DYNAMIC DESCRIPTION OF A GAS CHROMATOGRAPHIC COLUMN.

DECEMBER, 1969.

PREFACE

The work described in this thesis is presented in partial fulfilment of the requirements for the degree of M.Sc. in Chemical Engineering. The work is original except where stated and no part has been presented before at any other University.

The investigation was carried out in the Department of Chemical Engineering at the University of the Witwatersrand during 1968 and 1969.

The author gratefully acknowledges the help, inspiration and guidance afforded by Dr. D. Glasser and Dr. A.W. Bryson.

H.A. Greenberg

M.A. GREENBERG.

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CHAPTER I

1. INTRODUCTION.

The ability to simulate the dynamic behaviour of a gas-liquid chromatographic system has many interesting applications. The prediction of the effect of physical parameters on the performance of the column enables the development of transfer functions for process analysis and control. th eventually can be extended to simulation and on-line control of dependent integrated process systems.

Gas-liquid partition chromatography involves a mixture of volatile components injected into an inert gas stream and contacted in a packed column with a stationary liquid supported on an inert solid. The components of the mixture are separated as they are swept through the column and emerge at the outlet as solute bands.

A model based on an isothermal fixed bed in which there was longitudinal dispersion, forced convection and linear interphase mass transfer at a finite rate was proposed. The model produced two simultaneous partial differential equations, involving four parameters, which were examined by using Laplace Transforms and then applying a numerical inversion technique.

The mathematical and experimental behaviour of a typical system was examined. Experimental arbitrary input pulses were imposed on a column and the response analysed. The input and output signals were represented as a harmonic series of sinusoidal functions and the

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impulse response determined in the same form.

The results predicted by the model were compared with the experimental results and the model was simplified to one in which instantaneous equilibrium occurred.

Regeneration of the output curves and analysis of the system using both the proposed models indicated that they provide an adequate dynamic description of the gas chromatograph.

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CHAPTER II

2.1 INTRODUCTION.

In this section three models providing descriptions of isothermal fixed beds are proposed.

MODEL 1, describes longitudinal dispersion, forced convection and linear interphase mass transfer at a finite rate.

MODEL 2, which is a simplification of model 1, describes longitudinal dispersion, and forced convection only.

MODEL 3, describes longitudinal dispersion, forced convection and instantaneous linear interphase mass transfer.

The models result in a set of partial differential equations in one dimension. Laplace Transforms are taken in both the time and distance domains and mathematical manipulations performed. An analytical inversion is then carried out in the distance domain resulting in a system transfer function which cannot be analytically inverted.

A numerical technique for inversion of the Laplace transform is then proposed. From this the impulse response of the system is obtained expressed as a harmonic series in a selected time interval.

A frequency analysis is conducted, solving for the system

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parameters at each selected frequency in this series.

In order to do this, the experimental impulse response is determined from an arbitrary impulse input and the corresponding output by fitting Fourier curves and manipulating the resulting coefficients.

However, the mathematics of the system is such that only two parameters may be independently evaluated at any given frequency. This dilemma is overcome by postulating that longitudinal dispersion and forced convection are characteristic of the column and conditions only and are not affected by the particular solute. Experiments are then chosen to enable determination of two parameters at a time from relevant models.

Evaluation of the parameters from the harmonic series coefficients is accomplished using a method suggested by Law and Bailey. This involves an iterative procedure which requires reasonable starting values. The method of Moment Analysis is used to provide these values as well as a preliminary check on the procedure.

Finally, the dynamic description is studied by considering a least squares analysis and then by regenerating the output curves corresponding to particular impulse inputs.

2.2 MATERIAL BALANCE.

Consider a differential element of a gas-liquid chromatographic

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column, The various transfer processes are described in FIGURE 2.1.

2.2.1 MATERIAL BALANCE IN THE GAS-PHASE

$$\text{Mass in} = \begin{matrix}\text{Mass in}\\ \text{by diffusion}\end{matrix} + \begin{matrix}\text{mass in}\\ \text{by bulk flow}\end{matrix}$$

$$= -D \left.\frac{\partial Cg}{\partial x}\right|_x AFg + uCg\Big|_x A\,Fg$$

$$\text{Mass out} = \begin{matrix}\text{Mass out}\\ \text{by diffusion}\end{matrix} + \begin{matrix}\text{Mass out}\\ \text{by bulk flow}\end{matrix}$$

$$= -D \left.\frac{\partial Cg}{\partial x}\right|_{x+\Delta x} AFg + uCg\Big|_{x+\Delta x} AFg + k\left(\frac{Ce}{M} - Cg\right)\Delta x$$

$$\text{Mass accumulated} = AFg \frac{\partial Cg}{\partial t}\,\Delta x$$

$$\therefore \frac{\partial Cg}{\partial t} = D\frac{\partial^2 Cg}{\partial x^2} - u\frac{\partial Cg}{\partial x} + \frac{k}{AFg}\left(\frac{Ce}{M} - Cg\right)$$

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2.2.2 MATERIAL BALANCE IN THE LIQUID PHASE

$$\text{Mass in} = -k \left(\frac{Ce}{M} - Cg \right) \Delta x$$

$$- \text{Mass out}$$

$$\text{Mass accumulated} = \Delta x \; A \; Fe \; \frac{\partial Ce}{\partial t}$$

$$\therefore \quad \frac{\partial Ce}{\partial t} = \frac{k}{AFe} \left(Cg - \frac{Ce}{M} \right)$$

Let $k_1 = \frac{k}{AFg}$

$k_2 = \frac{k}{AFe}$

$F = \frac{k_1}{k_2} = \frac{Fe}{Fg}$

Thus the model produces the following set of one-dimensional partial differential equations:

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$$\frac{\partial Cg(x,t)}{\partial t} = D\frac{\partial^2 Cg(x,t)}{\partial x^2} - u\frac{\partial Cg(x,t)}{\partial x} + k_1\left\{\frac{Ce(x,t)}{M} - Cg(x,t)\right\} \qquad (2.1)$$

$$\frac{\partial Ce(x,t)}{\partial t} = k_2\left\{Cg(x,t) - \frac{Ce(x,t)}{M}\right\} \qquad (2.2)$$

These equations are based on the model originally proposed by Van Deemter (1)(2).

A paper by Lai and Roth (3) failed to recognise the existence of different k's in these equations.

When there is no interphase mass transfer these equations reduce to the well known Taylor Equations:

$$\frac{\partial Cg(x,t)}{\partial t} = D\frac{\partial^2 Cg(x,t)}{\partial x^2} - u\frac{\partial Cg(x,t)}{\partial x} \qquad (2.3)$$

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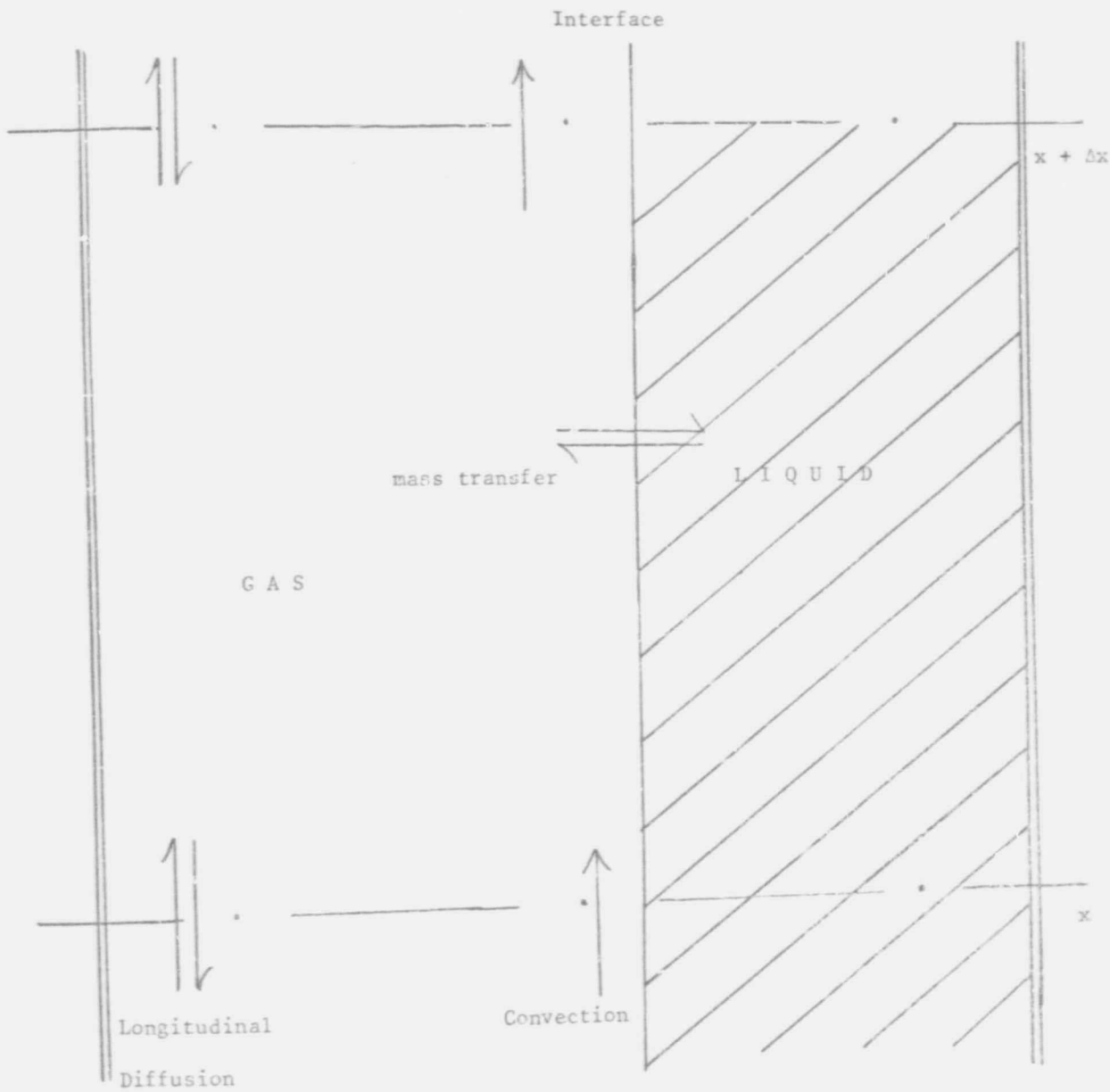

FIGURE 2.1

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2.3 THE MATHEMATICAL TRANSFORMATION.

A dynamic description of a gas-liquid chromatographic column requires the solution of the partial differential equations

$$\frac{\partial Cg(x,t)}{\partial t} = D \frac{\partial^2 Cg(x,t)}{\partial x^2} - u \frac{\partial Cg(x,t)}{\partial x} + k_1 \left\{ \frac{Ce(x,t)}{M} - Cg(x,t) \right\}$$

$$\frac{\partial Ce(x,t)}{\partial t} = k_2 \left\{ Cg(x,t) - \frac{Ce(x,t)}{M} \right\}$$

subject to the following initial and boundary conditions.

C.1 $Cg(0,t) = \delta(t)$ at $t = 0$

This condition implies an ideal impulse input at time zero.

C.2 $Cg(\infty,t) =$ finite at all t

This condition implies that for the hypothetical case of an infinitely long column, the concentration at all time t is finite.

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C.3 $\underline{Cg(x,t) = 0}$ for $t \leq 0$

This condition implies that the concentration of solute in the gas phase at all points within the column is zero for time less than or equal to zero, i.e. the column has been completely purged.

C.4 $\underline{Ce(x,t) = 0}$ for $t \leq 0$

This is the same as C3 but applies to the liquid phase.

Using standard mathematical techniques, transfer functions corresponding to these differential equations may be formulated. [APPENDIX I].

2.4 SUMMARY OF TRANSFER FUNCTIONS.

MODEL I An analysis based on the assumptions of perfect mixing, plug flow and isothermal linear equilibrium yields,

$$F(S) = \exp\left[\frac{ux}{2D} - \left(\frac{u^2x^2}{4D^2} - \frac{x^2}{D}\left(\frac{k_1}{\frac{M}{k_2}\cdot S + 1} - k_1 - S\right)\right)^{\frac{1}{2}}\right] \quad (2.4)$$

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MODEL II An analysis as above but neglecting the interphase mass transfer yields,

$$F(S) = \exp\left[\frac{ux}{2D} - \left(\frac{u^2x^2}{4D^2} + \frac{x^2s}{D}\right)^{\frac{1}{2}}\right] \tag{2.5}$$

MODEL III An analysis based on the assumption of perfect mixing plug flow and instantaneous isothermal linear equilibrium yields,

$$F(S) = \exp\left[\frac{ux}{2D} - \left(\frac{u^2x^2}{4D^2} + \frac{x^2s}{D}(MF + 1)\right)^{\frac{1}{2}}\right] \tag{2.6}$$

2.5 AN INVERSION TECHNIQUE FOR THE LAPLACE TRANSFORM

An approximate real time solution f(t), can be obtained from the Laplace Transform, F(S), in the form

$$f(t) = e^{\alpha t}\left[\sum_{n=1}^{\infty} a_n \sin\frac{n\Pi t}{T} + \sum_{n=0}^{\infty} b_n \cos\frac{n\Pi t}{T}\right]$$

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where

$$a_n = -\frac{1}{T} \cdot \mathrm{Im}\left[F\left(\alpha + \frac{in\Pi}{T}\right)\right]$$

$$b_n = \frac{1}{T} \cdot \mathrm{Re}\left[F\left(\alpha + \frac{in\Pi}{T}\right)\right]$$

$$b_o = \frac{1}{2T} \cdot F(\alpha)$$

for $n = 1(1)\infty$

It has been shown that for an impulse input and response,

$\alpha = 0$

[See appendix 7]

Hence

$$f(t) = \sum_{n=1}^{\infty} a_n \sin\frac{n\Pi t}{T} + \sum_{n=0}^{\infty} b_n \cos\frac{n\Pi t}{T}$$

$$a_n = \frac{1}{T} \cdot \mathrm{Im}\left[F\left(\frac{in\Pi}{T}\right)\right]$$

$$b_n = \frac{1}{T} \cdot \mathrm{Re}\left[F\left(\frac{in\Pi}{T}\right)\right] \qquad (2.7)$$

$$b_o = \frac{1}{2T} \cdot F(0) \qquad n = 1(1)\infty$$

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2.6 FOURIER SERIES REPRESENTATION

A wide range of arbitrary functions can be represented by this harmonic series in a fundamental interval (0,2T) provided that certain conditions known as the DIRICHLET conditions are met.

CONDITION I f(t) must be defined at every point in the interval (0,2T).

CONDITION II f(t) must everywhere be single valued, finite and sectionally continuous.

CONDITION III f(t) must have a finite number of maxima and minima in the interval (0,2T).

Under these conditions the function f(t) can be represented as a convergent series of the form,

$$f(t) = \sum_{n=1}^{\infty} a_n \sin \frac{n\pi t}{T} + \sum_{n=0}^{\infty} b_n \cos \frac{n\pi t}{T}$$

where

$$a_n = \frac{1}{T} \int_0^{2T} f(t) \sin \frac{n\pi t}{T} \, dt$$

$$b_n = \frac{1}{T} \int_0^{2T} f(t) \cos \frac{n\pi t}{T} \, dt \qquad (2.8)$$

$$b_o = \frac{1}{2T} \int_0^{2T} f(t) \, dt \qquad n = 1(1)^{\infty}$$

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2.7 RELATIONSHIP BETWEEN INPUT AND OUTPUT CURVES.

Let an inpulse input $\theta_i(t)$ be imposed on the system and let the response to this input be $\theta_o(t)$. (See FIGURE 2.2.)

$$\theta_i(t) = \sum_{n=1}^{\infty} p_n \sin \frac{n\Pi t}{T} + \sum_{n=0}^{\infty} q_n \cos \frac{n\Pi t}{T}$$

$$\theta_o(t) = \sum_{n=1}^{\infty} u_n \sin \frac{n\Pi t}{T} + \sum_{n=0}^{\infty} v_n \cos \frac{n\Pi t}{T}$$

$$f(t) = \sum_{n=1}^{\infty} a_n \sin \frac{n\Pi t}{T} + \sum_{n=0}^{\infty} b_n \cos \frac{n\Pi t}{T}$$

It can be shown that (SEE APPENDIX 2)

$$b_n = \frac{1}{T}\left(\frac{v_n q_n + u_n p_n}{q_n^2 + p_n^2}\right)$$

$$a_n = \frac{1}{T}\left(\frac{u_n q_n - v_n p_n}{q_n^2 + p_n^2}\right) \qquad (2.9)$$

and $$v_n = T\,(b_n q_n - a_n p_n)$$

$$u_n = T\,(a_n q_n + b_n p_n)$$

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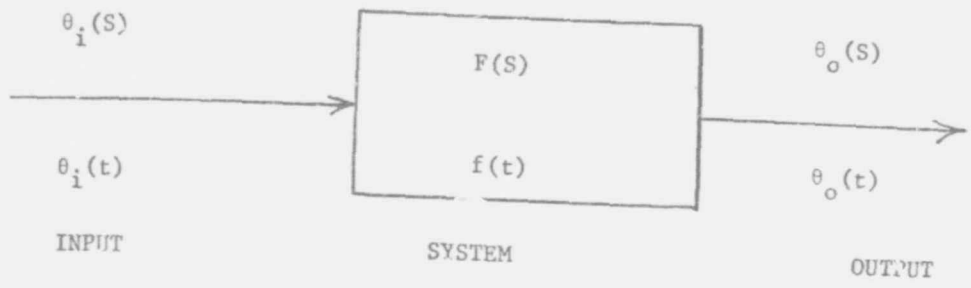

FIGURE 2.2

2.8 EVALUATION OF U AND D.

Consider a packed gas-liquid chromatographic column in which no interphase mass transfer occurs. This corresponds to MODEL 2 and the transfer function is described by equation 2.5.

$$F(S) = \exp\left[\frac{ux}{2D} - \left(\frac{u^2x^2}{4D^2} + \frac{-sx^2}{D}\right)^{\frac{1}{2}}\right]$$

Let $S=iw$

and $x = L$

$$F(iw) = \exp\left[\frac{uL}{2D} - \left(\frac{u^2L^2}{4D^2} + \frac{iwL^2}{D}\right)^{\frac{1}{2}}\right]$$

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The following mathem·tic transformations will be used:

$$Z = x + iy = r(\cos\theta + \sin\theta)$$

where $r = (x^2 + y^2)^{\frac{1}{2}}$

$$\theta = \arctan\left(\frac{y}{x}\right)$$

also $(r \text{ cis } \theta)^{1/n} = r^{1/n} \text{ cis } \left(\frac{\theta}{n} + \frac{2\pi k}{n}\right)$

for $k = 0(1)\ n-1$

Examine the square root in equation (2.5). This must be positive because as $x \to \infty$, $Cg(\infty,t)$ must remain finite. ie. the exponential must be negative. Thus for $n = 2$ only $k = 0$ requires consideration.

Thus $(r \text{ cis } \theta)^{1/n} = r^{1/n} \text{ cis } \left(\frac{\theta}{n}\right)$ for $n = 2$

Let $p = \frac{u^2L^2}{4D^2}$

$$q = \frac{wL^2}{D}$$

$$(p + iq)^{\frac{1}{2}} = (p^2 + q^2)^{1/4} \text{ cis } \left(\tfrac{1}{2}(\arctan \frac{q}{p})\right)$$

$$= j \text{ cis } \ell$$

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