VARI (variance). A value of $T \approx 150$ seconds was then selected.

Fourier curves were fitted to both input and output and the amplitude ratios calculated. These values are tabulated on Page C8.

From these Fourier coefficients the system coefficients were evaluated and the amplitude ratio and phase lag calculated.

Values of the parameters D and u were then fitted in the least squares sense at each selected frequency. The results are again tabulated on page C8.

FIGURE 4.1A shows a plot of D and u vs. w. This plot has been extrapolated to produce values of D and u at zero frequency.

4.3 k AND M AS A FUNCTION OF w

The evaluation and analysis of k and M as a function of w is presented under the heading RUN NUMBER 2 (pages C14 and C15) for n-butane, RUN NUMBER 3 (pages C16 and C17) for butene-1 and RUN NUMBER 5 (pages C18 and C19) for n-butane in a gas mixture.

The format is exactly the same as for the inert gas analysis except that the values of D and u are presented alongside k and M for convenience.

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FIGURES 4.2A and 4.2B show plots of k and M vs. w.

These plots have also been extrapolated to produce values at zero frequency.

4.4 REGENERATION OF THE OUTPUT CURVE.

Using experimentally determined values of D, u, k and M the output curve was regenerated using MODEL 1 and MODEL 3. Two distinct investigations were performed. Firstly, to pragmatically test the validity of the numerical approximations, values of the parameters as a function of w were used to regenerate the output. Secondly, to test the validity of the models, a Rosenbrock Search (9) was used to find the parameters which produced an overall sum of squares minimum and these single values were then used to regenerate the output. (See pages C30 to C42).

The results, described in terms of start point number, finish point number, time axis interval and concentration profile, are tabulated on pages C26, C29 , C46 and C49.

FIGURES 4.3A and 4.3B show the comparison of experimental and predicted curves for n-butane.

4.5. SENSITIVITY ANALYSIS.

The variation of the sum of squares of errors with D, w, k and

Continued/...39

M was examined.

Similar fractional changes in the respective parameters were selected.

The results are tabulated on pages C22 and C23.

FIGURES 4.4 and 4.5 show graphically the effect of D, U, k and M on the sum of squares of errors.

4.6 SAMPLE RUN.

Complete results of a particular run are shown from pages C49 onwards and FIGURE 4.6.

4.7 COMPARISON OF REPORTED AND DETERMINED M VALUES.

Mellado (8) has reported values of the partition coefficient for n-butane in n-dodecane, at infinite dilution, as a function of temperature and pressure. (SEE APPENDIX 6). The relevant value is

$$M^{o} = 53.2$$

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CHAPTER V

5.1 DISCUSSION AND CONCLUSIONS.

The aim of this thesis was to formulate a model and mathematical procedure to provide a dynamic description of a gas-liquid chromatographic column. This aim has been achieved as it has been shown that MODEL 1 adequately describes the physical system. Further, the simplified MODEL 3 satisfactorily describes the particular system investigated but obviously cannot be used as a general model of a chromatographic column. The technique should prove useful in studying any packed bed in which simultaneous longitudinal dispersion, forced convection and interphase mass transfer occurs. The ease with which the experimentation and computation can be achieved suggests that the technique can be extended to investigate further dynamic models with comparitively little modification.

The mathematical procedure used for the inversion of the Laplace Transform has been studied in detail by Turner in his M.Sc. thesis (5). In the application of this technique two points were of particular interest. Firstly, how many Fourier coefficients are necessary to ensure exclusion of noise, avoid loss of portion of the actual signal and limit the processing and computing time to a minimum. Secondly, what range of frequencies should be studied and how should a value for T be chosen.

In this study, conclusions arrived at by Turner have been accepted and pragmatically verified. The conclusions are that:

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a. The relationship between the number of Fourier coefficients and data or sample points should be such that the number of data points is greater than or equal to 4 times the number of coefficients selected.

b. The choice of T should be such that truncation of the series occurs before noise completely swamps the signal. This truncation point is determined by plotting the amplitude ratio as a function of frequency and looking for a turning point. As indicated in CHAPTER 2.8 the analysis of D and u utilizes a numerical technique. It has however, subsequently been found that an analytic solution of equations 2.13 is possible. This fact does not alter any of the computer programs other than MG51.

The mathematical procedure required that MODEL 2 be formulated to evaluate parameters D and u for use in MODEL 1. The results show that, for the frequency range studied, the model adequately describes the physical system. This is apparent from the ability to regenerate the output curve.

The numerical procedure adopted for evaluating the four parameters in two searches resulted in a sum of squares error which was not an absolute minimum. However, the improvement in error using a four variable search technique (9) was insignificant, and the results as determined in the separate searches were used throughout.

The results produced using MODEL 1 show that, even although k varies irregularly with w, the model adequately descrives a gas-liquid chromatographic column. The explanation of this phenomenon is that the model, under these particular experimental conditions, is insersitive to variations in k. The sum of squares-sensitivity analysis shows the model to be insensitive to both k and D. It is suggested

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that the model will, in general, be insensitive to D but that the sensitivity to k will vary according to solute and substrate.

As a result, MODEL 1 was modified to exclude the finite rate transfer term. Using this MODEL 3, regeneration of the output curve indicated that, although not as suitable as MODEL 1, it produced a satisfactory description of the experimental output curve. It is however, not proposed that the modified model be adopted as the effect of various solutes and substrates must be examined to clearly define its limits of application.

The inference that the system studied is insensitive to values of k offers an explanation of the fact that Lai and Roth (3) were able to produce acceptable regenerated output curves even though they failed to recognize the existance of k_1 and k_2.

The method used by Lai and Roth (3) to evaluate D and u independently involved experimentation with a packed column in which the liquid substrate had been omitted. This study made use of an inert solute, hydrogen, which did not undergo mass transfer. A worthwhile refinement to both these techniques would be the use of an inert solute with a similar molecular weight to the active solute.

The technique is comparable, as far as regeneration of output, with the method used by Lai and Roth but is, in addition, able to predict dead times. The regenerated output shows discrepencies particularly at the tail end of the curve. An explanation i[illegible] tail may not be produced by chromatographic mechanisms but re[illegible], other factors

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such as adsorption onto the packing and diffusion in the liquid phase.

It is of interest to note that in the run in which butane was studied in a gas mixture, the analysis produced results which correlated well with those obtained with the pure gas.

Finally it is encouraging to note that the values of M determined using this method of analysis are not inconsistant with those reported in the literature.

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NOMENCLATURE

A	Cross-section column area, L^2
AR_T	Amplitude ratio
a_n, b_n	Coefficients in Fourier Series
Cg(x,t)	Concentration of solute in gas, mols L^{-3}
Ce(x,t)	Concentration of solute in liquid, mols L^{-3}
D	Effective longitudinal diffusivity, L^2t^{-1}
Fg	Volume fraction of gas phase
Fe	Volume fraction of liquid phase
F(s)	Laplace transform of f(t)
f(t)	Real time solution
Im	Imaginary part of
i	square root of -1
k	Mass transfer coefficient/unit length of column, L^2t^{-1}
L	Column length, L
M	Distribution coefficient (C_e/C_g)
n	Positive integer
p	Complex distance variable
P_n, q_n	Coefficients in Fourier series
Re	Real part of
s,S	complex time variable
T	Time range variable
T_m	Mean
T_s^2	Variance
T_a^3	Skewness

Continued/... 45

t	Time, t
u	Average interstitial gas velocity, L^2t^{-1}
u_n, v_n	Coefficients in Fourier series
x	Distance variable, L
ζ	Real part of S
α_n	n'th Moment of f(t)
$\delta(t)$	Dirac delta
$\theta(t)$	Real time curve
ϕ_T	Phase lag
w	frequency, t^{-1}

Continued/...46

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Continued/...A1

APPENDIX I

TRANSFORMATION AND MANIPULATION OF THE DIFFERENTIAL EQUATIONS. (2.1 and 2.2)

EQUATION (2.1): Taking Laplace Transforms on both sides with respect to time

$$sC_g(x,s) - \underbrace{C_g(x,0)}_{\text{zero by C3}} = D\frac{d^2}{dx^2} C_g(x,s) - u\frac{d}{dx} C_g(x,s)$$

$$+ \frac{k_1}{M} \cdot C_e(x,s) - k_1 C_g(x,s)$$

Taking Laplace Transforms on both sides with respect to distance

$$sC_g(p,s) = Dp^2 C_g(p,s) - \underbrace{D\,p\,C_g(0,s)}_{\text{unity by C1}} - Dg'(0,s) - u\,p\,C_g(p,s)$$

$$+ \underbrace{uC_g(0,s)}_{\text{unity by C1}} + \frac{k_1}{M} C_e(p,s) - k_1 C_g(p,s)$$

(A.1.1.)

where $C_g'(0,s) = \left.\frac{dC_g(x,s)}{dx}\right|_{x=0}$

Continued/...A2

EQUATION (2.2): Transform with respect to time.

$$sCe(x,s) - \underbrace{\cancel{Ce(x,0)}}_{\text{zero at C4}} = k_2\, Cg(x,s) - \frac{k_2}{M}(Ce(x,s))$$

Transform with respect to distance

$$sCe(p,s) = k_2\, Cg(p,s) - \frac{k_2}{M} Ce(p,s)$$

Now

$$sCe(p,s) + \frac{k_2}{M}(Ce(p,s)) = k_2\, Cg(p,s)$$

$$Ce(p,s)\left\{s + \frac{k_2}{M}\right\} = k_2 Cg(p,s)$$

$$\therefore \quad Ce(p,s) \qquad \frac{M}{/k_2 \cdot s + 1} \cdot Cg(p,s) \qquad (A.1.2)$$

Substituting back into equation (A.1.1)

$$sCg(p,s) = D\,p^2\, Cg(p,s) - Dp - DCg(0,s) - u\,p\,Cg(p,s) + u$$

$$+ \frac{k_1}{M} \cdot \frac{M}{M/k_2 \cdot s + 1} Cg(p,s) - k_1 Cg(p,s)$$

Continued/A3

$$Cg(p,s) = \frac{Dp - u + D\,Cg'(0,s)}{\left[Dp^2 - up + \left(\frac{k_1}{M/k_2 \cdot s + 1} - s - k_1\right)\right]}$$

$$= \frac{p - \frac{u}{D} + Cg'(0,s)}{\left[p^2 - \frac{u}{D} \cdot p + \frac{1}{D}\left(\frac{k_1}{M/k_2 \cdot s + 1} - s - k_1\right)\right]}$$

(A.1.3)

The denominator has the form

$$x^2 + bx + C$$

which has roots

$$x = -\frac{b}{2} \pm \left(\frac{b^2}{4} - C\right)^{\frac{1}{2}}$$

Now let $B_o = -\frac{u}{D} + Cg'(0,s)$

$$B_1 = -\frac{u}{2D} + \left(\frac{u^2}{4D^2} - \frac{1}{D}\left[\frac{k_1}{M/k_2 \cdot s + 1} - s - k_1\right]\right)^{\frac{1}{2}}$$

$$B_2 = -\frac{u}{2D} - \left(\frac{u^2}{4D^2} - \frac{1}{D}\left(\frac{k_1}{M/k_2 \cdot s + 1} - s - k_1\right)\right)^{\frac{1}{2}}$$

Equation (A.1.3) can then be written

$$Cg(p,s) = \frac{p + B_o}{(p + B_1)(p + B_2)}$$

Continued/...A4

Inverse transforming with respect to p

$$Cg(x,s) = \frac{\left(B_o - B_1\right) e^{-B_1 x} - \left(B_o - B_2\right) e^{-B_2 x}}{B_2 - B_1} \qquad (A.1.4)$$

Consider B_1 : $M > 0, \quad k_1 > 0, \quad k_2 > 0$

$$\therefore \frac{M}{k_2} > 0$$

By definition s is a positive constant

$$\therefore \frac{M}{k_2} \cdot s + 1 > 0$$

$$\therefore \frac{k_1}{\frac{M}{k_2} \cdot s + 1} < k_1$$

$$\therefore s + k_1 > \frac{k_1}{\frac{M}{k_2} \cdot s + 1}$$

i.e. $$\frac{k_1}{M/k_2 \cdot s + 1} - k_1 - s < 0$$

Thus B_1 is always positive and as $x \to \infty$, $e^{-B_1 x} \to 0$

Consider B_2 Using the same argument as above, B_2 is always

Continued/...A5

negative and as $x \to \infty$ $e^{-B_2 x} \to \infty$

Hence for C2 to hold

$$B_o - B_2 = 0$$

Thus

$$\frac{u}{D} - Cg'(0,s) = -\frac{u}{2D} - \left(\frac{u^2}{4D} - \frac{1}{D} \left(\frac{k_1}{M/K_2 \cdot s + 1} - s - k_1 \right) \right)^{\frac{1}{2}}$$

$$\therefore \quad Cg'(0,s) = \frac{u}{2D} - \left[\frac{u^2}{4D} - \frac{1}{D} \left(\frac{k_1}{M/k_2 \cdot s + 1} - s - k_1 \right) \right]^{\frac{1}{2}}$$

Also, from equation (A.1.4)

$$Cg(x,s) = \frac{B_0 - B_1}{B_2 - B_1} \cdot e^{-B_1 x}$$

$$= e^{-B_1 x}$$

$$\therefore \quad Cg(x,s) = \exp \left[\frac{ux}{2D} - \left(\frac{u^2 x^2}{4D^2} - \frac{x^2}{D} \left[\frac{k_1}{M/k_2 \cdot s + 1} - k_1 - s \right] \right)^{\frac{1}{2}} \right] \qquad \text{(A.1.5)}$$

Equation (A.1.5) is the system transfer function corresponding to the original partial differtial equations.

Consider the special case of no interphase mass transfer. Equation (A.1.5) reduces to

Continued/...A6

$$Cg(x,s) = \exp\left[\frac{ux}{2D} - \left(\frac{u^2x^2}{4D^2} - \frac{x^2 s}{D}\right)^{\frac{1}{2}}\right] \qquad (A.1.6)$$

Also consider the case where interphase mass transfer does occur but $k \to \infty$

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

Now

$$\frac{k_1}{M/k_2 \cdot s + 1} - k_1 = \frac{k_1 k_2}{Ms + k_2} - k_1$$

$$= \frac{k_1 k_2 - k_1 Ms - k_1 k_2}{Ms + k_2}$$

$$= \frac{-MsF\ k_2}{Ms + k_2}$$

where $F = \frac{k_1}{k_2}$ (by definition)

Using Le Hopital's rule for indeterminate forms,

$$\lim_{k_2 \to \infty}\left[\frac{-MsF\ k_2}{Ms + k_2}\right] = \lim_{k_2 \to \infty}\left[\frac{-MsF}{1}\right]$$

$$= -MsF$$

Continued/...A7

Hence equation (A.15) becomes

$$F(s) = \exp\left[\frac{ux}{2D} - \left(\frac{u^2x^2}{4D^2} + \frac{sx^2}{D} (MF + 1) \right)^{\frac{1}{2}} \right] \quad (A.1.7)$$

Continued/...A8

APPENDIX II

RELATIONSHIP BETWEEN INPUT AND OUTPUT COEFFICIENTS.

Let

$$\theta_i(t) = \sum p_n \sin \frac{n\Pi t}{T} + \sum q_n \cos \frac{n\Pi t}{T}$$

$$\theta_o(t) = \sum u_n \sin \frac{n\Pi t}{T} + \sum v_n \cos \frac{n\Pi t}{T} \qquad \text{(A.2.1)}$$

$$f(t) = \sum a_n \sin \frac{n\Pi t}{T} + \sum b_n \cos \frac{n\Pi t}{T}$$

where $w = \frac{n\Pi}{T}$

By definition of the Laplace Transform in the time domain

$$F(s) = \int_o^\infty e^{-st} f(t)\, dt \qquad \text{(A.2.2)}$$

and in the frequency domain

$$F(iw) = \int_o^\infty e^{-iwt} f(t)\, dt \qquad \text{(A.2.3)}$$

For all $t > 2T$, $f(t) = 0$

$$\therefore F(iw) = \int_0^{2T} e^{-iwt} f(t)\, dt$$

$$= \int_0^{2T} (\cos wt - i \sin wt) f(t)\, dt$$

$$= Tb_n - i\, Ta_n \qquad \text{(A.2.4)}$$

Continued/...A9

also

$$F(s) = \frac{\theta_o(s)}{\theta_i(s)}$$

or

$$F(iw) = \frac{\theta_o(iw)}{\theta_i(iw)} \qquad \text{(A. 2.5)}$$

$$\therefore Tb_n - i\,Ta_n = \frac{Tv_n - iTu_n}{Tq_n - iTp_n}$$

$$= \frac{T(v_n - iu_n)(q_n + ip_n)}{T(q_n - ip_n)(q_n + ip_n)}$$

Multiplying by the complex conjugate.

$$= \frac{(v_n q_n + u_n p_n)}{\left(q_n^2 + p_n^2\right)} - i\,\frac{(u_n q_n - v_n p_n)}{\left(q_n^2 + p_n^2\right)}$$

and equating real and imaginary parts

$$b_n = \frac{1}{T}\left\{\frac{v_n q_n + u_n p_n}{q_n^2 + p_n^2}\right\} \qquad \text{(A.2.6)}$$

$$a_n = \frac{1}{T}\left\{\frac{u_n q_n - v_n p_n}{q_n^2 + p_n^2}\right\} \qquad \text{(A 2.7)}$$

Continued/...A10

APPENDIX III

SOLUTION OF THE EQUATIONS BY THE METHOD OF LAW AND BAILEY (6) (MODEL 2)

The least squares method is used to find the values of u and D which give the best solution to the equations (2.13) in the least squares sense.

To do this, the sum

$$s^2 = \sum_{i=1}^{n} (y_i - \phi_i)^2 \qquad (A.3.1)$$

must be minimised, where

n = number of observation points

y_i = observed values

ϕ_i = theoretical or predicted values

Let

AR_a = experimental (actual) amplitude ratio

AR_T = theoretical amplitude ratio

ϕ_a = experimental phase lag

ϕ_T = theoretical phase lag

b_p = model parameters (u and D)

Thus the equation

$$s^2 = (\ln AR_a - \ln AR_T)^2 + (\tan \phi_a - \tan \phi_T)^2 \qquad (A.3.2)$$

Continued/...A11