overall rate of adsorption is best expressed in terms of Rosen's⁴⁰ solution for this case. Rosen⁴¹ has presented tabulated values and curves for his dimensionless groups, namely, the film resistance, the bed length and the contact time parameter. The main limitation for the extended use of Rosen's solution is the fact that it is based on a linear isotherm.

The conservation equation contains a term for longitudinal

diffusion, which is usually disregarded as negligible. It may however become an important factor in determining the breakthrough slope when fluid particle equilibrium is closely approached, as Vermeulen⁴⁷ indicates. Lapidus and Amundson²⁴ have reviewed the effect of longitudinal diffusion combined with external mass transfer for the case of a linear isotherm. Acrivos¹ has discussed how, under certain circumstances, an approximate analytical solution can be obtained for the combined effect of longitudinal diffusion and external mass transfer for a non-linear (but favourable) isotherm.

In all the rigorous treatments of the problem reviewed above, the general procedure consists in first expressing the physical variables in terms of partial differential equations, one to account for the mass balance, and another to represent the point mass transfer or 'reaction' rate. The isotherm relationship is used to define the driving force in the second equation in suitable terms. The solutions of these simultaneous partial differential equations are then obtained under specified initial and boundary conditions, considering the first inflow of the gas into the column as equivalent to the occurrence of a step change in the inlet concentration at zero time. In order to permit analytical solutions, one is driven to make simplifying assumptions either regarding the isotherm or regarding the pattern of flow through the bed. The final form of the solution generally involves special mathematical

functions which have tabulated values or for which values can be computed. In certain ranges, however, it is not uncommon to find the combination of these special functions yielding a nearly indeterminable result. From this point of view it would not be too much to say that, in the final analysis, these methods turn out to be rigorous solutions for particular situations, rather than generalizations of wide applicability.

The solution of the partial differential equations mentioned above can also be obtained by finite difference techniques. What limits their use, however, is the extensive and laborious calculations required which generally call for the use of a computing machine. Granted that a computer is available, numerical techniques can be used to solve even more complicated cases, or cases which have so far failed to yield to analytical treatment. Such situations arise, for example, where the bed is initially partially saturated, or the adsorption isotherm or mass transfer relations are non-linear, or where radial symmetry of the bed cannot be assumed and calculations have to be extended to two or three dimensions. Opler³⁵ has discussed the applications of these techniques for the prediction of fixed-bed performance, but they are not a panacea, and it is easy to formulate problems which will tax the capabilities of even the largest and fastest of present-day computers.

While the search for rigorous methods of design continues,

it has been the case with every unit operation that the practical design of equipment is, in the meanwhile, carried out by empirical or semi-empirical procedures. Adsorption has been no exception to this rule. In a way, there is some justification for using such methods since it is difficult to estimate separately the magnitude of each of the resistances that go to define the mass transfer under the actual conditions obtaining in the fixed-bed. In a fixed-bed, the situation is neither strictly isothermal nor strictly adiabatic; much depends upon the way the heat of adsorption is dissipated. The consequent temperature rise may affect not only the local individual mass transfer coefficients, but also the equilibrium. Apart from this, there may also be a variation in the rate-controlling mechanism, even as the adsorption proceeds. Hence, in many instances, rigorous treatment may not appear worth the trouble, and so the transfer mechanisms are approximated by coefficients whose variations with important parameters can be correlated experimentally. Foster and Daniels¹², Rathmell and Bateman,³⁹ Ross and McLaughlin,⁴² Luibimov and Smirnov,²⁷ and Miller and Roberts³⁰ have attempted such empirical correlations for specific systems. Carter⁸ summarizes their work in his review cited earlier. Barry's⁴ suggestion to extend correlations based on the mass transfer zone concept of Michaels²⁹ should also be considered as a useful semi-empirical approach. Monet³⁴ cites the procedure given by Moison and O'Hern³² for the correlation of their experimental results on fixed-bed ion exchange as a very useful semi-empirical method.

It is felt that much more can be done along these lines, and what is vitally needed is a series of reliable experimental results for typical systems, which can serve as a basis for the testing and critical evaluation of existing mathematical solutions. No simplifying assumptions are ever exactly satisfied, and when a theoretical solution involves such assumptions, it is important to know how sensitive it is to deviations from them.

Programme of Present Work

The object of the present work was to provide a comprehensive set of data for one particular system, the range of measurements and conditions being specifically chosen to test the validity of the various simplifying assumptions commonly made, and the effect of relaxing them as well as to discover the rate-controlling mechanisms in different circumstances.

The system chosen was the adsorption of carbon dioxide from air, using molecular sieve pellets (type 4A). The choice was largely a matter of practical convenience, although, of course, this represents an important industrial purification problem in the low-temperature separation of air. Molecular sieves too are an important new class of adsorbents for which little data of this kind are available and which are specially adapted to gas separation problems of this type.

Most commercial adsorbents have an ill-defined internal structure with a wide range of pore sizes and shapes; they

also tend to deteriorate with repeated cycles of adsorption and regeneration. In both these respects molecular sieves are greatly superior; they have a definite crystalline structure, giving pores of uniform size and shape which are capable of exact measurement by X-ray techniques, and the loss of capacity with repeated use is small. One can therefore expect good reproducibility with beds of molecular sieves.

In the work to be described, in order to obtain true comparability between successive runs, the bed was left undisturbed for the experimental programme, thus eliminating any variability due to changes in packing characteristics of the pellets. Also, provision was made for measurements at ten equally spaced points within the bed, so that results for variable bed-length were obtained without the need for repacking the bed between runs.

Carbon dioxide is a convenient gas for analysis, especially in mixtures with air. The molecular diameters of carbon dioxide, nitrogen and oxygen are small enough for all three gases to enter readily the crystal cavities of molecular sieve 4A, so that no specific "sieve-action" is involved. The adsorptive capacity of the molecular sieve for carbon dioxide is also appreciable at room temperature,

In most investigations the concentration of the solute in the gas phase is kept low enough to permit the assumptions of

a linear isotherm and a constant gas velocity. In the present work the effects of higher solute concentrations were investigated and provision was also made for measuring the radial variations of gas concentrations at different points in the bed.

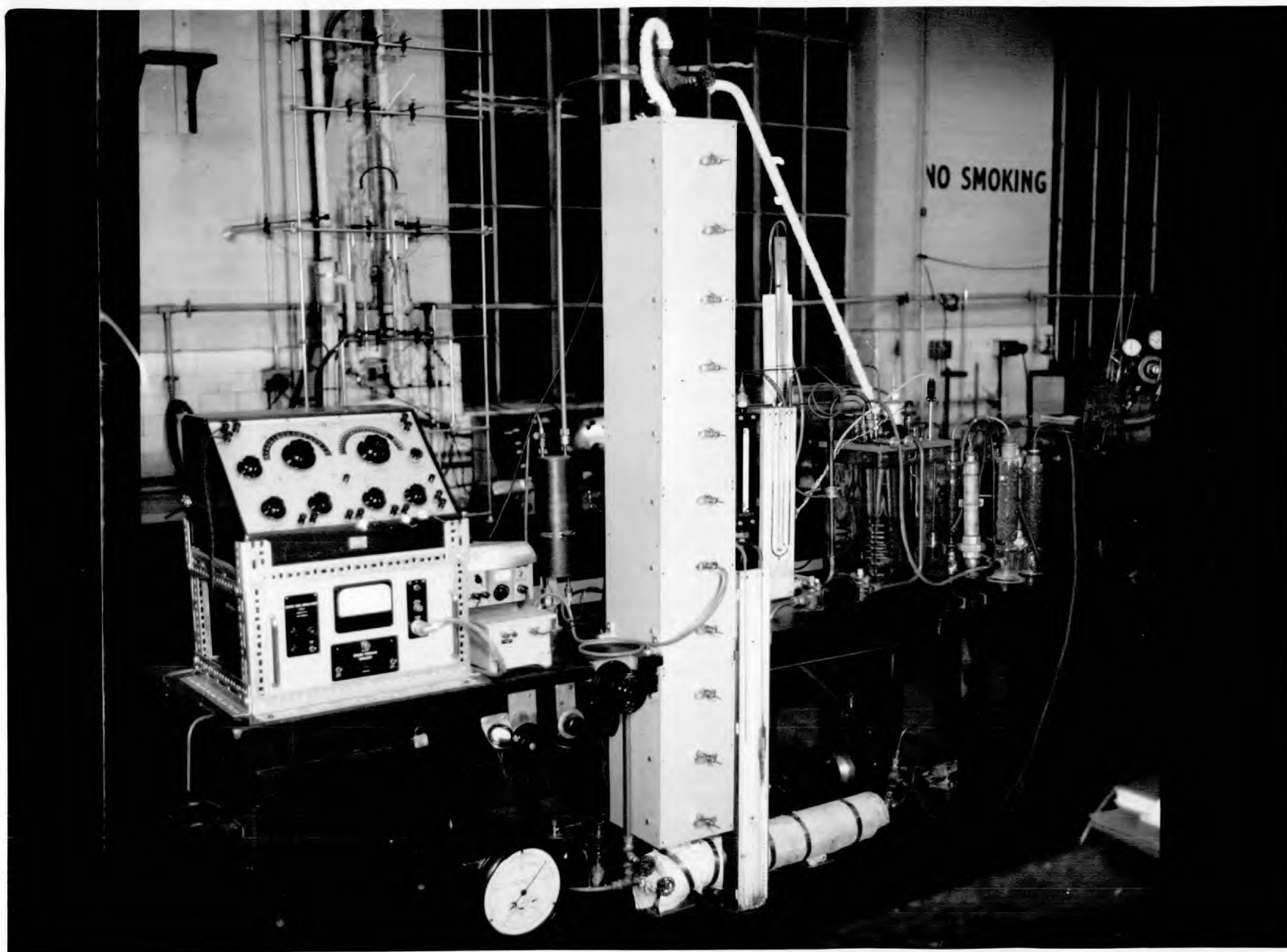


PLATE 2.1

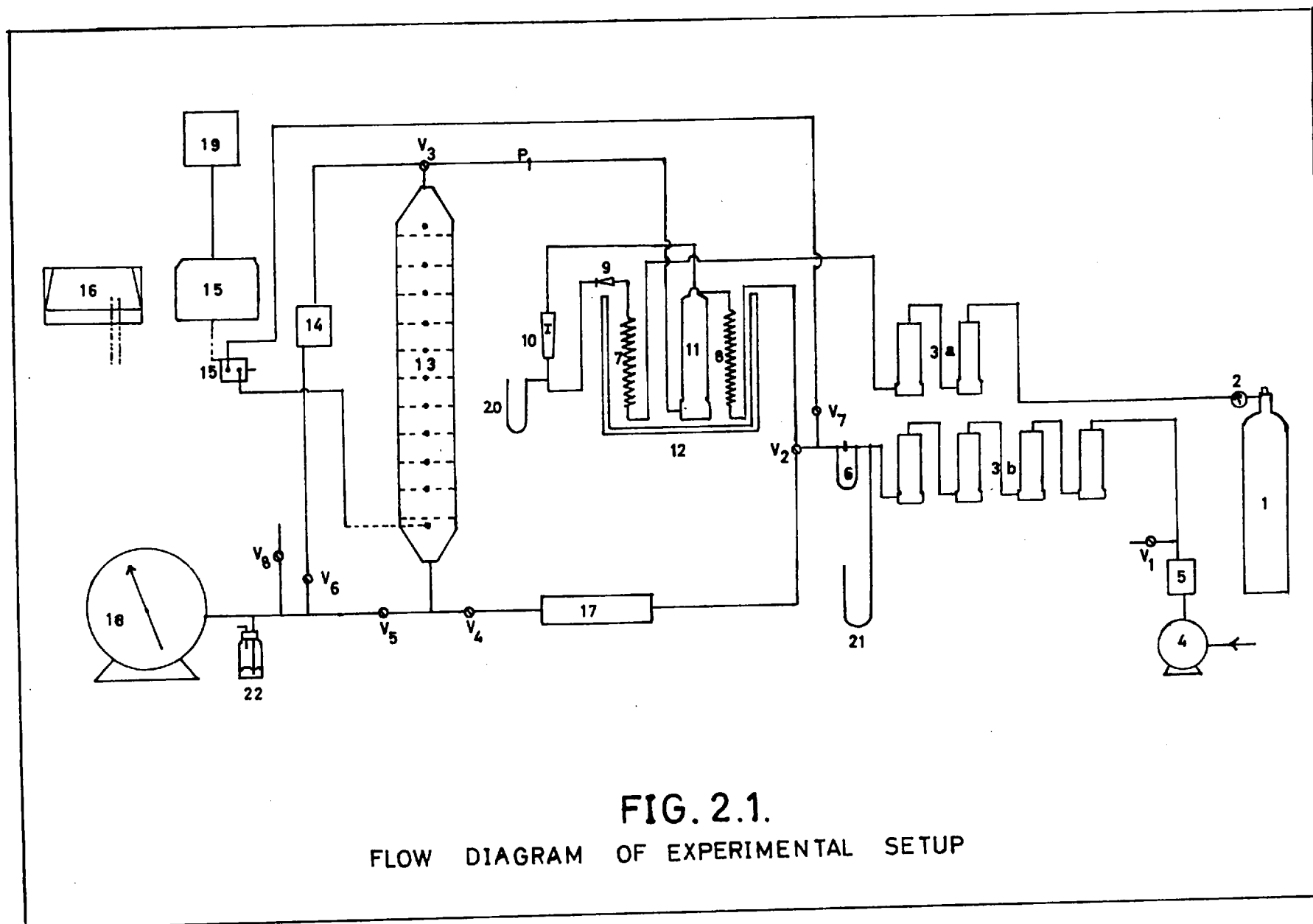
Chapter 2

EQUIPMENT

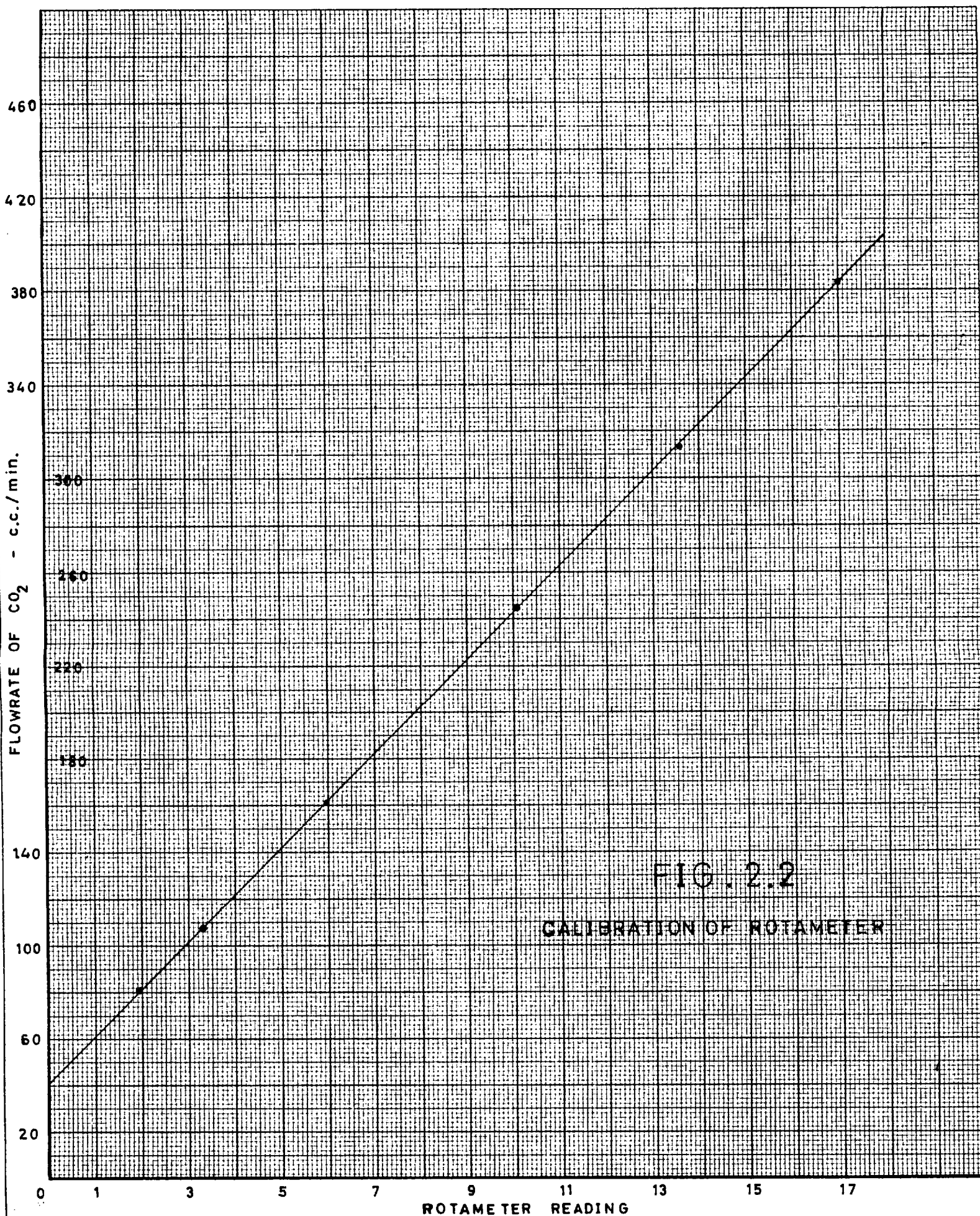
General Arrangement:

In Fig. 2.1, a flow-diagram of the experimental setup that was used for the investigation is shown. In the following description of the apparatus the numbers given in brackets refer to the corresponding items in the flow-diagram. (Plate 2.1 shows a photograph of the setup).

Carbon dioxide from cylinder (1) was throttled in a reducing valve (2), passed through two towers (3a) filled with silica gel for drying the gas, and then through the copper coil (7) immersed in a constant temperature bath (12) maintained at 25°C, finally reaching the fine adjustable needle valve (9). The needle valve was operated at greater than the critical pressure ratio of upstream to downstream pressure so that a constant discharge of gas, unaffected by downstream conditions was obtained. The constancy of flow was observed and the rate of flow metered in a rotameter (10) which was suitably calibrated (vide Fig. 2.2, for rotameter calibration graph). The carbon dioxide then joined the air stream in chamber (11) entering it through a jet to ensure adequate mixing. The chamber (11), constructed of mild steel piping and packed with aluminium Lessing rings, provided additional mixing of the two gases and attainment of the bath temperature before their entering the adsorption column via the lagged pipe-line P_1 and the three-way valve V_3 .



Air was drawn from outside the laboratory through the compressor (4), passed through a filter (5), then through four silica gel towers (3b) for drying, and metered in an orifice meter (6) before it reached the three-way valve V_2 . During the adsorption cycle, the valve V_2 was turned to make the air pass through the copper coil (8) in the constant temperature bath (12) and then into the chamber (11) where it was mixed with the carbon dioxide. During the regeneration cycle, the valve V_2 was turned so as to make the air pass through the heater (17) and then through valve V_4 into the adsorption column (13) from below. In its passage through the heater (17) the air came into direct contact with electrically heated nichrome wire wound on asbestos strip held longitudinally in the heater tube. The output of the heater was controlled by a "Dimmerstat" regulator included in the circuit. The heater and the piping leading to the adsorption column were well lagged on the outside with glass wool to minimize heat losses. The hot gases coming out of the column during the regeneration cycle were cooled in the cooler (14). The wet gas meter (18) in the final exit line measured the gas flow rate thus serving as a check on the rotameter readings. A gas wash bottle (22), with a small quantity of mercury covering a dip-tube connected to the exit gas line, served as a safety device by allowing the gas to escape by bubbling out through the mercury, in case of accidental build-up of pressure in the system. Mercury Manometers (20) and (21),

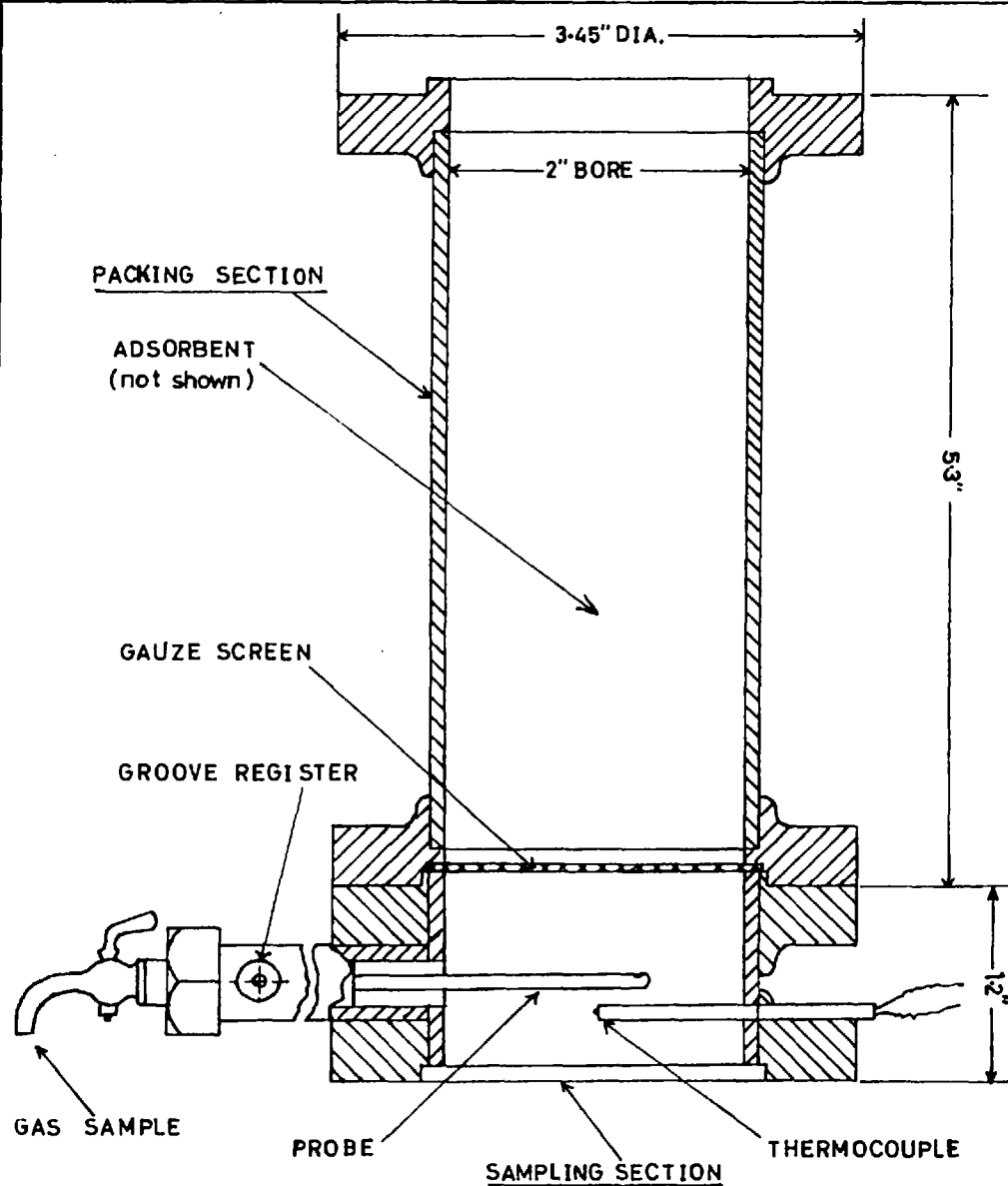


helped in the controlled operation of the valves in the carbon dioxide and air lines respectively. Valve V_1 served as an air leak from the compressor to control the quantity flowing into the system.

The analysis of the gas phase sampled through the probes provided in the column was carried out in a Sonic Gas Analyser (15). The sample of inlet air needed for the zero-adjustment of the sonic gas analyser could be drawn through the passage (not shown in the figure) controlled by valve V_7 . Valve V_8 , operated suitably in conjunction with V_3 provided a by-pass to the sonic gas analyser, of the gas mixture during the initial adjustment of the composition of the gas, prior to starting of the actual run. The sonic gas analyser was also coupled to a Cambridge Recorder (19) on which the breakthrough curve could be directly obtained. A spare point in the recorder was used to register the changes in the voltage of the thermocouple at the corresponding level, during the course of the adsorption. The Potentiometer (16), connected to the thermocouples through a multipoint selector switch (not shown in the flow-diagram), enabled measurement of the other thermocouple voltages and hence the corresponding temperatures.

The Adsorption Column:

The adsorption column was constructed of 2 in. (i.d.) brass piping in ten flanged packing sections, separated by an equal number of sampling sections. The height of each packing



DETAILS OF PROBE

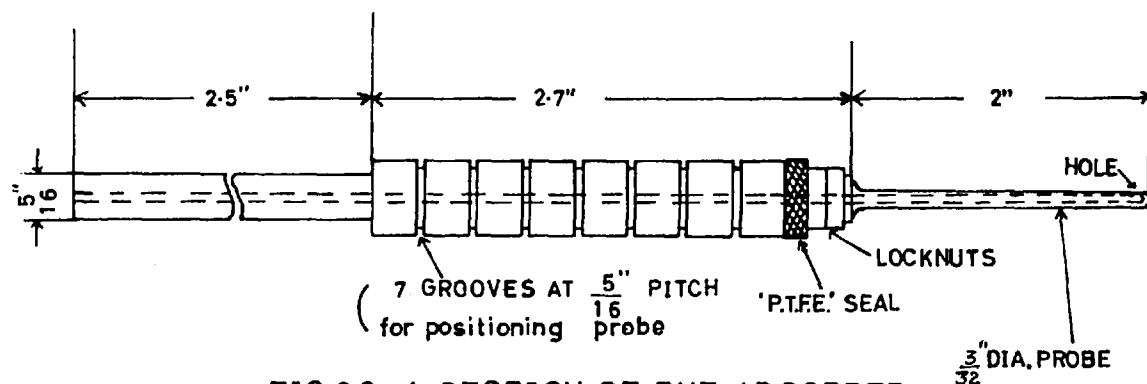


FIG.2.3-A SECTION OF THE ADSORBER

section was 5.3 ins. and the packing was supported on 20 mesh copper wire screen, held rigidly between the bottom flange of the section and the top flange of the sampling section below. Each sampling section was 1.2 ins. in height and carried a probe inserted through the wall radially, for sampling the gas.

The probe was $3/32$ in. in diameter and was $\frac{1}{8}$ in. below the level of the wire screen support for the packing. (Fig. 2.3. illustrates the details of a section and the traverse mechanism). Each sampling section also carried a copper-constantan thermocouple, whose sensitive point alone was exposed to the gas, for registering the gas temperature at the axis of flow. The thermocouple was about an eighth of an inch below the level of the probe.

When assembled (after filling each section to the desired level with the adsorbent) the overall height of the column was 65 ins. between the two sampling probes at the inlet and outlet ends of the column. The column was connected to the rest of the assembly through tapering conical sections at the two ends to minimize end-effects. The entire column was enclosed in a rectangular hardboard box filled with santocel to minimize heat losses during the regeneration cycle, and in order to assist in maintaining the desired regeneration temperature each packing section was wound on the outside with nichrome wire, over mica insulation, for

electrical heating. These heater coils were connected in series, and the heat input manually controlled by means of a Variac included in the circuit.

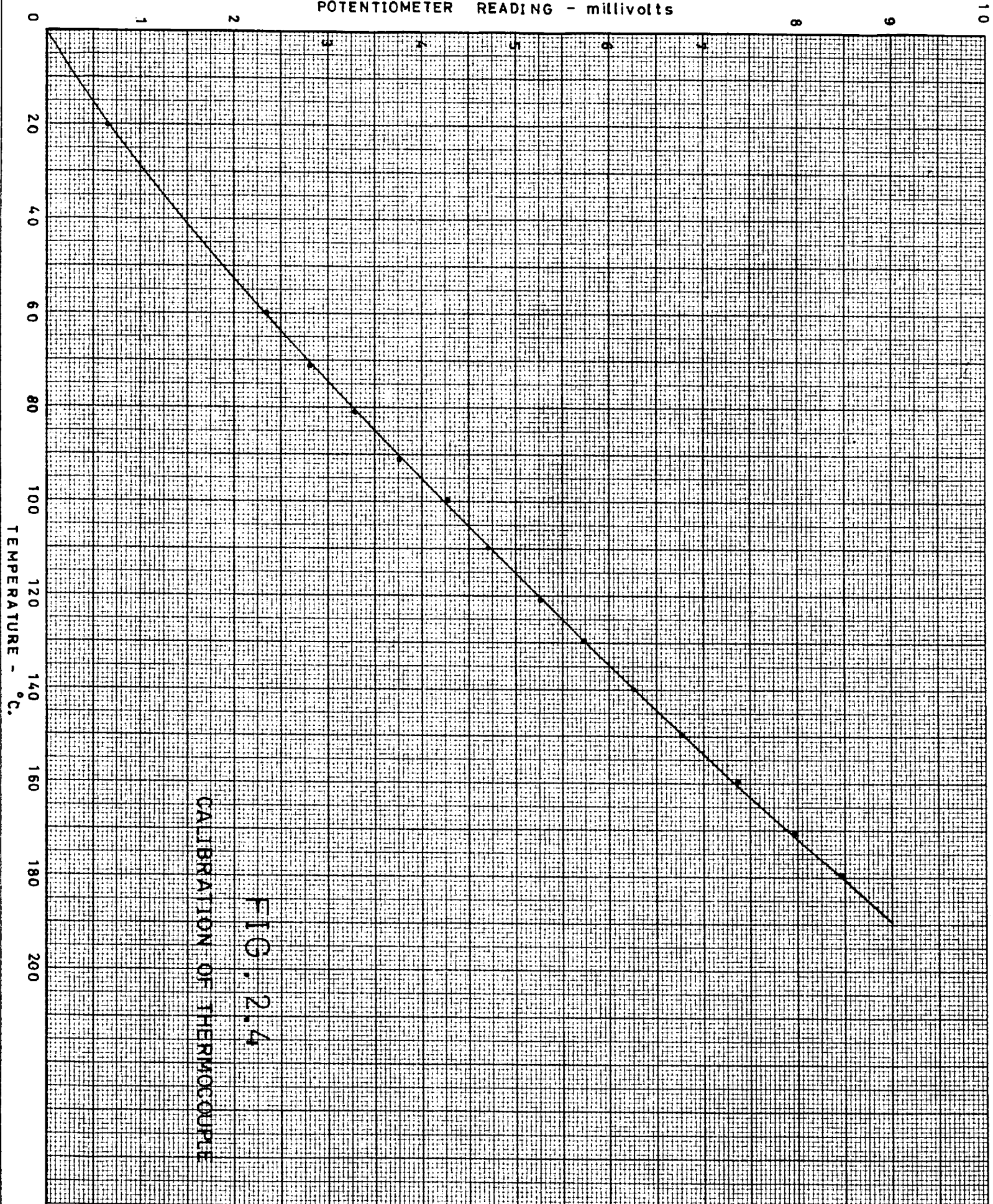
The division of the column into ten sections with intervening sampling sections, was to facilitate the movement of the probe and to obtain breakthrough curves for ten different depths of the packing without disturbing it every time a change in the bed depth was made. As the adsorbent was supported on wire screen at each stage, the question of consolidation of the bed due to its own weight and the consequent effect on the voidage distribution did not arise. The residence time of the gas phase in the sampling section was also quite small compared with the times involved in the observation of the concentration-history for these runs. Thus the column, as designed, provided a close approach to a system in which the effect of bed depth on the effluent concentration-history could be studied under reasonably identical conditions of the bed.

The need for heating coils around each section arose from two main reasons. Firstly, the heat capacity of the body of the metallic column and the heat losses to outside had to be met from a source other than the hot purge gas in order to reduce the time for the initial 'heating-up' period during the regeneration. Secondly, the unavoidable temperature gradient that would exist over the length of the column even towards the end of the regeneration period, if heated by the purge gas alone,

had to be reduced as much as possible; and this could be done by keeping the walls of the column "hot", by external heating. A useful result of this arrangement was that the regeneration cycle could be terminated every time under identical conditions of longitudinal temperature gradient of the column, by observing the thermocouple readings and suitably controlling the output of the heater coils with the Variac. This, it was hoped, would result in the same pattern of residual moisture gradient being left in the packing over the length of the column, after every regeneration.

The probes in the adsorption column were designed to be movable across the diameter of the sampling sections. The slight pressure in the column during operation was sufficient to push the sample gas through the narrow passage of the probe when the stopcock on the external end of the probe was opened. A rubber tube led the sample of gas from the probe through a copper coil (to bring the sample to room temperature) and thence to the comparison-tube of the sonic gas analyser. In calculating the elapsed time for the effluent gas from the time of initial gas entry into the column, necessary allowance was made for the time taken by the sample gas to move through the probe to the sonic gas analyser. This could be easily computed by knowing the rate of flow of the gas through this passage and the actual volume of the passage experimentally determined. The probe could be turned on its axis; and

POTENTIOMETER READING - millivolts



this allowed its use for measuring pressure drop by keeping the aperture at 90° to the direction of flow when static pressure alone would be registered. The probe could have also been used as a pitot tube to measure the velocity profile across the column; but in view of the very low pressure differences between the static and stagnation pressures of the flow over the range of operation of the column, such a use of it was not made. Normally, during the runs, the probe was positioned to make the aperture coincide with the axis of flow, facing the direction of flow.

The thermocouples, made from copper-constantan wires, were suitably protected by double-conduit porcelain sheaths passing through the radial brass tubes provided in the sampling sections. Only the tips of the thermocouples were exposed to the gas, sealing the other parts with epoxy resin cured at high temperature. The thermocouples were suitably calibrated before mounting against a standard thermometer. The necessary cold junction for the thermocouples was provided.

Fig 2.4. gives a calibration chart for the thermocouple used.

The Sonic Gas Analyser:

The Sonic Gas Analyser, manufactured by Grubb Parsons Ltd., was used for the continuous analysis of the carbon dioxide in the effluent gas.

This instrument works on the principle that the velocity of sound in a gas depends upon the nature of the gas and is given by the expression $V = \sqrt{\frac{\gamma RT}{M}}$, where γ is the ratio of the specific heats of the gas, R the gas constant, T the absolute temperature and M the average molecular weight. Since γ varies only from unity to 1.67 for all gases, then, if T is kept constant, the velocity of sound in the gas will depend mainly on the molecular weight.

In the practical instrument there are two tubes to contain the gases. One is used as a standard and the other as a comparison tube. Sound at a frequency of about 3 kilocycles/sec. is transmitted along both tubes by means of miniature "earphones" excited by an oscillator, and is received at the other end by similar earphones. If the two tubes contain different gases, then there will be a difference in the velocity of sound transmitted. This velocity variation is measured as a phase change Θ between the two received signals which is given by $\Theta = 2\pi f d \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$, where f is the frequency of the sound, d the distance from transmitter to receiver in either tube (30 cm for this instrument), and V_1 and V_2 are the velocities of sound in the respective tubes. This phase shift is measured electronically and an output proportional to the phase angle is presented on a meter. By employing the two tubes in this way, temperature effects are largely cancelled out.

Since $V = \sqrt{\frac{Y_{RT}}{M}}$, the phase change can also be expressed as $\Theta = \frac{2\pi f}{\sqrt{RT}} d \left(\sqrt{\frac{M_2}{Y_2}} - \sqrt{\frac{M_1}{Y_1}} \right)$, and hence

calculated for any given mixture. However, in actual practice, a direct calibration is preferably carried out with pure gas in one tube and various concentrations of the binary mixture in the other. Usually the calibration graph is practically linear, unless the instrument is desensitised for measuring higher ranges of concentrations. In the experiments carried out in this investigation, the air used as carrier gas for the runs was employed as the standard in the standard tube of the sonic gas analyser. This compensated for the presence of traces, if any, of moisture or other gases in the carrier air affecting the observed value on the sonic gas analyser for the analysis of carbon dioxide. Zero-adjustment of the gas analyser was done periodically by using the same air in the comparison tube also. At all other times during the course of a run, the comparison tube had the effluent gas flowing (at a low velocity) through it so that continuous analysis was carried out by the instrument. A recorder was connected to the sonic gas analyser and the breakthrough curves directly registered on a moving chart. A certain amount of magnification of the readings could be obtained in the recorder and this could be varied to some extent by an adjustable resistance included in the circuit. All values were finally expressed in terms of the sonic gas analyser meter reading for which a calibration chart had

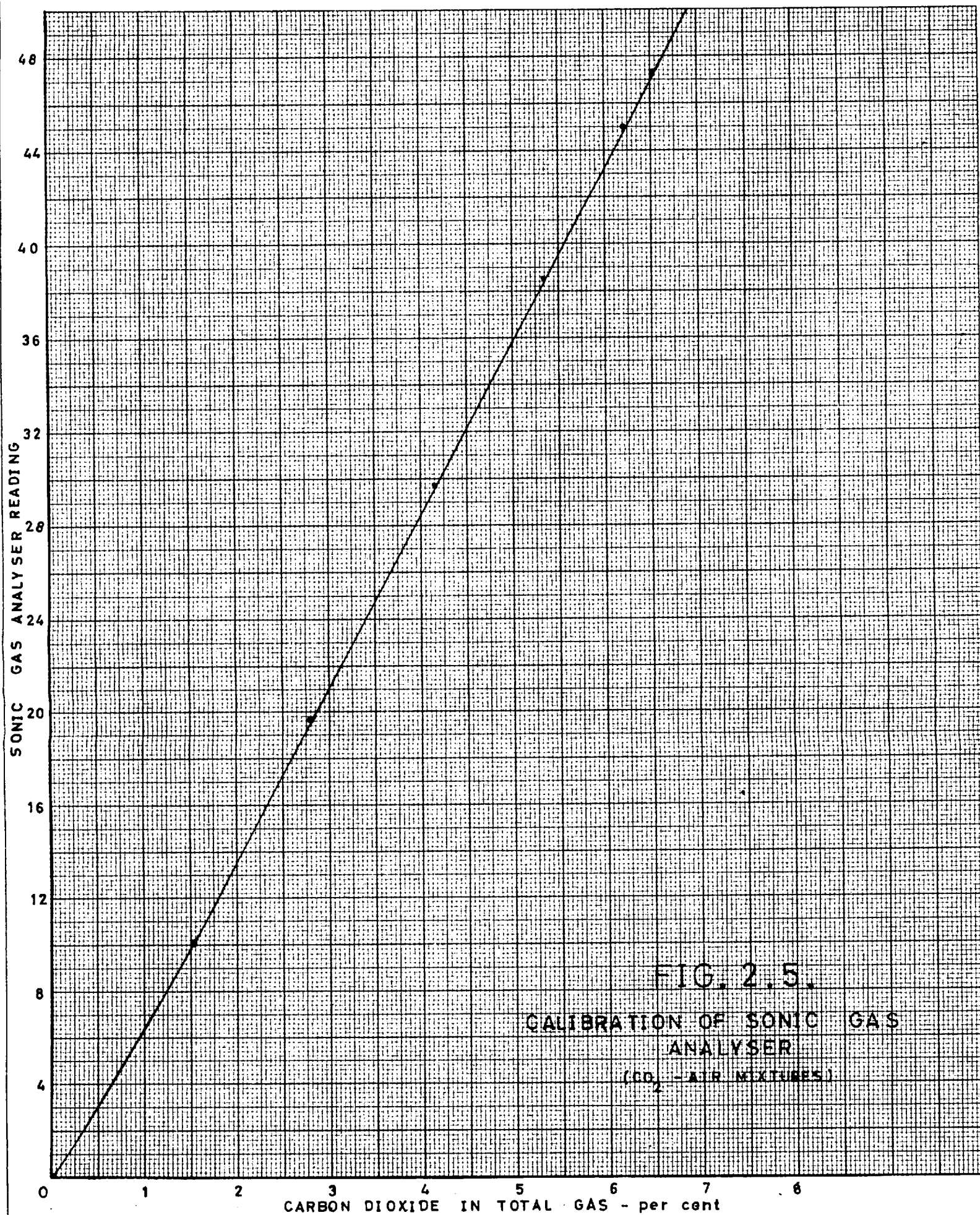


FIG. 2.5.
CALIBRATION OF SONIC GAS
ANALYSER
(CO₂ - AIR MIXTURES)

separately been prepared using made up mixtures of carbon dioxide and air. Fig. 2.5 illustrates this calibration chart.

The full scale of the meter on the sonic gas analyser had 50 divisions. With the aid of the magnification obtainable through the recorder, it was possible, usually, to read correct to a tenth of a division of the gas analyser meter. Approximately 8 divisions of the meter represented 1 per cent carbon dioxide in the air (though it must be stated that this value depended on the setting of the sensitivity control on the analyser). By suitable adjustment of the recorder magnification it was possible, in essence, to get the analysis of carbon dioxide up to 0.01 per cent.

Chapter 3

EXPERIMENTAL

Preparation of the Column:

The column was initially filled with Linde Molecular Sieves,³³ type 4A, $\frac{1}{8}$ in. pellets, to a depth of 4 inches in each section, and then assembled. The weight and the bulk volume of the packing were measured and the moisture-content and the true density of the pellets determined. Hence the porosity was calculated. (Pressure drop measurements were made for three velocities of air flow and these checked up with the order of the value for the porosity directly measured.) The relevant results are given in Section 3 of Appendix III.

Drying of Gases:

Before every run, the four towers for drying the air were filled with a fresh batch of silica gel (indicating type 4 to 6 mesh) which had been regenerated after use in a previous run, by drying for over 6 hours in a vacuum dryer. In a sample test, the air leaving the silica gel towers, when passed through a Casella Dew Point Apparatus showed no detectable moisture (clouding of the mirror) even at as low a temperature as -80°F .

Initial Activation of the Molecular Sieves:

The molecular sieves in the column had first to be activated. This was done by passing hot air at about 330°F

through the packing for several hours during the day and repeating the procedure for five consecutive days. Cooling was done by leaving the column to cool overnight by itself. During the cooling, all the passages to the column were closed except for a vent through the silica gel towers so that only dry air entered to fill up the partial vacuum created in the column. The same procedure was adopted for the cooling after every regeneration cycle that followed the adsorption runs.

Direction of Flow:

During adsorption the gas flow was from top to bottom of the column and during regeneration the gas flowed from bottom to top. For gases the direction of flow is immaterial except that it would be preferable to have the direction of flow for regeneration opposite to that for adsorption. In the setup used for this investigation, upward flow was chosen for regeneration because of practical convenience in fixing up the heater.

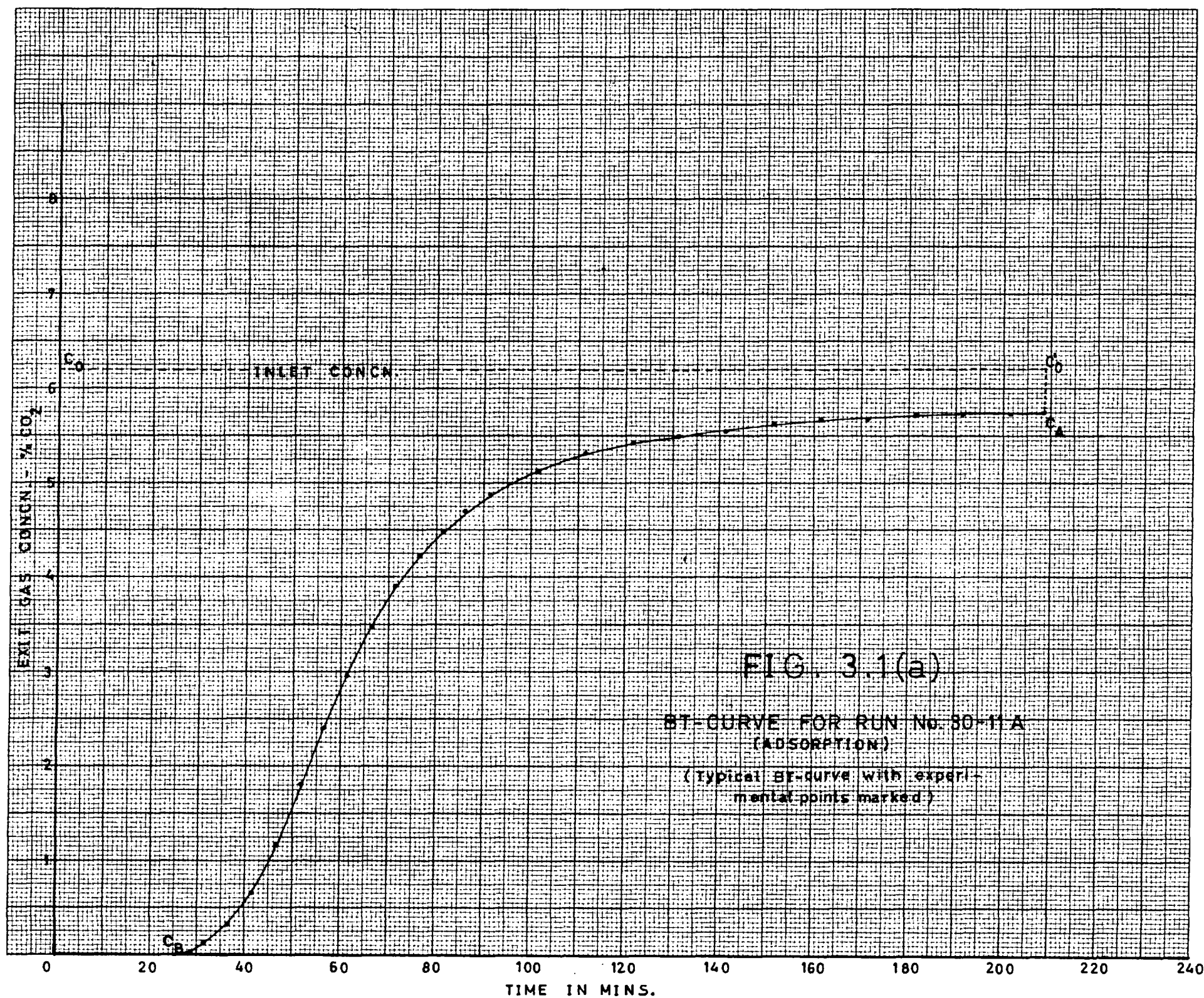
Allowable Gas Velocity:

The actual velocities used for adsorption were below the maximum allowable gas velocity correlated by Ledoux²⁵. The calculations are shown in Section 3 of Appendix I. This ensured that the column was operated well below the conditions that might cause attrition and carry over of the particles.

The Adsorption Run:

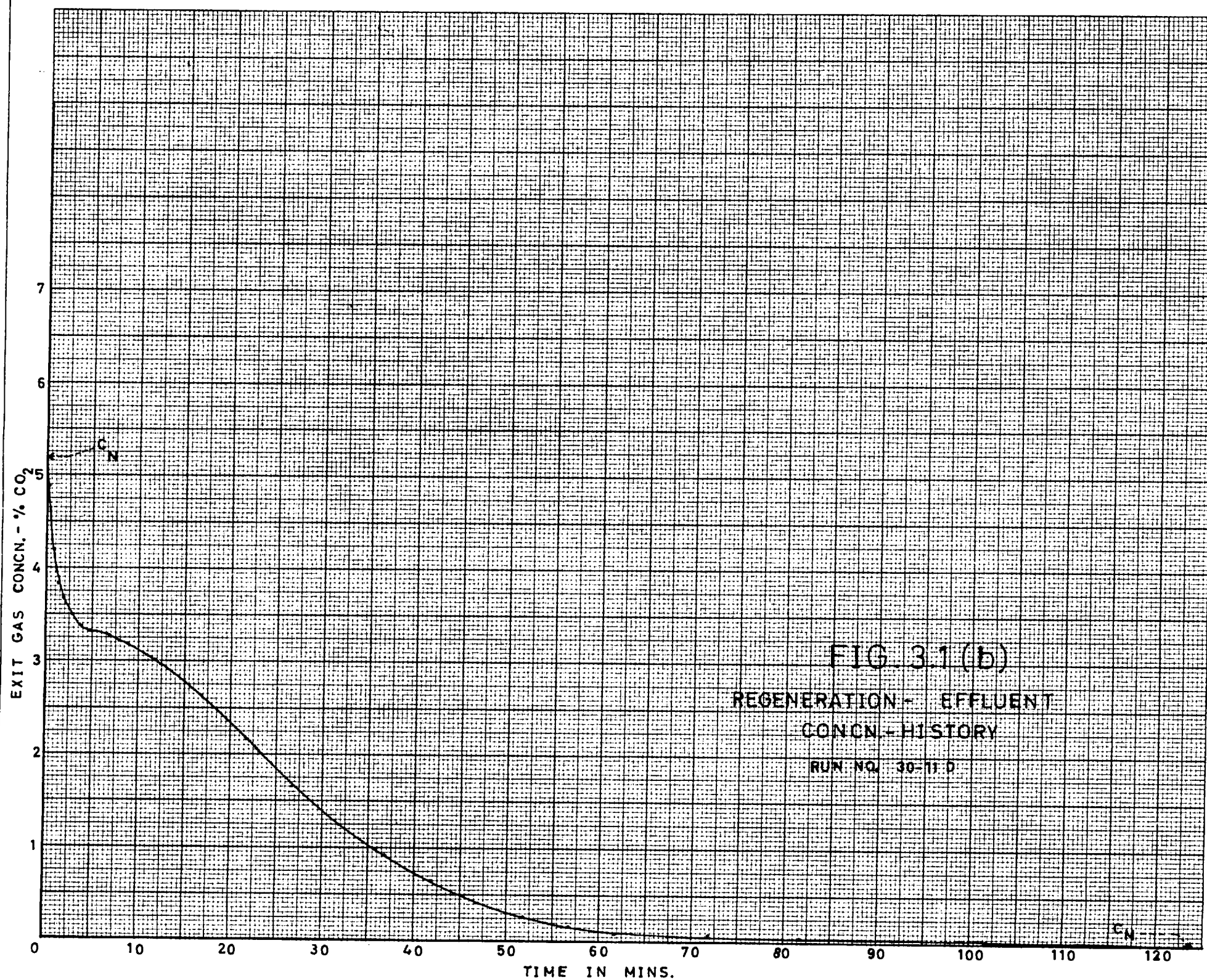
The constant temperature bath, the sonic gas analyser and the recorder were first brought to suitable conditions. Next, the three-way valve V_3 at the top of the column was turned to cut off entry to the column and provide a by-pass for the gas mixture straight to the gas meter. The side passage at the valve point V_8 was connected to the sonic gas alayser. The compressor was switched on and the air flow in the system adjusted approximately to the value desired, by observing the orifice meter. Carbon dioxide was then introduced into the system and the flow rate observed on the rotameter. The composition of the gas mixture was then adjusted more accurately by observing the sonic gas analyser reading. Similarly, the initial gas rate was adjusted more accurately with the help of the the gas meter.

When these arrangements were complete, the gas was passed into the column by suitable adjustment of valves, and the time of start noted on the recorder sheet. Due to the additional pressure drop through the column the flow tended to fall slightly from its initial value. This was corrected with the minimum delay by the following procedure: The carbon dioxide flow remained unaffected by variations in the condition of the column since the needle valve (9) was operated with greater than the critical pressure ratio. This was confirmed by the steady reading obtained on the rotameter. The air flow



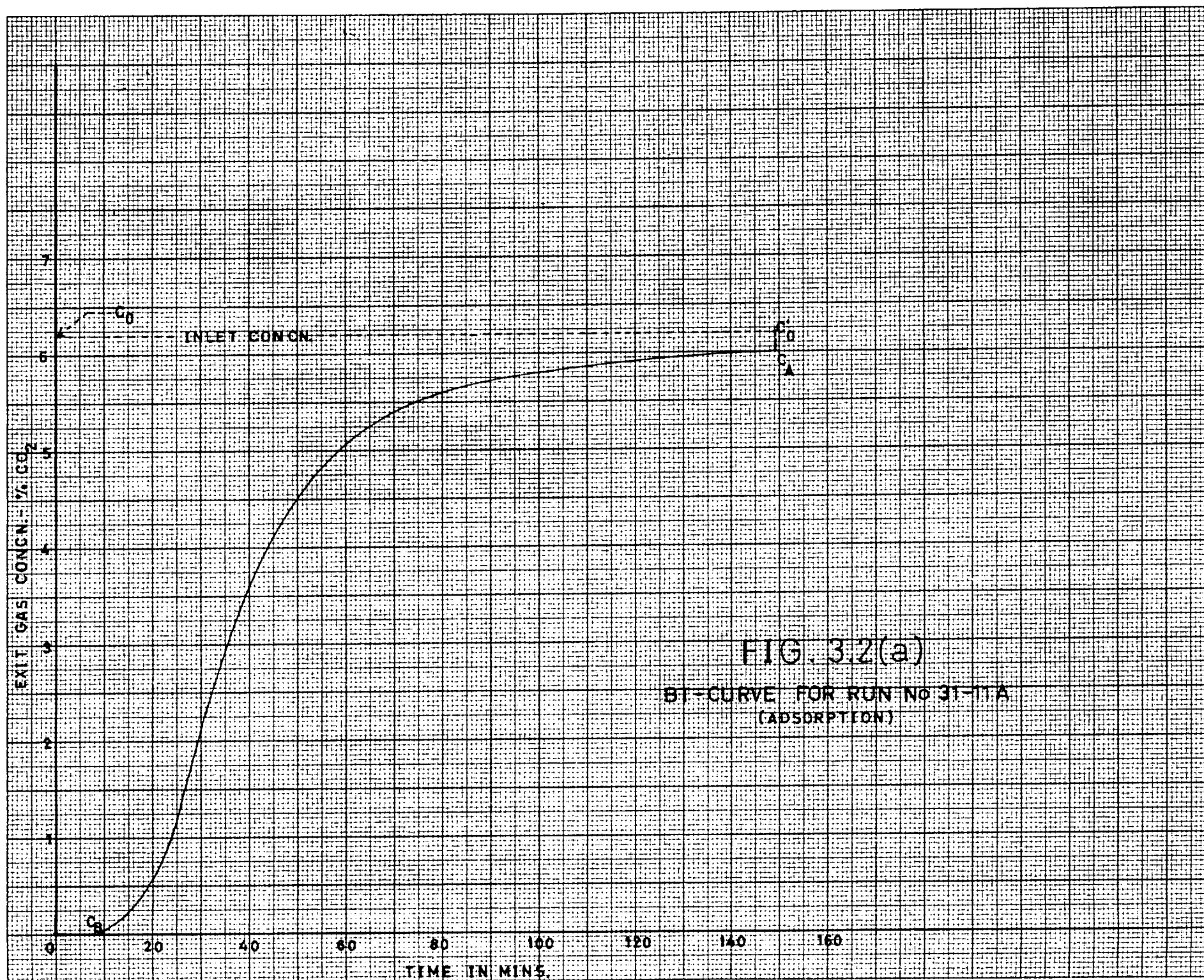
was slightly affected by the column having been brought into the path of flow. This could be checked by observing the gas composition at level 1 (i.e. the sampling section prior to entry into the column). For this purpose the probe at level 1 was usually kept connected to the sonic gas analyser during the starting period of the run. Any variation in the composition was quickly corrected by suitably altering the air flow only. As there was always some considerable time before the breakthrough occurred, this adjustment could always be safely carried out. In fact, this technique of sampling from level 1 was used as a method for the occasional checking of the entry gas composition and applying corrections to air flow (usually slight), if found necessary, even during the course of the runs.

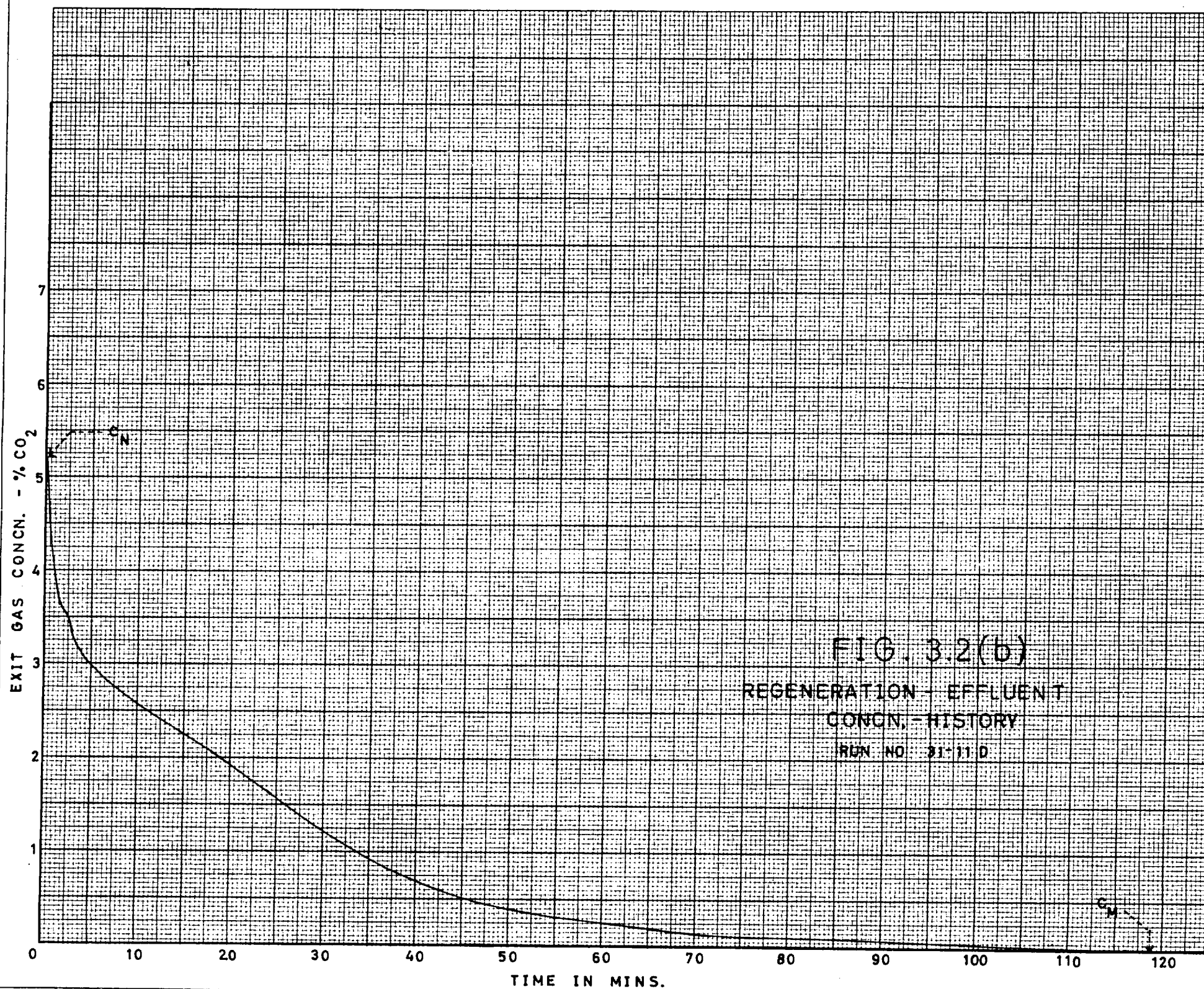
The breakthrough curve obtained on the recorder chart was then used to read off the exit gas composition versus time relationship for the run in question and the results suitably summarised in a table. The results for the various runs thus obtained are given in sections 1 to 3 of Appendix II. Fig. 3.1(a) shows the breakthrough curve obtained for a typical adsorption run, from which it can be seen how closely the points fall on a smooth curve. This was the case with all the runs carried out, except for some occasional deviations of a few points. Hence, in all the other figures where families of such curves are examined, only the smooth breakthrough curves without the points marked on them, are shown.



Regeneration:

The adsorption run was followed by a regeneration run. The regeneration was carried out with a higher air velocity than was used for the adsorption runs. The volumetric flow rate was of the order of 1.5 c.ft. (nearly 42 litres) per minute. The inlet air was heated to about 200°C in the external heater, while the heating coils around the column were also switched on. The initial 'warming up' period for the column to heat up and the first thermocouple to show the desired high temperature, was about an hour but the regeneration cycle was continued for approximately 3½ hours. This period for the regeneration cycle was fixed after an initial set of experiments in which it was found that the carbon dioxide adsorbed during the adsorption run was all removed in a matter of about 2 hours of regeneration at this air velocity and temperature. This was indicated not only by the carbon dioxide concentration of the exit gas reaching zero, but also by material balance against the carbon dioxide adsorbed in the adsorption run that preceded the regeneration cycle. Fig.3.1(b) gives the concentration-history curve for such a regeneration run carried out after an adsorption run. The area under the curve measured with a planimeter gave the amount of carbon dioxide adsorbed, and this agreed to within 2% of the amount calculated from the corresponding adsorption run (vide section 1 of Appendix III). In view of the approximations involved in the use of a planimeter, this could be considered as satisfactory agreement.





Towards the end of the regeneration cycle, the heat input to the heating coils around the column was adjusted in such a way that there was as little difference as possible in the temperatures measured by the successive thermocouples starting from the inlet end. By this means, it was hoped to supply to the column the equivalent of the "heat-losses" suffered by the hot gas as it travelled up the column. However, it was found difficult to obtain a small difference of temperature across the topmost section as there was much heat conducted away by the cold piping at this end. Section 4 of Appendix I gives the pattern of temperature gradient along the column, obtained towards the end of the regeneration cycles.

The Isotherm:

The available data for the isotherm for adsorption of carbon dioxide on molecular sieves are based on the thoroughly dried solid. In the packed column the conditions of activation were not severe enough to drive off all the moisture. The published data²⁶ could not, therefore, be made use of in the column performance calculations, and hence the isotherm was determined for conditions obtaining at the middle of the column as follows:

Fig. 3.3 gives a sketch of the apparatus used for this purpose. The numbers given in brackets refer to the items bearing corresponding numbers in the sketch. A basket (1) made from brass tubing with perforated wall was used to hold

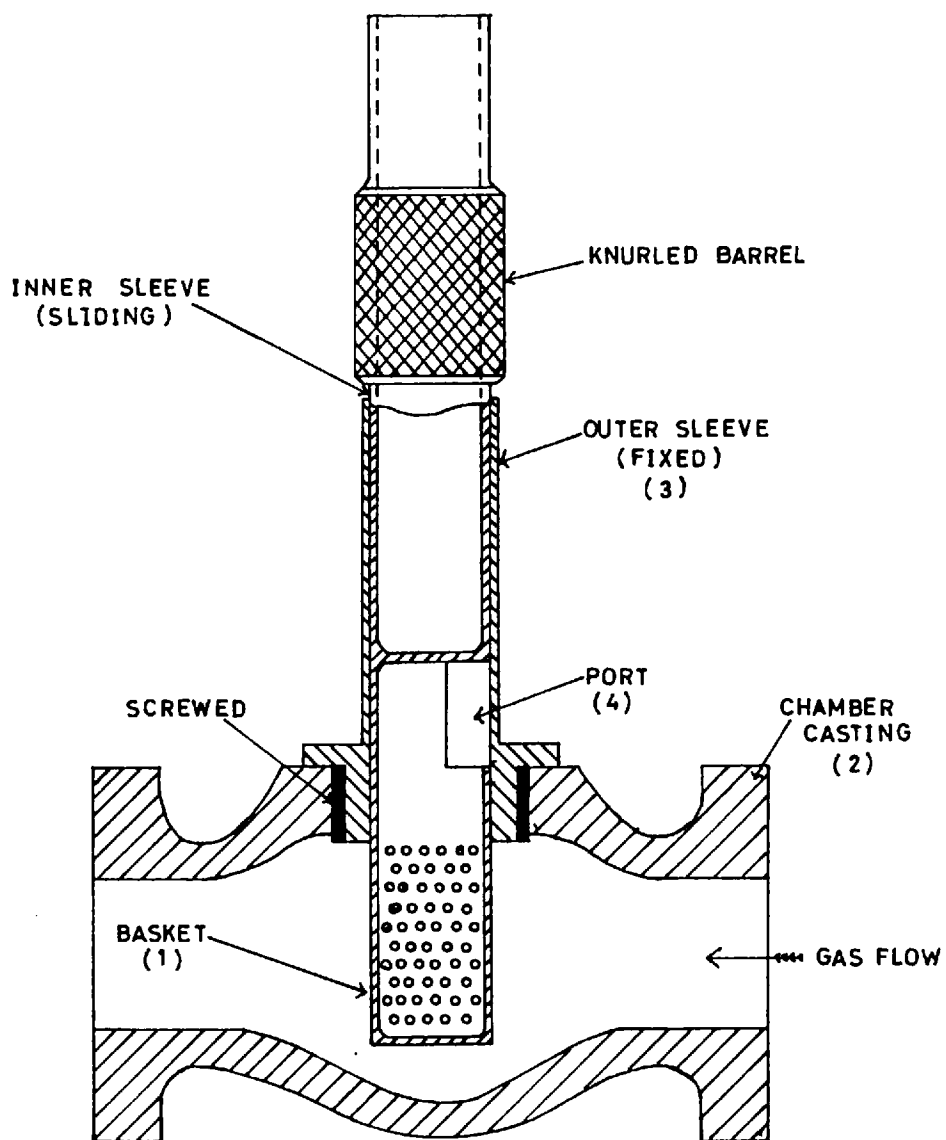
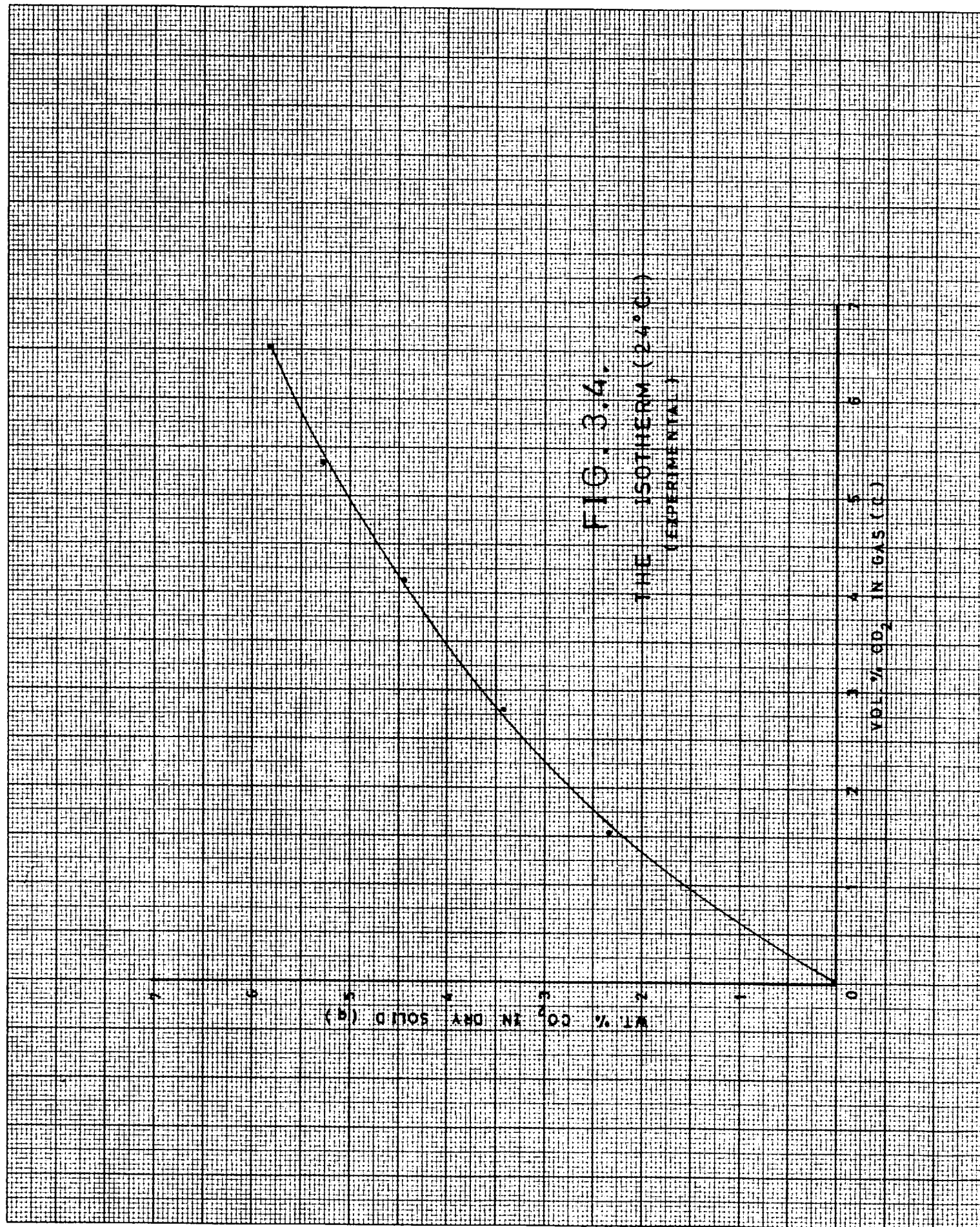


FIG. 33 EQUILIBRIUM APPARATUS

the sample of molecular sieve pellets in a current of the gas passing through a chamber (2) well lagged on the outside. The temperature of the gas was measured by means of a thermocouple provided in the chamber. Entry of the gas into the chamber was through copper tubing which could be heated electrically during the regeneration period by a nichrome wire winding. The heat output of the nichrome wire was controlled by a Variac included in the circuit. Whenever the sample had to be taken out for weighing, the basket was simply pulled out, about an inch, through the outer brass sleeve (3) so that the latter completely covered the perforated portion of the basket. The sleeve could now be unscrewed from the chamber and, with the basket held in, transported safely with the contents kept out of contact with the air outside. The contents could then be quickly transferred into a weighing bottle through the side hole (4) in the top section of the basket, which could be uncovered by pulling the basket out by about another inch through the sleeve.

About 2 gm. of the molecular sieve pellets were put in the basket and first activated by passing air at the same temperature as at the middle of the column during the regeneration cycle. The gases were obtained from the same set up used for the column runs. For determining the isotherm, the regenerated sample was then exposed to the gas (CO_2 - air mixture) of the desired composition passing through the chamber, for a period



of six hours, by which time the rate of adsorption (noted by the rate of increase in the weight of the solid) had become sufficiently small. The period of six hours mentioned above was arbitrarily fixed on practical considerations since the entire operation of regeneration and adsorption took nearly 9 hours, and the system could not be left (unattended) overnight as the gas composition was being maintained by dynamic mixing. The results obtained, were however, satisfactory as can be seen from the graph Fig. 3.4. The data could be fitted to a Langmuir form of equation the constants of which were obtained by the method of least squares. These results are given in section 6 of Appendix I. Published data obtained from static experiments also show that the isotherm is of the Langmuir form.

Chapter 4

THEORETICAL

In Chapter 1, a general review of the literature on fixed-bed performance was given. In this chapter the results of some of the theoretical papers dealing with the prediction of the concentration-history of a fixed-bed effluent are summarised for use in the discussion of the results of the present investigation in Chapter 5. The nomenclature has been modified to provide uniformity. Original papers should be referred to for fuller details.

The Anzelius³-Schumann⁴³ Solution:

Strictly speaking the Anzelius-Schumann solution is a mathematical solution for the analogous problem of heat transfer in fixed-beds. Schumann⁴³ and Furnas¹⁴ have presented the solution in graphical form and Hougen and Marshall¹⁸ have shown that it may be applied to the case of fixed-bed adsorption.

In essence, this solution is for the case involving a linear isotherm and with the diffusion in the external gas film rate-controlling, the effect of solid diffusion being negligible. The driving force for mass transfer is then given by the concentration difference across the gas film and is therefore a function of the average concentration in the solid and not the surface value. Hougen and Marshall further assumed that the adsorbate content of the gas present in the bed at any instant was negligible in comparison with the total quantity

of the adsorbate involved in the operation. These assumptions simplify the general mass balance and rate equation to

$$-G \left(\frac{\partial C_H}{\partial z} \right) = \rho_B \left(\frac{\partial q}{\partial t} \right) = k_g a (C_H - C_H^{\#}) \quad \dots\dots (4.1)$$

and the linear equilibrium relationship is given by

$$C_H^{\#} = K_H q \quad \dots\dots\dots (4.2)$$

where

G = mass velocity ($M.L.^{-2} T^{-1}$),

C_H = adsorbate concentration in gas ($M.M^{-1}$),

q = average adsorbate concentration in solid ($M.M^{-1}$),

ρ_B = bulk density of solid in bed ($M.L^{-3}$),

a = specific surface area of the adsorbent particles ($L^2.L^{-3}$),

k_g = mass transfer coefficient defined by the above equation,

K_H = constant in the linear equilibrium relationship,

z = height of the bed (L), and

t = time (T).

Hougen and Marshall have expressed the solution to the above equation for a constant influent concentration of C_0 and the flow starting at $t=0$, as

$$u = \frac{C}{C_0} = 1 - \int_0^E e^{-Bt - \xi} i_0 \quad (2\sqrt{\xi \cdot Bt}) d\xi \quad \dots\dots (4.3)$$

where

$$E = \frac{G}{k_g a} = \frac{1}{(HTU)_{og}}$$

$\xi = Ez$ = "thickness modulus" (dimensionless)

$$B = B_H K_H ; B_H = \frac{G}{\rho_B (HTU)_{og}}$$

Bt = time modulus (dimensionless)

I_0 = Modified Bessel function of the first kind and zero order.

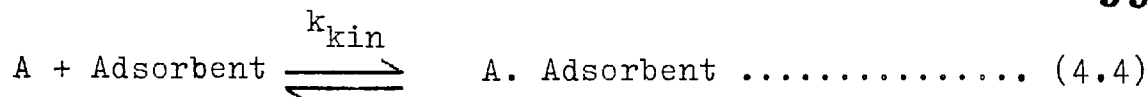
Brinkley et al⁵ have tabulated the integral appearing in equation (4.3) and Hougen and Marshall have also evaluated and plotted the values of u against the time modulus with the thickness modulus as parameter in the form of Schumann-Furnas curves.

Thomas's Solution:

Thomas⁴⁵ originally established his solution for the case of an ion exchange column. He assumed that the exchange was governed by 'a law of the concentration product type'. Thus his approach is a 'reaction-kinetic' approach and this has certain advantages of simplicity over the diffusional approach and serves as an expedient, particularly in cases where many steps are involved in the mass transfer and the equilibrium is non-linear. However, when applied to handle diffusional cases the model should be expected to be only approximate since it does not represent the real physical situation.

Hiester and Vermeulen¹⁷ have extended the application of Thomas's solution to the case of adsorption, and it is best to follow their^{17,36} treatment for this case.

The adsorption process can be considered as a reversible second order-first order surface reaction and represented as



where k_{kin} = rate constant for the adsorption (cc/m.mol./min.)

The surface reaction rate according to equation (4.4) is

$$\left(\frac{\partial q_A}{\partial t} \right)_L = k_{\text{kin}} C_A \left[(Q^{\text{ad}} - q_A) - \frac{1}{K_A^{\text{ad}}} q_A \right] \dots\dots (4.5)$$

where L = packed volume of solids, (cc)

t = time, (min.)

When the solid is homogeneous with uniform adsorptive forces throughout, the equilibrium mass action constant K_A^{ad} (cc/m.mol) for the above reaction is given by

$$K_A^{\text{ad}} = \frac{q_A}{C_A (Q^{\text{ad}} - q_A)} \dots\dots\dots (4.6)$$

C_A = concentration of component A in the fluid phase at a specified point in the column, (m.mol / cc)

q_A = concentration of component A in the solid phase at a specified point in the column, (m.mol/gm)

Q^{ad} = total concentration of components in the solid (i.e., the adsorptive capacity), (m.mol./gm)

ad = value for adsorption.

kin = value on the basis of a reaction-kinetic approach.

Equation (4.5) conveniently rearranges into the Langmuir isotherm form as $q^{\#} = \frac{Q^{\text{ad}} K_A^{\text{ad}} C_A}{1 + K_A^{\text{ad}} C_A} \dots\dots\dots (4.7a)$

or in its complementary form, as

$$C_A^{\#} = \frac{q_A}{K_A^{ad} Q^{ad} - K_A^{ad} q_A} \dots\dots\dots (4.7b)$$

Where $\#$ indicates the concentration in equilibrium with the actual concentration in the coexisting phase.

The conservation equation for an infinitesimal thickness of bed at any given cross section can be expressed as

$$- \left(\frac{\partial C_A}{\partial L} \right) = \frac{\epsilon_B}{F} \left(\frac{\partial q_A}{\partial t} \right)_L + \frac{e}{F} \left(\frac{\partial C_A}{\partial t} \right)_L \dots\dots (4.8)$$

where

F = volumetric flow rate of the fluid, (c.c./min.)

e = external void fraction, dimensionless.

ϵ_B = bulk density of the solid (gm/c.c. of packed volume)

If the time co-ordinate is transformed to $(t - \frac{Le}{F})$, the total time of flow past a given point in the bed, the conservation and the rate equations given above become

$$\begin{aligned} - \frac{F}{\epsilon_B} \left[\frac{\partial C_A}{\partial L} \right] \left(t - \frac{Le}{F} \right) &= \left[\frac{\partial q_A}{\partial (t - \frac{Le}{F})} \right]_L \\ &= k_{kin} C_A (Q^{ad} - q_A) - \frac{1}{K_A^{ad}} q_A \dots\dots\dots (4.9) \end{aligned}$$

At this stage certain dimensionless parameters may be defined

u = concentration ratio of the solute in the fluid.

w = concentration ratio of the solute in the solid.

r = a factor related to equilibrium conditions called 'the equilibrium parameter.'

S = a factor related to position in the column.

T = a factor related to total time of fluid flow

For the case where the bed is initially free of the solute and the solute concentration of the fluid is $(C_A)_0$ at the entrance of the column, the above parameters are given by

$$u = \frac{C_A}{(C_A)_0} \dots\dots\dots (4.10a)$$

$$w = \frac{q_A}{(q_A)_0} \dots\dots\dots (4.10b)$$

$$r = \frac{1}{1 + K_A^{ad} (C_A)_0} \dots\dots\dots (4.10c)$$

$$S = \frac{k_{kin} Q^{ad} e_B L}{F} \dots\dots\dots (4.10d)$$

and

$$T = \frac{k_{kin}}{K_A^{ad}} (1 + K_A^{ad} (C_A)_0) (t - \frac{Le}{F}) \dots\dots\dots (4.10e)$$

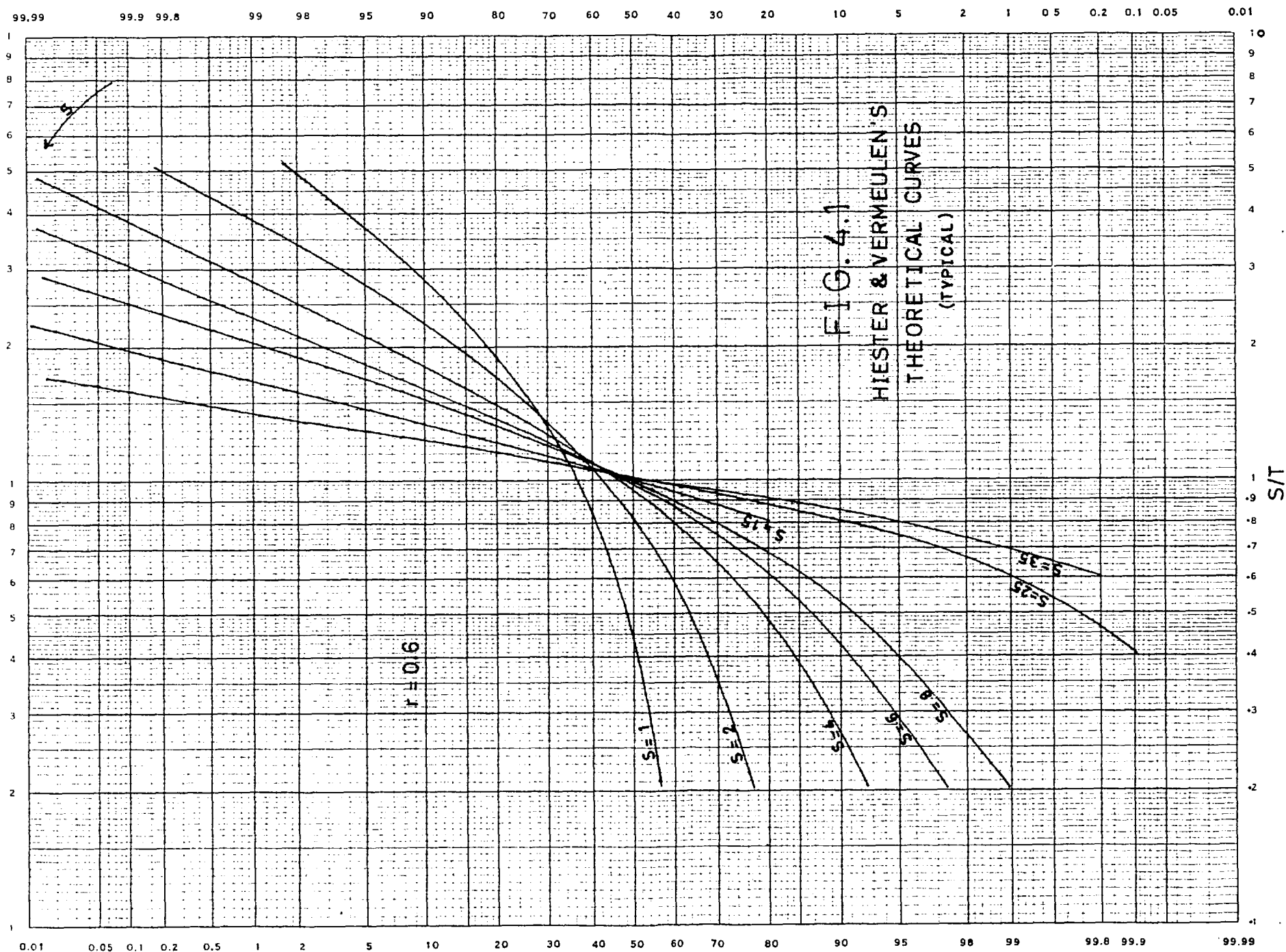
In terms of these parameters, the conservation and rate relations given by equation (4.9) reduce to

$$- \left(\frac{\partial u}{\partial s} \right)_T = \left(- \frac{\partial w}{\partial T} \right)_S = u (1-w) - rw (1-u) \dots\dots\dots (4.11)$$

Under these conditions Thomas's solution to equation (4.9) for 'saturation' boundaries is also the solution to equation (4.11). In terms of the present parameters, the solution can be expressed as,

$$u = \frac{J(r S, T)}{J(r S, T) + e^{(r-1)(T-S)} [1 - J(S, r T)]} \dots\dots (4.12)$$

$$u = CK_0(\%)$$



with

$$J(X, Y) = 1 - \int_0^X e^{-Y-\xi} I_0(2\sqrt{Y\xi}) d\xi \dots\dots (4.13)$$

where $J(X, Y)$ = function of two quantities X and Y , defined by the above equation.

and $I(\xi)$ = modified Bessel function of the first kind and Zero order for argument ξ .

This function is identical in form with the Anzelius solution given in equation (4.3), so that tabulations of this solution can be used to evaluate u in equation (4.12), which in fact reduces to equation (4.3) when $r = 1$.

A similar type of solution for w can be obtained, and Opler and Hiester³⁶ have computed numerical values for u and w and have tabulated these for a wide range of r , S and T values. Using these values, one can plot u versus $\frac{S}{T}$ for each value of r , with S as parameter, and obtain theoretical master curves, similar to those shown by Hiester and Vermeulen¹⁷. Fig. 4.1, illustrates a typical case of such a graph, where a logarithmic scale for the x-axis and a probability scale for the y-axis have been used in order to obtain graphs of relatively small curvature and with an expanded scale for plotting the terminal values of U .

The value of $\frac{S}{T} = Z$, is called the throughput parameter and is defined by the relation

$$Z = \frac{V - Le}{V_{\text{stoic}}} = \frac{C \bullet (V - Le)}{(q_A)_0^* C_{BL}} \dots\dots\dots(4.14)$$

where

$V = Ft$ = the volume of fluid that has entered the column up to a particular time t , (c.c.) and

V_{stoic} = the stoichiometric volume of the fluid, (c.c.).

The throughput parameter reaches a value of unity when the volume of feed which has passed through the column becomes stoichiometrically equivalent to the adsorption capacity of the column, and it can be obtained directly from experimental data.

For comparing the experimental data against the theoretical solution, one uses scales similar to those of the master curves drawn for the appropriate r value, and plots the experimental data for C/C_0 against $\log Z$, $\log (t - \frac{Le}{F})$ or $\log (V - Le)$, on tracing paper. This curve is then matched against the master curves, using horizontal displacement if necessary, in order to determine the value of S giving the best fit. From the value of S so obtained, the value of k_{kin} can be calculated from equation (4.10d).

Rosen's Method:

Since in most cases of practical adsorption, both the fluid film resistance and solid diffusion take a significant part in the overall mass transfer, a theoretical analysis which takes account of both of these factors should be highly welcome. Such an analysis has been made by Rosen⁴¹ who has also provided tabulated values of u , the concentration ratio, for a range of values of certain dimensionless parameters defined by him.

Unfortunately; however, mathematical difficulties have necessitated restriction of the solution to a linear isotherm. Rosen's⁴⁰ solution provides a very convenient method of evaluating the solid diffusion coefficient from experimental data, if other factors are known.

By neglecting variations, if any, in velocity or concentration over a given cross section of the bed of spherical particles of adsorbent as insignificant, one can consider the fixed-bed as a one-dimensional column in space with bed length z and time t alone as variables determining the concentration of the solute in the gas phase and write the conservation equation as,

$$v \left(\frac{\partial C}{\partial z} \right) + \frac{\partial C}{\partial t} - D_L \frac{\partial^2 C}{\partial z^2} = -\frac{1}{m} \frac{\partial q_v}{\partial t} \dots (4.15)$$

where

v = linear flow velocity (assumed constant), (cm/sec.)

D_L = longitudinal diffusion coefficient, (cm²/sec)

$m = \frac{e}{1-e}$ = void volume per unit volume of solid particles, (dimensionless).

q_v = average volumetric concentration of adsorbate on adsorbent particle (cm³/cm³).

If the term $-D_L \frac{\partial^2 C}{\partial z^2}$ is eliminated assuming

*The basic assumptions are repeated here in order to give a fuller treatment of Rosen's solution as it has assumed importance in the discussion of our results in the chapter to follow.

negligible effect of longitudinal diffusion, equation (4.15) reduces to

$$v \left(-\frac{\partial c}{\partial z} \right) + -\frac{\partial c}{\partial t} = \frac{1}{m} \left(-\frac{\partial q_v}{\partial t} \right) \dots\dots (4.16)$$

By a change of variables

$$x = \frac{z}{mv} \dots\dots\dots (4.17)$$

$$\text{and } \theta = t - \frac{z}{v} \dots\dots\dots (4.18)$$

Equation (4.16) can be transformed to

$$\frac{\partial c}{\partial x} = - \frac{\partial q_v}{\partial \theta} \dots\dots\dots (4.19)$$

The rate $\frac{\partial q_v}{\partial t} = \frac{\partial q_v}{\partial \theta}$ at which the material is taken up from the fluid phase by the solid particles is determined by the combined effect of gas film and solid diffusion into the particles and is given by

$$\frac{\partial q_v}{\partial \theta} = \frac{3h}{b} (c - c^*) = \frac{1}{R_f} (c - c^*) \dots\dots (4.20)$$

for the transfer through the boundary layer and by

$$\frac{\partial q_i}{\partial \theta} = \left(\frac{D_s}{R^2} \right) \frac{\partial}{\partial R} \left[R^2 \left(-\frac{\partial q_i}{\partial R} \right) \right] \dots\dots (4.21)$$

for the transfer into the granules,

where,

D_s = effective solid diffusion coefficient in the spherical particles ($\text{cm}^2/\text{sec.}$)

h = gas film mass transfer coefficient (cm./sec.).

b = radius of the spherical particles: (assumed uniform throughout the bed (cm.)

q_i = concentration of adsorbate in the particle at radius R ; (volumetric).

R = radial distance from centre of spherical particle. (cm.)

$R_f = \frac{b}{3h}$ effective surface film resistance (sec.)

Since $\frac{\partial q_v}{\partial \theta} = \frac{\partial q_i}{\partial \theta}$ at the surface, equations (4.20) and (4.21) can be combined to give

$$\left(\frac{\partial q_v}{\partial t} \right)_{R=\ell} = \frac{3h}{\ell} \left(C - \frac{q_s}{K} \right) = \left(\frac{D_s}{\ell^2} \right) \left\{ \frac{\partial}{\partial R} \left[R^2 \left(\frac{\partial q_i}{\partial R} \right) \right] \right\}_{R=\ell} \dots\dots(4.22)$$

where

$q_s = K C^*$, K being the constant defining the linear isotherm

q_s = adsorbate concentration on the particle (volumetric) in equilibrium with C^* .

Also, the average concentration in the particles q_v is related to the internal concentration q_i at radius R , by

$$q_v = \frac{3}{b^3} \int_0^b q_i R^2 dR \dots\dots\dots(4.23)$$

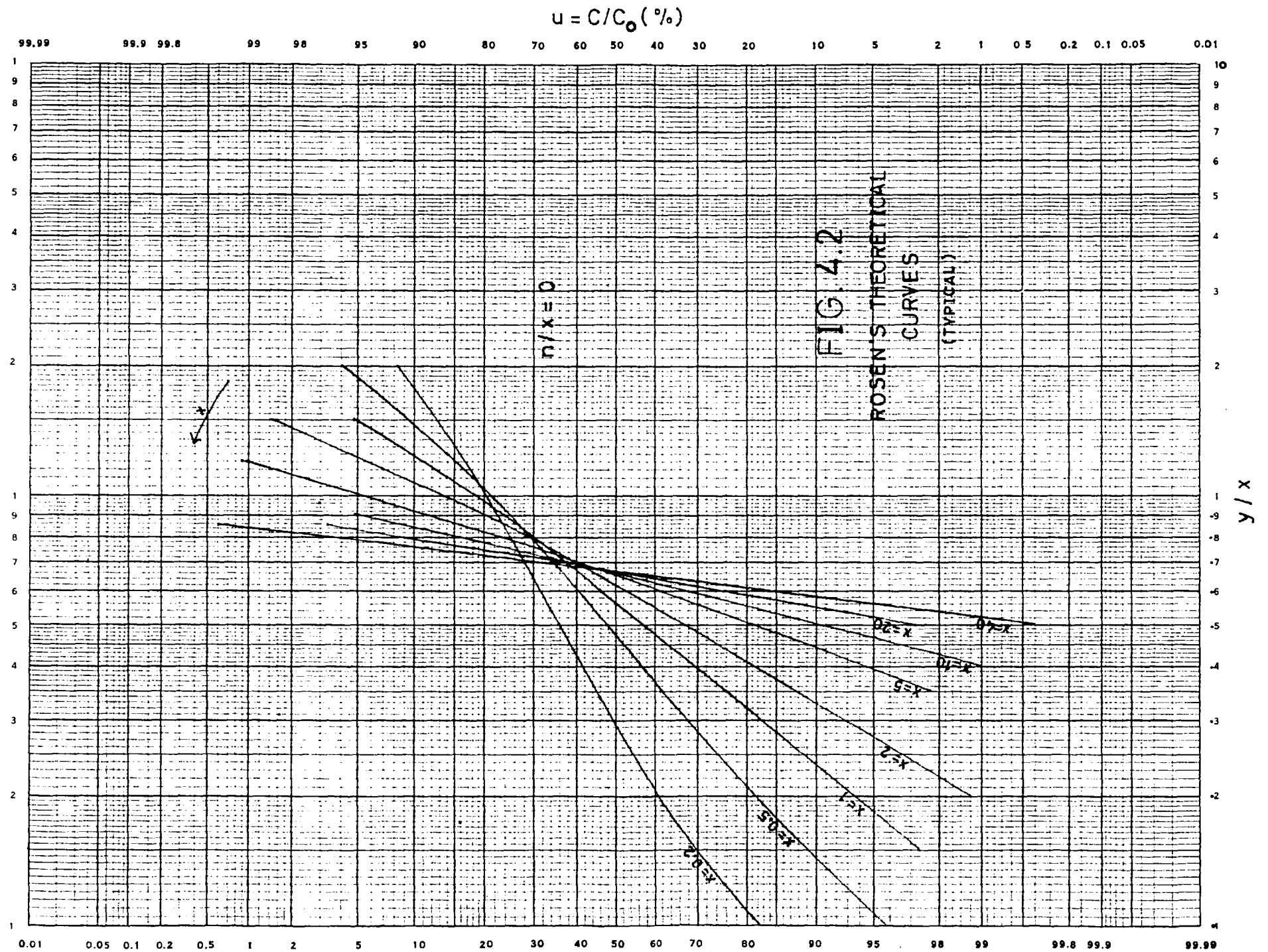
Under conditions where the bed is initially free of adsorbate, and for a step increase in the influent concentration from zero to C_0 at time $t = 0$, and for constancy of gas film and solid diffusion coefficients, Rosen has solved these equations for the effluent concentration as a function of time and bed length, in terms of three dimensionless parameters.

The solution can be expressed as

$$u = \frac{C}{C_0} = \frac{1}{2} + \phi \quad (n, x, y) \dots\dots\dots(4.24)$$

where

$$n = -\frac{3D_s K R_f}{b^2} ; \quad \text{film resistance parameter (dimensionless)} \dots\dots\dots(4.25)$$



$$x = \frac{3 D_s K z}{m v b^2} ; \text{ bed length parameter (dimensionless) } \dots (4.26)$$

$$y = \frac{2 D_s (t - \frac{z}{v})}{b^2} ; \text{ contact time parameter (dimensionless) } \dots (4.27)$$

and

$$\phi(n, x, y) = \int_0^\infty e^{-x H_1(\sqrt{\beta}, n)} \sin \left[y \beta - x H_2(\sqrt{\beta}, n) \right] \frac{d\beta}{\beta} \dots (4.28)$$

The functions H_1 and H_2 are defined in Rosen's paper.

Using a digital computer, Rosen has evaluated the integral for a range of numerical values of u , x and y and has presented the values of u in tabular and graphical forms against the values of y/x , x and n/x . It will be seen that

$$\frac{y}{x} = \frac{2m}{3K} \left(\frac{vt}{z} - 1 \right) ; \text{ (dimensionless) } \dots (4.29)$$

$$\text{and } \frac{n}{x} = \frac{m v R_f}{z} ; \text{ (dimensionless) } \dots (4.30)$$

Fig. 4.2, gives a typical case of Rosen's theoretical curves. In this, probability-logarithmic scales have been used instead of the arithmetic-logarithmic scales used by Rosen, since the former gives relatively straightened curves making it easy for comparison against experimental curves. It also enlarges the scale at terminal values of u .

The curve-matching technique is similar to the one described for Vermeulen's adaptation of Thomas's solution. One plots the experimental data on a probability-logarithmic graph with u (probability scale) against y/x (logarithmic scale). Sets of master curves of Rosen's solution are prepared on similar paper for different n/x values with x as parameter. One can also

prepare and use plots of theoretical curves for different values of x with n/x as parameter, depending upon the needs. The experimental curve is then matched against the theoretical curves, using horizontal shift if necessary, until an appropriate fit is obtained. The value of x or n/x so obtained can be used for interpretation.

It will be seen from equation (4.29) that the horizontal shift needed, if any, will give the ratio of the K value actually used to the mean K value giving the best fit to the curves, since the y/x values have been plotted on a logarithmic scale.

If one has breakthrough data for various bed depths, one can, by using the above curve-matching technique, obtain values of x as a function of z , the bed depth. If K and D_s are constant for all bed depths, then from equation (4.26) it can be seen that a plot of x versus z on arithmetic coordinates should result in a straight line passing through the origin, with slope

$$\lambda = \frac{3 D_s K}{m v b^2} \dots\dots\dots (4.32)$$

from which the value of D_s , the effective solid diffusion coefficient can be evaluated, using for b , the mean particle diameter, the value obtained from pressure drop experiments, as given in section 3, of Appendix III.

Even though the solutions of Anzelius, Thomas and Rosen are presented separately, in their respective nomenclature, for convenience in treatment, it can be seen that they are

basically the same in certain respects. For example, the conservation equations (4.8) and (4.16) are the same except that the q value in equation (4.8) is expressed in wt./wt. units while in the latter it is in vol./vol. units. Transformation of the length and time variables, allowing for the 'delay' due to mass transfer, results in the simplified form of the conservation equation (4.19) in either case. The corresponding conservation equation in Hougen and Marshall's solution (vide equation 4.1) is also similar, with the $\frac{\partial C}{\partial t}$ term neglected.

It is only with regard to the rate equations that the three solutions differ according to the different controlling mechanisms assumed. Hougen and Marshall's equation (4.1) is the simplest in form because it is for external mass transfer controlling and for a linear isotherm. Thomas's equation is based on a reaction-kinetic approach, but the resultant equation can be transformed to a Langmuir isotherm form thus gaining a wider range of applicability. It is Rosen's equation that takes into account both the surface resistance and the solid diffusion and hence becomes more complicated. The restriction of a linear isotherm for this case is a mathematical necessity for obtaining an analytical solution. The reason for the differences in the form of the rate equations can now be seen.

Another point of similarity is in the use of dimensionless parameters which ultimately resolve to the same physical meaning.

In the case of the parameter used for representing 'time', for example, it can be seen that the numerical value of the parameter calculated from equation (4.29) (Rosen's) will be exactly $\frac{2}{3}$ rds of that given by equation (4.14) (Vermeulen's), for the same set of operating conditions of the column.

Chapter 5

RESULTS AND DISCUSSIONS

The experimental work described in Chapter 3 has provided us with breakthrough data for ten different lengths of a column packed with molecular sieve pellets type 4A, adsorbing carbon dioxide from air at room temperature. These data are presented in sections 1 to 3 of Appendix II. The sets of runs designated as series 10 and series 20, are for the same inlet concentration of 6.2% by volume of carbon dioxide, a value chosen to be within the range of the sonic gas analyser and yet well on the nonlinear portion of the isotherm. The two sets of runs were however made at different gas flow rates, 6.19 litres per min. for series 10 and 23.48 litres per min. for series 20, values chosen arbitrarily to fall within the limits of experimental convenience.

The runs designated as series 50, have an inlet concentration of 1.9% carbon dioxide which is nearer the initial linear portion of the isotherm and yet not too low to upset the accuracy of analysis by the sonic gas analyser. The flow rate is 5.67 litres per min. of gas at the inlet. These experiments should provide sufficient data to check the validity of the theories described in Chapter 4, which has been our main objective.

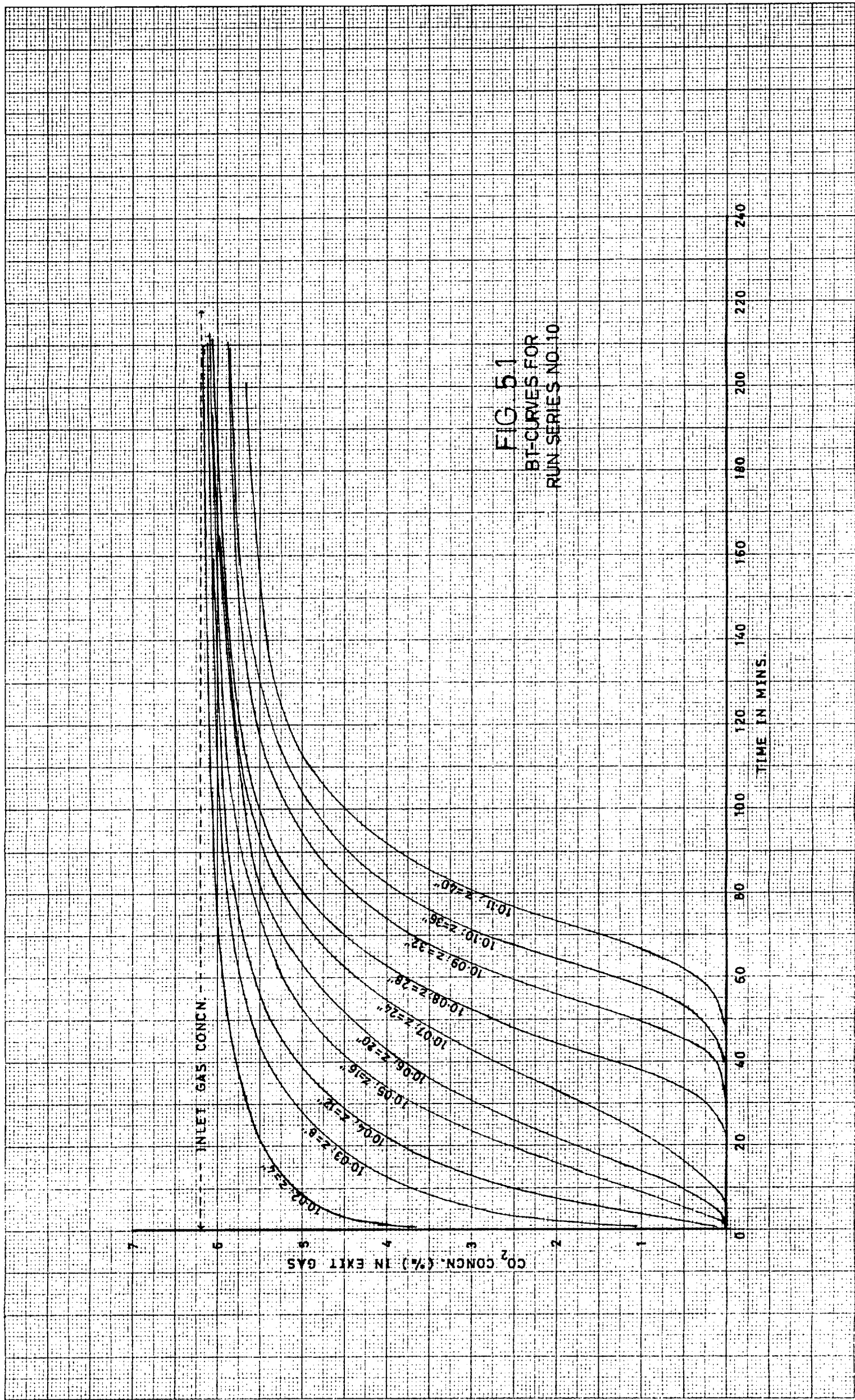


FIG 51
BT-CURVES FOR
RUN SERIES NO.10

Data for certain other experiments are presented in sections 1 to 3 of Appendix III. These serve as auxiliary experiments and have been conducted with the following objectives:

- (a) Checking reproducibility of initial bed conditions
- (b) Checking the magnitude of radial effects.
- (c) Checking voidage by pressure drop measurements and determining equivalent diameter of the particles.

Two of the results of the auxiliary experiments are worth mentioning at this stage as they have a bearing on the application of the theories to our experiments. The first is the confirmation that our regeneration procedure was effective enough to remove the adsorbed carbon dioxide completely from the bed, thereby enabling us to assume a value of zero for the initial concentration of carbon dioxide in the bed. The second is the confirmation that radial effects on concentration is of an order that can be neglected.

If, in addition to these, we assume the effect of longitudinal diffusion to be negligible, application of the theories enumerated in Chapter 4, becomes straight forward. No special experiments were conducted to test the significance of longitudinal diffusion, but the fact that theories neglecting the effect provide an adequate correlation of the results is indirect evidence that it is indeed negligible.

We now proceed to describe the treatment of the main

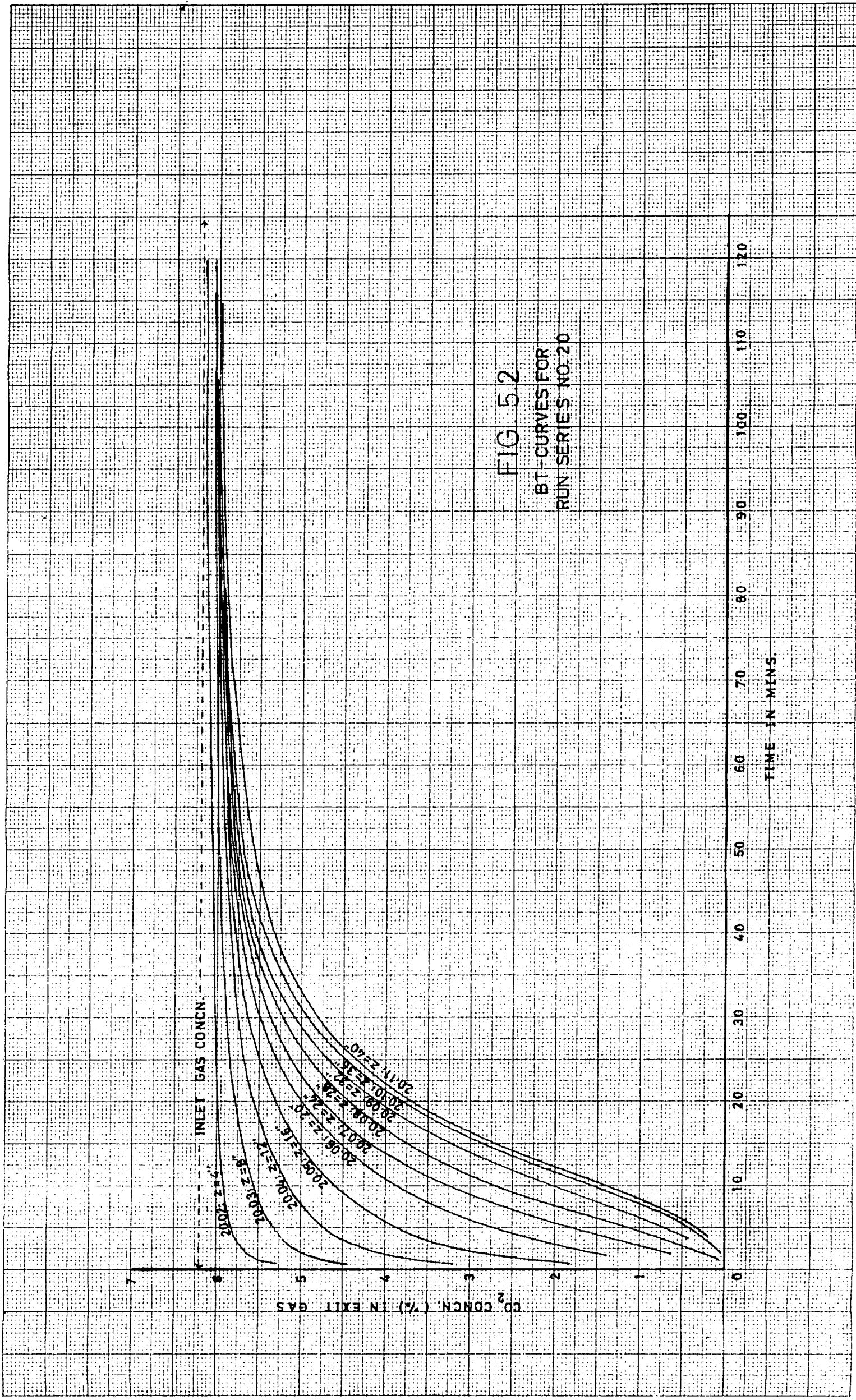


FIG 5.2
BT-CURVES FOR
RUN SERIES NO. 20

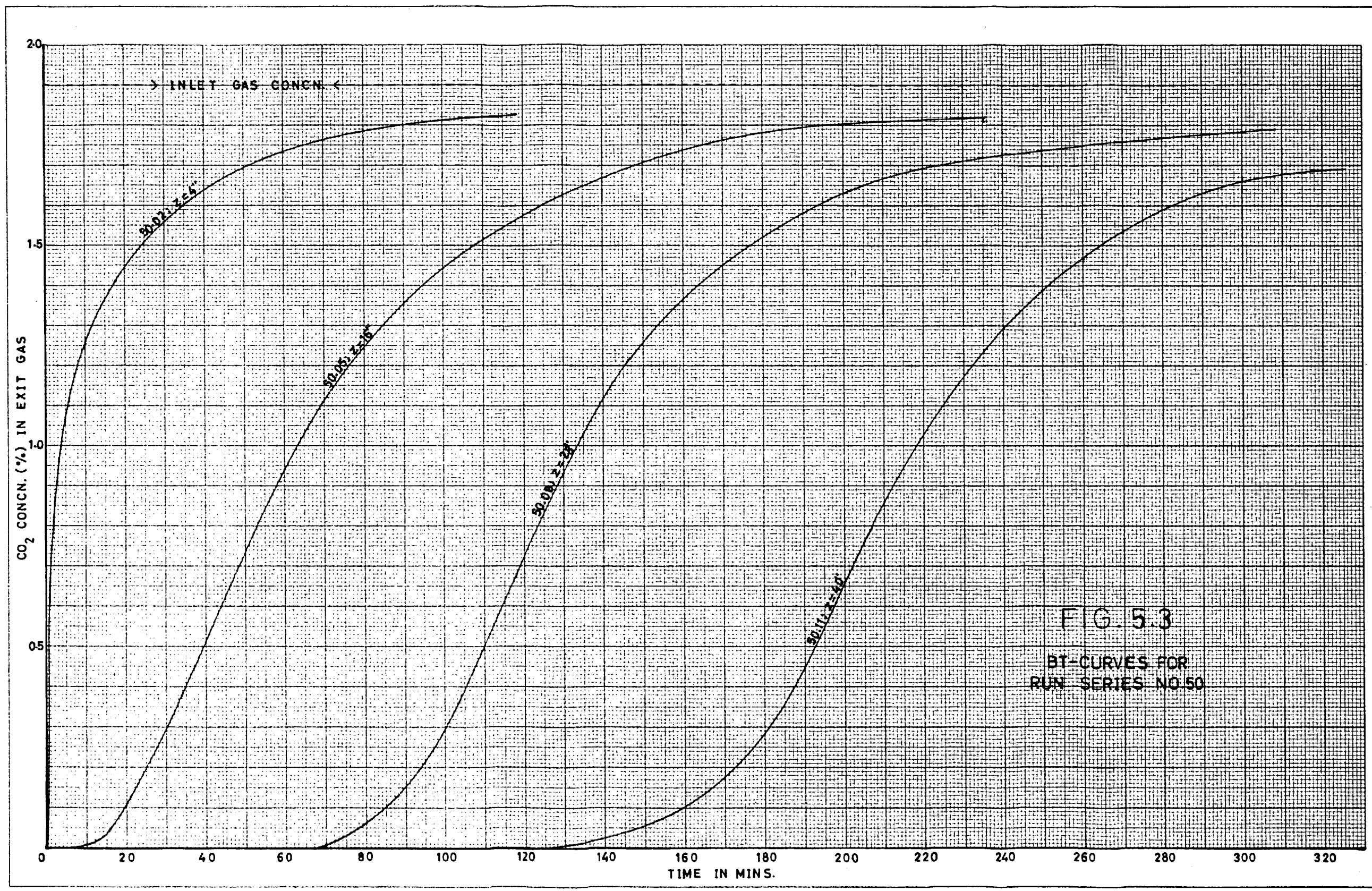
data we have obtained from the runs of series 10, 20 and 50 and the inferences that can be drawn from them.

The Concentration History:

The breakthrough data for the various series of runs were represented as in Figs. 5.1, 5.2 and 5.3 on arithmetic co-ordinates, with t , the time in minutes, as abscissa, the value of u or $\frac{C}{C_0}$, the effluent concentration ratio, as the ordinate and with z , the bed depth, as parameter. It may be seen that for runs of lower gas flow and higher values of z , the breakthrough curves* conform to the general S-shape to be expected. At lower values of z for these runs the 'break point' starts quite early and hence the lower asymptotic portion of the BT curves is either short or is non-existent. In the case of set 20, this effect is noticeable for practically all the z values in the range, presumably because of the low residence time occurring as a result of the high rate of flow of gas.

The slope of the BT curves also show a regular tendency to decrease as the value of z increases, except that at very high values of z in the case runs 10 and 50, which have lower rates of flow of gas, the slope tends to reach a constant value. Since the isotherm is of the Langmuir type it should be expected that the BT curve will normally be of the "constant-pattern". Even so, and assuming that a certain

* to be henceforth designated as BT curves.



amount of bed length would be required for the "pattern" to establish itself, it is not clear at first sight why there should be so much deviation from the "constant-pattern" at most of the z values investigated. There are, perhaps, other factors that have to be taken into account and we shall revert to this point again at a later stage of the discussion.

The Isotherm:

Since, for any consideration of the theoretical aspects, data on the "equilibrium" is necessary, this was determined by separate experiments simulating the conditions obtaining at the middle of the column, as described in Chapter 3. The data obtained are presented in section 5 of Appendix I. Fig. 3.4, shows the form of the isotherm. The Langmuir constants were determined by the method of least squares as shown in section 6 of Appendix I. The final result is expressed as

$$q_e = \frac{1.8615C_e}{1 + 0.1692C_e} \dots\dots\dots (5.1)$$

where

q_e = concentration of carbon dioxide in the solid phase at equilibrium, (gm/100 gm. dry solid)

C_e = concentration of carbon dioxide in the gas phase (cc./100 cc. of gas)

Equation (5.1) can also be expressed in another form for application to Vermeulen's theory as

$$q_e = Q^{ad} \frac{K_e C_e}{1 + K_e C_e} = 11.001773 \times \frac{0.1692C_e}{1 + 0.1692C_e} \dots\dots\dots (5.2)$$

When applying equilibrium data to the experimental runs, the values calculated from the above equations have been used.

The Anzelius-Schumann Solution:

This solution has been described in Chapter 4. Since it is based on external mass transfer rate controlling, one would not expect it to be very successful in interpreting our results. In any case the Anzelius solution can be considered as a special case of Thomas's solution when the value of $r = 1$. Hence fitting our data to the Anzelius-Schumann solution as such was not attempted.

Thomas's Solution:

In applying Thomas's solution for the interpretation of our data the curve-matching technique described in Chapter 4 was used. The value of r for runs 10 and runs 50 are 0.48 and 0.76 respectively (vide section 4 of Appendix II). From the Opler-Hiester³⁶ tables the values of C/C_0 and T/S for various values of S and the nearest tabulated value of r , were read and master-curves prepared with S as parameter. To represent the experimental data, there is no need to calculate the value of Z separately, since a logarithmic scale is used for the abscissa. One can even use the graphs of experimental data prepared on Rosen's parameters of u and $\frac{Y}{X}$, because the latter is exactly $\frac{2}{3}$ of the calculated value of Z for identical conditions, and only a horizontal shift of the scale is necessary for curve-matching.

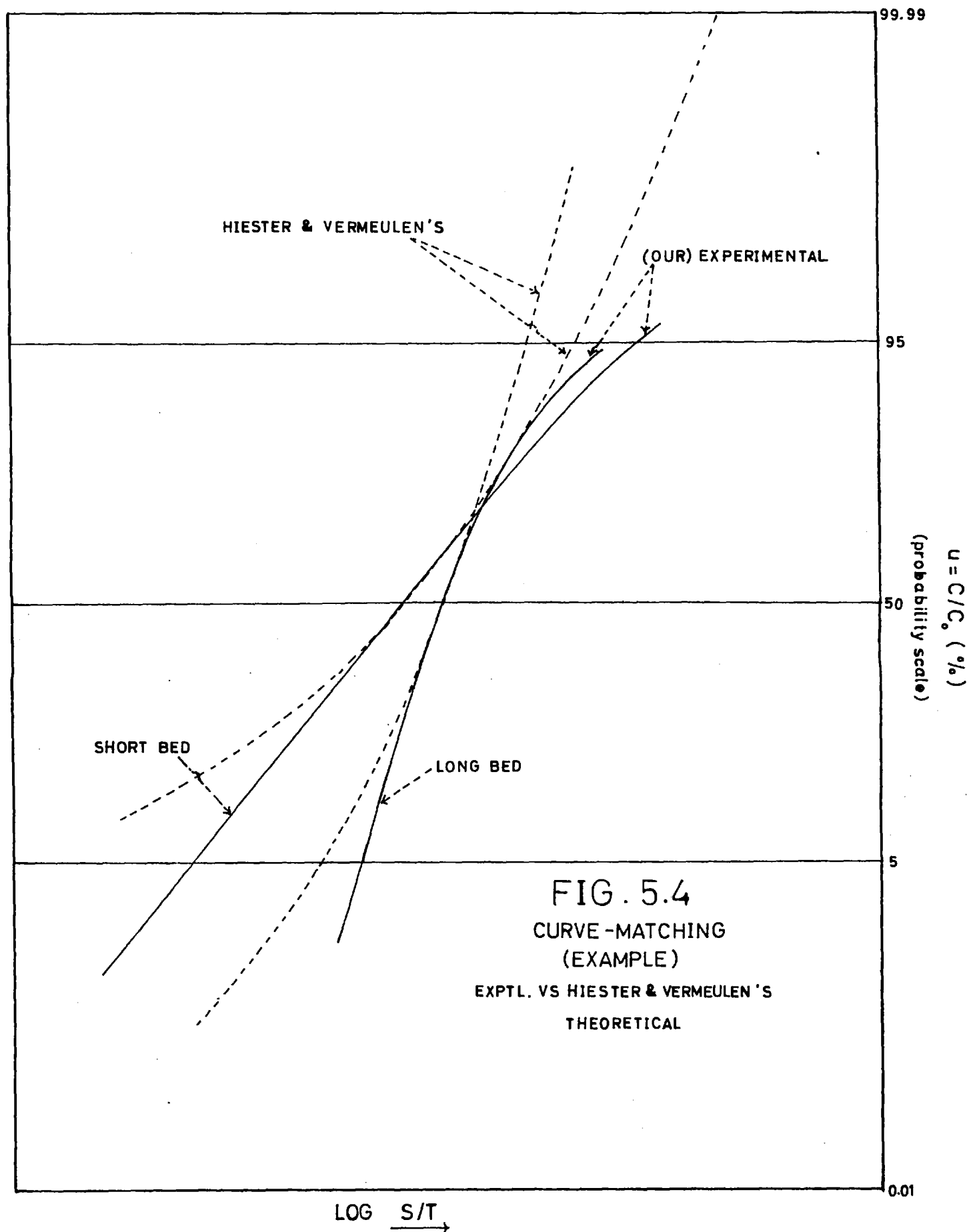


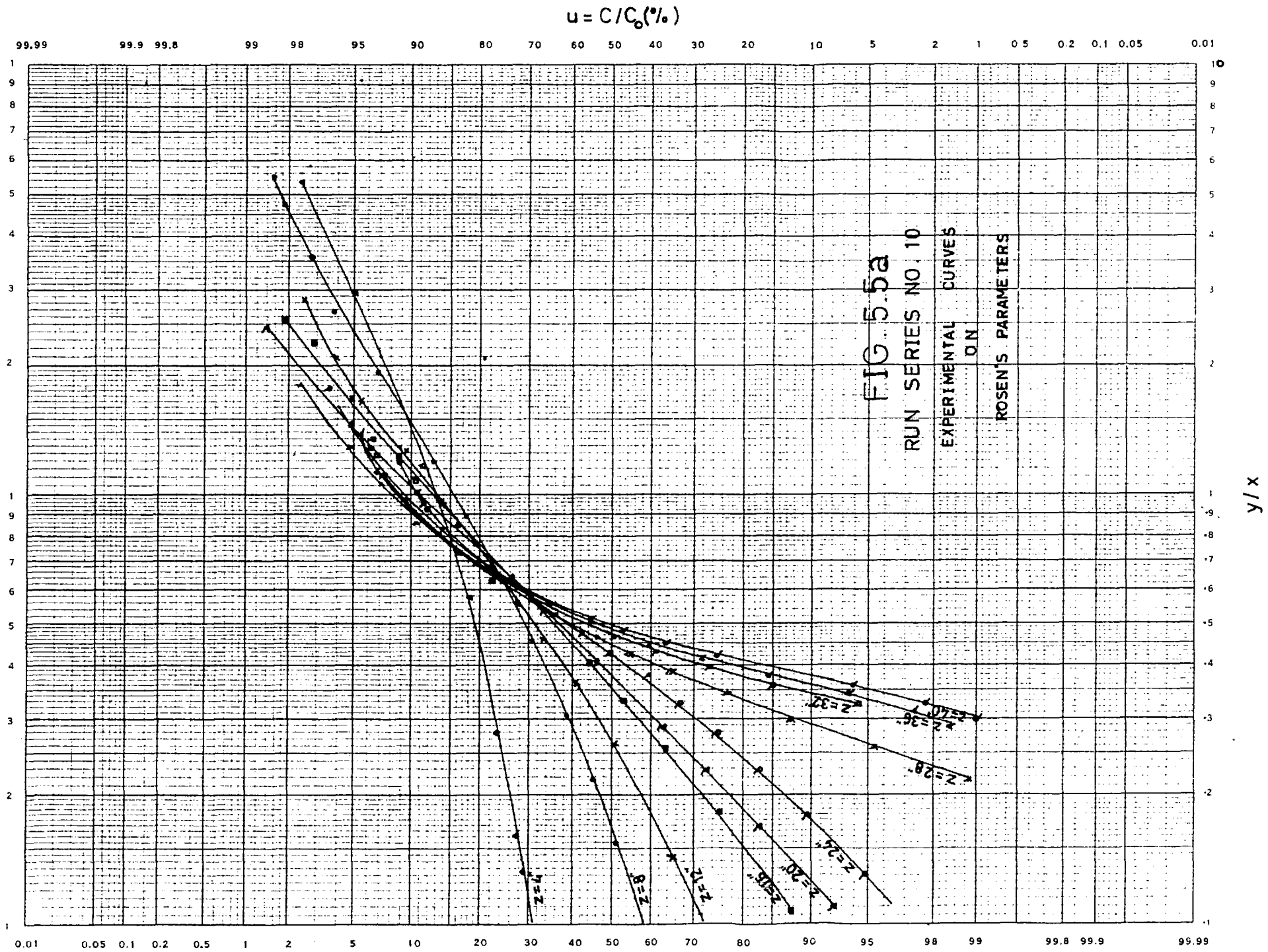
FIG. 5.4
 CURVE-MATCHING
 (EXAMPLE)
 EXPTL. VS HIESTER & VERMEULEN'S
 THEORETICAL

It was found that the experimental curves do not match Vermeulen's theoretical curves based on the kinetic approach. Even when the slopes are matched at the value of $u = 0.5$, the experimental curves deviate widely from the theoretical curves, as illustrated in Fig. 5.4. The theoretical curves are actually more curved than the experimental ones and this is probably due to the inadequacy of the reaction-kinetic model in representing cases where diffusional mechanisms seem to predominate. This is supported by the fact that even in the 'empirical' approach followed by Hiester and Vermeulen¹⁷ to treat the diffusional cases, the generalized BT- curves for the case of internal diffusion controlling are more straight than those for external diffusion controlling (vide, Fig. 7 in the reference cited). However, correlation with their generalized BT curves for the diffusional cases was not attempted in view of the empirical nature of their approach, and the doubtful validity of the resulting curves.

It may also be noticed, in Fig. 5.4, that the deviations of the experimental curves from the theoretical ones are very large at values of u greater than 0.7.

Rosen's Solution:

In applying Rosen's solution the curve-matching technique described in Chapter 4 has been followed. From the experimental data, values of y/x are computed as described in section 5 of Appendix II for various values of t . These are shown

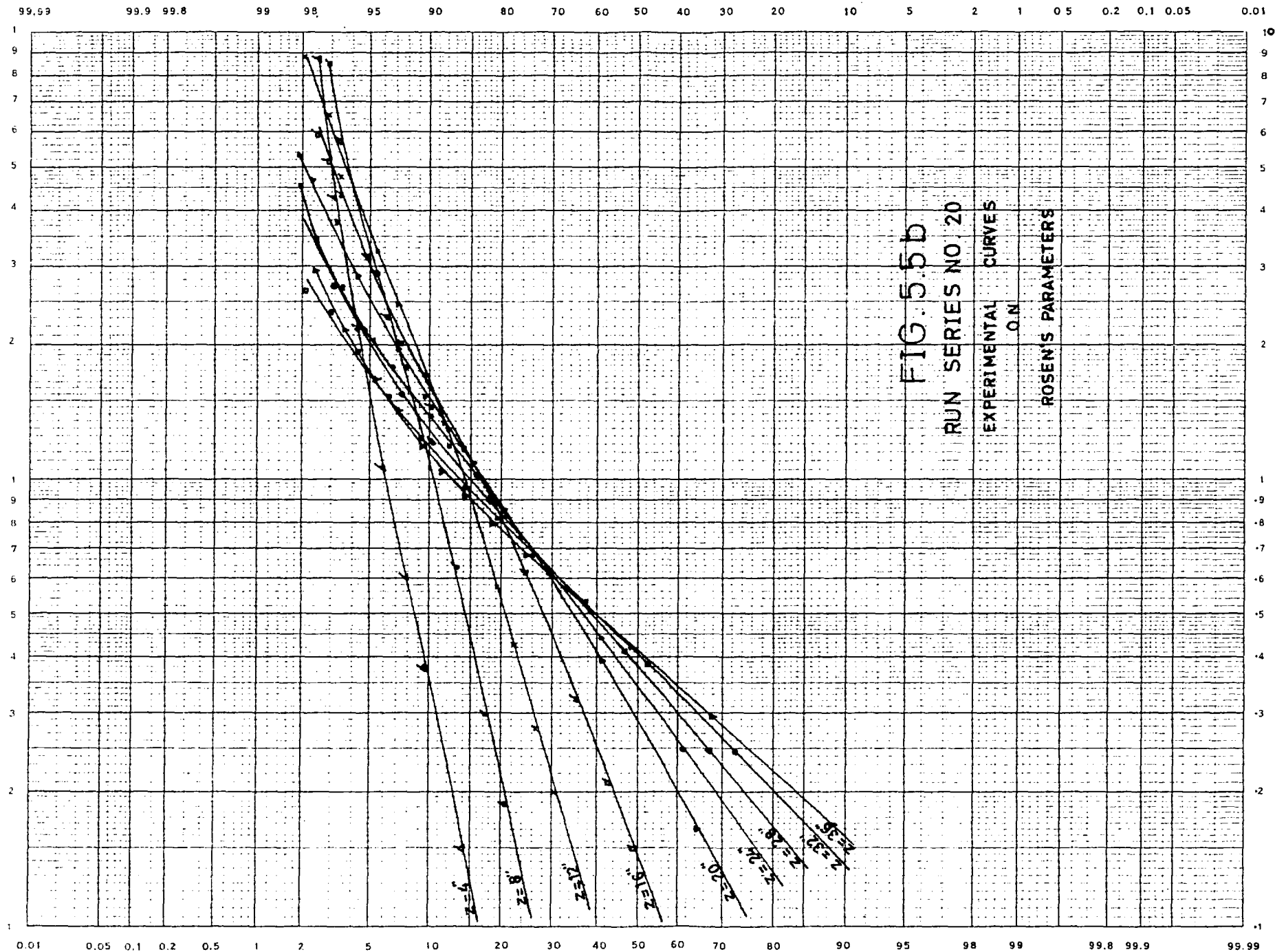


tabulated against u in section 6, of Appendix II.

Figs. 5.5a, b, c, show the corresponding graphs plotted on probability-logarithmic paper. From the tabulated values of u against y/x given by Rosen in his paper⁴¹, master-curves are prepared for values of $n/x = 0$ and $n/x = 0.025$ with x as parameter on tracing paper. The experimental graphs are then matched against the theoretical ones, using horizontal shift only, where found necessary. It is first assumed that the surface film resistance is insignificant and hence $n/x = 0$. This, on trial, is found to give a good match. As a further check the curve-matching is repeated for $n/x = 0.025$, the next higher value tabulated by Rosen, but this is not found to give such a close match as the former one. Thus, fixing the most suitable value of n/x as zero, the values of x for the breakthrough curves for the different values of z are read off, where necessary by graphical interpolation. These values are shown tabulated in section 7 of Appendix II. x is then plotted against z as shown in Figs. 5.7, 5.8 and 5.9

Fig. 5.6 illustrates the degree of **fit** obtained in the curve-matching, with the experimental and the theoretical curves drawn side by side in the 'matched' position for a few typical cases. It will be seen that Rosen's solution provides a reasonable fit of curves up to about $u = 0.7$, but for values of $u > 0.7$, large deviations occur as in the case of Vermeulen's theory.

$$u = C/C_0 (\%)$$



y/x

From the curve-matching procedure it is in principle possible to obtain three parameters: the appropriate mean value of K from the required shift of the logarithmic (y/x) scale, the surface resistance to mass transfer R_f from the value of n/x , and the solid diffusion coefficient from the slope of the x versus z curve. However, it must be appreciated that the curve-matching procedure is a rather crude and inaccurate method of determining these parameters, especially as the precise shape of the curves tends to be rather insensitive to the way in which the parameters are chosen.

Thus, although the best fit was obtained in all cases by taking $n/x = 0$, it is difficult to assert that the surface resistance is definitely negligible, but we may safely conclude that its effect is small. Nevertheless, this uncertainty in the precise value of n/x will be reflected in some uncertainty in the value of x itself, and hence in the apparent solid diffusion coefficient.

In contrast, the correction to the value of K obtained from the shift of the y/x scale is quite precise. It was found that the same shift matched simultaneously all the curves in a given set, and further that these resulted in the same value of K for sets 10 and 20 which have the same inlet concentration (6.2%) although the gas flow rates are different. The results are as follows:

$$u = C/C_0(\%)$$

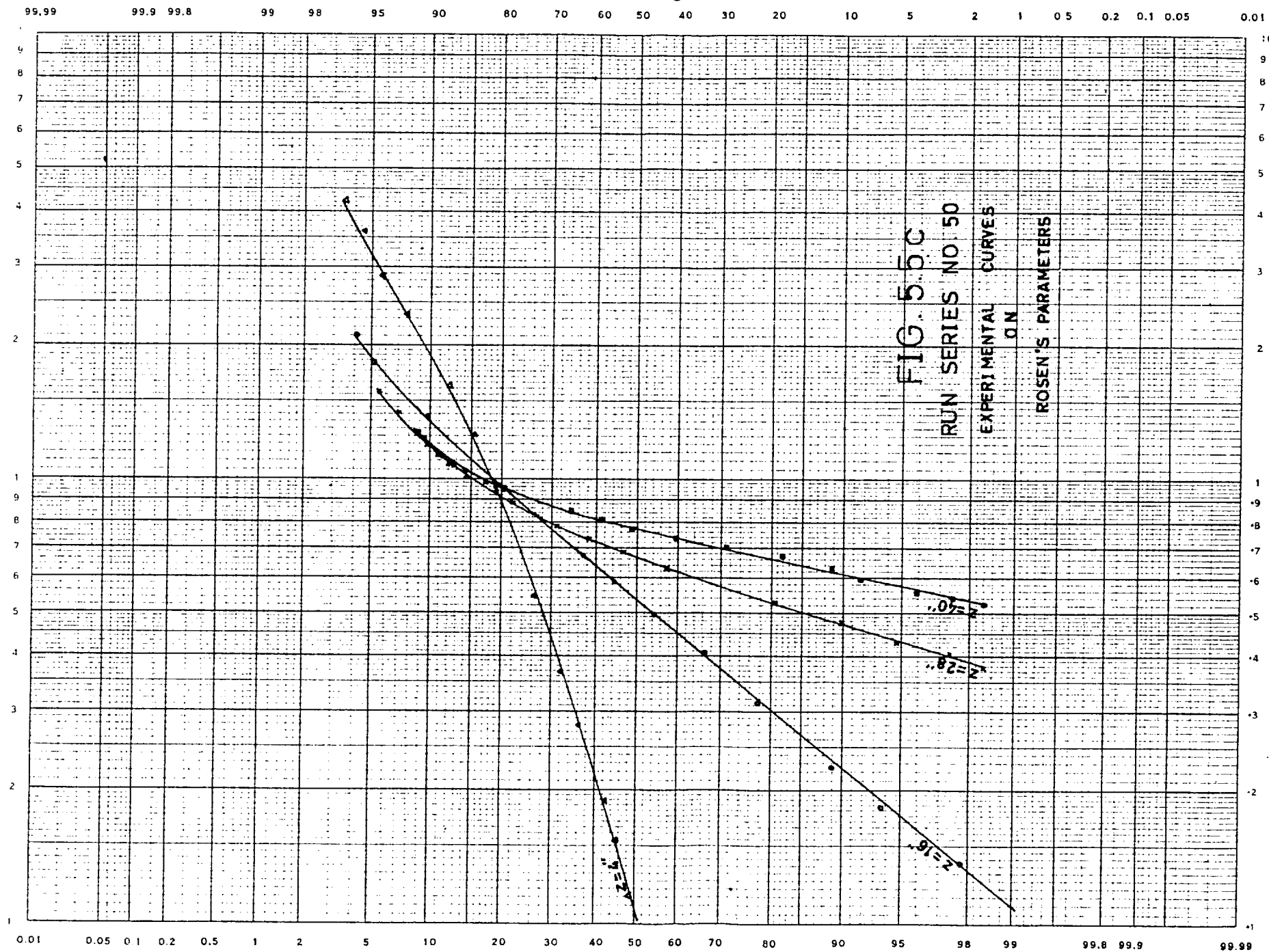
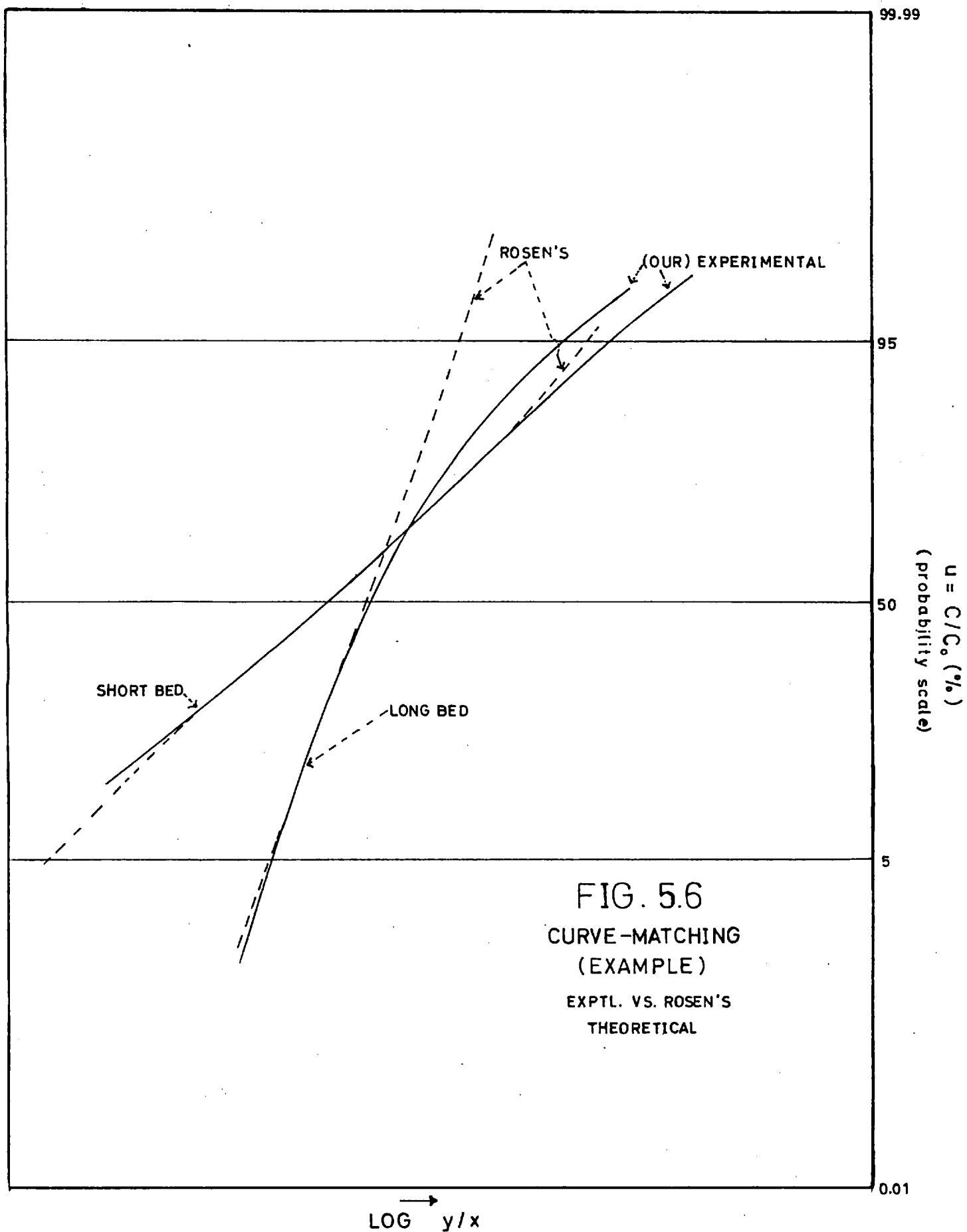


TABLE NO. 5.1

Series No.	Inlet gas concn. (%)	Flow rate l./min.	K-value used (q_0/c_0)	Correction factor from Shift	Proper mean K- value
10	6.2	6.19	548.8	0.74	406
20	6.2	23.48	548.8	0.74	406
50	1.9	5.67	850.4	0.96	816

It should be mentioned that two of the individual curves did not conform with the other curves in their sets. The curve for run 20.11 was found to cut across its neighbours at an odd slope and was rejected, whilst that for the run 50.11 seemed to have a reasonable slope but required a slightly different K-value to obtain the best fit. This deviation did not seem sufficient to invalidate the general conclusion that the appropriate mean K-value is independent of bed-length and gas flow rate and is a function only of the gas inlet concentration.

This in itself is a striking confirmation of the usefulness of Rosen's model in predicting fixed-bed behaviour, but if it is to form the basis of a design procedure it is necessary to provide in addition a satisfactory means of obtaining the proper mean K-value from the true equilibrium isotherm. Rosen's solution assumes that the isotherm is a straight line passing through the origin; it is therefore natural to seek such an approximation to the real isotherm, and to try and correlate the mean K-value with the terminal values of C/q obtained from this isotherm. These values are given in Table 5.2, and it



is immediately obvious that no such correlation is possible since the mean K-value falls outside the range in both cases.

TABLE NO. 5.2

Run Series No.	Proper Mean K-value *	q_0/C_0	Slope at $C = 0$	Slope at $C = C_0$
10 and 20	406	548.8	1124	268
50	816	850.4	1124	644

* Derived from horizontal shift needed for curve-matching.

Values of slope are given on the same basis as for K.

A straight line through the origin is in fact not the best straight-line approximation to the isotherm, and it is therefore worthwhile investigating the possibility of extending Rosen's solution to allow a general linear equilibrium relation of the form

$$q = q_0 + K C \quad \dots\dots\dots(5.3)$$

The initial conditions require modification since q is no longer zero when $C = 0$. The logical and self-consistent modification is to assume that the bed is still initially at equilibrium so that $q = q_0$ and $C = 0$ at zero time. With this assumption, it is easily seen that the function $(q - q_0)$ now satisfied all the equations and conditions required for q in Rosen's theory, so that his solution is still valid, subject only to this reinterpretation of q . In particular, the expressions for C itself remain unchanged, provided that K is interpreted as

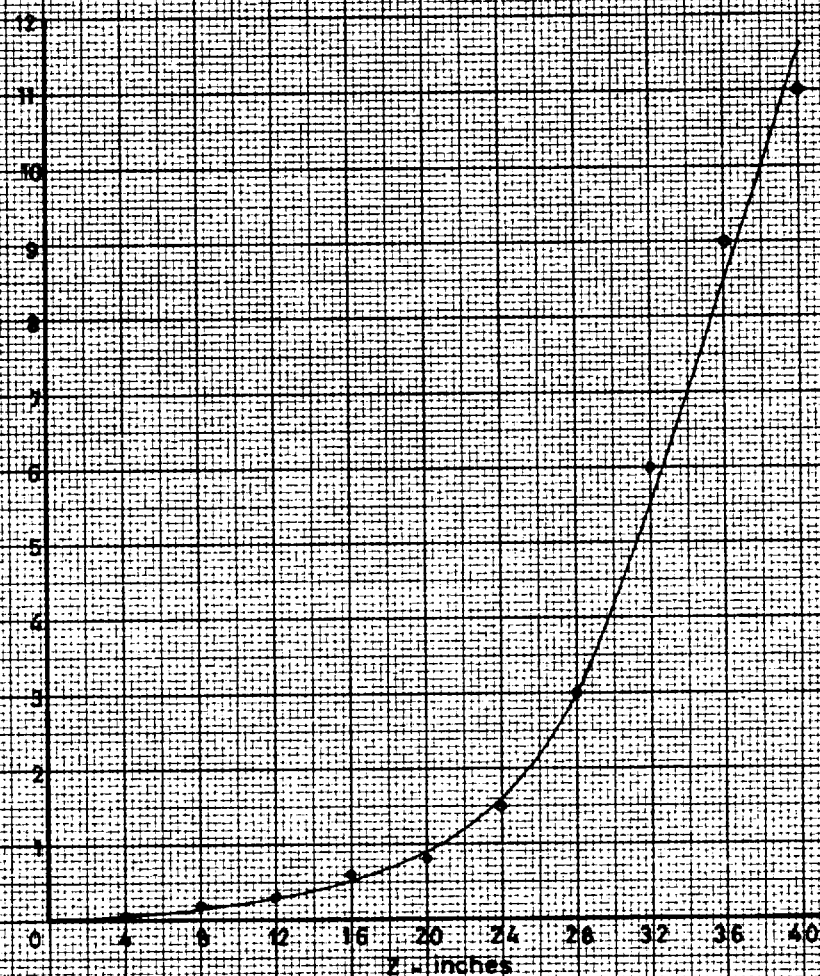


FIG. 5.7 - 'x' vs 'z' GRAPH FOR RUN SERIES
NO. 10

the mean slope of the real isotherm. Terminal values of the slope of the real isotherm are also given in Table 5.2, and it will be seen that the mean K-values as determined from the dynamic experiments now fall satisfactorily between the terminal values. Unfortunately, however, there seems to be no simple rule to predict the mean K-value from these terminal values, nor is it in any way related to the slope of the best straight line fit for the isotherm over the range involved.

It remains to consider the x-z curves, which are shown in Figs. 5.7, 5.8, 5.9, and it is here that we encounter serious deviations from Rosen's hypotheses since these plots do not in fact yield straight lines. Although this means that the theory is not strictly applicable, we can nevertheless calculate an apparent diffusion coefficient (D_a) from x, as indicated in Chapter 4, and the resulting values are plotted in Fig. 5.10.

There is of course no logical reason why D_a should be an explicit function of z, and since the degree of saturation of the solid decreases steadily along the bed, it seems natural to conclude that the diffusion coefficient decreases as the amount of gas adsorbed increases. The original curve-matching was based mainly on the portions of the curves below $u = 0.7$ in view of the strong deviations above this value, and a closer look at these curves will reveal that the matched portions for the shorter bed-lengths lie completely in regions where u is relatively high. As the bed-length increases, the short-time

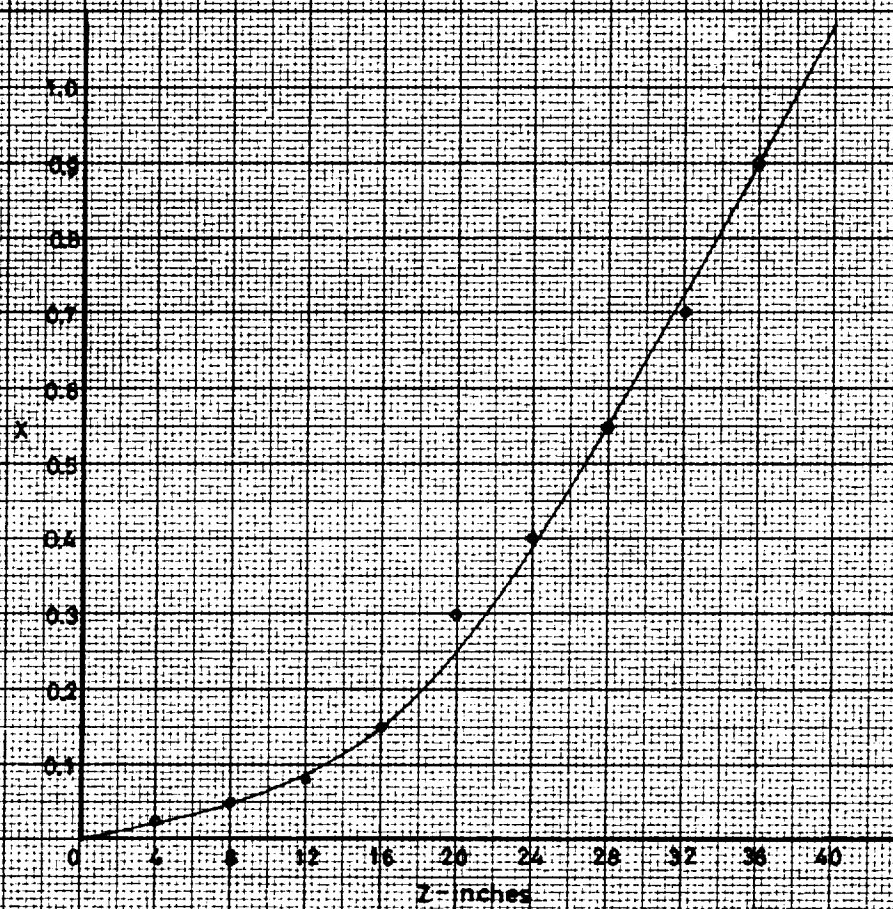


FIG. 5.8 - 'X' VS 'Z' GRAPH FOR RUN SERIES
NO. 20

portion of the curve descends progressively into the region of low u , and for series 10 and 50 this tendency is strongly accentuated for the last few curves near the end of the bed. This explains satisfactorily the initial low value of D_a , the slow rise with bed-length. and the sudden very large increase in D_a for runs 10 and 50 towards the end of the bed.

The process of adsorption into a molecular sieve crystal is not a surface effect, but a process of diffusion of the gas molecules into cavities formed by the crystal lattice. It is not unreasonable to suppose that the mobility of the gas molecules will be reduced as the cavities are filled and that there may well be a drastic reduction of mobility in the final stages of saturation. This intuitive notion accords well with the hypothesis put forward above to explain the variation of D_a .

For the shorter bed-lengths, as has already been noted the solid becomes appreciably saturated almost immediately, and the diffusion coefficient remains relatively constant at a low value for almost the whole of the run; the corresponding breakthrough curve (of Fig. 5.6) thus conforms well with the Rosen solution over the whole period. For the long bed-lengths on the other hand the solid remains relatively unsaturated in the early part of the run with a high value of the diffusion coefficient. As the adsorption wave-front arrives, the diffusion coefficient falls sharply causing the sudden deviation of the experimental breakthrough curve from the

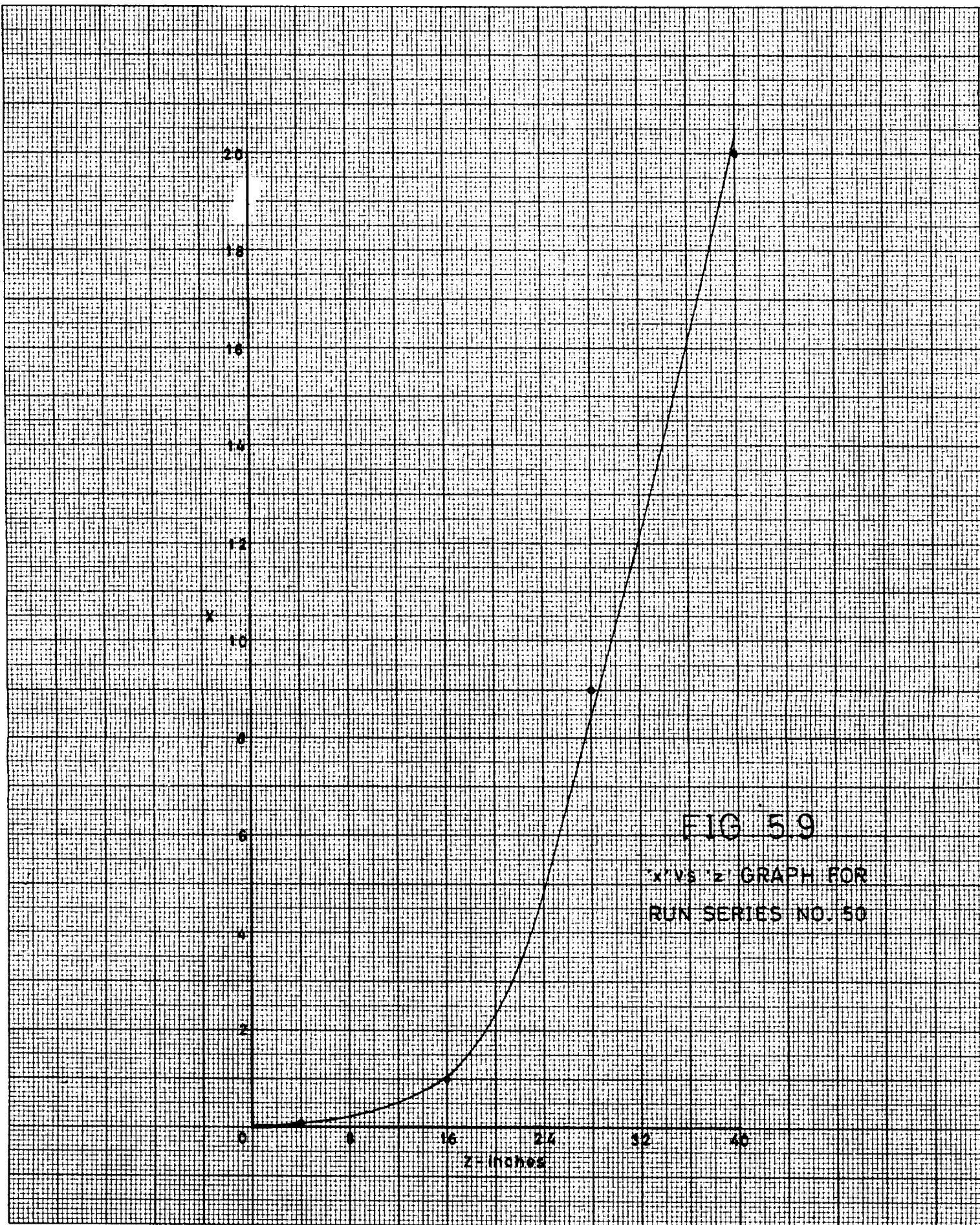


FIG 5.9
 'x' VS 'z' GRAPH FOR
 RUN SERIES NO. 50

Rosen solution, which is evident above $u = 0.7$ for these longer bed-lengths. It may be noted that these curves then become approximately parallel with those for the short bed-lengths indicating a similar low value of the diffusion coefficient.

It may be seen from the table given in section 7 of Appendix II, that the apparent diffusion coefficient has a value of the order of 2×10^{-8} ft.²/sec. initially and then decreases continuously to an average value of about a tenth of this, during the later stages of saturation.

Before concluding, it is necessary to consider a possible alternative explanation of the variation in the diffusion coefficient. The initial portion of the bed was regenerated at a slightly lower temperature than the remainder and so might contain a greater amount of residual moisture, which in turn may decrease the diffusion coefficient. There are several reasons why this explanation is less satisfactory. First, it is well known that the moisture content has a significant effect on the equilibrium isotherm, and no abnormalities in this respect were obtained from the y/x -axis shift for these short bed-lengths. Secondly, the regeneration temperature profile (see section 4 of Appendix I) shows that at most the first three sections of the bed would be significantly affected, whilst low values of D_a are found over most of the length, particularly for run 20. Finally, a specific property of the initial portion of the bed cannot explain the deviations at large time for the greater bed-lengths, nor the several secondary effects mentioned in the

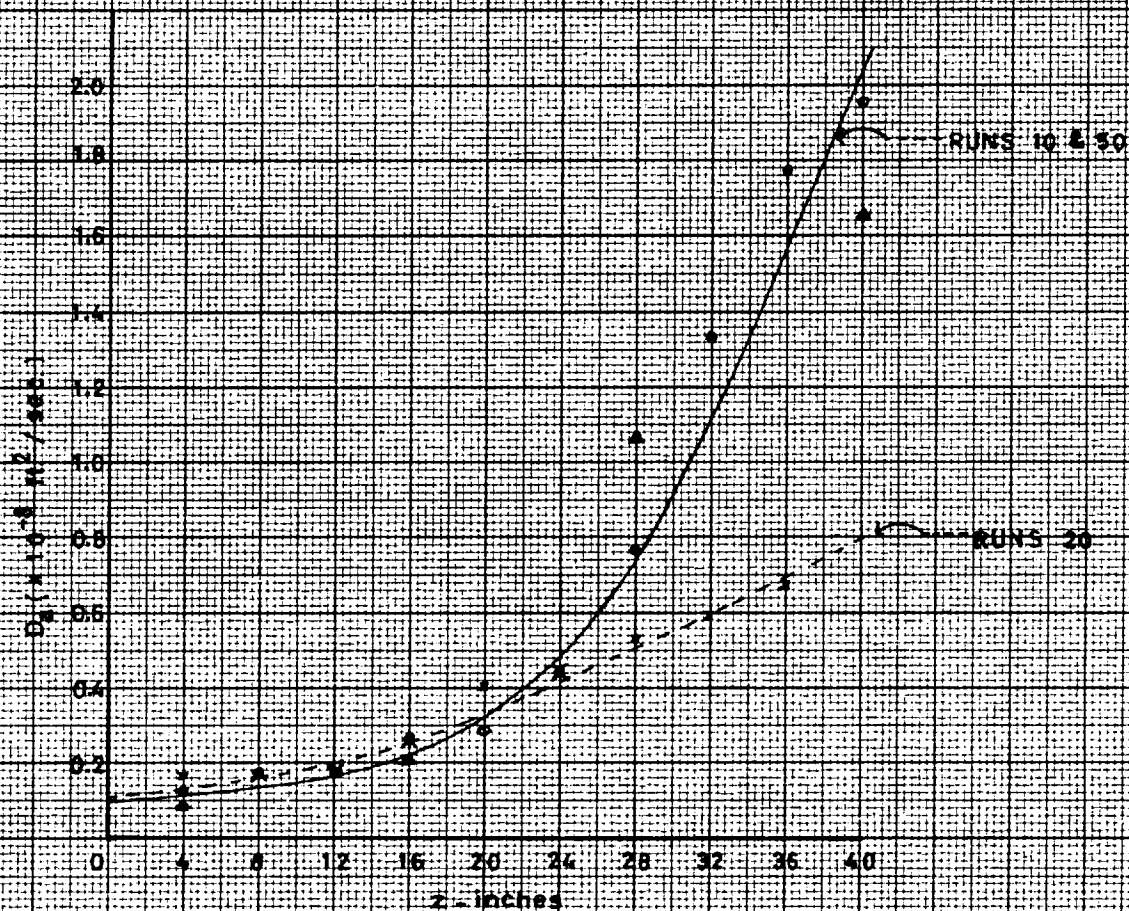


FIG. 5.10-APPARENT DIFFUSION COEFFICIENT (D_a) AT VARIOUS BED DEPTHS, z , FOR RUNS 10($\circ$), 20($\times$) and 50(Δ).

earlier discussion.

We therefore conclude that the most plausible hypothesis which provides a satisfactory explanation of all the facts, is that the rate-controlling process is that of solid diffusion, and that the diffusion coefficient is probably a function only of the degree of saturation, decreasing as the amount of gas adsorbed increases.

Computer Work:

In order to investigate further the variations of the solid diffusion coefficient with the amount adsorbed, it is necessary to calculate the latter, as a function of bed-length and time, from the experimental results.

A programme was therefore written for this purpose for use on the University of London Mercury Computer and, since Rosen's solution is not strictly valid when the solid diffusion coefficient varies, the programme was made to obtain the result by direct numerical integration of the true non-linear mass balance equation:

$$D_L \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - \frac{\partial c}{\partial t} = \frac{1}{m} \frac{\partial q}{\partial t} \quad \dots\dots\dots(4.15)$$

(using Rosen's symbols).

Any value of the longitudinal diffusion coefficient (D_L) may be assigned, although this has been taken as zero in the preliminary work. The relevant data and computer programme are given in Appendix IV.

The general procedure consisted of utilizing the Library Programme - 1007 developed by Dr. J.H. Cadwell of R.A.E. (Farnborough) and available with the London University Computer Unit, in its two stages, to fit a bivariate least squares polynomial to our data. The third stage consisted of using the polynomial coefficients so obtained in a specially written programme to compute the appropriate differential coefficients at various points in the fitted surface, the concentration in the solid at these levels by numerical integration, and ultimately the best value of the apparent solid mass transfer coefficient for the system under the conditions of experimentation.

Unfortunately, however, the work could not be completed in view of the fact that the University Computer was being moved to new premises and insufficient computing time was available to obtain the necessary results.

Our data are therefore presented here with the hope that the work may eventually be completed when the computer is again in service and may also serve as a basis for computing the true variation of diffusion coefficient within the solid, during the later stages.

Chapter 6

CONCLUSIONS

A review of the work described in the previous chapters leads to a number of general conclusions which, it is hoped, will be of value in guiding design procedures for fixed-beds or in future research on molecular sieves.

The experimental data obtained in this investigation has made possible a thorough test of the applicability of the existing theories to the case of adsorption of carbon dioxide from air by molecular sieves in fixed-beds. It is shown that the Anzelius-Schumann solution is too simple a model for application to this system, whilst the reaction-kinetic approach based on Thomas's solution (adapted by Vermeulen et al) does not predict the breakthrough curve shape properly. It seems necessary to take account of the true physical process of solid diffusion in order to obtain a successful fit to the data. Rosen's solution which takes into account the solid diffusion, would serve as a better basis for design.

In industrial applications to gas purification, it is the initial portion of the breakthrough curve (where C/C_0 is small) that is of importance; and here, except for very short bed lengths which have in any case no practical interest, Rosen's solution provides a successful and satisfactory means of predicting the performance. The experimental results show

that for this system satisfactory performance is obtained with relatively low regeneration temperatures of about 160°C.

The experiments have also shown that the radial concentration gradients are negligible, and the results are satisfactorily correlated on the assumption that longitudinal diffusion and gas-solid surface resistance are both negligible. Thus the only parameters necessary for use of Rosen's solution in a design procedure are the effective mean slope of the equilibrium isotherm and the effective mean solid diffusion coefficient. Although it has not been possible to deduce a formula for the prediction of the mean slope from the parameters of the true isotherm, it has been shown to be within the proper limits of the initial and terminal slopes of this isotherm. As for the solid diffusion coefficients, under the conditions of experiment, the data give evidence to support the view that it varies with the amount of gas adsorbed; but further analysis is needed before definite conclusions can be drawn. The programme proposed for calculations with the computer would be helpful in the analysis. However, curves have been presented which indicate the order of magnitude of the diffusion coefficients (calculated by assuming Rosen's formula to be applicable) for the particular conditions of these experiments.

It should be mentioned that experiments on fixed-beds are not ideally suited to the study of the details of the mechanism of the diffusion taking place within the solid.

The type of investigations being carried out by L.O. Dworjanyn in this Department on single pellets and small samples of pure crystals using radioactive tracer technique is the more appropriate one for the study of this aspect of the problem and this forms a natural continuation of the work presented here.

NOMENCLATURE*

- a ... specific surface area of the adsorbent particles.
- b ... radius of the spherical particles.
- B ... $=B_H K_H$; $B_H = \frac{G}{e_B (HTU)_{og}}$ in equation (4.3)
- C ... concentration of the solute in the gas phase (volumetric)
- C_A ... concentration of component A in the fluid phase at a specified point in the column.
- C_e ... concentration of the solute in the gas phase in the equation for isotherm (5.1)
- C_H ... adsorbate concentration in gas in equation (4.2)
- C_o ... concentration of the solute in the gas entering the column
- D_a ... apparent diffusion coefficient obtained by curve-matching against Rosen's solutions, and from equation (II.7.1.)
- D_L ... longitudinal diffusion coefficient.
- D_s ... effective solid diffusion coefficient in spherical particles.
- e ... external void fraction.
- E ... $= \frac{G}{k_g a} = \frac{I}{(HTU)_{og}}$ in equation (4.3)
- F ... volumetric flow rate of gas.
- G ... mass velocity
- h ... gas film mass transfer coefficient in equation (4.20)
- HTU... height of transfer unit.
- I_o ... modified Bessel function of the first kind and zero order.

* The dimensions of the various items are not given here as the units vary to some extent depending on the context. They are however given in the body of the text.

- $J(X,Y)$... function of X and Y as defined in equation (4.13)
- k_g ... mass transfer coefficient as defined in equation (4.1)
- K_{kin} ... rate constant for adsorption.
- K ... constant defining the linear isotherms in equation (4.22)
- K_H ... Constant in the equilibrium relationship in equation (4.2)
- K_A^{ad} ... equilibrium mass action constant as defined in equation (4.6)
- L ... packed volume of solids.
- m ... $= \frac{e}{1-e}$. void volume per unit volume of solid particles.
- n ... film resistance parameter, defined by equation (4.25)
- q ... average adsorbate concentration in solid.
- q_e ... adsorbate concentration in solid in the equation for isotherm (5.1)
- q_i ... adsorbate concentration in the particle at radius R
- q_s ... adsorbate concentration in the particle (volumetric) in equation (4.22)
- Q^{ad} ... the total adsorptive capacity, as defined in equation (4.6)
- r ... the equilibrium parameter, defined by equation (4.10 c)
- R ... radial distance from centre of spherical particle.
- R_f ... effective surface film resistance, in equation (4.20)
- S ... (column capacity) parameter defined by equation (4.10 d)
- t ... time.
- T ... (solution capacity) parameter defined by equation (4.10 e)

- u ... $\frac{C}{C_0}$, ratio of concentration of solute in the gas at a point in column to the concentration at inlet.
- v ... linear flow velocity.
- V ... $=Ft$, volume of gas that has entered the column up to a particular time t .
- w ... $\frac{q}{q_s}$, ratio of the solute concentration in the solid at a point in the column to the solute concentration, in solid which will be in equilibrium with c_0 .
- x ... bed length parameter, defined by equation (4.26)
- y ... contact time parameter, defined by equation (4.27)
- z ... bed depth.
- Z ... throughput parameter, defined by equation (4.14)

Greek Letters

- ζ ... $= Ez$, thickness modulus, in equation (4.3)
- θ ... transformed time variable, defined by equation (4.18)
- λ ... slope of x vs. z graph, defined by equation (4.32)
- ξ ... integrating variable in equation (4.13)
- ρ ... density,

(Contd.)

Greek Letters
(Contd.)

ρ_B ... bulk density of solid in bed.

Subscripts

A ... component A.
 g ... gas film.
 og ... overall gas film.
 o ... initial conditions.
 kin ... value on the basis of a reaction-kinetic approach

Superscripts

*, $\#$... concentration in equilibrium with the actual concentration in the co-existing phase.
 ad ... value for adsorption.

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A P P E N D I X I

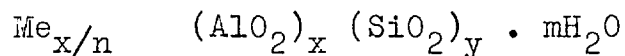
SECTION I. 1Column Characteristics

Diameter of the column (internal)	= 2 inches
Area of cross section of empty column	= 0.02182 sq. ft.
Number of Sections	= 10
Total (empty) volume of each section (packing and sampling sections together)	= 334.7 c.c.
Packed height in each section	= 4 inches
Adsorbent (used as packing) :	(Molecular Sieve Pellets, (Type 4A; nominal size $\frac{1}{8}$ in.
Packed volume in each section	= 206 c.c.
Pellet volume " " "	= 122.4 c.c.
Void fraction	= 0.406
Dry weight of packing in each section	= 133.7 gm.
Pellet density (dry)	= 1.093 gm./c.c.
Packing bulk density (dry)	= 0.649 gm./c.c.
Surface area of packing	= 346.2 sq.ft./c.ft.
Equivalent diameter of particles in) packing }	=(0.1235 ins. { or { 0.01029 ft.

SECTION 1.2Molecular Sieves

The following brief extract on molecular sieves is presented here. More details are available in the publications cited under reference 33:

The molecular sieves are synthetic crystalline zeolites, and consist of a three-dimensional network of alternating aluminium dioxide and silicon dioxide tetrahedra arranged in a cubic crystal structure. The type A has a structural formula



where Me represents exchangeable cations of charge n. The unit cell dimension is 12.3 Å with central cavities of 11.4-Å in diameter and are interconnected by 4.2-Å - diameter holes which are responsible for the so called 'sieve action'. The position and size of the exchangeable cations, however, determine the "effective" diameter of these passage ways.

The zeolite is precipitated as a powder with an average particle size of about 2 μ . The powder is bonded with 20% clay and extruded as 1/16 in. and 1/8 in. diameter pellets or formed into roughly spherical beads from 4 to 12 mesh in size. The adsorbent is activated with heat to drive off the water of crystallization when a very porous but robust crystal structure will be left behind.

Type 4A is the crystalline sodium alumin~~o~~-silicate.

SECTION I. 3Allowable Gas Velocity

This was calculated using the correlation given by Ledoux²⁵:

$$\frac{G^2}{d_g d_a D g} = 0.0167 \dots\dots\dots(1.3.1)$$

where

G = mass velocity of the gas, lb./((sec)(sq.ft))

d_g = gas density (flow conditions), lb./c.ft.

d_a = adsorbent bed density, lb./c.ft.

D = average particle diameter, ft.

g = acceleration due to gravity, ft./sec.²

Since higher velocities were used during the regeneration cycle only in our experiments, the allowable gas velocity was calculated for these conditions.

Maximum temperature during regeneration = 167°C

d_g = 0.0501 lb./C.ft.

d_a = 40.5 lb./c.ft.

D = 0.01029 ft.

g = 32.174

Hence, by substitution of above values in equation (1.3.1),

$$G = 0.1059 \text{ lb./((sec) (sq.ft))} \dots\dots\dots(1.3.2)$$

The order of mass velocity actually used during regeneration in our experiments was about 0.8 of the above value.

Temperature Profile

Temperatures read by the thermocouples at various levels of the column at the end of a typical regeneration cycle.

TABLE NO: I.4.1.

LEVEL NO.	TEMP. °C.
11 (bottom inlet)	167.0
10	166.2
9	166.0
8	165.8
7	165.3
6	164.6
5	162.5
4	160.6
3	157.2
2	152.0
1 (top exit)	133.2

Note: During adsorption, the direction of flow of gas was from top to bottom, and the temperature between 24° and 25°C.

Isotherm

The results of the experiments described under the section on 'Equilibrium' in Chapter 3 are as follows:

TABLE NO: I.5.1

CO ₂ concn. in gas phase % by volume C	CO ₂ concn. in solid phase % by weight of dry solid q
6.516	5.815
5.327	5.261
4.122	4.432
2.776	3.406
1.510	2.328

Isotherm - Formula by Least Squares

For this, the procedure and the symbols given by Milne³¹ (page 242 of the reference) are used.

The Langmuir form of the isotherm is given by

$$q = \frac{k_2 C}{1 + k_1 C} \dots\dots\dots (I.6.1)$$

which is also

$$\frac{C}{q} = \frac{1}{k_2} + \left(\frac{k_1}{k_2} \right) C \dots\dots\dots (I.6.2)$$

where

C and q have the usual meanings and k_1 and k_2 are constants.

The following symbols given by Milne³¹, are used as they are: $a_0, a_1, S_0, S_1, S_2, V_0, V_1, x, y$,

$$\begin{aligned} \text{If } \frac{1}{k_2} &= a_0, & \left(\frac{k_1}{k_2} \right) &= a_1, \\ C &= x & \text{and } \frac{C}{q} &= y \end{aligned}$$

the values of k_1 and k_2 are obtained by solving the following two equations after substituting the numerical values for S_0, S_1, S_2, V_0 and V_1

$$S_0 a_0 + S_1 a_1 = V_0 \dots\dots\dots (I.6.3)$$

$$S_1 a_0 + S_2 a_1 = V_1 \dots\dots\dots (I.6.4)$$

Thus $k_1 = 0.1692$

and $k_2 = 1.8615$

The final formula for calculating q_e under the experimental conditions for a given value of C_e is,

$$q_e = \frac{1.8615 C_e}{1 + 0.1692 C_e} \dots\dots\dots (I.6.5)$$

or in the alternative form,

$$q_e = 11.001773 \left(\frac{0.1692 C_e}{1 + 0.1692 C_e} \right) \dots\dots\dots (I.6.6)$$

The following table summarizes the course of the calculations and the results:

TABLE NO: I.6.1

x or C	q	y or C_e/q_e	x^0	x^2	xy	q_e calculated from (I.6.6.)	% error $\pm \frac{q_e}{q} \times 100$
6.516	5.815	1.120	1	42.458	7.298	5.769	-0.79
5.327	5.261	1.013	1	28.377	5.396	5.215	-0.87
4.122	4.432	0.9301	1	16.991	3.834	4.520	+1.98
2.776	3.406	0.8150	1	7.706	2.262	3.516	+3.23
1.510	2.328	0.6486	1	2.280	0.9794	2.239	-3.82
S_1		V_0	S_0	S_2	V_1		
20.251		4.5267	5	97.812	19.7694		

The following table gives the values of q_e calculated from equation (I.6.6) for the inlet concentrations (C_0) used in the run series Nos. 10, 20 and 50.

TABLE NO: I.6.2

Run Series No.	CO ₂ concn. in Inlet gas % by volume C _o	CO ₂ concn. in solid (corresponding to C _o) % by weight (q _e) _o
10	6.2	5.635
20	6.2	5.635
50	1.9	2.676

A P P E N D I X I I

SECTION II.1Breakthrough Data for Runs: Series No.10

Inlet gas concentration = 6.2% CO₂

Volumetric rate of flow of gas into column = 6.19 litres per min.

TABLE NO: II. 1.1Run No. 10.11^{*}

Bed depth = 40 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
45.2	0.0	0.0
48.2	0.01	0.002
50.2	0.06	0.010
55.2	0.14	0.023
60.2	0.38	0.061
65.2	0.91	0.147
70.2	1.58	0.255
75.2	2.28	0.368
80.2	2.90	0.468
85.2	3.39	0.547
90.2	3.73	0.602
(contd.)		

^{*} The number after the decimal point indicates the level no. from the inlet, at which the exit gas concentration was measured. In this run, for instance, the level no. was 11 which means that (11-1) or 10 sections of the bed (each 4 ins. in packed depth) were involved.

(contd)

Time from start (mins) t	CO ₂ concn. in ² exist gas (%) C	Exit concn./ Inlet concn. C/C _c
95.2	4.04	0.652
100.2	4.50	0.726
105.2	4.83	0.780
110.2	4.94	0.784
115.2	5.06	0.816
120.2	5.23	0.844
125.2	5.24	0.845
130.2	5.32	0.858
135.2	5.36	0.865
140.2	5.40	0.871
145.2	5.41	0.873
150.2	5.45	0.879
155.2	5.46	0.881
160.2	5.48	0.884
165.2	5.51	0.889
170.2	5.53	0.892
175.2	5.54	0.894
180.2	5.56	0.897
185.2	5.59	0.902
190.2	5.61	0.905
195.2	5.64	0.910
200.2	5.65	0.911

Run No. 10.10

Bed depth = 36 inches

Time from start (mins)	CO ₂ concn. in ² exit gas (%)	Exit concn./ Inlet concn.
t	C	C/C _c
0	0.0	0.0
35.2	0.0	0.0
39.2	0.03	0.005
43.2	0.10	0.016
47.2	0.17	0.027
52.2	0.40	0.065
57.2	0.98	0.158
62.2	1.74	0.281
67.2	2.50	0.403
72.2	3.16	0.510
77.2	3.62	0.584
82.2	4.03	0.650
87.2	4.33	0.698
92.2	4.59	0.740
97.2	4.80	0.774
102.2	4.98	0.803
107.2	5.11	0.824
112.2	5.23	0.844
117.2	5.32	0.858
122.2	5.39	0.869
127.2	5.46	0.881
132.2	5.53	0.892
137.2	5.58	0.900
142.2	5.62	0.907
147.2	5.67	0.915
152.2	5.72	0.923
157.2	5.73	0.924

(contd)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. c/c.
162.2	5.76	0.929
167.2	5.78	0.932
172.2	5.80	0.936
177.2	5.81	0.937
182.2	5.82	0.939
187.2	5.83	0.940
192.2	5.83	0.940
197.2	5.85	0.944
202.2	5.85	0.944
208.2	5.86	0.945

TABLE NO: II. 1.3

Run No. 10.09

Bed depth = 32 inches.

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. c/c ₀
0	0.0	0.0
29.2	0.0	0.0
31.2	0.01	0.002
33.2	0.03	0.005
38.2	0.09	0.015
43.2	0.34	0.058
48.2	0.93	0.150
53.2	1.63	0.263
58.2	2.37	0.382
63.2	3.04	0.490
68.2	3.58	0.577
73.2	3.99	0.644
78.2	4.31	0.695
83.2	4.57	0.737
88.2	4.77	0.769
93.2	4.98	0.803
98.2	5.14	0.829
103.2	5.26	0.848
108.2	5.37	0.866
113.2	5.44	0.877
118.2	5.50	0.887
123.2	5.56	0.897
128.2	5.61	0.905
133.2	5.66	0.913
138.2	5.68	0.916
143.2	5.70	0.919

(contd.)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_o
148.2	5.72	0.923
153.2	5.74	0.926
158.2	5.76	0.929
163.2	5.78	0.932
168.2	5.79	0.934
173.2	5.80	0.936
178.2	5.80	0.936
183.2	5.81	0.937
188.2	5.81	0.937
193.2	5.84	0.942
198.2	5.85	0.944
203.2	5.85	0.944
208.2	5.86	0.945

TABLE NO: II. 1.4

Run No. 10.08

Bed depth = 28 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_o
0	0.0	0.0
20.2	0.0	0.0
25.2	0.07	0.011
30.2	0.28	0.045
35.2	0.75	0.121
40.2	1.40	0.226
45.2	2.12	0.342
50.2	2.79	0.450

(contd.)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
55.2	3.34	0.539
60.2	3.83	0.618
65.2	4.22	0.681
70.2	4.55	0.734
75.2	4.80	0.774
80.2	4.99	0.805
85.2	5.16	0.832
90.2	5.31	0.857
95.2	5.40	0.871
100.2	5.53	0.892
105.2	5.58	0.900
110.2	5.61	0.905
115.2	5.66	0.913
120.2	5.72	0.923
125.2	5.76	0.929
130.2	5.81	0.937
135.2	5.85	0.944
140.2	5.88	0.948
145.2	5.89	0.950
150.2	5.90	0.952
155.2	5.92	0.955
160.2	5.93	0.957
165.2	5.95	0.960
170.2	5.95	0.960
175.2	5.95	0.960
180.2	5.99	0.966
185.2	6.00	0.968
190.2	6.02	0.971
195.2	6.03	0.973
200.2	6.04	0.974
205.2	6.04	0.974
210.2	6.05	0.976

Run No. 10.07*

Bed depth = 24 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0.	0.0	0.0
3.2	0.0	0.0
8.2	0.08	0.013
13.2	0.33	0.053
18.2	0.65	0.105
23.2	1.06	0.171
28.2	1.57	0.253
33.2	2.04	0.329
38.2	2.51	0.405
43.2	3.10	0.500
48.2	3.55	0.573
53.2	3.93	0.634
58.2	4.27	0.689
63.2	4.55	0.734
68.2	4.76	0.768
73.2	5.01	0.808
78.2	5.19	0.837
83.2	5.33	0.860
88.2	5.43	0.876
93.2	5.54	0.893
98.2	5.60	0.903
103.2	5.66	0.913
108.2	5.70	0.919
113.2	5.73	0.924
118.2	5.75	0.927
123.2	5.78	0.932
128.2	5.81	0.937
133.2	5.84	0.942
138.2	5.86	0.945
143.2	5.88	0.949
148.2	5.89	0.950

* Values obtained by graphical interpolation.

TABLE NO: II. 1.6

Run No. 10.06

Bed depth = 20 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
2.2	0.0	0.0
4.2	0.09	0.015
9.2	0.48	0.077
14.2	1.08	0.174
19.2	1.71	0.276
24.2	2.31	0.373
29.2	2.88	0.465
34.2	3.35	0.540
39.2	3.76	0.607
44.2	4.10	0.662
49.2	4.37	0.705
54.2	4.54	0.732
59.2	4.84	0.781
64.2	5.03	0.812
69.2	5.20	0.839
74.2	5.38	0.868
79.2	5.50	0.887
84.2	5.59	0.902
89.2	5.61	0.905
94.2	5.64	0.910
99.2	5.66	0.913
104.2	5.69	0.918
109.2	5.73	0.924
114.2	5.78	0.932
119.2	5.80	0.935
124.2	5.82	0.939
129.2	5.84	0.942
134.2	5.86	0.946

(contd.)

(contd)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. c/c_o
139.2	5.88	0.949
144.2	5.92	0.955
149.2	5.97	0.963
154.2	6.01	0.970
159.2	6.02	0.971
164.2	6.03	0.973
169.2	6.02	0.973
174.2	6.04	0.975
179.2	6.04	0.975
184.2	6.05	0.976
189.2	6.05	0.976
194.2	6.06	0.978
199.2	6.07	0.979
204.2	6.09	0.983
209.2	6.12	0.987
214.2	6.14	0.991

TABLE NO: II. 1.7

Run No. 10.05

Bed depth = 16 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. c/c_o
0	0.0	0.0
1.2	0.01	0.002
2.2	0.07	0.011
7.2	0.75	0.121
12.2	1.50	0.242
17.2	2.23	0.360
22.2	2.88	0.464

(contd.)

Time from start (mins)	CO ₂ concn. in ² exit gas (%)	Exit concn./ Inlet concn.
t	C	C/C ₀
27.2	3.43	0.553
32.2	3.85	0.621
37.2	4.24	0.684
42.2	4.53	0.731
47.2	4.78	0.771
52.2	5.00	0.807
57.2	5.18	0.836
62.2	5.28	0.852
67.2	5.39	0.857
72.2	5.47	0.882
77.2	5.57	0.898
82.2	5.64	0.910
87.2	5.67	0.915
92.2	5.73	0.924
97.2	5.79	0.934
102.2	5.81	0.937
107.2	5.86	0.945
112.2	5.89	0.950
117.2	5.91	0.953
122.2	5.92	0.955
127.2	5.93	0.957
132.2	5.93	0.957
137.2	5.94	0.958
142.2	5.95	0.960
147.2	5.98	0.965
152.2	6.01	0.970
157.2	6.04	0.974
162.2	6.06	0.977
167.2	6.06	0.977
172.2	6.08	0.981

(contd.)

(contd)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
177.2	6.08	0.981
182.2	6.07	0.979
187.2	6.07	0.979
192.2	6.08	0.981
197.2	6.08	0.981
202.2	6.09	0.982
207.2	6.09	0.982
212.2	6.09	0.982

TABLE NO: II.1.8

Run No. 10.04

Bed depth = 12 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
0.2	0.11	0.018
3.2	0.94	0.152
7.2	2.13	0.344
13.2	3.00	0.484
18.2	3.65	0.589
23.2	4.12	0.665
28.2	4.47	0.721
33.2	4.74	0.765
38.2	4.98	0.803
43.2	5.16	0.832
48.2	5.33	0.860
53.2	5.45	0.879
58.2	5.53	0.892

(contd.)

(contd)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
63.2	5.60	0.903
68.2	5.66	0.913
73.2	5.73	0.924
78.2	5.78	0.932
83.2	5.84	0.942
88.2	5.87	0.947
93.2	5.90	0.952
98.2	5.93	0.957
103.2	5.95	0.960
108.2	5.95	0.960
113.2	5.96	0.961
118.2	5.97	0.963
123.2	5.98	0.965
128.2	5.99	0.966
133.2	6.00	0.968
138.2	6.01	0.969
143.2	6.04	0.974
148.2	6.06	0.977
153.2	6.08	0.981
158.2	6.11	0.986
163.2	6.13	0.989
168.2	6.14	0.990
173.2	6.16	0.994
178.2	6.17	0.995
183.2	6.18	0.997
188.2	6.18	0.997
193.2	6.18	0.997
198.2	6.18	0.997
203.2	6.17	0.995
208.2	6.18	0.997

Run No. 10.03

Bed depth = 8 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
0.2	1.06	0.171
1.2	1.67	0.269
2.2	2.10	0.339
3.2	2.48	0.400
5.2	2.99	0.482
7.2	3.37	0.544
10.2	3.80	0.613
15.2	4.28	0.690
20.2	4.62	0.745
25.2	4.90	0.790
30.2	5.10	0.823
35.2	5.26	0.848
40.2	5.40	0.871
45.2	5.52	0.890
50.2	5.60	0.903
55.2	5.67	0.915
60.2	5.72	0.923
65.2	5.78	0.932
70.2	5.84	0.942
75.2	5.86	0.945
80.2	5.92	0.955
85.2	5.93	0.957
90.2	5.96	0.961
95.2	5.99	0.966
100.2	6.00	0.966
105.2	6.00	0.966
110.2	6.00	0.966
115.2	6.01	0.969

(Contd.)

(contd)

Time from start (mins) t	CO ₂ concn. in ² exit gas	Exit concn./ Inlet concn.
	(%) C	C/C ₀
120.2	6.02	0.971
125.2	6.03	0.973
130.2	6.04	0.974
135.2	6.06	0.977
140.2	6.07	0.979
145.2	6.07	0.979
150.2	6.08	0.981
155.2	6.08	0.981
160.2	6.08	0.981
165.2	6.08	0.981
170.2	6.09	0.982
175.2	6.09	0.982
180.2	6.09	0.982
185.2	6.10	0.984
190.2	6.10	0.984
195.2	6.11	0.986
200.2	6.11	0.986
205.2	6.12	0.987
210.2	6.12	0.987

TABLE NO. II. 1.10

Run No. 10.02

Bed depth = 4 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
0.2	3.67	0.592
0.7	3.82	0.616
1.2	4.18	0.674
1.7	4.26	0.687
2.2	4.38	0.707
2.7	4.47	0.721
3.7	4.62	0.745
4.7	4.75	0.766
9.7	5.10	0.823
14.7	5.31	0.857
19.7	5.52	0.888
29.7	5.64	0.910
39.7	5.78	0.932
49.7	5.87	0.947
59.7	5.94	0.958
69.7	6.00	0.966
79.7	6.02	0.971
89.7	6.04	0.974
99.7	6.06	0.977
109.7	6.08	0.981
119.7	6.09	0.982
129.7	6.10	0.984
139.7	6.13	0.989
149.7	6.14	0.990
159.7	6.15	0.992
169.7	6.16	0.994
179.7	6.18	0.997
189.7	6.19	0.998
199.7	6.19	0.998
209.7	6.19	0.998

SECTION II.2Breakthrough Data for Runs: Series No. 20.Inlet gas concentration = 6.2% CO₂

Volumetric rate of flow of gas into column = 23.48 litres per min.

TABLE NO: II. 2.1Run No. 20.11

Bed depth = 40 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
1.66	0.0	0.0
3.66	0.23	0.045
5.66	0.46	0.074
7.66	0.87	0.140
12.66	2.14	0.345
17.66	3.30	0.537
22.66	4.08	0.658
27.66	4.63	0.747
32.66	4.98	0.804
37.66	5.24	0.845
42.66	5.41	0.873
47.66	5.51	0.889
52.66	5.60	0.904
57.66	5.69	0.918
62.66	5.73	0.924
67.66	5.79	0.934
72.66	5.87	0.947
82.66	5.92	0.955
92.66	5.95	0.960
102.66	5.97	0.963
114.66	5.98	0.965

TABLE NO: II. 2.2Run No. 20.10

Bed depth = 36 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
1.66	0.05	0.008
6.66	0.71	0.114
11.66	2.00	0.321
16.66	3.22	0.520
21.66	4.05	0.653
26.66	4.64	0.749
31.66	5.04	0.813
36.66	5.29	0.853
41.66	5.49	0.886
46.66	5.61	0.905
51.66	5.70	0.920
56.66	5.76	0.929
61.66	5.84	0.943
66.66	5.86	0.946
76.66	5.91	0.954
86.66	5.96	0.962
96.66	6.02	0.971
116.66	6.04	0.975

TABLE NO: II. 2.3

Run No. 20.09

Bed depth = 32 inches

Time From start (mins.) t	CO ₂ concn. in exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
3.66	0.46	0.074
8.66	1.68	0.271
13.66	2.95	0.476
18.66	3.89	0.628
23.66	4.55	0.734
28.66	4.98	0.803
33.66	5.29	0.853
38.66	5.51	0.889
43.66	5.61	0.905
48.66	5.72	0.923
53.66	5.79	0.934
58.66	5.85	0.944
63.66	5.88	0.949
68.66	5.93	0.957
73.66	5.98	0.965
78.66	6.00	0.968
83.66	6.01	0.970
88.66	6.04	0.975
93.66	6.06	0.978

TABLE NO: II. 2.4Run No. 20.08

Bed depth = 28 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
1.16	0.09	0.015
2.66	0.45	0.073
7.66	2.00	0.323
12.66	3.32	0.536
17.66	4.16	0.671
22.66	4.71	0.760
27.66	5.08	0.819
37.66	5.57	0.899
43.66	5.62	0.907
47.66	5.72	0.923
52.66	5.78	0.932
57.66	5.83	0.941
62.66	5.86	0.946
72.66	5.92	0.955
82.66	5.98	0.965
92.66	6.03	0.973
102.66	6.04	0.974
112.66	6.06	0.978
117.66	6.07	0.979

TABLE NO: II. 2.5

Run No. 20.07

Bed depth = 24 inches.

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
1.66	0.64	0.103
6.66	2.37	0.382
11.66	3.61	0.582
16.66	4.41	0.711
21.66	4.89	0.789
26.66	5.21	0.840
31.66	5.44	0.878
36.66	5.57	0.898
41.66	5.68	0.916
46.66	5.77	0.931
51.66	5.84	0.942
56.66	5.90	0.952
61.66	5.94	0.958
71.66	6.00	0.968
81.66	6.03	0.973
91.66	6.04	0.975
101.66	6.05	0.976
111.66	6.06	0.978
119.66	6.07	0.980

TABLE NO: II. 2.6

Run No. 20.06

Bed depth = 20 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn. Inlet concn. C/C_0
0	0.0	0.0
1.66	1.39	0.224
3.66	2.22	0.358
8.66	3.63	0.586
13.66	4.37	0.705
18.66	4.87	0.786
23.66	5.23	0.844
28.66	5.44	0.878
33.66	5.58	0.900
38.66	5.67	0.915
43.66	5.76	0.929
53.66	5.86	0.945
63.66	5.93	0.957
73.66	5.96	0.962
83.66	5.99	0.967
93.66	6.04	0.975
103.66	6.05	0.976
113.66	6.06	0.978
118.66	6.07	0.980

TABLE NO: II. 2.7

Run No. 20.05

Bed depth = 16 inches

Time from start (mins) t	CO ₂ concn. in exit has (%) C	Exit concn. Inlet concn. C/C_0
0	0.0	0.0
0.66	1.83	0.295
1.16	2.30	0.371
1.66	2.66	0.429
2.66	3.20	0.516
3.66	3.55	0.578
5.66	4.00	0.645
10.66	4.65	0.750
15.66	5.06	0.816
20.66	5.31	0.857
25.66	5.56	0.897
30.66	5.62	0.907
35.66	5.74	0.926
40.66	5.79	0.934
45.66	5.84	0.942
55.66	5.89	0.950
60.66	5.91	0.954
75.66	5.98	0.965
85.66	6.00	0.968
90.66	6.01	0.970
100.66	6.02	0.971
105.66	6.04	0.975
115.66	6.08	0.981
119.66	6.10	0.984

TABLE NO: II. 2.8

Run No. 20.04

Bed depth = 12 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn. Inlet concn. c/c ₀
0	0.0	0.0
0.66	3.20	0.516
1.66	3.92	0.632
2.66	4.28	0.691
3.66	4.54	0.732
5.66	4.81	0.776
7.66	4.98	0.803
12.66	5.27	0.850
17.66	5.46	0.881
22.66	5.60	0.903
27.66	5.70	0.920
32.66	5.76	0.929
37.66	5.80	0.936
42.66	5.85	0.944
52.66	5.91	0.954
62.66	5.98	0.965
72.66	5.99	0.967
82.66	6.00	0.968
87.66	6.02	0.971
102.66	6.07	0.979
117.66	6.07	0.979
119.66	6.07	0.979

TABLE NO: II. 2.9Run No. 20.03

Bed depth = 8 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
0.66	4.52	0.729
1.66	4.92	0.793
2.66	5.14	0.829
5.66	5.37	0.866
10.66	5.54	0.894
15.66	5.70	0.920
20.66	5.78	0.933
25.66	5.84	0.942
35.66	5.92	0.955
50.66	5.98	0.965
60.66	6.00	0.968
75.66	6.01	0.970
85.66	6.02	0.971
95.66	6.05	0.976
115.66	6.06	0.978

Run No. 20.02

Bed depth = 4 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
0.66	5.33	0.860
1.66	5.60	0.903
2.66	5.70	0.920
4.66	5.82	0.939
9.66	5.91	0.954
18.66	5.99	0.967
28.66	6.01	0.970
38.66	6.03	0.973
53.66	6.07	0.979
63.66	6.10	0.984
72.66	6.12	0.987
80.66	6.13	0.989
87.66	6.14	0.991
93.66	6.14	0.991
109.66	6.15	0.992
119.66	6.16	0.994

SECTION II.3Breakthrough Data for Runs: Series No. 50Inlet gas concentration = 1.9% CO₂

Volumetric rate of flow of gas into column = 5.67 litres per min.

TABLE NO: II. 3.1Run No. 50.11

Bed depth = 40 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) c	Exit concn./ Inlet concn. c/c _o
0	0.0	0.0
125.2	0.0	0.0
135.2	0.02	0.011
145.2	0.03	0.016
150.2	0.05	0.026
155.2	0.08	0.042
165.2	0.16	0.084
175.2	0.21	0.111
185.2	0.35	0.184
195.2	0.55	0.290
205.2	0.77	0.405
215.2	0.97	0.511
225.2	1.11	0.584
235.2	1.24	0.653
245.2	1.35	0.710
255.2	1.43	0.753
265.2	1.50	0.790
275.2	1.56	0.821
285.2	1.61	0.847
290.2	1.63	0.858
295.2	1.65	0.869
300.2	1.66	0.874

(contd)

Time from start (mins) t	CO ₂ concn. in exit gas (%) C	Exit concn./ Inlet concn. C/C_0
305.2	1.67	0.879
310.2	1.68	0.884
320.2	1.68	0.884
325.2	1.69	0.890
330.2	1.69	0.890
335.2	1.70	0.895
340.2	1.71	0.900
345.2	1.72	0.905
348.2	1.73	0.911

TABLE NO: II. 3.2

Run No. 50.08

Bed depth = 28 inches

Time from start (mins) t	CO ₂ concn. in exit gas (%) C	Exit concn./ Inlet concn. C/C_0
0	0.0	0.0
68.2	0.0	0.0
73.2	0.03	0.016
78.2	0.05	0.026
83.2	0.10	0.053
93.2	0.19	0.100
103.2	0.37	0.195
113.2	0.58	0.305
123.2	0.80	0.421
133.2	1.01	0.532
143.2	1.17	0.616
153.2	1.30	0.684
163.2	1.40	0.737
173.2	1.47	0.774

(Contd)

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn. Inlet concn. C/C_0
183.2	1.53	0.805
193.2	1.58	0.832
198.2	1.62	0.853
203.2	1.64	0.863
208.2	1.67	0.879
213.2	1.68	0.884
218.2	1.69	0.890
223.2	1.70	0.895
233.2	1.71	0.900
243.2	1.72	0.905
253.2	1.73	0.911
263.2	1.74	0.916
273.2	1.76	0.927
283.2	1.77	0.932
293.2	1.78	0.937
308.2	1.79	0.942

TABLE NO: II. 3.3

Run No. 50.05

Bed depth = 16 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
5.2	0.0	0.0
10.2	0.01	0.005
15.2	0.04	0.021
20.2	0.12	0.063
25.2	0.21	0.111
35.2	0.42	0.221
45.2	0.64	0.337
55.2	0.86	0.453
65.2	1.05	0.553
75.2	1.18	0.621
85.2	1.29	0.679
95.2	1.40	0.737
105.2	1.49	0.785
115.2	1.54	0.811
125.2	1.60	0.842
135.2	1.64	0.863
145.2	1.67	0.879
155.2	1.71	0.900
165.2	1.75	0.921
175.2	1.78	0.937
185.2	1.79	0.942
195.2	1.79	0.942
205.2	1.80	0.948
215.2	1.81	0.953
225.2	1.81	0.953
235.2	1.82	0.958

Run No. 50.02

Bed depth = 4 inches

Time from start (mins) t	CO ₂ concn. in ² exit gas (%) C	Exit concn./ Inlet concn. C/C ₀
0	0.0	0.0
0.7	0.65	0.342
1.2	0.72	0.379
1.7	0.79	0.416
2.2	0.84	0.442
2.7	0.91	0.479
3.2	0.96	0.505
3.7	1.00	0.527
4.2	1.03	0.542
4.7	1.05	0.553
5.2	1.09	0.574
7.7	1.20	0.631
10.2	1.28	0.674
15.2	1.39	0.732
20.2	1.46	0.768
25.2	1.51	0.795
35.2	1.60	0.843
40.2	1.65	0.869
45.2	1.67	0.879
55.2	1.72	0.905
60.2	1.73	0.911
65.2	1.75	0.921
70.2	1.77	0.932
75.2	1.77	0.932
80.2	1.79	0.942
85.2	1.79	0.942
90.2	1.79	0.942
100.2	1.81	0.953
110.2	1.82	0.958
118.2	1.83	0.963

SECTION II.4Calculations for Applying Thomas's Solution

For this the value of r , the equilibrium parameter is needed.

$$\text{From equation (4.10c), } r = \frac{1}{1 + K_1 C_o}$$

where K_1 is the Langmuir constant of equation (I.6.6)
(Vide reference No.17).

The values of r so calculated for the run series Nos. 10, 20 and 50 are tabulated as below.

TABLE NO: II.4.1

Run Series No.	CO ₂ concn. of inlet gas % by volume C _o	Equilm. parameter r
10	6.2	0.4881
20	6.2	0.4881
50	1.9	0.7565

Calculations for Rosen's Parameters

The value of m:

$$m = \frac{e}{1 - e} = \frac{0.406}{(1 - 0.406)} = 0.6834$$

Mean Velocity (v):

To allow for change in velocity of gas due to adsorption of the solute gas as it flows down the column, the mean velocity was taken to correspond to the composition $C/C_0 = 0.5$, and the value so computed was used for the v in Rosen's equations.

Thus, for run series 10,

$$v = \frac{6.19 \times 0.969}{60} \times \frac{1}{28.32} \times \frac{1}{0.02182} \times \frac{1}{0.406} = 0.3984 \text{ ft/sec.}$$

Slope of Isotherm (K)

According to Rosen the value of K is given by $K = \frac{q}{C}$ in volumetric units. In applying Rosen's theory to our data, K was calculated as

$K = \frac{(q_v)_0}{C_0}$ in volumetric units. For example, for the run series No. 10,

$$C_0 = 6.2\% \text{ (by volume); } q_e = 5.635\% \text{ (by weight)}$$

$$(P_{CO_2})_{25^\circ C} = 0.00181 \text{ gm./c.c.}$$

$$\rho_{\text{solid}} = 1.093 \text{ gm./c.c.}$$

$$\therefore K = \frac{0.05635 \times 1.093}{0.00181 \times 0.062} = 548.8$$

The values of v and K for the run series 10, 20 and 50 are tabulated below:

TABLE II. 5.1

Run Series No.	$\bar{v}$ ft./sec.	K
10	0.3984	548.8
20	1.511	548.8
50	0.373	850.4

The value of y/x

$$y/x = -\frac{2m}{3K} \left(\frac{vt}{z} - 1 \right) \quad \text{from equation (4.29)}$$

As an example, for run 10.11

$m = 0.6834$; $K = 548.8$; $v = 0.3984$ ft./sec; $z = 3.3333$ ft.

$t = \text{mins.}$

$$\begin{aligned} \therefore \frac{y}{x} &= \frac{2 \times 0.6834}{3 \times 548.8} \left(\frac{0.3984 \times 60}{3.3333} t - 1 \right) \\ &= 8.303 \times 10^{-4} (7.17 t - 1) \end{aligned}$$

SECTION II.6Tables of Rosen's Parameters Calculated forExperimental RunsTABLE NO. II.6.1Run No. 10.11

$$y/x = 8.303 \times 10^{-4} (7.17 t - 1)$$

<u>t</u> mins.	<u>y/x</u>	<u>u = C/C₀</u> (experimental)
50.2	0.298	0.010
55.2	0.328	0.023
60.2	0.358	0.061
65.2	0.387	0.147
70.2	0.417	0.255
75.2	0.447	0.368
80.2	0.477	0.468
85.2	0.506	0.547
95.2	0.566	0.652
105.2	0.625	0.780
120.2	0.715	0.844
155.2	0.923	0.881
170.2	1.012	0.892
185.2	1.102	0.902
200.2	1.191	0.911

TABLE NO. II. 6.2Run No. 10.10

$$y/x = 8.303 \times 10^{-4} (7.967 t - 1)$$

t mins.	y/x	u = C/C ₀ (experimental)
43.2	0.285	0.016
47.2	0.311	0.027
52.2	0.344	0.065
57.2	0.378	0.158
62.2	0.411	0.281
67.2	0.444	0.403
72.2	0.477	0.510
77.2	0.510	0.584
87.2	0.576	0.698
97.2	0.642	0.774
112.2	0.741	0.844
127.2	0.841	0.881
147.2	0.973	0.915
167.2	1.105	0.932
182.2	1.245	0.939
208.2	1.376	0.945

TABLE NO. II. 6.3Run No. 10.09

$$y/\bar{x} = 8.303 \times 10^{-4} (8.963 \ t^{-1})$$

t mins.	y/ $\bar{x}$	u = C/C _o (experimental)
38.2	0.284	0.015
43.2	0.321	0.058
48.2	0.358	0.150
53.2	0.395	0.263
58.2	0.432	0.382
63.2	0.470	0.490
68.2	0.506	0.577
73.2	0.544	0.644
83.2	0.619	0.737
93.2	0.693	0.803
108.2	0.804	0.866
128.2	0.953	0.905
153.2	1.140	0.926
168.2	1.251	0.934
178.2	1.326	0.936

TABLE NO: II. 6.4Run No. 10.08

$$y/x = 8.303 \times 10^{-4} (10.243 t^{-1})$$

t	y/x	u = C/C _o
mins.		(experimental)
25.2	0.214	0.011
30.2	0.256	0.045
35.2	0.299	0.121
40.2	0.341	0.226
45.2	0.384	0.342
50.2	0.426	0.450
55.2	0.469	0.539
60.2	0.511	0.618
70.2	0.596	0.734
85.2	0.724	0.832
100.2	0.851	0.892
125.2	1.064	0.929
150.2	1.277	0.952
170.2	1.447	0.960
190.2	1.618	0.971
200.2	1.702	0.974
210.2	1.786	0.976

TABLE NO: II. 6.5Run No. 10.07 *

$$y/x = 8.303 \times 10^{-4} (11.95 t - 1)$$

t mins.	y/x	C/C ₀
13.2	0.130	0.053
18.2	0.180	0.105
23.2	0.229	0.171
28.2	0.279	0.253
33.2	0.329	0.329
38.2	0.378	0.405
43.2	0.428	0.500
48.2	0.477	0.573
53.2	0.527	0.634
63.2	0.626	0.734
73.2	0.729	0.808
83.2	0.824	0.860
98.2	0.973	0.903
113.2	1.121	0.924
128.2	1.271	0.937
148.2	1.470	0.950

* By graphical interpolation.

TABLE NO: II. 6.6Run No. 10.06

$$y/\bar{x} = 8.303 \times 10^{-4} (14.34 t^{-1})$$

t mins.	y/ $\bar{x}$	u = C/C _o (experimental)
9.2	0.109	0.077
14.2	0.168	0.174
19.2	0.228	0.276
24.2	0.287	0.373
34.2	0.406	0.540
44.2	0.524	0.662
54.2	0.645	0.732
64.2	0.764	0.812
79.2	0.942	0.887
109.2	1.300	0.924
129.2	1.538	0.942
149.2	1.775	0.963
159.2	1.894	0.971
194.2	2.313	0.978
204.2	2.430	0.983

TABLE NO: II . 6.7Run No. 10.05

$$y/x = 8.303 \times 10^{-4} \quad (17.925 \pm -1)$$

t mins.	y/x	u = C/C ₀ (experimental)
7.2	0.106	0.121
12.2	0.181	0.242
17.2	0.255	0.360
22.2	0.330	0.464
27.2	0.404	0.553
37.2	0.553	0.684
47.2	0.702	0.771
57.2	0.850	0.836
72.2	1.073	0.882
82.2	1.223	0.910
112.2	1.669	0.950
142.2	2.116	0.960
152.2	2.265	0.970
172.2	2.563	0.981

TABLE NO: II. 6.8Run No. 10.04

$$y/x = 8.303 \times 10^{-4} \quad (23.9 \pm -1)$$

t	y/ x	u = C/C _o
mins.		(experimental)
7.2	0.142	0.344
13.2	0.261	0.484
18.2	0.360	0.584
23.2	0.460	0.665
28.2	0.559	0.721
38.2	0.757	0.803
48.2	0.956	0.860
63.2	1.253	0.903
83.2	1.650	0.942
103.2	2.046	0.960
143.2	2.841	0.974
158.2	3.140	0.986
168.2	3.336	0.990
188.2	3.735	0.997

TABLE NO: II. 6.9Run No. 10.03

$$y/x = 8.303 \times 10^{-4} \quad (35.85 \pm -1)$$

t mins.	y/x	u = C/C ₀ (experimental)
5.2	0.154	0.482
7.2	0.214	0.544
10.2	0.303	0.613
15.2	0.452	0.690
20.2	0.601	0.745
30.2	0.898	0.823
40.2	1.195	0.871
50.2	1.494	0.903
65.2	1.940	0.932
90.2	2.685	0.961
120.2	3.576	0.971
160.2	4.768	0.981
185.2	5.513	0.984

TABLE NO: II. 6.10Run No. 10.02

$$y/x = 8.303 \times 10^{-4} \quad (71.7 \pm -1)$$

t mins.	y/x	u = C/C ₀ (experimental)
2.2	0.132	0.707
2.7	0.160	0.721
4.7	0.279	0.766
9.7	0.577	0.823
14.7	0.874	0.857
19.7	1.171	0.888
29.7	1.767	0.910
49.7	2.957	0.947
69.7	4.149	0.966
89.7	5.338	0.974
129.7	7.720	0.984

TABLE NO: II. 6.11Run No. 20.11

$$y/x = 8.303 \times 10^{-4} \quad (27.204 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
5.66	0.127	0.074
7.66	0.172	0.140
12.66	0.285	0.345
17.66	0.398	0.537
22.66	0.511	0.658
27.66	0.624	0.747
32.66	0.737	0.804
37.66	0.850	0.845
42.66	0.963	0.873
52.66	1.188	0.904
67.66	1.528	0.934
82.66	1.866	0.955
114.66	2.590	0.965

TABLE NO: II. 6.12Run No. 20.10

$$y/x = 8.303 \times 10^{-4} (30.227 t - 1)$$

t mins.	y/x	u = C/C ₀ (experimental)
6.66	0.166	0.114
11.66	0.292	0.321
16.66	0.417	0.520
21.66	0.543	0.653
26.66	0.669	0.749
31.66	0.794	0.813
36.66	0.920	0.853
41.66	1.044	0.886
46.66	1.170	0.905
56.66	1.420	0.929
66.66	1.672	0.946
86.66	2.174	0.962
116.66	2.928	0.975

TABLE NO: II. 6.13Run No. 20.09

$$y/x = 8.303 \times 10^{-4} \quad (34.005 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
3.66	0.103	0.074
8.66	0.244	0.271
13.66	0.385	0.476
18.66	0.526	0.628
23.66	0.667	0.734
28.66	0.808	0.803
33.66	0.950	0.853
43.66	1.232	0.905
53.66	1.514	0.934
68.66	1.938	0.957
83.66	2.360	0.970
93.66	2.643	0.978

TABLE NO: II. 6.14Run No. 20.08

$$y/x = 8.303 \times 10^{-4} \quad (38.863 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
7.66	0.246	0.323
12.66	0.408	0.536
17.66	0.571	0.671
22.66	0.731	0.760
27.66	0.892	0.819
37.66	1.214	0.899
47.66	1.537	0.923
62.66	2.020	0.946
82.66	2.666	0.965
117.66	3.796	0.979

TABLE NO: II. 6.15Run No. 20.07

$$y/x = 8.303 \times 10^{-4} (45.34 t - 1)$$

t mins.	y/x	u = C/C _o (experimental)
6.66	0.250	0.382
11.66	0.438	0.582
16.66	0.626	0.711
21.66	0.815	0.789
26.66	1.003	0.840
31.66	1.190	0.878
36.66	1.379	0.898
46.66	1.755	0.931
56.66	2.131	0.952
71.66	2.695	0.968
91.66	3.448	0.975
119.66	4.504	0.980

TABLE NO: II.6.16Run No. 20.06

$$y/x = 8.303 \times 10^{-4} (54.408 t - 1)$$

t mins.	y/x	u = C/C _o (experimental)
1.66	0.074	0.224
3.66	0.165	0.358
8.66	0.391	0.586
13.66	0.617	0.705
18.66	0.842	0.786
23.66	1.068	0.844
28.66	1.294	0.878
33.66	1.520	0.900
43.66	1.972	0.929
63.66	2.875	0.957
83.66	3.781	0.967
103.66	4.680	0.976
118.66	5.360	0.980

TABLE NO: II. 6.17Run No. 20.05

$$y/x = 8.303 \times 10^{-4} (68.01 \pm -1)$$

t mins.	y/x	u = C/C ₀ (experimental)
2.66	0.149	0.516
3.66	0.206	0.578
5.66	0.319	0.645
10.66	0.601	0.750
15.66	0.884	0.816
20.66	1.166	0.857
25.66	1.448	0.897
35.66	2.013	0.926
40.66	2.296	0.934
55.66	3.142	0.950
75.66	4.270	0.965
90.66	5.117	0.970
105.66	5.965	0.975

TABLE NO: II. 6.18Run No. 20.04

$$y/x = 8.303 \times 10^{-4} \quad (90.68 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
0.66	0.049	0.516
1.66	0.124	0.632
2.66	0.199	0.691
3.66	0.275	0.732
5.66	0.425	0.776
7.66	0.576	0.803
12.66	0.953	0.850
17.66	1.328	0.881
22.66	1.704	0.903
32.66	2.458	0.929
42.66	3.210	0.944
62.66	4.714	0.965
87.66	6.595	0.971
117.66	8.860	0.979

TABLE NO: II. 6.19Run No. 20.03

$$y/x = 8.303 \times 10^{-4} (136.02 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
0.66	0.074	0.729
1.66	0.187	0.793
2.66	0.300	0.829
5.66	0.639	0.866
10.66	1.203	0.894
15.66	1.768	0.920
25.66	2.897	0.942
50.66	5.718	0.965
75.66	8.535	0.970
95.66	10.80	0.976
115.66	13.06	0.978

TABLE NO: II. 6.20Run No. 20.02

$$y/x = 8.303 \times 10^{-4} (272.04 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
0.66	0.148	0.860
1.66	0.374	0.903
2.66	0.600	0.920
4.66	1.052	0.939
9.66	2.181	0.954
18.66	4.214	0.967
38.66	8.736	0.973

TABLE NO: II. 6.21Run No. 50.11

$$y/x = 5.358 \times 10^{-4} (6.714 t^{-1})$$

t mins.	y/x	u = C/C _o (experimental)
145.2	0.522	0.016
150.2	0.540	0.026
155.2	0.558	0.042
165.2	0.594	0.084
175.2	0.630	0.111
185.2	0.666	0.184
195.2	0.702	0.290
205.2	0.738	0.405
215.2	0.774	0.511
225.2	0.810	0.584
235.2	0.846	0.653
245.2	0.882	0.753
265.2	0.954	0.790
275.2	0.990	0.821
290.2	1.043	0.858
300.2	1.079	0.874
310.2	1.116	0.884
325.2	1.170	0.890
345.2	1.241	0.905
348.2	1.252	0.911

TABLE NO: II. 6.22Run No. 50.08

$$y/x = 5.358 \times 10^{-4} \quad (9.591 \pm -1)$$

t mins.	y/x	u = C/C _o (experimental)
73.2	0.376	0.016
78.2	0.401	0.026
83.2	0.427	0.053
93.2	0.479	0.100
103.2	0.530	0.195
113.2	0.582	0.305
123.2	0.633	0.421
133.2	0.684	0.532
143.2	0.736	0.616
153.2	0.787	0.684
163.2	0.839	0.737
173.2	0.890	0.774
183.2	0.941	0.805
198.2	1.018	0.853
208.2	1.069	0.879
218.2	1.121	0.890
233.2	1.198	0.900
273.2	1.404	0.927
308.2	1.583	0.942

TABLE NO: II. 6.23

Run No. 50.05

$$y/x = 5.358 \times 10^{-4} (16.785 t - 1)$$

t mins.	y/x	u = C/C _o (experimental)
15.2	0.136	0.021
20.2	0.181	0.063
25.2	0.226	0.111
35.2	0.316	0.221
45.2	0.406	0.337
55.2	0.496	0.453
65.2	0.586	0.553
75.2	0.676	0.621
85.2	0.766	0.679
95.2	0.856	0.737
105.2	0.947	0.785
115.2	1.036	0.811
135.2	1.215	0.863
155.2	1.395	0.900
175.2	1.576	0.937
205.2	1.846	0.948
235.2	2.115	0.958

TABLE NO: II. 6.24Run No. 50.02

$$y/x = 5.358 (67.14 t^{-1})$$

t mins.	y/x	u = C/C _o (experimental)
3.2	0.115	0.505
4.2	0.151	0.542
5.2	0.187	0.574
7.7	0.277	0.631
10.2	0.367	0.674
15.2	0.546	0.732
25.2	0.906	0.795
35.2	1.266	0.843
45.2	1.626	0.879
65.2	2.346	0.921
80.2	2.884	0.942
100.2	3.604	0.953
118.2	4.252	0.963

SECTION II.7Results of curve-matching
against Rosen's solutionTABLE NO. II. 7.1Run Series No.10

m = 0.6834, v = 0.3984; b = 0.00515 and K = 406

Run No.	z ins	x	Apparent value [*] $D_a, \text{ft}^2/\text{sec.}$ (x 10 ⁻⁸)
10.11	40	11	1.956
10.10	36	9	1.777
10.09	32	6	1.334
10.08	28	3	0.762
10.07	24	1.5	0.445
10.06	20	0.8	0.284
10.05	16	0.6	0.267
10.04	12	0.3	0.178
10.03	8	0.2	0.178
10.02	4	0.07	0.124

* Calculated from

$$D_a = \frac{x}{z} \cdot \frac{mvb^2}{3K} \dots\dots\dots(\text{II.7.1})$$

using for K the value obtained from the horizontal shift
 needed for curve-matching.

TABLE NO. II. 7.2Run Series No. 20.

$m = 0.6834$; $v = 1.511$; $b = .00515$ and $K = 406$

Run No.	z ins	x	Apparent value $D_a, \text{ft}^2/\text{sec.}$ ($\times 10^{-8}$)
20.11	40	-	-
20.10	36	0.9	0.675
20.09	32	0.7	0.591
20.08	28	0.55	0.531
20.07	24	0.4	0.450
20.06	20	0.3	0.405
20.05	16	0.15	0.253
20.04	12	0.08	0.180
20.03	8	0.05	0.169
20.02	4	0.025	0.169

TABLE NO. II. 7.3Run Series No. 50

$m = 0.6834$; $v = 0.3730$; $b = 0.00515$ and $K = 816$

Run No.	z ins	x	Apparent value $D_a, \text{ft}^2/\text{sec.}$ ($\times 10^{-8}$)
50.11	40	20	1.657
50.08	28	9	1.065
50.05	16	1	0.207
50.02	4	0.1	0.083

TABLE NO. III.1. 1.Mass BalanceRun No: 30.11A (Adsorption)Inlet gas concentration = 6.2% CO₂

Volumetric rate of flow of gas into column = 8.28 litres per min.

Bed depth = 40 inches.

Time from start (mins.) t	CO ₂ concn. in exit gas (%) C
0	0.0
25.87	0.01
28.87	0.04
31.87	0.13
36.87	0.32
41.87	0.67
46.87	0.18
51.87	1.80
56.87	2.40
61.87	2.95
66.87	3.47
71.87	3.90
76.87	4.22
81.87	4.47
86.87	4.68
91.87	4.86
101.87	5.11
111.87	5.30
121.87	5.42
131.87	5.48
141.87	5.54
151.87	5.61
161.87	5.67
171.87	5.68
181.87	5.71
191.87	5.72
201.87	5.74
208.87	5.75

TABLE NO. III. 1.2Run NO: 30.11 -D(Desorption of CO₂ adsorbed in Run 30.11-A)Volumetric flow rate of exit gas (after cooling) = 38.8 litres per
min.

Bed depth = 40 inches.

Time from start (mins) t	CO ₂ concn. in exit gas (%) C
0.28	4.87
0.53	4.47
0.78	4.20
1.28	3.84
1.78	3.69
2.78	3.50
3.78	3.39
4.78	3.33
6.78	3.26
7.78	3.21
8.78	3.18
11.78	3.02
16.78	2.63
21.78	2.16
26.78	1.65
31.78	1.25
36.78	0.93
41.78	0.65
46.78	0.41
51.78	0.27
56.78	0.17
61.78	0.09
71.78	0.08
81.78	0.05
91.78	0.04
101.78	0.02
111.78	0.01
123.78	0.00

TABLE NO. III. 1.3Run No. 31. 11-A (Adsorption)Inlet gas concentration = 6.2% CO₂

Volumetric rate of flow of gas into column = 12.90 litres per min.

Bed depth = 40 inches.

Time from start (mins) t	CO ₂ concn. in exit gas (%) C
0	0.0
8.34	0.01
9.34	0.03
11.34	0.08
14.34	0.17
19.34	0.50
24.34	1.14
29.34	2.01
34.34	2.83
39.34	3.57
44.34	4.04
49.34	4.45
54.34	4.78
59.34	5.04
64.34	5.24
69.34	5.38
74.34	5.47
79.34	5.55
84.34	5.61
89.34	5.67
94.34	5.73
99.34	5.78
104.34	5.81
109.34	5.85
114.34	5.88
124.34	5.93
134.34	5.96
144.34	6.00
149.34	6.02

TABLE No: III. 1.4Run No. 31.11 -D(Desorption of CO_2 adsorbed in Run 31.11 -A)Volumetric flow rate of exit gas (after cooling = 38.84 litres
per min.)

Bed depth = 40 inches.

Time from start (mins) t	CO_2 concn. in exit gas (%) C
0.29	4.87
0.54	4.47
0.79	4.18
1.29	3.82
1.79	3.60
2.79	3.43
3.79	3.13
5.79	2.92
10.79	2.53
15.79	2.20
20.79	1.88
25.79	1.49
30.79	1.16
35.79	0.90
40.79	0.67
45.79	0.50
50.79	0.37
55.79	0.31
60.79	0.27
65.79	0.19
70.79	0.13
75.79	0.10
80.79	0.09
90.79	0.07
95.79	0.05
100.79	0.03
105.79	0.02
110.79	0.01
118.79	0.0

To check the effectiveness of the regeneration procedure, the data of runs 30.11A, 30.11-D, 31.11-A and 31.11-D (given above) were used. First, graphs were prepared as shown in Figs. 3.1.(a), 3.1(b), 3.2(a) and 3.2(b) for the adsorption and the corresponding regeneration runs. Using a planimeter, the areas $OC_B C_A C'_O C_O$ for the adsorption runs and $OC_M C_N$ for the regeneration runs were measured and converted to a common scale. These areas should be inversely proportional to the respective gas rates used for adsorption and regeneration if the material balance is allright. The results are shown in the Tables given below. The material balance can be seen to be satisfactory.

TABLE NO. III. 1.5

No.	Item	Run No. 30.11-A adsorption	Run No. 30.11-D desorption
1.	Average flow rate of gas	8.02 l./min.	37.8 l./min.
2.	Area, $OC_B C_A C'_O C_O$	95.4 sq.cm.	-
3.	Area, $OC_M C_N$ (reduced to same scale as 2).	-	20.18 sq.cm.
4.	Area reduced to velocity 8.02/l/min.	95.4 sq.cm.	95.1 sq.cm.
5.	Difference	-	0.3 sq.cm.
6.	Percentage difference	-	0.314%

TABLE NO. III. 1.6

No.	Item	Run 31.11-A adsorption	Run 31.11 desorption
1.	Average flow rate of gas	12.5 l./min	37.81 l./min
2.	Area, $OC_B C_A C_O C_O$	55.31 sq.cm.	-
3.	Area, $OC_M C_N$ (reduced to same scale as 2)	-	18.5 sq.cm
4.	Areas, reduced to velocity 8.02 l./min	55.31 sq.cm	56.2 sq.cm
5.	Difference	-	0.89
6.	Percentage difference	-	1.61%

Radial Effects

The very low difference between the static and stagnation pressures over the range of operation of the column did not permit the measurement of velocity profile. Instead, the concentration profile was measured, this being the ultimate effect which is of interest to us.

The sampling was done by means of the probe. Attempts to measure the concentration profile at various levels were not successful in view of the superimposition of the unsteady state which made comparison of the concentrations at various radial positions, even at the same level, practically impossible. To get over this difficulty, an alternative procedure that could be applied to level 11 (i.e., exit level at the bottom of the column during adsorption) was adopted. The Valve V_8 provided a point at which the exit gas from level 11 could be assumed to have reached a uniform concentration due to sufficient mixing, all radial effects, if any, having disappeared. If this sample could be continuously passed through the standard tube of the sonic gas analyser, then samples drawn from level 11 at different radial positions by means of the probe could be passed through the comparison tube of the sonic gas analyser, and the difference in concentration read on the analyser meter. This would measure the difference between the point concentration and the mean concentration provided the time lag in sampling

between these two points was ignored.

Fluctuations were observed in the sonic gas analyser reading when it was used this way, presumably because of the continuous flow of non -standard gas through the standard tube which should normally be kept closed, and the 'zero-adjustment' had to be done more often. This showed that the method was not very reliable. Fortunately, however, for the range of flow used in the investigations, the maximum shift that was noticed in the sonic gas analyser reading as the probe was moved across the diameter, was 0.2 of a division which is equivalent to 0.03% of CO_2 , though it averaged less. Hence it was decided to ignore the radial concentration effect and base all the breakthrough data on the analyses of samples taken with the probe at the central position, (i.e.) the axis of the column.

SECTION III. 3

Checking Voidage by Pressure Drop Measurements

Three runs were conducted at 3 different rates of flow of air through the column. The following correlation given in Perry's Handbook (p.394 of the Third Edition, 1950) in conjunction with Fig.36 (of the same reference) were used:

$$\Delta P = \frac{f_c L S \rho V_o^2}{g_c \epsilon^3} \dots\dots\dots (III. 3.1)$$

which is also

$$\epsilon^3 = \frac{f_c L S \rho V_o^2}{g_c \Delta P} \dots\dots\dots (III. 3.2)$$

$$f_c = f (\text{Re.No.}) \dots\dots\dots (III. 3.3)$$

$$\text{Re.No.} = \frac{\rho V_o}{\mu S} \dots\dots\dots (III. 3.4)$$

$$\text{and } S = \frac{6 (1-e)}{\phi (D_p)} \dots\dots\dots (III. 3.5)$$

where

ΔP = Pressure drop, lb force /sq.ft.

f_c = friction factor (using Fig.36 of Perry's)

L = bed depth, ft .

S = area of particle surface per unit volume of bed, sq.ft./c.ft.

ρ = fluid density, lb.mass/c.ft.

V_o = Superficial velocity, ft./sec.

g_c = Conversion factor, 32.1740, $\frac{\text{lb.mass} \times \text{ft.}}{\text{lb. force} \times \text{sec}^2}$

D_p = Particle diameter, ft.

$\epsilon, (e)$ = voidage, dimensionless

ϕ = shape factor (unity for spheres)

The data and results are given in the following table:

TABLE NO. III. 3.1

No.	Item	Observed Data and Results		
		Run No. 40.11	Run No. 41.11	Run No. 42.11
1.	Bed depth, inches	40	40	40
2.	Pressure drop, cm.of water	5.45	3.45	0.95
3.	Friction factor, f_c	0.73	0.88	1.8
4.	Surface area (assumed) } sq.ft./c.ft.	370	370	370
5.	Voidage, ϵ , (calculated from eqn.) III.3.2) (average = 0.4154) }	0.4151	0.417	0.4141
6.	Voidage, e , determined from sp.gr. measurements. }	0.406	0.406	0.406
7.	Flow Rate: litres/min	23.03	16.77	6.12

Calculation of Equivalent Diameter

Though the voidage calculated from pressure drop measurements **checked** up with the order of the voidage determined by separate experiments, the latter was used in all calculations, since S was an assumed value based on suppliers' general data. Using the experimentally determined value of e instead of one can calculate the value of S corresponding to this from equation III. 3.1, as 346.2 sq.ft./c.ft. Substituting the value of S and e in equation III. 3.3, the value of ϕD_p , the equivalent diameter of the particles is obtained as 0.01029 ft (= 0.1235 ins.)

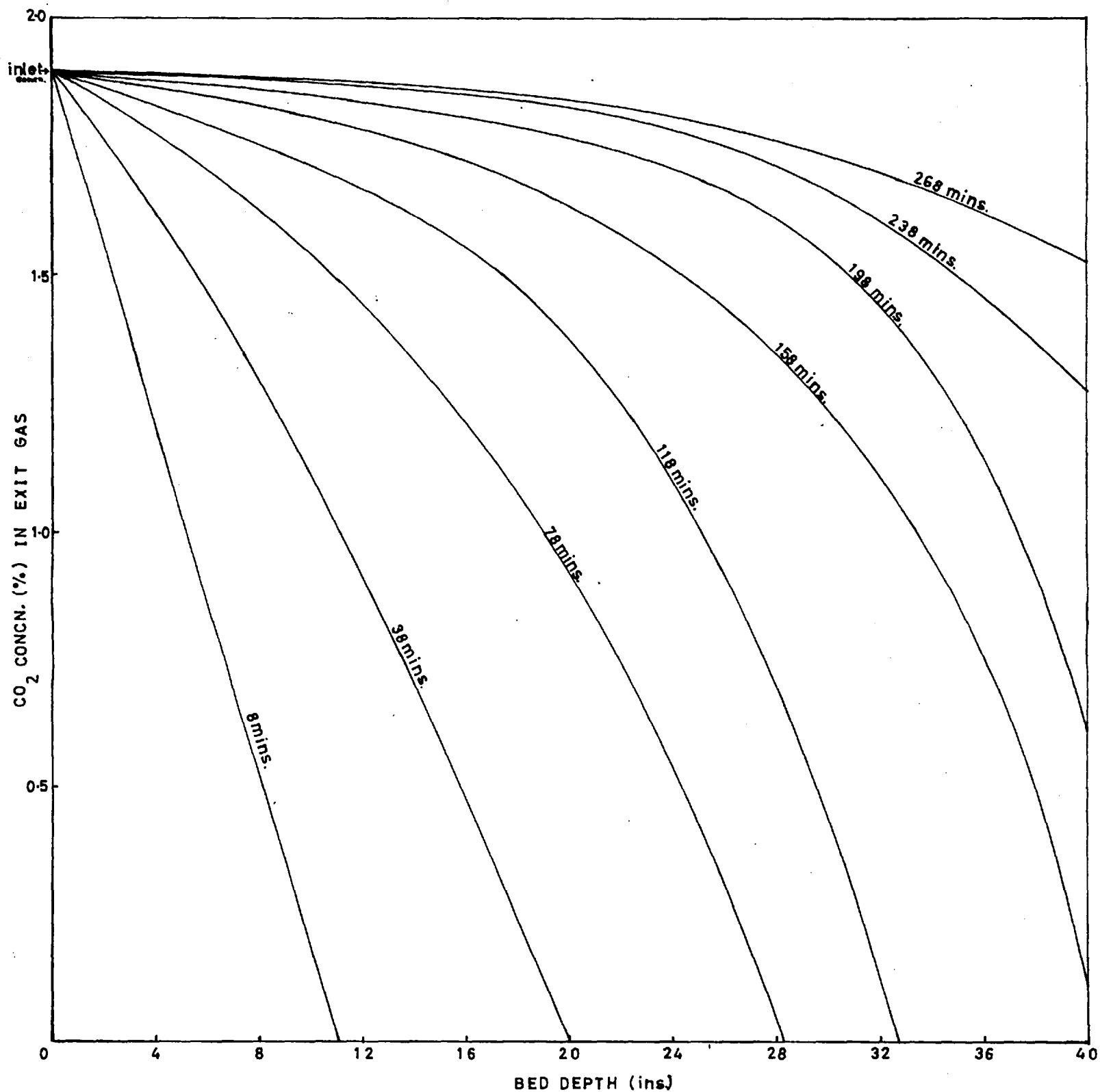


FIG. IV.1.1 - EXAMPLE OF CROSS-PLOT OF
GAS CONC.N. vs BED DEPTH
(RUN SERIES NO. 50)

TABLE NO: IV. 1.1

Concentration of CO₂ in gas phase as a function of bed depth and time read from cross-plots of experimental data.

Run Series No. 10

Inlet gas concentration = 6.2% CO₂

Volumetric rate of flow of gas into column = 6.19 litres per min.

Time in mins.	CO ₂ concentration (%) at various bed depths										
	0"	4"	8"	12"	16"	20"	24"*	28"	32"	36"	40"
0	6.20	0	0	0	0	0	0	0	0	0	0
3.2	"	4.53	2.48	0.94	0.17	0.03	0	0	0	0	0
8.2	"	5.00	3.50	2.13	0.91	0.38	0.08	0	0	0	0
13.2	"	5.25	4.10	3.02	1.65	0.93	0.33	0	0	0	0
18.2	"	5.44	4.49	3.66	2.37	1.57	0.65	0	0	0	0
23.2	"	5.57	4.79	4.12	3.00	2.19	1.06	0.03	0	0	0
28.2	"	5.66	5.02	4.47	3.50	2.75	1.57	0.19	0	0	0
33.2	"	5.72	5.19	4.74	3.92	3.25	2.04	0.53	0.02	0	0
38.2	"	5.77	5.34	4.98	4.29	3.67	2.51	1.13	0.09	0.01	0
43.2	"	5.81	5.47	5.17	4.58	4.02	3.10	1.84	0.35	0.08	0
48.2	"	5.85	5.56	5.32	4.83	4.31	3.55	2.51	0.94	0.19	0.01
53.2	"	5.88	5.63	5.44	5.04	4.57	3.93	3.13	1.65	0.49	0.09
58.2	"	5.92	5.70	5.53	5.21	4.79	4.27	3.67	2.37	1.15	0.26
63.2	"	5.96	5.76	5.61	5.33	5.00	4.55	4.08	3.03	1.92	0.92
68.2	"	5.98	5.81	5.67	5.42	5.17	4.76	4.42	3.58	2.65	1.82
73.2	"	6.00	5.86	5.73	5.51	5.32	5.01	4.69	3.98	3.75	2.03
78.2	"	6.02	5.89	5.78	5.57	5.43	5.19	4.92	4.30	3.73	2.67

(contd)

Time in mins.	CO ₂ concentration (%) at various bed depths										
	0"	4"	8"	12"	16"	20"	24"*	28"	32"	36"	40"
83.2	6.20	6.03	5.92	5.83	5.64	5.53	5.33	5.11	4.57	4.10	3.20
88.2	"	6.04	5.95	5.87	5.69	5.60	5.43	5.26	4.79	4.39	3.67
93.2	"	6.05	5.97	5.89	5.75	5.67	5.54	5.38	4.97	4.64	4.07
98.2	"	6.06	5.99	5.92	5.79	5.70	5.60	5.48	5.13	4.84	4.40
103.2	"	6.07	6.01	5.94	5.83	5.73	5.66	5.56	5.26	5.00	4.66
108.2	"	6.08	6.02	5.95	5.87	5.76	5.70	5.59	5.36	5.14	4.86
113.2	"	6.09	6.02	5.96	5.89	5.78	5.73	5.67	5.44	5.25	5.01
118.2	"	6.10	6.03	5.97	5.91	5.81	5.75	5.72	5.51	5.35	5.13
123.2	"	6.12	6.04	5.98	5.93	5.83	5.78	5.75	5.57	5.42	5.23
128.2	"	6.13	6.05	5.99	5.94	5.85	5.81	5.78	5.61	5.49	5.30
133.2	"	6.13	6.05	6.00	5.95	5.87	5.84	5.82	5.65	5.54	5.34
138.2	"	6.14	6.05	6.00	5.95	5.88	5.86	5.84	5.68	5.59	5.38
143.2	"	6.14	6.06	6.01	5.96	5.89	5.88	5.87	5.71	5.63	5.41
148.2	"	6.15	6.07	6.02	5.97	5.90	5.89	5.88	5.72	5.68	5.43

* Interpolated values from cross plots.

TABLE NO: IV. 1.2

Concentration of CO_2 in gas phase as a function of bed depth and time read from cross-plots of experimental data.

Run Series No. 20

Inlet gas concentration = 6.2 % CO_2

Volumetric rate of flow of gas into column = 23.48 litres per min.

Time in mins.	CO_2 concentration (%) at various bed depths										
	0"	4"	8"	12"	16"	20"	24"	28"	32"	36"	40"
0	6.20	0	0	0	0	0	0	0	0	0	0
2.16	"	5.66	5.03	4.11	2.95	1.66	0.83	0.33	0.20	0.09	0.02*
4.66	"	5.82	5.30	4.67	3.78	2.59	1.76	1.07	0.66	0.40	0.30*
7.16	"	5.87	5.44	4.93	4.21	3.30	2.50	1.85	1.28	0.80	0.75
9.66	"	5.90	5.54	5.11	4.53	3.79	3.17	2.58	1.94	1.43	1.36
12.16	"	5.93	5.62	5.25	4.78	4.17	3.70	3.21	2.60	2.12	2.01
14.66	"	5.95	5.68	5.36	4.99	4.49	4.11	3.69	3.16	2.76	2.63
17.16	"	5.97	5.73	5.45	5.16	4.75	4.44	4.08	3.64	3.31	3.19
19.66	"	5.98	5.77	5.52	5.30	4.96	4.70	4.39	4.044	3.76	3.64
22.16	"	5.99	5.80	5.58	5.42	5.13	4.91	4.65	4.37	4.12	4.02
24.66	"	6.00	5.83	5.63	5.51	5.27	5.08	4.87	4.64	4.42	4.32
27.16	"	6.00	5.85	5.68	5.58	5.38	5.22	5.05	4.87	4.68	4.58
29.66	"	6.01	5.88	5.72	5.63	5.46	5.34	5.21	5.06	4.88	4.79
32.16	"	6.02	5.90	5.75	5.68	5.53	5.44	5.34	5.21	5.06	4.96
34.66	"	6.02	5.92	5.78	5.72	5.59	5.52	5.44	5.33	5.19	5.09
37.16	"	6.03	5.93	5.80	5.76	5.65	5.59	5.54	5.45	5.31	5.20
39.66	"	6.03	5.94	5.82	5.78	5.69	5.65	5.60	5.53	5.42	5.30
42.16	"	6.04	5.95	5.84	5.81	5.73	5.69	5.64	5.60	5.50	5.39
44.66	"	6.05	5.96	5.86	5.83	5.77	5.73	5.68	5.66	5.57	5.46

* Interpolated values from cross-plots.

TABLE NO: IV. 1.3

Concentration of CO₂ in gas phase as a function of bed depth and time read from cross-plots of experimental data.

Run Series No. 50

Inlet gas concentration = 1.9% CO₂

Volumetric rate of flow of gas into column = 5.67 litres per min.

Time in mins.	CO ₂ concentration (%) at various bed depths.										
	0"	4"	8"*	12"*	16"	20"*	24"*	28"	32"*	36"*	40"
0	1.90	0	0	0	0	0	0	0	0	0	0
8.2	"	1.21	0.53	0	0	0	0	0	0	0	0
18.2	"	1.43	0.97	0.53	0.08	0	0	0	0	0	0
28.2	"	1.55	1.15	0.72	0.26	0	0	0	0	0	0
38.2	"	1.63	1.30	0.92	0.48	0.01	0	0	0	0	0
48.2	"	1.68	1.42	1.09	1.70	0.27	0	0	0	0	0
58.2	"	1.73	1.51	1.24	0.90	0.50	0.04	0	0	0	0
68.2	"	1.76	1.57	1.35	1.07	0.75	0.41	0	0	0	0
78.2	"	1.78	1.63	1.45	1.22	0.93	0.55	0.05	0	0	0
88.2	"	1.79	1.67	1.52	1.33	1.07	0.69	0.12	0	0	0
98.2	"	1.81	1.70	1.58	1.43	1.18	0.82	0.27	0	0	0
108.2	"	1.82	1.73	1.63	1.50	1.29	0.96	0.47	0	0	0
118.2	"	1.83	1.75	1.67	1.56	1.38	1.10	0.70	0.12	0	0
128.2	"	1.84	1.78	1.70	1.61	1.44	1.21	0.90	0.52	0.08	0
138.2	"	1.85	1.80	1.73	1.65	1.52	1.33	1.09	0.79	0.44	0.02
148.2	"	1.86	1.81	1.75	1.69	1.59	1.44	1.24	0.96	0.59	0.05
158.2	"	1.87	1.83	1.78	1.72	1.64	1.52	1.35	1.11	0.76	0.10
168.2	"	1.87	1.84	1.80	1.76	1.68	1.57	1.44	1.23	0.88	0.17
178.2	"	1.88	1.85	1.82	1.78	1.71	1.63	1.51	1.31	0.97	0.26

(contd)

Time in mins.	CO ₂ concentration (%) at various bed depths.										
	0"	4"	8"*	12"*	16"	20"*	24"*	28"	32"*	36"*	40"
188.2	1.90	1.89	1.86	1.83	1.79	1.74	1.67	1.59	1.38	1.07	0.05
198.2	"	1.89	1.86	1.84	1.80	1.76	1.71	1.62	1.44	1.15	0.61
208.2	"	1.89	1.86	1.84	1.81	1.78	1.73	1.66	1.51	1.25	0.83
218.2	"	1.89	1.87	1.84	1.81	1.79	1.75	1.69	1.57	1.37	1.01
228.2	"	1.89	1.87	1.84	1.82	1.79	1.76	1.71	1.60	1.42	1.15
238.2	"	1.89	1.87	1.85	1.84	1.81	1.78	1.72	1.62	1.46	1.27
248.2	"	1.89*	1.87	1.86	1.85	1.82	1.79	1.74	1.64	1.52	1.38
258.2	"	1.89*	1.88	1.87	1.86	1.83	1.80	1.75	1.67	1.57	1.46
268.2	"	1.89*	1.88	1.87	1.86	1.84	1.81	1.76	1.70	1.62	1.53

* Interpolated values from cross-plots

Computer Programme for Calculating Solid-phase
Mass Transfer Coefficient

```

title
icst-chem.engg-chandrasekharan and sargent-u748/q-adsorption
title
to find best value of solid-phase mass transfer coefficient

chapter 1
a→80
d→3
u→8
v→8
w→2
x→2
4)i=o(1)s
newline
newline
caption
length=
print(ih)3,2
newline
j=o(2)t
jumpdown 1
x' :=Ødivide (100-a,100-c)
x' :=vu'x'
newline
print (jh') 3,2
print (c)0,5
print (u')0,5
print (v'/x')0,5
print (w'/x')0,5
repeat
hoot 1
repeat
newline

```

(Contd.)

```

read (d)
f = 0
f' = 0
g' = 0
i = 0 (1)s
newline
newline
newline
caption
length =
print (ih) 3,2
newline
b = 0
k = 0
j = 0 (1) t
jumpdown 1
£0 = 0 divide (100-a,100-c)
£1 = dv'-vu'£0-w'
wk = 0 divide (e£1d1d3, d2-ed2)
k=k + 1
jump 3, k=2
jump 2, k=1
£2=0 divide (4w1+wo+w2,3)
b=b+h'£2
k=1
wo=w2
2)£1=ca'
c'=0 divide (b'£1, 1+£1)
£2=c'-b
u=wo/£2
f=f+wowo
f'=f'+wo£2
g'=g'+£2£2
newline
print (jh')3,2
print (c)o,5
print (c')o,5
print (b)o,5
print (u)o,5
3)repeat
hoot4
repeat
u=f'/g'
£0=t/2+1
£1=0 divide (f-uf', s £0+s)
£2=0 sqrt (£1)
newline
newline
caption
axial diffusivity=
print (d) o,5
newline

```

```

caption
mass transfer coefficient=
print (u)o,5
newline
caption
standard deviation=
print (&2)o,5
end
l)p=o(1)8
q=o(1)8
r=9p+q
uq=ar
repeat
vp=0poly(jh')uo,8
repeat
c=0poly(ih)vo,8
p=l(1)8
u(p-1)=pvp
repeat
u'=0poly(ih)uo,7
p=l(1)7
v(p-1)=pup
repeat
v'=0poly(ih)vo,6
p=o(1)8
q=l(1)8
r=9p+q
u(q-1)=qar
repeat
vp=0poly(jh')uo,7
repeat
w'=0poly(ih)vo,8
hoot 8
return
psa
close

```

```

chaptero
a→8o
d→3
u→8
v→8
w→2
&→2
r=o(1)8o
read(ar)
repeat
read(a')
read(b')
read(d1)
read(d2)
read(d3)
read(e)
read(v)

```

(contd)

```
read(a)
read(z')
read(y')
read(h)
read(h')
newline
caption
isotherm constants- a'=
print(a')o,5
space
caption
b'=
print(b')o,5
newline
caption
gas density=
print(d1)o,5
newline
caption
solid density=
print(d2)o,5
caption
solute gas molecular weight=
print(d3)3,2
newline
caption
porosity=
print(e)o,5
newline
caption
inlet velocity=
print(v)3,2
newline
caption
inlet gas concentration=
print(a)o,5
newline
caption
total length=
print(z')3,2
space
caption
increment=
print(h)3,2
newline
caption
total time=
print(y')3,2
space
caption
increment=
```

(Contd)

```

print(h')3,2
h'=h'/2
z'=z'+0.01
y'=y'+0.01
s=@intpt(z'/h)
t=@intpt(y'/h')
across4/l
psa
close
→

```

(Data Tape follows)

The data tape for the above Programme is prepared inserting the necessary numerical values against the items in the same sequence, as given below:

a_r : Polynomial coefficients, 81 in number, obtained from Library Programme - 1007 (substituting the value of zero for a_r where powers higher than the degree of polynomial fit obtained are involved).

$\left. \begin{matrix} a' \\ b' \end{matrix} \right\}$: Langmuir isotherm parameters in $b = b' \frac{a'c'_{ij}}{1+a'c'_{ij}}$

d_1 : Gas density, (moles/cc.)

d_2 : Solid density, (gm./cc.)

d_3 : Solute gas molecular weight (gm./mole.)

e : bed porosity

v : initial gas velocity, (ins./min.)

a : initial gas concentration, (cc/100cc. of gas)

z' : total bed length, (ins.)

y' : total time, (mins.)

h : length increment (ins.)

h' : time increment (mins.)

d : bed longitudinal diffusion coefficient (assumed zero)

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