$$= j \cos \ell + i j \sin \ell$$

where $j = (p^2 + q^2)^{1/4}$

$$\ell = \tfrac{1}{2} \arctan \left(\frac{q}{p} \right)$$

now $F(iw) = \exp \left[\frac{uL}{2D} - j \cos \ell - i j \sin \ell \right]$

$$= \exp \left[y + i Z \right]$$

$$= e^y \cdot \left[\cos Z + i \sin Z \right]$$

where $y = \frac{uL}{2D} - j \cos \ell$

$$Z = - j \sin \ell$$

and using equations (2.7)

$$\boxed{\begin{aligned} a_n &= - \frac{1}{T} \cdot e^y \sin Z \\ b_n &= \frac{1}{T} \cdot e^y \cos Z \end{aligned} \qquad (2.10)}$$

For convenience the following two relationships involving u and D can be defined:

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$$\text{Amplitude Ratio} = T\left(a_n^{\ 2} + b_n^{\ 2}\right)^{\frac{1}{2}} = AR_T \quad (2.11)$$

$$\text{Phase Lag} = \arctan\left(\frac{b_n}{a_n}\right) = \phi_T \quad (2.12)$$

$$\text{Thus} \quad AR_T = \left\{ T\left[\frac{1}{T}\,2\left[e^{2y}\sin^2 Z + e^{2y}\cos^2 Z\right]\right]^{\frac{1}{2}} \right\}$$

$$\text{and} \quad = e^{y}$$

$$\text{and} \quad \phi_T = \arctan\left(-\frac{-1}{\tan\ Z}\right)$$

$$\therefore\ \ln AR_T = y$$

$$\tan\ \phi_T = -\frac{1}{\tan\ Z} \qquad (2.13)$$

Equations (2.13) are two simultaneous equations in the two unknowns u and D.

These equations may be solved by using a method proposed by Law and Bailey (6) and fully described in APPENDIX 3.

It has been subsequently found that an analytical solution to equation (2.13) is possible. However, for the purposes of this investigation the numerical technique has been used.

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2.9 EVALUATION OF k AND M.

Consider a packed gas-liquid chromatographic column in which isothermal, linear interphase mass transfer occurs. This corresponds to MODEL 1 and the transfer function is described by equation (2.4).

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

let $s = iw$

and $x = L$

Consider $\left[\frac{M}{k_2} \cdot iw + 1\right]^{-1}$

$$= \left(\frac{M^2w^2}{k_2^2} + 1\right)^{-\frac{1}{2}} \operatorname{cis}\left(-\arctan\frac{Mw}{k_2}\right)$$

as before, let

$$\beta = -\arctan\frac{Mw}{k_2}$$

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

$$Y = \left(\frac{M^2w^2}{k_2^2} + 1\right)^{-\frac{1}{2}}$$

Continued/...20

then $\left\{\frac{u^2L^2}{4D^2} - \frac{L^2}{D}\left[\frac{k_1}{\frac{M}{k_2}\cdot S+1} - k_1 - S\right]\right\}^{\frac{1}{2}}$

$$= \left[Z - \frac{L^2k_1}{D}(Y\cos\beta - 1) + i\left\{\frac{L^2w}{D} - \frac{L^2k_1}{D}\cdot Y\sin\beta\right\}\right]^{\frac{1}{2}}$$

$$= (U + i\,v)^{\frac{1}{2}}$$

where $U = Z - \frac{L^2k_1}{D}\left[Y\cos\beta - 1\right]$

$$v = \frac{L^2}{D}\left[w - k_1 Y\sin\beta\right]$$

$$\theta = \arctan\frac{v}{U}$$

Hence $(U + iv)^{\frac{1}{2}} = \left[\left\{U^2 + v^2\right\}^{\frac{1}{2}} \text{cis}\,\theta\right]^{\frac{1}{2}}$

$$= \left\{U^2 + v^2\right\}^{1/4}\left\{\cos\frac{\theta}{2} + i\sin\frac{\theta}{2}\right\}$$

$$\therefore F(iw) = \exp\left[\frac{uL}{2D} - \left\{U^2 + v^2\right\}^{1/4}\text{cis}\,\frac{\theta}{2}\right]$$

$$= \exp\left[\frac{uL}{2D} - \left\{U^2 + v^2\right\}^{1/4}\cos\frac{\theta}{2} + i\left\{\left\{U^2 + v^2\right\}^{1/4}\cdot -\sin\frac{\theta}{2}\right\}\right]$$

$$= e^x\cdot(\cos y + i\sin y)$$

Continued/...21

where $$x = \frac{uL}{2D} - \left(U^2 + v^2\right)^{1/4} \cos\frac{\theta}{2}$$

$$y = -\left(U^2 + v^2\right)^{1/4} \sin\frac{\theta}{2}$$

and by equation (2.7)

$$a_n = -\frac{1}{T} \cdot e^x \sin y$$

$$b_n = -\frac{1}{T} \cdot e^x \cos y \qquad (2.14)$$

As before

$$\ell n\ AR_T = \frac{uL}{2D} - \left(U^2 + v^2\right)^{1/4} \cos\frac{\theta}{2}$$

and $$\tan\phi_T = \frac{-1}{\tan\left[-\left(U^2 + v^2\right)^{1/4} \sin\frac{\theta}{2}\right]} \qquad (2.15)$$

Equations (2.15) are two simultaneous equations in the two unknowns k and M and may once again be solved by the method proposed

Continued/...22

by Law and Bailey. (APPENDIX 4)

2.10 EVALUATION OF a_n AND b_n AS $k \to \infty$

A packed gas-liquid chromatographic column in which $k \to \infty$ can be described by a transfer function of the form,

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

Let $S = iw$

and $x = L$

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

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

$$q = \frac{L^2w}{D} \cdot (MF + 1)$$

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

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

$$= j\cos\ell + i\, j\sin\ell$$

where $j = (p^2 + q^2)^{1/4}$

$$\ell = \tfrac{1}{2}\arctan\left(\frac{q}{p}\right)$$

Continued/...23

$$\therefore \quad F(iw) = e^{y} (\cos Z + i \sin Z)$$

where $\quad y = \frac{uL}{2D} - j \cos \ell$

$\quad Z = - j \sin \ell$

and from equations (2.7)

$$\boxed{\begin{aligned} a_n &= -\frac{1}{T} \cdot e^{y} \sin Z \\ b_n &= \frac{1}{T} \cdot e^{y} \cos Z \end{aligned} \qquad (2.16)}$$

2.11 MOMENT ANALYSIS

Using the method of Moments (5) it is possible to evaluate the system parameters U, D, M and k at zero frequency.

It can be shown (5) that if F(t) is the response to an ideal impulse input then :

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$$\ln F(S) = \ln \alpha_0 - T_m S + \frac{T_s^2}{2} \cdot S^2 - \frac{T_a^3}{6} S^3 + \cdots \quad (2.17)$$

where

$$\alpha_0 = \int_0^\infty f(t)\, dt$$

$$\alpha_1 = \int_0^\infty t f(t)\, dt \quad (2.18)$$

$$\alpha_n = \int_0^\infty t^n f(t)\, dt$$

$$= \quad \text{n'th moment of the system}$$

and $$T_m = \frac{\alpha_1}{\alpha_0} \quad \text{(MEAN)}$$

$$T_s^2 = \left(\frac{\alpha_2}{\alpha_0}\right) - \left(\frac{\alpha_1}{\alpha_0}\right)^2 \quad \text{(VARIANCE)}$$

(2.19)

$$T_a^3 = \frac{\alpha_3}{\alpha_0} - \frac{3\alpha_1\alpha_2}{\alpha_0^2} + 2\left(\frac{\alpha 1}{\alpha 0}\right)^3 \quad \text{(SKEWNESS)}$$

For the case of a non-ideal impulse input the values of T_m, T_s^2 can be evaluated from the input and output curves by the use of the relationships

$$T_m = T_{m_o} - T_{m_i}$$

$$T_s^2 = T_{s_o}^2 - T_{s_i}^2$$

$$T_a^3 = T_{a_o}^3 - T_{a_i}^3 \quad (2.20)$$

Where O refers to the output curve and i to the input curve.

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The mathematical analysis (APPENDIX 5) produces the following results:

$$u = \frac{L}{T_{m_1}}$$

$$D = \frac{L^2 T_{s_1}^{\,2}}{2\, T_{m_1}}$$

$$M = \frac{(UT_{m\,2} - L)}{FL}$$

$$k_2 = \frac{2M^2\, FL\, u^2}{(u^3\, Ts_2^{\,2} - 2L(MF + 1)^2\, D\,)} \qquad (2.21)$$

Inspection of the models and these results points out the intuitive dependencies:

u and M	$\rightarrow$	MEAN
D and k_2	$\rightarrow$	SPREAD

The method of moment analysis has yielded the equations

$$T_{s_1}^{\,2} = \frac{2DL}{u^3}$$

Continued/...26

$$T_{m_1} = \frac{L}{u}$$

$$T_{s_2}^{\;2} = \frac{2M^2LF}{u\,k_2} + \frac{2L(MF + 1)^2D}{u^3}$$

$$T_{m_2} = \frac{(MF + 1)\,x}{u}$$

For a process to be independent of k, it is necessary that

$$T_{s_1}^{\;2} \rightarrow T_{s_2}^{\;2}$$

ie. $$T_{s_2}^{\;2} \rightarrow \frac{2M^2LF}{u\,k_2} + \frac{2L(MF + 1)^2 \cdot u^3T_{s_1}^{\;2}}{u^3 \cdot 2L}$$

ie. $$T_{s_2}^{\;2} \rightarrow (MF + 1)^2\;T_{s_1}^{\;2} \qquad (2.22)$$

The appearance of the factor (MF + 1) is once again as expected.

2.12 LEAST SQUARES ANALYSIS.

In order to measure the "goodness of fit" of a model it is

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possible to make use of the method of least squares.

Let $\theta(t)$ be the experimental curve evaluated from $\theta_i(t)$ and $\theta_o(t)$ and $f(t)$ be the theoretical curve evaluated from a model.

$$\theta(t) = \sum_{n=1}^{\infty} a_n' \sin \frac{n\Pi t}{T} + \sum_{n=0}^{\infty} b_n' \cos \frac{n\Pi t}{T}$$

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

By definition

$$S^2 = \text{sum of squares of errors}$$

$$= \frac{1}{2T} \int_0^{2T} \left[f(t) - \theta(t) \right]^2 dt$$

$$= \frac{1}{2T} \int_0^{2T} \left\{ \sum_{n=1}^{\infty} (a_n - a_n') \sin \frac{n\Pi t}{T} + \sum_{n=0}^{\infty} (b_n - b_n') \cos \frac{n\Pi t}{T} \right\}^2 dt$$

$$\boxed{\therefore \quad S^2 = \frac{1}{2} \left[\sum_{n=1}^{\infty} (a_n - a_n')^2 + \sum_{n=0}^{\infty} (b_n - b_n')^2 \right] \qquad (2.23)}$$

Thus it is possible to examine the Fourier Coefficients rather

Continued/...28

than the curves $f(t)$ and $\theta(t)$ when considering the suitability of the models.

2.13 REGENERATION OF THE OUTPUT CURVE.

Suppose that the input to the system is expressed in the form

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

then the output from the system may be regenerated by using equations (2.7) and (2.9). Values of the parameters D, U, k and M may be chosen using a ROSENBROCK SEARCH (9) with 4 variables and minimizing the objective function

$$\sum_{n=1}^{\infty} (a_n - a_n')^2 + \sum_{n=0}^{\infty} (b_n - b_n')^2$$

Thus

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

$$b_n = \frac{1}{T} \text{ Re } \left[F \left(\frac{in\Pi}{T} \right) \right]$$

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

Continued/...29

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

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

finally

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

2.14 SENSITIVITY ANALYSIS

The sensitivity of MODEL 1 to the parameters D, U, k and M can be examined.

The values of the parameters at zero frequency are obtained by plotting each as a function of n or w and extrapolating back to the origin. (SEE FIGURES 4.1 AND 4.2)

Substituting these values in equations (2.14), a_n and b_n can be evaluated. From a knowledge of $\theta_i(t)$ and $\theta_o(t)$, a_n' and b_n' can then be found and finally S^2 computed from equation (2.23).

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CHAPTER III

3. EXPERIMENTAL

3.1. INTRODUCTION.

The experimentation was conducted in a constant temperature room using a standard gas chromatograph with a hot wire detector coupled to a fast response millivolt recorder.

An input signal was injected into the inert gas stream by means of a sample valve. The input was recorded by substituting the column with a capillary tube whilst the output was recorded in the normal fashion.

Experiments were conducted on firstly, an inert solute which did not undergo mass transfer and secondly, on a number of active solutes.

3.2 THE APPARATUS.

The apparatus consisted essentially of a gas chromatograph, a fast response millivolt recorder and a soap bubble tube for measuring gas flowrates.

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3.2.1. THE GAS CHROMATOGRAPH.

The chromatograph used was a PERKIN-ELMER Model F6 Fractometer which incorporated a hot wire detector, gas sampling valve and constant temperature jacket. The entire apparatus was located in a constant temperature room.

3.2.2. THE RECORDER.

The recorder used was a BRISTOL DYNAMASTER millivolt recorder. The chart was operated at maximum speed (530 cm/min.) which proved adequate.

3.2.3. THE COLUMN.

The column was constructed from 1/4 " I.D. copper tubing and was 6 feet long. The substrate was n-dodecane and the packing 44/60 mesh EMBACEL. The column was packed by the recognized method of slurrying using n-hexane as the solvent. TABLE 3.1 details the column characteristics.

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COLUMN CHARACTERISTICS		
Substrate		n-dodecane
Support		44/60 EMBACEL.
Length	183	cm
Ratio of support/substrate	100:17.75	
Cross-sectional area	0.2086	cm^2
Column volume	38.15	cm^3
Support volume	4.02	cm^3
Substrate volume	2.08	cm^3
Free gas volume	32.07	cm^3
Mass stationary phase	10.3050	g
Free gas cross-section	0.175	cm^2
Free liquid cross-section	0.0136	cm^2
Volume fraction of gas	0.84	
Volume fraction of liquid	0.055	

TABLE 3.1

Continued/...33

3.3 THE PROCEDURE

The temperature in the constant temperature room was stabilized at 20°C.

A gas sample capillary of 0.1 ml was chosen in accordance with Van Deemters criterion for negligible sample volume effect(1).

The column was removed from the chromatograph and replaced by a capillary tube.

A flowrate of 100 ml/minute of carrier gas was chosen and the needle valves carefully adjusted. The flowrate was measured by means of a soap bubble tube.

The apparatus was turned on and the system left to settle down until a steady base-line was produced on the chart.

Input pulses and their reproducibility were then studied. After some practice, perfectly standard pulses were mastered.

The system was then pulsed with the gases listed in TABLE 3.2 and the input recorded. The flowrates were periodically checked but no variations were encountered.

The column, which had previously been swept clean by carrier gas, was then replaced in the chromatograph and allowed to settle in.

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Pulses of the same gases were then imposed and the output recorded.

TABLE 3.3 details the experimental conditions.

GASES STUDIED.	
Carrier Gas Inert Gas	Nitrogen Hydrogen
Active Gas	n-butane butene-1 "handigas"

TABLE 3.2

EXPERIMENTAL CONDITIONS	
Global Temperature	$20^{\circ}C$
Inlet Gas Pressure	30 psig.
Carrier Gas Flowrate	100 ml/min.
Sample Volume	0.1 ml.
Chart Speed	530 cm/min.

TABLE 3.3

Continued/...35

3.4 DISCUSSION.

The experimental procedure, although very simple, was found to be effective. In all cases reproducible curves were obtained for both input and output. A desirable feature was the use of a constant temperature room which ensured complete temperature equilibrium of all the apparatus.

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CHAPTER IV

4. RESULTS.

4.1 INTRODUCTION.

The computer programs used for all the analyses are presented in the accompanying folder. The programs have been carefully documented by the liberal use of comment statements. It is suggested that these listings be consulted for details of methods and sequences used in the analysis.

The program listings are followed immediately by the results they produced.

4.2 D AND u AS A FUNCTION OF w.

The evaluation and analysis of D and u as a function of w is presented under the heading RUN NUMBER 1 (pages C7 and C8).

An impulse input of hydrogen gas described by a start point number, finish point number, time axis interval and concentration profile resulted in an output described in the same fashion.

A moment analysis produced valued of D, u, TME(mean) and

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