1991

Radial Flow Chromatography in Compressed Pancake-Shaped Beds.

Brian Keith Heft

Louisiana State University and Agricultural & Mechanical College

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Heft, Brian Keith, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1991

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**RADIAL FLOW CHROMATOGRAPHY
IN COMPRESSED PANCAKE-SHAPED BEDS**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and Mechanical College
in partial fulfillment of the requirements for
the degree of Doctor of Philosophy**

**in
The Department of Chemical Engineering**

**by
Brian Keith Heft
B.S., Rensselaer Polytechnic Institute, 1980
M.S., Lehigh University, 1983
May, 1991**

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Abstract

The separation of a methane/n-butane mixture was demonstrated using radial flow through compressed, pancake-shaped beds of fine alumina powder. The compacted stationary phase improved performance relative to an uncompressed sorbent by assuring flow uniformity through the bed, reducing band-broadening and tailing (by decreasing interstitial hold-up) and decreasing effective plate height (through an increase in the capacity ratio of the chromatograph).

Dispersion was identified as the key dissipative effect in the prototype radial flow adsorber. An exact analytical solution derived for the transport equations describing such a device compared favorably with experimental data. The dispersion coefficients were found to be strong functions of the individual solute sorption constants. The dispersion coefficient for weakly adsorbed solutes such as methane was found to reduce to molecular diffusivity. This phenomenon is believed to result from a combination of classical Taylor dispersion and pore hold up effects such as that suggested by Dayan and Levenspiel (D2) for conventional, axial flow patterns.

The elementary Peclet number defining the order of the Bessel functions appearing in the analytical solution was shown to control the shape of the response curve. The system time constant that determines retention is seen to vary with - among other parameters - the equilibrium sorption constant and the radius of the adsorber. The inverse dependence of both the Peclet number and the time constant on interstitial porosity indicates that increased compression will sharpen the response while increasing retention.

A theoretical comparison of inward and outward flow configurations indicates that the order of the Bessel functions defining the response is higher for the inward flow option. This suggests that the inward flow configuration may ultimately offer performance advantages. Unfortunately, mechanical difficulties prevented experimental verification of this trend.

Methods for improving separation - including the use of greater sorbent bed compression, temperature programming and stacking of individual sorbent discs - are discussed briefly.

NOMENCLATURE

a_p	surface area of sorbent particles per unit particle volume, cm^{-1}
A_i	interstitial cross-sectional area of the bed, cm^2
A_o	superficial cross-sectional area of the bed, cm^2
C_m	mobile phase concentration, moles/cc
C_p	concentration of rectangular pulse input, moels/cc
C_s	stationary phase concentration, moles/cc
C_m^*	equilibrium mobile phase concentration, g/cc
C_s^*	equilibrium stationary phase concentration, g/cc
C_o	impulse strength, moles/cc
D_{AB}	binary molecular diffusion coefficient, cm^2/sec
D_{AB}^*	constant for Eq. 2.5, cm^2/sec
D_e	eddy diffusivity, cm^2/sec
D_{eff}	effective dispersion coefficient, including the impact of both eddy and molecular diffusion, cm^2/sec
D_p	pore diffusion coefficient for Fickian-like diffusion within large, fluid-filled pores, cm^2/sec
D_s	total solid phase diffusivity, including Knudsen, pore and surface diffusion effects, cm^2/sec
d_p	particle diameter, cm
E_o	superficial axial dispersion coefficient, cm^2/sec
f	friction factor for flow through a packed bed
h	height of radial flow bed, cm
H	height equivalent to a theoretical plate, cm
H'	reduced plate height, dimensionless
j_v	volumetric flow per unit bed height ($j_v = Q/2\pi h\epsilon$), cm^2/sec
k_d	apparent mass conductance, cm/sec
k_f	general rate parameter accounting for all mass transfer effects in the model of Huang, et al. (H3), sec^{-1}
k_m	film transfer coefficient, cm/sec
K_p	equilibrium partition coefficient C_s^*/C_m^* , dimensionless
K_s	sorption equilibrium constant, dimensionless
l_{mix}	mixing length, cm
L	length of packed, axial flow column, cm
p	Peclet number defining the order of the Bessel functions that compose the analytical solution for the mobile phase dispersion model. $p = j_v/2D_{eff}$, dimensionless
Pe_e	Peclet number based on particle diameter and the superficial axial dispersion coefficient, dimensionless (see Eq. 2.8)
Pe_o	Peclet number based on superficial velocity
Pe_p	Peclet number based on particle diameter and interstitial voidage (see Eq. 2.21)
q	solid phase composition, moles/cc

Q	volumetric flow, cc/sec
r	radial distance coordinate, cm
R	retention parameter equal to the equilibrium fraction of a given solute present in the mobile phase at any instant
R_g	ideal gas constant
R_f	radius of central feed tube in radial adsorber, cm
R_p	particle radius, cm
R_s	peak resolution (see Eq. 2.1)
S	superficial cross-sectional area available to flow, cm ²
t_R	peak retention time, sec
t_R^*	retention time for a non-adsorbing solute, sec
U	ratio of mobile phase composition to that of a step input, dimensionless
v	superficial mobile phase velocity, cm/sec
v_{ia}	interstitial mobile phase velocity through an axial flow column, cm/sec
v_{ia}^*	reduced interstitial mobile phase velocity through an axial flow column, dimensionless
v_{ir}	interstitial mobile phase velocity through a radial flow column, cm/sec
v_{ia}	interstitial mobile phase velocity through an axial flow column, cm/sec
v_{oa}	superficial mobile phase velocity through an axial flow column, cm/sec
v_{or}	superficial mobile phase velocity through a radial flow column, cm/sec
v_r	interstitial mobile phase velocity in the radial direction, cm/sec
V^*	ratio of compacted to original bed volume, dimensionless
V_m	mobile phase volume, cc
V_s	stationary phase volume, cc
W_b	Peak width measured at the baseline, mm
X	distance variable for moving coordinate system, sec
z	distance coordinate for axial columns, cm

Greek Letters

ϵ	interstitial bed porosity
ϵ_o	interstitial bed porosity prior to compression
ρ	fluid density, g/cc
η	capacity ratio or bed voidage, $= \epsilon/(1-\epsilon)$
λ	empirical packing factor dependent on the shape of the packing (Eq. 2.9)
ξ	combined mass transfer resistance term, seconds, (see Eq. 2.23)
θ	time variable for moving coordinate system, sec
σ_t	standard deviation with respect to time, sec
σ_l	standard deviation with respect to distance, cm

CHAPTER 1

INTRODUCTION and RESEARCH STATEMENT

1.1 Introduction

Chromatographic techniques encompass a variety of methods for the separation of chemical species according to differences in their affinity for specific stationary phases. The effectiveness of these methods lies in their ability to resolve solutes into distinct zones within a mobile phase that passes through a stationary phase on the way to a suitable detector.

Resulting separations are either analytical or preparative in nature. The high resolution achieved with analytical techniques allows identification of sample components according to the response generated by a detector. Preparative techniques sacrifice resolution for higher throughput, and thus favor concentration of a highly pure product or removal of trace impurities from a large sample.

Much research has been directed towards improving the speed, resolution and versatility of chromatographic techniques. The concept investigated here involves the use of radial flow patterns established by forcing the mobile phase through a cylindrically shaped stationary phase. The obvious advantage of this approach is the pressure drop reduction achieved with the radial flow configuration. This reduction permits both an increase in throughput and, through the use of smaller stationary phase particles, a decrease in dissipative effects associated with film and intraparticle mass transfer resistances.

Other advantages of the radial flow configuration stem from its simplicity. Note that a compact, disc-like radial flow bed can be heated mechanically via direct contact, thus eliminating the need for the bulky convection ovens used for temperature control of conventional axial flow columns.

The radial flow configuration also facilitates compression of the stationary phase - a formidable task when utilizing the longer, coiled columns of conventional axial flow chromatographs. The increase in stationary/mobile phase ratio resulting from compression should enhance separation by decreasing the height of each theoretical plate (thereby packing more stages into a shorter contact length) and sharpening resolution (through a reduction in the deleterious effects of fluid mixing).

The most intriguing advantage is the potential use of differences in the diffusivity of the individual solutes to enhance separation. Such "kinetic" effects have been utilized as the sole separating mechanism for the resolution of non-adsorbing species such as the permanent gases in axial columns (K1). In these cases, differing diffusion rates determine retention by changing the amount of time each solute species spends "trapped" in stagnant pools associated with intraparticle pores.

Kinetic effects in radial flow chromatography arise from an alternate mechanism that involves competition between interparticle convection and mobile phase diffusion. Although high interstitial velocities eliminate such effects in axial flow columns, the larger flow area available in the radial flow devices considered here reduces convective effects so that they are of the same order as diffusion. It will be shown later that, under such conditions, convective-diffusive competition defines both retention and band spreading.

1.2 Research Statement

Radial flow chromatography dates back to 1947 when Peter Hopf (H1) invented the so-called chromatofuge for separating liquid solutes. This device and its successors (L1, W1) were large, cumbersome, and devoted solely to preparative scale separations.

Little has been done to refine the use of radial flow patterns for quantitative, analytical separations. This effort, and those of Rice (R1) and Yee (Y1) on which it is based, are apparently the first to examine the use of pressure-induced radial flow for gas phase, analytical chromatographic separations. Specific objectives of the research program included:

- Quantification of pressure drop across the radial flow chromatograph.
- Investigation of the dynamics of the impulse response.
- Investigation of potential diffusional enhancement of separations.
- Development of models to quantify and explain the impulse response.
- Performance forecasts and comparison with experimental data.
- Experimental comparison of axial and radial flow chromatographs.

Pressure drop quantification was based heavily on the work of Yee. His efforts were extended by noting that the particle size reduction that accompanies bed compression must be accurately assessed in order to derive estimates of bed porosity from his radial flow analogue of the Blake-Kozeny relation. An alternate method of quantifying bed porosity based on impulse response data is discussed in Chapter 5.

Impulse modeling was initially based on Rice's work for systems in which intraparticle diffusion and film resistances control (R3). The inability to fit experimental data to this model led to the development of the fluid-phase dispersion model discussed in Chapter 3. This model accurately quantifies competition between convection and mobile phase diffusion, and demonstrates that some separation enhancement can be achieved through an appropriate choice of operating conditions - including the choice of solvent used as the mobile phase.

CHAPTER II

BACKGROUND and LITERATURE REVIEW

2.1 The Early History of Radial Flow Chromatographic Efforts

Early investigations of radial flow chromatographic methods centered on development of preparative techniques that utilized a liquid mobile phase to effect desired separations. Most of this work was experimental in nature, with little effort devoted towards development of the mathematical models needed to describe sorption and transport processes.

Peter Hopf, et al., (H1, H8) produced the first publication describing the use of a radial flow chromatographic device. He invented the chromatofuge, which utilized centrifugation to drive a liquid mobile phase through a packed bed in the desired radial flow pattern. This device was used to separate binary mixtures of organic liquids, and to resolve dilute sulfuric acid solutions containing various metals into clearly defined zones.

Lynam, et al. (L1) improved the chromatofuge sufficiently for use in crude industrial separations by the early 1950's. The columns employed were large by chromatographic standards - four feet in diameter and approximately 20 inches high - and consisted of concentric beds separated by perforated walls. Emphasis was again placed on the use of centrifugal force (i.e., rotating the chromatograph) to improve fluid distribution and increase throughput. Separate elution vessels were required to recover the desired product. This was accomplished by mechanically removing the section of the bed in which the desired solute had concentrated and treating it in a separate "recovery" vessel.

Weil (W1) discussed the perceived advantages of the chromatofuge relative to standard, axial flow chromatographs. They included higher throughput, improved packing uniformity through the use of centrifugal force, less distortion of the solute band, better observation of the bands within the device, and reduced floor-space requirements. One disadvantage, that of the re-mixing of the solutes when attempts were made to operate the chromatofuge in an elution mode, was also noted.

Weil also argued that inward flow is preferable to outward flow because it causes the solute band to widen as it passes through the bed. This widening results from a decrease in the cross sectional area available for flow with the square of the distance from the central axis of the chromatofuge. He noted that the development of similar (wide) bands from the same amount of mixture in an axial flow column requires the use of small bed diameters, which, owing to the larger pressure drop of the axial device, necessitates lower throughputs and thus longer treatment times. Hence, inward radial flow was presumed to be preferable to both conventional axial and outward radial flow devices.

Although this intuitive argument is attractive at first glance, one must not forget that it applies only to batch separations in which solutes are mechanically recovered as fixed bands in the stationary phase. When elution chromatography is considered, the advantage of band-widening (as the central axis is approached) is offset by a proportional increase in velocity. Hence, although a band widens in terms of the radial increment of the stationary phase it occupies, increasing flow velocity negates this effect by causing the solute to elute over a smaller time.

The early work on the chromatofuge appears to have been the only effort directed towards development of radial flow chromatographic techniques prior to the introduction of the Topsoe Radial Flow Converter for ammonia synthesis in the late 1960's (J1). By that time production demands in excess of 1000 tons per day per unit had stretched the performance of conventional axial flow reactors to the point that resulting pressure drops were economically prohibitive. Since the fabrication of conventional reactors with sufficient diameters to cut pressure drop to acceptable levels proved to be both mechanically and logistically difficult, the only way to meet capacity requirements with conventional converters was the costly approach of installing multiple reactor trains.

The Topsoe Radial Flow Converter resolved this problem by minimizing pressure drop through the use of a radial flow configuration. This innovation generated large power savings, since it permitted operation at lower pressures and thus reduced compression requirements. In addition, reduced pressure drop permitted the use of smaller catalyst particles, which, owing to their higher effectiveness factor, increased per pass conversion. Resultant efficiency improvements increased throughput and reduced variable costs dramatically. Whether coincidental or not, sparse references to radial flow chromatography began to re-appear at around this same time.

Sussman (S1, S2) reported on the use of the radial flow configuration for continuous chromatographic separations in 1974. He and his co-workers separated gaseous hydrocarbons continuously utilizing radial flow between two discs rotating at about 20 rpm. Their device consisted of a stationary feed bonnet that injected both the carrier gas (nitrogen) and the solutes (methane, propylene and butane) into the channel between two 12-inch, parallel, solvent-coated rotating discs spaced 50-150 microns apart. The close surface spacing was supposed to produce the small HETP, as is the case for conventional axial flow capillary columns, needed to achieve separation with relatively short flow paths.

Each of the solutes was swept radially through the rotating channel by the carrier gas at a rate inversely proportional to its affinity for the stationary phase (the solvent coating the discs). Since each solute traverses an arc of differing slope on its journey, they reach the periphery of the device at an angle proportional to its residence time. Suitable location of multiple detectors (initially determined by trial and error) allowed the response for each solvent to be measured independently.

Sussman suggested that such "crossflow" configurations would be useful for preparative operation on mixtures not easily separated by other techniques. However, he also noted that although such separations can be accomplished with amazing speed - often less than a second - resolution capabilities are considerably less than those of conventional, long axial flow devices due to the inherently smaller number of theoretical plates. More recently the Separagen Corporation has begun to market "Superflow" columns that employ a radial flow configuration for preparative separations of liquids. These columns, which are ideally suited for biological separations, have been used to isolate the various components of egg white, separate proteins, and fractionate plasma (S3). Separagen claims that, by maintaining a constant height to diameter ratio, scale-up problems associated with conventional, axial flow columns can be eliminated. Hence, the transfer of laboratory operations to the industrial level is greatly simplified. The reduced pressure drop of the radial flow device also eliminates compression of the gels typically employed as the stationary phase. This problem can be quite severe with much longer axial flow columns.

The preceding review of published work specific to radial flow chromatography reveals that the majority of the investigative effort into the utilization of the radial flow configuration has been experimental in nature

and directed towards development of preparative, liquid techniques. Most of these efforts utilized the centrifugal force generated by spinning the column as a means to move the carrier fluid and the solutes it contained through the bed.

The present work, and those of Rice (R1) and Yee (Y1) on which it is based appear to be the only efforts directed towards the development of radial flow gas chromatographic techniques sufficiently refined for analytical separations. Here the driving force for flow is not centrifugation, but the imposition of a pressure differential across the bed. A number of problems related to flow uniformity had to be resolved before the need for centrifugation could be eliminated.

The following sections will review factors affecting chromatographic separations, models of fixed bed adsorbers, and extrapolations of relevant concepts and models to the radial flow problem.

2.2 Chromatographic Separations and Band Broadening

The effectiveness of an analytical chromatographic separation depends on its ability to resolve individual solutes into distinct, compact bands. This separation must be accomplished with a minimum of band spreading or the segregated solutes will interfere with each other as they elute through a detector.

The resolution, or separability, of a pair of solutes is equally enhanced by either doubling the difference between their respective migration rates or halving the spread of their peaks. It is quantified in terms of the difference between the retention times of the peaks in question and their average peak width:

$$R_s = \frac{2[t_{R,2} - t_{R,1}]}{W_{b,1} + W_{b,2}} \quad (Eq. 2.1)$$

Here the retention time of each peak (t_R) is measured with respect to its concentration maximum, while the peak width (W_b) is measured relative to the baseline of the chromatograph. Since the subscript "1" refers to the solute eluting from the column first, resolution always assumes a positive value. Although satisfactory resolution is achieved for all values of $R_s \geq 1.0$, values ≥ 1.5 are required for complete baseline resolution (S4).

2.2.1 Separation of Zone Centers

As a solute band moves through a column, its individual molecules progress via a "stop and go" sequence. Each time a molecule is sorbed onto the stationary phase, its forward motion ceases while the zone as a whole passes over it. Differences in the affinity of each solute for the stationary phase give rise to separation by causing the molecules of one solute to, on average, spend more time "stopped" in the sorbed state than another.

The fraction of solute in the mobile and stationary phases at any instant can be given as R and $(1-R)$, respectively, if equilibrium exists within the column. This ratio can be equated to the volume of the mobile (V_m) and stationary (V_s) phases as follows:

$$\frac{R}{1 - R} = \frac{C_m^* V_m}{C_s^* V_s} \quad (\text{Eq. 2.2})$$

Replacing C_s^*/C_m^* , the equilibrium ratio of concentration of the two phases, by the partition coefficient, K_p , and solving for R yields:

$$R = \frac{V_m}{V_m + K_p V_s} \quad (\text{Eq. 2.3})$$

Since only a fraction " R " of the solute is present in the mobile phase at a given time, the zone moves through the column at a fraction of the superficial mobile phase velocity, v_{oa} (the subscript "oa" indicates a superficial quantity pertaining to an axial flow column), this fraction being Rv_{oa} .

The fraction " R " is thus a measure of the retention of a solute by the column. Since solutes with a high affinity for the stationary phase (larger K_p) spend more time in the "sorbed" state, they transverse the column at a lower average velocity (Rv_{oa}). Such solutes will be more strongly retained (smaller R) and exhibit larger retention times (t_R).

The expression for R can be generalized (G1) for a case in which several phases contribute to retention. Hence:

$$R = \frac{V_m}{V_m + \sum K_{p,i} V_{s,i}} \quad (\text{Eq. 2.4})$$

where the $K_{p,i}$ and $V_{s,i}$ represent individual partition coefficients and volumes for each phase present.

A second factor that can - in specific instances - affect retention in a chromatographic column is molecular diffusion. Such "diffusive retention" was first noted by Kaizuma (K1), who studied differences between the retention times of non-adsorbed solutes in a column packed with a porous stationary phase. These differences were observed to increase as carrier gas flow decreases.

Kaizuma deduced that diffusive retention occurs under specific conditions in which solute molecules enter the micropores of the packing and are trapped for a finite time before diffusing back into the flow field. A stop and go mechanism similar to that discussed above for sorption results, and the displacement of solute molecules between the flowing and stagnant phases prolongs migration through the column. Since solutes with small diffusion coefficients take longer to diffuse out of stagnant pockets, they will also exhibit longer retention times.

A parabolic relation presented in a subsequent effort (K2) related the retention times of non-adsorbed species to their molecular diffusivity:

$$\left[\frac{t_R - t_R^\circ}{t_R^\circ} \right] \left[\frac{D_{ab} - D_{ab}^\circ}{D_{ab}^\circ} \right] = 1 \quad (Eq. 2.5)$$

Here t_R° is the time required for an inert solute to pass through a column of non-porous packing, t_R is the retention time for the same solute in a column containing a non-adsorbing, porous stationary phase, and D_{ab} is the diffusion coefficient for the solute in the carrier gas. The constant D_{ab}° , with the units of molecular diffusivity, is related to both the molecular diffusivity of the solute in the carrier and the pore diameter of the packing.

Kaizuma's studies of helium, neon and argon solutes in hydrogen and nitrogen carrier gases showed that two conditions must be met for diffusive retention to occur. Most obvious is the requirement that the pore diameter of the stationary phase be small enough to generate stagnant pools within a particle. If pore diameters are too large, intraparticle voids will be sufficiently exposed to the flow field to experience the convective effect of the carrier gas. Kaizuma determined that pore diameters less than $\approx 250 \text{ \AA}$ are required for diffusive retention to occur in the systems he studied.

A less obvious requirement is that stationary phase pore size and the mean free path of the carrier gas must preclude Knudsen diffusion. This criterion results from the impact of the carrier's mean free path and pore wall interactions on the molecular diffusion coefficient of the solute. If either the pore size or the mean free path criterion is not met, the value of the constant D_{ab}^* tends to zero and diffusive retention is mitigated.

Although Kaizuma has exploited diffusive retention for the separation of inert gases via a process he calls diffusion chromatography (K3), the phenomenon is not generally recognized as an important mechanism relative to conventional chromatographic systems. The reason is that mobile phase flowrates typical of chromatographic applications are several orders of magnitude greater than the motion created by diffusion. Hence, convective phenomena dominate the diffusive effects responsible for retention.

Flow dynamics are somewhat different when radial flow chromatography is considered. In this case the larger flow area and correspondingly smaller interstitial velocities employed reduce convective effects until they can be of the same order as diffusion. It thus seems likely that, given the proper choice of stationary phase pore structure and operating conditions (to set the mean free path of the carrier gas), diffusive retention could be utilized to enhance separations in radial flow chromatographs. As it will be shown later, because transport competition exists between interparticle convection and diffusion in the mobile phase, solute residence time can be significantly changed owing to diffusion in the mobile phase.

2.2.2 Spreading of Individual Solute Zones

The impact of zone spreading on peak resolution has already been noted. The physical processes responsible must thus be understood in order to regulate them sufficiently to control spreading. Vermeulen (V1) lists these processes, which can occur either in series or in parallel depending on conditions at the interface between the mobile and stationary phases, as:

- transport between the mobile and stationary phase
- sorption at the phase boundary
- diffusion in the sorbed state
- pore and Knudsen diffusion
- mixing in the mobile phase

The contribution of each of these processes to band spreading depends on the system in question. For example, one would expect a combination of fluid-side effects including transport from the mobile phase, pore diffusion and mixing to control applications (such as gas chromatography) in which mobile phase solute concentrations are low.

The earliest attempt to explain band broadening was a qualitative effort by Wilson (W2). He perceived that the width of a solute band will increase if weak adsorption causes the leading edge to migrate too rapidly, or if strong adsorption causes the trailing edge to migrate too slowly. Wilson also noted that although these effects can be minimized by decreasing flow through the column, any benefit realized will be partially offset by a concurrent increase in the relative magnitude of mobile phase diffusional transport. This strictly qualitative argument was the first to link excessive band broadening to both very high and very low flowrates.

Mixing in the fluid phase is generally referred to as dispersion. It can result from either diffusion in the direction of flow, void space mixing, concentration gradients across a velocity distribution, or some combination of these factors. Sir Geoffrey Taylor (T1) performed the original "first principles" analysis of a velocity-based dispersive process in 1953. He determined that radial concentration gradients tend to smooth parabolic concentration profiles established in liquids flowing through an open tube. Taylor defined a longitudinal dispersion coefficient to quantify this effect. First principles were used to show that this coefficient is inversely proportional to the molecular diffusion coefficient for the system and directly proportional to the square of fluid velocity.

Although Taylor studied liquids passing through open tubes, his findings raise concerns pertinent to the development of a radial flow gas chromatograph. These concerns stem from the fact that for a radial flow device the driving force for Taylor dispersion exists in both the angular and lateral directions. In an axial device such effects occur in a single (radial) direction.

Vermeulen (V1) addressed dispersion by empirically combining the effects of diffusion and void mixing into a single parameter, an apparent conductance, k_d so that:

$$k_d a_p = \frac{Q}{A_o l_{mix}} \quad (Eq. 2.6)$$

where a_p is the surface area of the sorbent particles per unit particle volume, Q is the volumetric flow through the bed, A_o is the superficial cross-sectional area available for flow and l_{mix} is the mixing length pertinent to the flow field.

The synergistic effects of diffusion and void mixing were addressed by summing a contribution from each to define the mixing length for the system:

$$l_{mix} = \frac{d_p}{Pe_e} + \frac{A_o D_{ab}}{2Q} \quad (Eq. 2.7)$$

The Peclet number, used to define the contribution of eddy dispersion to the mixing length, was based on particle diameter, d_p , and a superficial axial dispersion coefficient, E_o :

$$Pe_e = \frac{d_p Q}{E_o A_o} \quad (Eq. 2.8)$$

Klinkenburg and Sjenitzer (K4) studied the effect of intermittent operation, finite transfer coefficients, radial diffusion, axial diffusion and eddy dispersion on the residence-time distribution of fluids in vessels. They addressed eddy dispersion by defining an eddy diffusivity, D_E , in terms of the diameter of the packing particles, d_p , the interstitial velocity of the system, v_{ia} , and an empirical packing factor, λ , that depends on the shape of the packing. In the absence of molecular diffusion, D_E is given as:

$$D_E = \lambda d_p v_{ia} \quad (Eq. 2.9)$$

The parameter λ has been the object of much study. Van Deemter, et al. (V2) found that it increased with decreasing particle size. Evans and Kenney (E1) surveyed the literature and found values ranging from as low as 0.3 to as high as 8.

Klinkenburg and Sjenitzer determined that residence-time distributions (or band spreading in the case of chromatographic applications) resulting solely from eddy dispersion would be proportional to the particle diameter-column length ratio and independent of flow velocity:

$$\frac{\sigma_t}{\tau} = \sqrt{\frac{2\lambda d_p}{L}} \quad (Eq. 2.10)$$

Here σ_t is the standard deviation of the distribution about the mean residence time, $\tau = \frac{L}{v_{ia}}$

Conversely, the distribution resulting from axial diffusion was shown to be proportional to the square root of the molecular diffusivity:

$$\frac{\sigma_t}{L} = \sqrt{\frac{2D_{ab}}{v_{ia}L}} \quad (Eq. 2.11)$$

Since only phenomena yielding Gaussian residence-time distributions were considered, Klinkenberg and Sjenitzer were able to sum variances to determine the combined impact of several mechanisms operating independently and in series. For example, if both eddy dispersion and molecular diffusion are considered the variance of the resulting residence-time distribution is given by:

$$\left[\frac{\sigma}{\tau} \right]^2 = \frac{2\lambda d_p}{L} + \frac{2D_{ab}}{v_{ia}L} \quad (Eq. 2.12)$$

The concept of additive variances was ultimately applied to the plate theory originally proposed by Martin and Synge (M1). The union of these concepts was the cornerstone of most early efforts to describe band spreading quantitatively. It represented the first attempt to describe the development of a zone profile under the influence of a linear adsorption isotherm and dynamic conditions. Martin and Synge noted that, given sufficient development time, an ideal band profile will assume a Gaussian shape.

Taking the concept of Gaussian band-shapes from the plate theory, Van Deemter, et al., were able to sum variances to describe the net impact of several processes on band spreading (V2). This led to the development of the now-famous Van Deemter equation (V2), an empirical expression of the plate height:

$$H = \frac{\sigma^2}{L} = A + \frac{B}{v_{ia}} + C v_{ia} \quad (Eq. 2.13)$$

Here H is the thickness of a layer such that the solution issuing from it is in equilibrium with the mean concentration of the solute in the stationary phase throughout the layer (the plate height), and v_{ia} is the interstitial velocity of the mobile phase. The constants A, B and C depend on solute/solvent interactions, flow conditions,

and the configuration of the stationary phase. Comparison of this equation with the previously noted variance equation indicates that the constant "A" accounts for eddy dispersion and is equal to $2\lambda d_p$, while the constant "B" = $2D_{ab}$ addresses the impact of molecular diffusion in the mobile phase. The constant "C" accounts for mass transfer limitations to and within the stationary phase.

When particle mass transfer is negligible, the Van Deemter equation simplifies to:

$$H = 2\lambda d_p + \frac{2D_{ab}}{v_{ia}} \quad (Eq. 2.14)$$

This relation can be re-arranged to define an effective dispersion coefficient, D_{eff} :

$$D_{eff} = \frac{Hv_{ia}}{2} = \lambda d_p v_{ia} + D_{ab} \quad (Eq. 2.15)$$

Hence the plate theory developed by Van Deemter, et al., predicts that dispersion resulting from the combined effect of eddy dispersion and molecular diffusion will be a linear function of velocity which approaches a constant on the order of molecular diffusivity at low flowrates.

The simplicity of the van Deemter equation has led to its widespread use for quantification of the performance of chromatographic columns. Various modifications and extensions of this equation have also been proposed. For example, the Knox equation:

$$H' = A v_{ia}'^{\frac{1}{3}} + \frac{B}{v_{ia}'} + C v_{ia}' \quad (Eq. 2.16a)$$

gives a reduced plate height, H' , in terms of the reduced interstitial velocity:

$$v_{ia}' = \frac{v_{ia} d_p}{D_{ab}} \quad (Eq. 2.16b)$$

while the Golay equation:

$$H = \frac{A_1}{v_{oa}} + \frac{A_2}{v_{oa}} + B_1 v_{oa} + B_2 v_{oa} \quad (Eq. 2.17)$$

addresses open tubular columns. As with the original Van Deemter equation, the constants A and B account for diffusive and mass transfer effects, while the subscripts 1 and 2 refer to the mobile and stationary phases, respectively (K6).

Although the velocity dependence of each term in these extensions is consistent with Van Deemter's original effort, the definition of the constants varies according to the model used in their development. All such equations correctly predict excessive band broadening (ie, a large plate height) at both high and low superficial velocities as well as an optimum velocity that yields a minimum plate height.

In spite of their usefulness, one must remember that all of the plate equations are semi-empirical in nature. Note for example, that as has already been pointed out, values for λ have been found to vary widely even for similar particles. The assumption that eddy dispersion and molecular diffusion operate independently has also been questioned by several authors (E1, G1). In summary, although the plate equations provide a parameter useful for characterizing zone spreading and thus resolution (the plate height), they are inadequate for describing the physical and molecular events occurring in chromatographic processes.

Aris and Amundson (A1) utilized a mixing cell model to study the impact of axial dispersion on flow through packed beds. They considered a bed of uniformly spaced, spherical packing particles. The fluid velocity was assumed to increase as it crossed through a plane that passed through a row of sphere centers, then decrease as it entered a plane passing through the void space between rows of packing. These void spaces were considered to be mixing cells. The influent to each cell was considered to be a jet created by squeezing fluid through the small open spaces found in a plane passing through sphere centers. The effluent from the cell was assumed to have the composition of the cell.

The physical picture thus created is one of a jet feeding a CSTR. Aris and Amundson extrapolated this simple model to the case of random packing and determined that, for sufficiently high Reynolds numbers, mixing should be complete and the system Peclet number - $d_p v_{id}/D_{eff}$ - should approach 2. This projection is consistent with that of the Van Deemter equation which, as has already been noted, predicts a linear dependence of the dispersion coefficient on interstitial velocity.

McHenry and Wilhelm analyzed axial dispersion in H_2-N_2 and $C_2H_4-N_2$ systems at room temperature and atmospheric pressure. Under the conditions studied, ($26 \leq Re \leq 1000$) they determined that the Peclet number was constant and equal to 1.88 ± 0.15 . This finding is in good agreement with the projections of Van Deemter (that D_{eff} varies linearly with v_i) and Aris ($Pe = 2$).

Carberry and Bretton (C1) derived a bed-void, cell-mixing model similar to Aris' that established a direct proportionality between mixing efficiency and the Peclet number of the system. Under conditions of perfect mixing the Peclet number was again shown to attain a value of 2. Data collected on water flowing through beds of both spheres and rings confirmed a linear increase in the dispersion coefficient with Reynolds number in the laminar flow range. However, the Reynolds number dependency was observed to gradually decrease as flow moved through the transition region until a constant exponent of 0.25 was reached in the turbulent regime ($Re > 400$).

More pertinent to gas chromatography was Carberry and Bretton's limited work with an air-helium system operated at Reynolds numbers less than one. They observed a constant value for the dispersion coefficient under these conditions. Such a finding is in agreement with Van Deemter's predictions for low-velocity.

Evans and Kenny (E1) performed one of the more exhaustive studies of dispersion in gaseous systems. They determined that the relation between the effective dispersion coefficient and fluid velocity was not linear. Their correlations of experimental dispersion data over Reynolds numbers varying between 0.5 and 10 yielded the following empirical relation:

$$\frac{\epsilon D_{eff}}{D_{ab}} = 0.25 + 0.28 \left[\frac{\epsilon v_{ia} d_p}{D_{ab}} \right]^{1.4} \quad (Eq. 2.18)$$

Upon re-arrangement one obtains:

$$D_{eff} = 0.28 \left[\frac{\epsilon d_p v_{ia}}{D_{ab}} \right]^{0.4} d_p v_{ia} + 0.25 \left[\frac{D_{ab}}{\epsilon} \right] \quad (Eq. 2.19)$$

This relation, which was fit using their own data as well as that of other investigators, is consistent with Van Deemter's work in that it reflects a constant dispersion coefficient at low flow velocities that is of the same magnitude as the binary diffusion coefficient. However, it reflects a larger velocity dependence (to the 1.4 power) than the linear relation of Van Deemter.

By analogy with Van Deemter's analysis, the work of Evans and Kenny suggests that the constants in Equation (2-13) take the values $A = 0.28[(\epsilon d_p v_{ia})/D_{ab}]^{0.4}$ and $B = 0.25 \left[\frac{D_{ab}}{\epsilon} \right]$. Hence the λ in Van Deemter's plate equation appears to be a non-linear function of the dimensionless group $(\epsilon d_p v_{ia})/D_{ab}$ (or $\epsilon Re Sc$) that effectively modifies the system's mixing length, D_p , rather than retaining a constant value. The inclusion of ϵ in this expression is logical, since mixing is a function of the volume between bed particles.

Han, Bhakta and Carbonell (H2) reviewed a large amount of experimental data while looking for a time constant (similar to Taylor's for flow in open tubes) beyond which the dispersion coefficient could be considered a constant. They determined that:

$$\frac{D_{eff}}{D_{ab}} = a(Pe_p)^n \quad \text{for} \quad Pe_p > 1 \quad (Eq. 2.20a)$$

and

$$\frac{D_{eff}}{D_{AB}} = \sigma^* \quad \text{for} \quad Pe_p < 1 \quad (Eq. 2.20b)$$

Here Pe_p is given as

$$Pe_p = \frac{v_{ia} d_p}{D_{AB}} \left(\frac{\epsilon}{1 - \epsilon} \right) \quad (Eq. 2.21)$$

where ϵ is the bed voidage. The constant n was found to be greater than 1, while the constant σ^* was determined to be slightly less than 1.

These findings are consistent with those of Evans and Kenny in that they indicate the dispersion coefficient varies as velocity to some power greater than unity (recall that Van Deemter and Aris predicted a

proportional dependence on velocity). However, they differ from Evans and Kenny with respect to the fact that it predicts a constant dispersion coefficient that is less than that of molecular diffusivity at sufficiently low flowrates.

The emphasis placed on molecular diffusion in the preceding discussion of band spreading stems from its impact on radial flow gas chromatography. Molecular diffusion is the controlling resistance in the process because the lower interstitial velocities associated with the larger cross-sectional area of the radial flow column effectively reduce convective effects so that they are of the same magnitude as diffusional transport. Such is not the case for liquid radial flow chromatography, since diffusion coefficients for liquids are much lower than those for gasses.

2.2.3 Tailing

Tailing is a specific type of band broadening which causes a peak to deviate from the usual Gaussian shape. The resulting asymmetry may range from only a slight skewing of the peak to severe distortion in which much of the zone is strung-out behind the zone maxima.

There are many causes of tailing. Giddings (G2) lists some of them as excessive dead volume that permits a portion of the solute to hold-up in the column, the presence of non-uniform adsorption sites and too large a sample size. Non-uniform adsorption sites may occur naturally in the stationary phase, or they may be generated during the packing operation if rough handling fractures some of the particles exposing untreated surface area. Depending on the cause, tailing can be mitigated by eliminating excess dead volume, operating at higher temperatures, adding tail-reducing compounds to the stationary phase to "deadend" strong adsorption sites (S4), or reducing sample size.

Molecular diffusion can also be a primary cause of tailing, just as it is often a major contributor to the more common, Gaussian type band spreading discussed above. This fact was pointed out by both Levenspiel and Smith (L2), in their discussion of longitudinal mixing, and Klinkenberg and Sjenitzer (K4), in their discussion of the holding-time distributions. They noted that although the distribution of solute within a column is Gaussian with respect to position at any given instant, the distribution of solute in the effluent with respect to time will be skewed because different elements of solute have been diffusing for different times.

The skewness, or tail, observed in the effluent concentration will be small in an axial column if:

$$\frac{D_{AB}}{v_{ia}L} < 0.01 \quad (Eq. 2.22)$$

where D_{AB} is the molecular diffusivity of the solute in the carrier, v_{ia} is the interstitial velocity of the carrier, and L is the length over which the diffusion process occurs.

2.3 Adsorption Models for Axial Flow, Fixed Bed Adsorbers

Several attempts have been made to quantitatively account for the individual molecular processes that occur during the course of a chromatographic separation. As might be expected, assumptions regarding flow geometry and the relative importance of the various molecular processes are required to reduce the mathematics to a tenable level. Perhaps the most common assumption is that sorption-desorption kinetics proceed with only a slight departure from equilibrium. This assumption has led to the so-called "asymptotic" theories, which address sorption phenomena at sufficiently long times to ensure that the desired narrow, well-separated zones have developed.

Thomas (T2) produced one such analysis in 1948 by introducing a Langmuir rate equation (which reduces to linear kinetics at low solute concentrations) to the mass conservation equation. The solution to these equations was a complex mathematical expression giving effluent concentrations as a function of time. Thomas obtained simplified asymptotic solutions for cases in which flow was low enough to prevent large departures from equilibrium. Experimental solute concentration curves were used in conjunction with these formulas to determine adsorption and desorption rates.

Glueckauf (G3) is credited with the development of the first comprehensive model to account for the majority of the controlling processes for a given chromatographic technique. He considered solute diffusion through both ion exchange beads and the surrounding liquid, and evaluated several empirical diffusion equations for spherical ion exchange particles. These equations related the rate of change of the mean internal concentration and the concentration at the surface of the particles. Such relations are now referred to as linear driving force, or LDF, approximations. The models he developed can, of course, be extended beyond the range of ion chromatography.

Rosen (R2) addressed the kinetics of a fixed bed adsorber under conditions of negligible dispersion in which transport through a surface film and intraparticle diffusion control. He assumed a linear adsorption isotherm and integrated the partial differential equation describing Fickian-type diffusion through the particles in conjunction with the continuity equation and the equation for external mass transfer.

Liaw et al. (L3) simplified Rosen's analysis by assuming that the concentration profile within the solid particles was always parabolic. The partial differential equation describing the step response of a fixed bed adsorber was solved in the Laplace domain, but an analytical inversion was not obtained.

A single resistance parameter, ξ , including contributions from both transport through the surface film surrounding the particles and transport via intraparticle diffusion, was introduced to account for the total mass transfer resistance of the system:

$$\xi = \frac{K_s r_p}{3k_m} + \frac{r_p^2}{15D_s} \quad (\text{Eq. 2.23})$$

Here r_p is the particle radius, k_m is the film transfer coefficient, and D_s is the solid phase diffusivity of the sorbent.

Rice (R4) subsequently reported an elementary inversion formula for the original Laplace solution in a letter to the editor. He later (R1) tested this solution on packed beds of salt retardation resins.

Do and Rice (D1) determined that the parabolic profile approximation used by Liaw and others for modeling adsorption processes was valid for "long" contact times. In instances where solid phase diffusion controls, "long" contact times are determined as being greater than one-twentieth of the ratio of the square of the particle radius divided by the stationary phase diffusion coefficient. This inverse dependence on particle size indicates that small particles will develop a parabolic profile very quickly. When pore diffusion controls, this criteria is modified by multiplying the particle radius by the (dimensionless) sum of the (linear) equilibrium sorption constant and the voidage of the particle, and replacing the solid phase diffusivity with the effective diffusivity of the solute within a pore.

Eberly and Spencer (E2) developed an alternative model which considered only the effects of sorption kinetics. Both longitudinal diffusion in the fluid phase and intraparticle diffusion in the stationary phase diffusion were assumed to be insignificant when compared to adsorption/desorption kinetics. Their approach was similar to that of Thomas (T2), in that model development proceeded via simultaneous solution of the partial differential equation describing the rate of adsorption with the continuity equation. The resulting complex integral was simplified considerably by making use of the fact that adsorption constants for most systems of interest are generally much larger than unity. The resulting relation was subsequently integrated numerically to relate the impulse response to the mean residence time of a given solute.

They describe a series of experiments in which broadening due only to adsorption effects was measured and compared to their model. This was accomplished utilizing unusually high carrier gas flow rates (up to 150 cc/min at STP) through a short, relatively wide (0.18 inch internal diameter) axial flow column packed with unusually large (48 - 60 mesh) particles. The high superficial velocities and low pressure drop established in this column minimized band-broadening due to both longitudinal diffusion and convection (i.e., fluid mixing). This fact was verified by noting that a pulse of non-adsorbing argon eluted as a very sharp peak. The hydrocarbon pulses exiting the column from one to ten minutes later exhibited much lower and broader peaks.

2.4 Adsorption Models for Radial Flow, Fixed Bed Adsorbers

Lapidus and Amundson (L4) published the first detailed, theoretical analysis of a radial flow chromatographic process in 1950. They considered a flat, uniform adsorbent disc of infinite diameter with a hole through its center. A single solute introduced as a rectangular pulse was carried radially outward from this hole by the solvent. Mathematical solutions were developed for cases in which the relation between mobile and stationary phase solute concentrations were given by either a linear adsorption isotherm or a kinetic equation. Dispersive effects were ignored in both instances.

For the first case, solid phase compositions in a disc of thickness h with a central hole of radius R_1 were determined to vary with radial position r as follows:

$$C_m(r, V) = \begin{cases} 0, & \text{for } r < r_1 \\ C_p, & \text{for } r_1 < r < r_2 \\ 0, & \text{for } r > r_2 \end{cases} \quad (\text{Eq. 2.24a})$$

Here

$$r_1 = \left[\frac{V_m}{\pi h(\epsilon + K_s)} + R_I^2 \right]^{1/2} \quad (\text{Eq. } 2.24b)$$

and

$$r_2 = \left[\frac{V_m + \pi h K_s(a^2 + 2R_I a)}{\pi h(\epsilon + K_s) + R_I^2} \right]^{1/2} \quad (\text{Eq. } 2.24c)$$

V_m is the total volume of solvent admitted to the disc up to the time of interest, ϵ is the porosity of the adsorbent bed, and K_s is constant defining the (assumed) equilibrium sorption relation. This relation simply confirms that the sharp band originally formed in the center of the disc decreases in width as it is carried radially outward by the solvent.

In a subsequent effort Lapidus and Amundson (L5) considered various possible rate controlling mechanisms for the saturation of radial adsorbers. The analytical solutions they developed (assuming radial dispersion is negligible) predicted the now well-known dependence of some of these mechanisms on particle size. For example, film resistances were shown to vary linearly with particle diameter, while a squared dependence was predicted for solid phase diffusion effects. Saturation phenomena were shown to be independent of particle size when sorption kinetics controlled.

Lapidus and Amundson verified their equations experimentally in liquid systems, proving that the rate-determining step can be determined by quantifying the impact of changes in particle diameter on the sorption process. In particular, they observed that film resistances determined the rate of absorption of KCl on Dowex 50 resin, while solid diffusion limited the sorption of both CuSO_4 and acetic acid on activated alumina.

Rachinskii (R3), also considering a flat uniform disc in thermodynamic equilibrium with the mobile phase, noted that radial flow chromatography resembles gradient dynamic sorption techniques in axial columns. In the case of radial flow the gradient results from the reduction in solvent velocity that occurs as the solute travels outward from the center of the disc. Rachinskii observed (as had been noted by Weil $\approx$ 20 years earlier) that zone-sharpening occurs as a consequence of this gradient.

While such an effect may bear relevance for thin layer chromatography and other techniques in which the solute of interest is to be recovered from a stationary phase, it is not realized in elution chromatography. The reason for this is that reduced solvent velocity at the outer edge of the chromatograph extends the period of time over which the solute band elutes, thus causing even an internally sharp zone (with respect to radial position) to appear broad (with respect to time) as it elutes.

Huang, et al., investigated several modes of operation in which various resistances controlled the performance of a radial flow adsorber (H3). They noted that when fluid-phase dispersion due to molecular diffusion is negligible, the partial differential equation governing the relationship between solid and fluid phase compositions (C_s and C_m , respectively) is independent of bed configuration. The equation governing the flow of a single solute through any homogeneously packed bed under plug flow constraints thus becomes:

$$\frac{\partial(C_m + C_s)}{\partial t} + Q \frac{\partial C_m}{\partial V_m} = 0 \quad (\text{Eq. 2.25})$$

The volume coordinate, V_m , was defined for the axial case as $\partial V_m = A_0 \partial z$, where A_0 is the actual cross-sectional area of the bed and z is the axial distance coordinate. For radial flow the volume coordinate was given as $\partial V_m = 2\pi h r \partial r$, where h represents the thickness or height of the bed. The use of superficial quantities in the above equation is disappointing, especially in light of other recent efforts (eg., L3, R1, R4) which documented more detailed analyzes including bed porosity as a fundamental system parameter.

Huang and his co-workers also addressed situations in which fluid-phase dispersion affects the performance of the adsorber. The dependence of the dispersion term on the derivative of the fluid phase concentration gradient destroys the previously noted geometric symmetry, resulting in configuration-dependant governing equations. The differential equation applicable to the axial case was given as:

$$\frac{\partial(C_m + C_s)}{\partial t} + Q \frac{\partial C_m}{\partial V_m} = D_{eff} \frac{\partial^2 C_m}{\partial z^2} \quad (\text{Eq. 2.26})$$

while that for the radial case was stated to be:

$$\frac{\partial(C_m + C_s)}{\partial t} + Q \frac{\partial C_m}{\partial V_m} = \frac{D_{eff}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_m}{\partial r} \right) \quad (\text{Eq. 2.27})$$

Separate Laplace domain solutions were presented for radial flow adsorbers in which either linear adsorption equilibria or mass transfer to the stationary phase controlled the response of the adsorber in the presence of fluid-phase dispersion. All mass transfer effects were lumped into a single, general rate parameter, k_r . No attempt was made to quantify the contributions of various mass transfer resistances to this parameter, as has been done by others (L3, R4).

The Laplace domain solutions for radial adsorbers in which fluid phase dispersion is significant were shown to exist as a ratio of modified Bessel functions. The solutions for axial flow adsorbers operating under similar constraints take the form of simple exponential functions. The Laplace solution for a step-input to a radial flow adsorber was inverted via Bromwich integration. Time-domain solutions for the impulse response were not presented.

More revealing than the comparison of Laplace domain solutions was Huang's moments analysis of these equations. The results of this analysis are summarized in Table 2-1. The first moment, which represents the residence time of the impulse in the bed, was shown to be directly proportional to bed volume for both the axial and radial flow cases. However, whereas only the thermodynamic properties governing sorption phenomena (the equilibrium constant) affect residence time in the axial case, the dispersion coefficient was found to impact the radial case.

Table 2-1

Moments Analysis of Chromatographic Modes by Huang, et al.

Operating Model	First Moment, μ_1 (Residence Time)	Second Moment, μ_2 (Spread About Mean)
<i>Axial Flow</i> <ul style="list-style-type: none"> • Equilibrium Controls • Transport Controls 	$\frac{(K_s + 1) L}{(Q_o/A_o)}$ $\frac{(K_s + 1) L}{(Q_o/A_o)}$	$\frac{2D_{eff} (K_s + 1)^2 L}{(Q_o/A_o)^3}$ $\frac{2D_{eff} (K_s + 1)^2 L}{(Q_o/A_o)^3} + \frac{2K_s^2 L}{k_f (Q_o/A_o)}$
<i>Radial Flow</i> <ul style="list-style-type: none"> • Equilibrium Controls • Transport Controls 	$\frac{(K_s + 1) (r^2 - R_I^2)}{2 \left(\frac{Q_o}{2\pi h} - 2D_{eff} \right)}$ $\frac{(K_s + 1) (r^2 - R_I^2)}{2 \left(\frac{Q_o}{2\pi h} - 2D_{eff} \right)}$	$\frac{2D_{eff} (K_s + 1)^2 (r^4 - R_I^4)}{4 \left(\frac{Q_o}{2\pi h} - 2D_{eff} \right)^2 \left(\frac{Q_o}{2\pi h} - 4D_{eff} \right)}$ $\frac{2D_{eff} (K_s + 1)^2 (r^4 - R_I^4)}{4 \left(\frac{Q_o}{2\pi h} - 2D_{eff} \right)^2 \left(\frac{Q_o}{2\pi h} - 4D_{eff} \right)} + \frac{2K_s^2 (r^2 - R_I^2)}{2k_f \left(\frac{Q_o}{2\pi h} - 2D_{eff} \right)}$

The second central moment, a measure of the broadening of the impulse as it moves through the bed, was shown to depend in a similar fashion on dispersion and mass transfer in both the radial and axial flow cases. (Note that the mass transfer controlling case reduces to the equilibrium adsorption case when the transfer coefficient is large.) However, whereas the dispersive and mass transfer dependent contributions to band spreading vary linearly with position in the axial case, they are seen to vary with the fourth and second power of bed radius, respectively, for the radial case.

The moments analysis discussed above suggests several important conclusions regarding the performance of radial flow adsorbers. First, the analysis implies that large fluid-phase dispersion coefficients decrease residence time. This fact is confirmed by the time-domain solutions developed in Chapter 3 for the radial flow chromatographic problem.

More importantly, since the various contributions to the second moment are functions of radial position to a power, Haung's model predicts that band spreading will be more significant in radial flow adsorbers than in equivalent axial devices. Hence, attempts to improve separation by increasing the number of stages (i.e., adding length to the flow path) should increase band spreading by the square of the radius. Although this conclusion is directionally correct, the use of superficial quantities for model development prevented Haung, et al., from recognizing the importance of bed porosity in defining the performance of the adsorber. In fact, the more precise model developed in Chapter 3 will be used to show that the tendency towards greater band spreading in radial flow devices due to mobile phase dispersion can be partially mitigated by decreasing bed voidage via compression. Compression also increases the phase ratio, thus increasing the number of theoretical plates available per unit length of flow-path.

Several years prior to Huang's effort, Rice (R1), noting the equivalence of the radial and axial flow solutions in the absence of dispersion, extended the analysis of Liaw, et al. (L2) to radial flow adsorbers through the use of the following variable transformations for system length:

$$X = \frac{1}{2} \left(\frac{r}{\eta v_{ir}} \right) \quad (Eq. 2.28a)$$

and time:

$$\theta = t - \frac{1}{2} \left(\frac{r}{v_{ir}} \right) \quad (Eq. 2.28b)$$

Here r is the radial coordinate, v_{ir} is the interstitial radial velocity, and η is the capacity ratio, defined in terms of the bed porosity, ϵ , as $\eta = \frac{\epsilon}{1-\epsilon}$.

Rice also inverted Liaw's original result to obtain an analytical solution for the step response in the time domain in terms of the tabulated J function (R4). Differentiation of this solution yields the impulse, or chromatographic, response:

$$\frac{C_i(X, \theta)}{C_o} = \left(\frac{s}{\theta \xi} \right)^{\frac{1}{2}} \exp \left(\frac{-s - \theta}{\xi} \right) I_1 \left[\left(\frac{4s\theta}{\xi} \right)^{\frac{1}{2}} \right] \quad (Eq. 2.29)$$

where C_o is the strength of the initial pulse, $s = \frac{KX}{\xi}$, K is the equilibrium sorption constant, and I_1 is a modified Bessel function.

Yee (Y1) extended Rice's effort to account for a finite inner bed radius, R_i , by further modifying the length and time variable transformations. In terms of the volumetric flow per unit bed height, $j_v = \frac{Q}{2\pi h \epsilon}$, the distance coordinate becomes:

$$X = \frac{1}{2} \left(\frac{r^2 - R_i^2}{j_v \eta} \right) \quad (Eq. 2.30a)$$

while the time coordinate becomes:

$$\theta = t - \frac{1}{2} \left(\frac{r^2 - R_i^2}{j_v} \right) \quad (Eq. 2.30b)$$

The work of Yee and Rice will be reviewed later in much greater detail, since it served as the basis for this research effort.

2.5 The Importance of Fluid Distribution and Flow Direction

The importance of flow uniformity in chromatographic applications cannot be over-stated. Bypassing, hold-up, or the existence of even a slightly preferred flow path can generate a host of problems including a shortening or lengthening of column residence times, increased band width, multiple peaks and tails. Since the existence of uniform, plug flow is one of the simplifying assumptions common to all of the fixed bed models discussed above, the ramifications of deviations from this ideal and the impact of flow direction on performance must be understood.

Geometric considerations suggest that establishing and maintaining flow uniformity is more difficult in radial flow devices than it is in conventional axial flow configurations. Compare, for example, the difficulty of establishing a uniform inlet flow across the vertical height of a radial column to that of establishing a uniform inlet flow across the cross-section of an axial column. Note also that whereas flow in axial columns is restricted to two directions (the desired axial and the undesired radial), radial flow can occur in three (the desired radial as well as the undesired vertical and angular directions).

The various possible flow geometries that exist for the radial flow configurations complicate the issue further. There is centripetal flow, that utilizes fluid introduction at the periphery of the bed and inward flow to an exit tube along the centerline, and centrifugal flow, that requires the introduction of fluid along the centerline of the bed and uses outward flow to carry it to collection points at the periphery. The relative motion in annular inlet and exit piping can also be varied (G4). The configuration is denoted as "pi-flow" if the fluid in the central tube flows counter-current to that in the outer annulus. When the fluid in the two annuli flow co-currently, the configuration is referred to as "Z-flow". One must consider what - if any - effect the four possible combinations of this flow geometry might have on distribution.

Finally, one must consider the unique characteristic of radial flow devices - that of a variable velocity due to the constantly changing cross-sectional area available to flow - and the possible impact of this phenomena on distribution.

Lessons learned during development of axial flow chromatographic techniques ensured that the importance of uniform flow was recognized and pursued early on by radial flow researchers. Weil (W1) used conical inlet tubes in an attempt to establish a plug profile at the inlet to his chromatofuge. Lapidus and

Amundson (L5) ensured that channelling did not bias their experimental analyses of liquid systems by analyzing only those experiments in which the periphery of the solute rings they formed was completely wetted by the carrier solution. (Note, however, that this precaution does not guarantee plug flow!)

In spite of the experimental precautions noted above, there appears to have been no theoretical effort extended towards the analysis of the impact of maldistribution on radial flow chromatography. Hence, we are forced to look at other areas for guidance. Much research along these lines has been conducted on gas-phase, radial flow reactors. These devices are currently seeing widespread industrial use, particularly with respect to the production of ammonia.

Several investigators have studied the effect of flow direction on the conversion obtained in radial flow reactors. Hlavacek and Kubicek (H4) analyzed the two extremes of plug flow and CSTR operation for a constant volume, non-isothermal, first-order reaction. They noted that under some conditions multiple steady states may occur. For exothermic reactions with only one steady state, flow direction was found to have only a minor impact on conversion. They also determined that molecular dispersion can be ignored when considering reactors of commercial size.

Balakotaiah and Luss (B1) found that the preferred flow direction was dependent on both reaction order and stoichiometry. They analyzed single-reactant, isothermal systems and determined that centrifugal flow resulted in better conversion for all reactions with orders greater than one that do not result in a volume change, and for first-order reactions that cause a volume increase. Conversely, centripetal flow increases conversion for first-order reactions that generate a decrease in volume. For reaction systems not falling into these categories, the preferred flow direction depends on the magnitude of the kinetic parameters and the radial Peclet number. In all instances flow direction was found to have only a minor impact on conversion. Genkin et al. (G4) performed the first experimental investigation of velocity distributions in a packed, radial flow bed. They studied fluid distribution in radial flow reactors consisting of a central tube surrounded by a catalyst bed and an outer annular channel. Although only centrifugal flow was studied, they evaluated both the "pi" and "z" configurations.

Macroscopic energy equations derived for the central tube, the packed bed and the outer annulus were coupled by matching pressures at the interface between adjacent regions. When combined with the appropriate continuity equations these relations yielded differential equations describing gas distribution within the reactor. Yee (Y1) performed a similar analysis while studying design criteria for the radial flow chromatograph.

Genkin's analysis indicated that uniform velocity distributions are favored by systems with low free lateral surface area in the central tube (i.e., high pressure drop across the wall of the central tube), small central tube diameters, and pi-flow. They also noted that maldistribution was less of a problem for beds of low aspect ratio (defined as the ratio of bed height to outer bed radius). This fact suggests that a thin, flat plate may be the optimum configuration for a radial flow chromatograph.

Genkin collected experimental data by passing air in the turbulent flow regime through a fixed bed reactor. The reactor consisted of a central tube 5.3 cm in diameter, with a 100 cm high, 10.1 cm in diameter bed packed with 6.2 mm x 4.56 mm pellets. The experimental data agreed well with predictions from the differential equations.

Kaye (K5) extended Genkin's approach to account for centripetal flow. He identified three dimensionless parameters that can be used to assess whether or not uniform flow will be established outward across a radial bed from a central annulus. The primary parameter, β , is a complex expression relating the total pressure drop across the reactor to the pressure head at the inlet of the feed annulus. Large values of β imply that a large resistance to flow exists across the bed. Such a situation does, as might be expected, result in uniform flow.

The secondary parameter impacting distribution is the ratio of unpacked annular cross sectional area to that of the central feed pipe. This ratio determines the extent of maldistribution only if β is small. Then large values of area ratio are needed to ensure an initially uniform flow profile.

The final parameter affecting distribution is the Reynolds number within the central feed pipe. Kaye observed that the extent of maldistribution was generally negligible until a critical Reynolds number is reached. Then maldistribution increases rapidly with Reynolds number before leveling off at high Reynolds numbers.

The interpretations and conclusions outlined above were also experimentally verified. This was accomplished in a 2.4 meter 120° wedge shaped section of a radial flow bed. The standard deviation between model predictions and measured flow maldistribution ranged between 9.8% and 18%.

Ponzi and Kaye (P1) were the first to show that imperfect radial-flow profiles have a much larger influence on performance than does flow direction. They assumed plug, radial flow through an infinite array of parallel differential elements in a catalyst bed. Radial dispersion was taken to be negligible. Their analysis quantified the effect of maldistribution on the conversion obtained from both first and second order reactions, and on the selectivity observed in first order, series or parallel reactions.

They reported that increasing maldistribution always reduced conversion in isothermal reactors, and predicted that the reduction may be as great as 11%. Whereas increasing maldistribution was found to always decrease conversion for first-order, endothermic reactions, its impact on exothermic reactions was found to depend on observed conversion levels. At initially low, uniform conversions maldistribution was shown to increase conversion slightly. However, once a critical conversion level is achieved, maldistribution always works to reduce conversion.

Ponzi and Kaye used the continuity equation to establish a criterion for measuring maldistribution. They showed that, for flow introduced to the central annulus of a radial flow reactor, radial velocity will be proportional to the derivative of the (dimensionless) axial flow velocity in the annulus:

$$v_{or} = -\left(\frac{R_i}{2h}\right)\frac{\partial v_z}{\partial z} \quad (Eq. 2.31)$$

Here v_{or} , v_z and z are dimensionless parameters representing the radial velocity through the bed, the axial velocity through the annular feed pipe, and the distance along this pipe, respectively, while R_i is the radius of the feed pipe (or inner bed radius) and h is the height of the catalyst bed. If uniform radial flow is to be established, the axial velocity gradient through the feed pipe must have a constant value of -1. Deviations from this gradient serve as a measure of maldistribution.

Building both on their previous work and that of others, Chang, et al., developed design criteria to ensure uniform flow through radial, fixed bed reactors (C2).

In summary, flow direction was found to have only a small impact on the conversion achievable in a fixed bed, radial flow reactor regardless of the nature of the reaction. Flow distribution, on the other hand, can have a major effect. Application of these findings to radial flow chromatography suggests that, at this early developmental stage, emphasis must be placed on the establishment of uniform flow through the bed. The more subtle effects of flow direction can be evaluated at a later date once analytical models are more fully developed and a broader experimental data base is available for analysis.

2.6 Formation of Sorbent Bed Compacts

The importance of establishing flow uniformity was discussed in detail in the preceding section. Early investigations performed by Schwartz and Smith with gases (S5) revealed that, in the absence of external disturbances, essentially plug flow profiles can be established in uncompressed beds of particles provided the bed diameter is at least 30 times greater than the diameter of the particles.

The current experimental effort maintained the minimum diameter ratio recommended by Schwartz, and further attempted to improve flow uniformity by decreasing the interstitial porosity of the sorbent bed. These reductions were achieved through:

- implementation of a slurry-based packing technique designed to eliminate the formation of comparatively large voids during the initial packing procedure
- subsequent compression of the sorbent bed.

Bed compression offers advantages beyond that of improved fluid distribution. One is a decrease in interstitial hold-up, which contributes to dead volume and consequently band-broadening (see Section 2.2). Another is an increase in the ratio of convective to diffusive motion within the column, which, as discussed in Section 3.2.2, effectively sharpens the response peak.

The process of compressing a radial flow, chromatographic bed resembles industrial techniques developed for the production of tablets. It involves placing the desired powder in a die and applying sufficient pressure to generate the desired volume reduction. The resulting compact takes on the well-defined shape of the die.

Early investigators viewed the compaction process as the result of two separate mechanisms:

- at low pressures, particle rearrangement reduces interstitial volume through results in closer packing. The energy applied during this stage is dissipated primarily in overcoming friction.
- at high pressures, elastic and plastic deformation of the particles occurs, allowing them (or their fragments) to flow into smaller void spaces. This increases the area of interparticle contact and, for materials with both low thermal conductivities and low melting points, the heat generated at contact points may increase plasticity sufficiently to facilitate even greater particle deformation. Conversely, brittle materials will fracture, with additional volume reductions resulting from fragment rearrangement.

These mechanisms were presumed to occur either individually or simultaneously depending on the properties of the particles and the pressure applied during the compaction process (F1).

Cooper and Eaton (C3) reviewed several expressions used to correlate such behavior. Most of these were some variant of the following exponential relation:

$$\frac{\varepsilon}{\varepsilon_0} = \exp \left(-\frac{P}{R} \right) \quad (Eq. 2.32)$$

where P represents applied pressure and R is a constant specific to the particles undergoing compression.

They expanded the exponential model to address the independent contributions of particle rearrangement and plastic/elastic deformation separately. The resulting relation for V^* , the final volume compaction achieved, contained separate constants for each stage of the compression process:

$$V^* = a_1 \exp \left(-\frac{k_1}{P} \right) + a_2 \exp \left(-\frac{k_2}{P} \right) \quad (Eq. 2.33)$$

Here the constants a_1 and a_2 represent the ratios of compaction theoretically available in the independent rearrangement and plastic/elastic deformation steps, respectively, to the total theoretical compaction. The constants k_1 and k_2 have the units of pressure. Cooper and Eaton published experimentally determined values for these constants specific to several different types of particles.

Recently Zwan has extended the concept of the two stage compaction process by distinguishing between reductions in interstitial porosity via gross compaction of the particulate mass and reduction of intraparticle

porosity achieved through densification of individual porous particles (Z1). He noted that such distinctions are required when considering the compaction of granules composed of smaller, primary particles. The two compaction mechanisms mentioned previously thus become four:

- filling of the holes between granules.
- fragmentation and plastic deformation of granules.
- densification of individual particles via reductions in intraparticle porosity.
- fragmentation and plastic deformation of the primary particles comprising the granules.

Ramberger and Burger (R6) noted that several compaction processes can be described by using the Kawakita equation:

$$\frac{\epsilon}{1 - \epsilon} (P + P_o) = \psi \quad (\text{Eq. 2.34})$$

at low pressures and high porosities where densification results primarily from an increase in the number of particles per layer due to either slippage or fracture, and the Heckel relation:

$$\ln\left(\frac{1}{\epsilon}\right) = kP + A \quad (\text{Eq. 2.35})$$

at high pressures and low porosities where interparticle bonding (agglomeration) becomes significant. Here P_o is the initial pressure prior to compaction, P is the applied pressure, and k , A and ψ are constants.

Although the mathematics used to describe such compaction processes appears to be relatively simple, there are several factors that complicate their application to the production of ideal chromatographic beds. The most important of these is the effect of friction. Although compression of a particulate solid in a cylindrical die with frictionless walls would produce a uniform compact (since the compressive forces will be transmitted uniformly throughout, resulting in uniform internal pressures and hence uniform compact density) the presence of frictional shear forces at the die walls leads in actual practice to internal pressure variations that result in a nonuniform compact density. These variations may be as high as $\approx 10\%$ in dry compacts (F2). A reproduction of a typical density distribution within a cylindrical compact - looking vertically along the axis through its center - is presented in Figure 2.1.

FIGURE 2-1
DENSITY DISTRIBUTION WITHIN A NON-LUBRICATED
CYLINDRICAL COMPACT

COMPRESSION PRESSURE: 30,000 PSI
(DENSITIES GIVEN AS POUNDS/FT³)

General conclusions drawn from investigations of density variations within compacts formed under pressure are that density variations can be minimized by (F2):

- reducing the height of the specimen to be compressed while holding its diameter constant
- increasing the diameter of the die (regardless of specimen height)
- adding a lubricant to the walls of the die (which greatly reduces density variations) and/or the specimen itself (which slightly reduces density variations)

Density variations were also found to increase with increases in the pressure applied to the compact.

CHAPTER III

MODELING and ANALYSIS of the RADIAL FLOW CHROMATOGRAPH

3.1 Pressure Drop Across a Packed, Radial Flow Bed

The relationship between fluid flow rate and frictional energy losses can be derived from a macroscopic energy balance across a packed, radial flow bed of porosity ϵ , inner radius R_i and outer radius R_o (Yee, Y1):

$$\left(\frac{1}{\rho}\right)\frac{\partial P}{\partial r} + \frac{\partial}{\partial r}\left[\frac{\epsilon^2(rv_{ir})^2}{2r^2}\right] + \frac{1}{2\epsilon}\left[\frac{rv_{ir}}{r}\right]^2 f a_p(1-\epsilon) = 0 \quad (Eq. 3.1)$$

where mass continuity requires that (rv_{ir}) is constant at constant pressure. Here particle surface area per unit particle volume is denoted as a_p , and the friction factor for the system is symbolized by f . The lower case subscripts "i" and "r" refer to interstitial and radial values, respectively.

The low pressure drop generated by the radial flow configuration allows the fluid density, ρ , to be treated as a constant for all isothermal systems - even if the mobile phase is gaseous. This simplifies the task of integrating the energy balance, which yields:

$$\Delta P = -\left(\frac{1}{2}\right)\rho[\epsilon rv_{i,r}]^2\left[\frac{1}{R_i^2} - \frac{1}{R_o^2}\right] - \left(\frac{1}{2}\right)[rv_{i,r}]^2 a_p \left[\frac{1-\epsilon}{\epsilon}\right] \int_{R_o}^{R_i} \left[\frac{f}{r^2}\right] dr \quad (Eq. 3.2)$$

Yee (Y1) modified Ergun's analysis of the frictional losses for axial flow columns to develop an expression for the friction factor that is applicable to radial flow columns:

$$f = \frac{50(1-\epsilon)\mu}{d_p G_o} + \frac{7}{12} \quad (Eq. 3.3)$$

Note that since the friction factor is a function of G_o , the local mass velocity per unit area for flow, it is also - in the case of radial flow configurations - a function of bed position.

Insertion of this relation into Equation 3.2 yields an explicit expression for pressure drop as a function of the volumetric flow rate, Q :

$$\begin{aligned}
\Delta P = & 75 \frac{\mu}{d_p^2} \left[\frac{(1-\epsilon)^2}{\epsilon^3} \right] \frac{Q}{\pi h} \ln \left(\frac{R_o}{R_i} \right) \\
& + \left[\frac{7}{16} \right] \frac{\rho}{d_p} \left[\frac{(1-\epsilon)}{\epsilon^3} \right] \frac{1}{\pi^2 h^2} \left[\frac{1}{R_i^2} - \frac{1}{R_o^2} \right] Q^2 \\
& - \left(\frac{1}{2} \right) \left[\frac{\rho}{4\pi^2 h^2} \right] \left(\frac{1}{R_i^2} - \frac{1}{R_o^2} \right) Q^2
\end{aligned} \tag{Eq. 3.4}$$

Note the definition $Q = 2\pi h \epsilon j_v$, where, as was noted in Section 2.4, j_v is the volumetric flow rate per unit height of bed.

The three groups of terms on the right hand side of Equation 3.4 quantify the laminar, turbulent and kinetic contributions to the total bed pressure drop. The different dependency of these terms on the order of the volumetric flow rate allows the operating regime of a packed, radial flow device to be determined directly from pressure drop data. Given a suitable estimate of particle size, Equation 3.4 can also be used to estimate the dynamic porosity, ϵ , of the bed.

A detailed development of the pressure drop relation - similar to that first given by Yee (Y1) - is presented in Appendix I.

3.2 Sorption Modeling of the Radial Flow Chromatograph

Centrifugal pi-flow, the simplest radial flow configuration from a mechanical standpoint, will be addressed in the model development that follows. A material balance on a single component moving radially outward through such a packed bed yields:

$$D_{eff} \frac{\partial^2 C_m}{\partial r^2} = \frac{\partial C_m}{\partial t} + \left[\frac{j_v - D_{eff}}{r} \right] \frac{\partial C_m}{\partial r} + \left[\frac{1}{\eta} \right] \frac{\partial \bar{q}}{\partial t} \tag{Eq. 3.5}$$

Equation 3.5 was derived with the usual assumptions of a homogeneous bed, uniform plug flow, equilibrium between the mobile (C_m) and average stationary phase compositions ($\bar{q}$), and a dilute solution (so that sorption heat effects can be ignored and the system can be taken as isothermal). The capacity ratio, η , is defined with respect to bed porosity: $\eta = \epsilon/(1-\epsilon)$. The fluid phase dispersion coefficient, D_{eff} , accounts

for dispersion resulting from either molecular diffusion in the fluid phase, eddy dispersion associated with fluid flow, maldistribution, or some combination of these processes. Individual contributions to this constant are discussed in greater detail in section 5.3.2.

The movement of solute from the flowing phase (C_m) to the adsorbed state (q) is a complex process. In Section 3.2.1 we consider this relationship under conditions in which transport is controlled by film resistances and/or intraparticle diffusion. Section 3.2.2 explores the consequences of operation under conditions in which fluid phase dispersion controls. The constant j_v , previously defined as the volumetric flux per unit bed height, shall be shown to have special significance in the latter case. Note that j_v has the dimensions of diffusivity, and arises from convection due to flow through the bed. When fluid phase dispersion is significant the relative magnitudes of j_v and D_{eff} , and the competition between the fluxes they define, shall be seen to dictate the chromatographic response.

3.2.1 The Case of Negligible Fluid Phase Dispersion

If fluid phase dispersion is insignificant the relationship between average stationary and bulk fluid phase composition will depend solely on the film resistance and intraparticle diffusion. Under such conditions Equation 3.5 reduces to:

$$-\left(\frac{j_v}{r}\right)\frac{\partial C_m}{\partial r} = \left[\frac{1-\epsilon}{\epsilon}\right]\frac{\partial \bar{q}}{\partial t} + \frac{\partial C_m}{\partial t} \quad (Eq. 3.6)$$

The flux at the solid/fluid interface is defined by:

$$k_m \left[C_m - \frac{q_R}{K_s} \right] = \left[D_s \frac{\partial q}{\partial r} \right] \Big|_{r=R} \quad (Eq. 3.7)$$

Here the mass transfer coefficient through the fluid film surrounding the particles is given as k_m , while the subscript R indicates a property evaluated at the surface, or outer radius, of the particles. The equilibrium sorption constant, K_s , is defined in terms of the interfacial compositions q_R and C^* . The effective solid phase diffusivity, D_s , may include contributions from solid, surface, intrapore and Knudsen diffusion. The magnitude of these contributions is discussed in greater detail in Section 5.3.1.

The parabolic profile assumption popularized by Rice (R1, D1) for consideration of sorbent particles can be used to describe the composition within the stationary phase. For spherical particles of radius R this assumption yields:

$$\frac{\partial \bar{q}}{\partial t} = \left(\frac{15D_s}{R_p^2} \right) [q_R - \bar{q}] \quad (Eq. 3.8)$$

Equations 3.6 - 3.8 can be solved simultaneously to eliminate all reference to solid phase composition in favor of the more easily measured bulk fluid phase composition. The result for a step input becomes:

$$\xi \frac{\partial^2 U}{\partial X \partial \theta} + K_s \frac{\partial U}{\partial \theta} + \frac{\partial U}{\partial X} = 0 \quad (Eq. 3.9)$$

Here U is the ratio of the fluid phase composition to that of the step magnitude C_o , and ξ , the total mass transfer resistance resulting from contributions due to film and intraparticle diffusion effects, is given as:

$$\xi = R_p \left[\frac{K_s}{3k_m} + \frac{R_p}{15D_s} \right] \quad (Eq. 3.10)$$

Rice (R1) originally defined length and time coordinates for radial flow systems as follows:

$$X = \frac{r^2}{2j_v \eta} \quad (\text{sec}) \quad (Eq. 3.11 - a)$$

$$\theta = t - \frac{r^2}{2j_v} \quad (\text{sec}) \quad (Eq. 3.11 - b)$$

He also obtained an analytical solution for Equation 3.9, which had previously been derived by Liaw, et al. (L3) for an axial adsorber, in terms of the J function (R3):

$$U = \frac{C(X, \theta)}{C_o} = J(s, \tau) = 1 - \int_0^s \exp(-\tau - \beta) I_0[\sqrt{4\tau\beta}] d\beta \quad (Eq. 3.12)$$

where $s = K_s X / \xi$ and $\tau = \theta / \xi$. Differentiation of this relation with respect to θ yields the impulse, or chromatographic, response (R3):

$$\frac{C(X, \theta)}{C_0} = \sqrt{\frac{K_s X}{\theta \xi^2}} \exp\left[\frac{-(K_s X + \theta)}{\xi}\right] I_1\left[\sqrt{\frac{4K_s X \theta}{\xi^2}}\right] \quad (\text{Eq. 3.13})$$

As noted earlier, Yee (Y1) extended Rice's analysis to adsorbers with a finite inner bed radius through the use of the following variable change:

$$X = \frac{(r^2 - R_f^2)}{2j_v \eta} \quad (\text{Eq. 3.14-a})$$

$$\theta = t - \left[\frac{r^2 - R_f^2}{2j_v} \right] \quad (\text{Eq. 3.14-b})$$

Equations 3.12, 3.13, and 3.14-A and B are valid for all chromatographic situations in which fluid phase dispersion is negligible compared to film and/or solid phase diffusional resistances. The response in such cases is dictated by the equilibrium sorption constant, K_s , and the sum of the film and intraparticle diffusional resistances, ξ .

The predicted effect of these parameters is documented in Figures 3-1 and 3-2. They show that the combined resistance parameter exerts its greatest influence on the width of the response, and that its impact on retention is negligible (Figure 3-1). Conversely, the equilibrium sorption constant is seen to impact both band width and retention time (Figure 3-2). Hence, strongly adsorbed species (larger K_s) are retained longer and exhibit wider elution bands. Note that although the variations in ξ utilized to produce Figure 3-1 were generated via manipulation of particle radius, equivalent variations could have been achieved through adjustment of k_m and/or D_s .

FIGURE 3-1

RADIAL FLOW CHROMATOGRAPHIC RESPONSE: IMPACT OF RESISTANCE TERM WHEN FLUID PHASE DISPERSION IS NEGLIGIBLE

FIGURE 3-2

**RADIAL FLOW CHROMATOGRAPHIC RESPONSE:
IMPACT OF SORPTION CONSTANT WHEN FLUID PHASE DISPERSION IS NEGLIGIBLE**

Although the negligible dispersion model was shown to accurately predict the behavior of an axial flow column (see Section 5.3.1), attempts to fit it to radial flow data met with limited success. This fact is underscored in Figure 3-3, which documents the discrepancy between the nearly Gaussian model predictions and the skewed experimental response. The poor fit confirms that the negligible dispersion model does not accurately reflect physical phenomena occurring within the adsorber. This observation led to speculation that dispersion was significant in the radial flow devices considered, and resulted in development of the mobile phase dispersion model discussed below. One was especially alerted to the loss of physical reality by the large values of ξ required to attain the "best fit". These values bore no semblance to expectations (ie, $\xi \approx 0.01 - 0.001$ seconds).

FIGURE 3-3

TYPICAL POOR FIT FOR RICE'S NEGLIGIBLE DISPERSION MODEL

3.2.2 The Sorption Equilibria/Mobile Phase Dispersion Model

None of the terms in the solute material balance (Equation 3.5) can be cancelled when dispersion dominates. However, since film and intraparticle diffusion resistances are quite small ($10^{-2} - 10^{-3}$ seconds), local equilibrium is fast for the stationary phase and:

$$\bar{q} = K_s C_m \quad (\text{Eq. 3.15})$$

The simplified solute balance thus becomes:

$$\frac{\partial C_m}{\partial t} = \left(\frac{\eta}{K_s + \eta} \right) \left[D_{eff} \frac{\partial^2 C_m}{\partial r^2} - \left(\frac{j_v - D_{eff}}{r} \right) \frac{\partial C_m}{\partial r} \right] \quad (\text{Eq. 3.16})$$

The Laplace domain solution for this equation has been given previously (R5) as:

$$C(s, r) = r^p \left[AI_p \left(r \sqrt{s \left(\frac{K_s + \eta}{D_{eff} \eta} \right)} \right) + BI_{-p} \left(r \sqrt{s \left(\frac{K_s + \eta}{D_{eff} \eta} \right)} \right) \right] \quad (\text{Eq. 3.17})$$

where s is the Laplace variable and a Peclet number based on interstitial values, $p = \frac{j_o}{2D_{eff}}$, defines the order of the Bessel function.

Equation 3.17 is similar to the solution reported by Huang, et al. (H3), except that they did not consider the importance of interstitial porosity. Hence their Bessel functions took the order:

$$p = \frac{j_o}{2D_{eff}} \quad (\text{Eq. 3.18})$$

while the argument of these same functions was expressed as:

$$r \sqrt{s \left(\frac{K_s + 1}{D_{eff}} \right)} \quad (\text{Eq. 3.19})$$

Note that the constant j_o (in Equation 3.18) is a "superficial" volumetric flux $\left(j_o = \frac{Q}{2\pi h} \right)$ that does not depend on the interstitial porosity, ϵ .

The author would like to emphasize once again (as was done in section 2.4) that omission of the porosity term eliminates from consideration a parameter that is of great importance in determining the response of an adsorber. As shall be shown in Section 3.2.2.1, increasing the capacity ratio (decreasing ϵ) via bed compression

(i.e., decreasing porosity) reduces both band spreading and retention. The absence of porosity in Huang's model prevented their recognition of this important effect. Indeed, our results suggest that suitable radial flow chromatographic performance can only be achieved at high bed compression.

An analytical solution for Equation 3-16 in the time domain can be developed beginning with the introduction of appropriate dimensionless variables. Following along the lines of Rice and Heft (R7):

$$p = \frac{j_v}{2D_{eff}} \quad (\text{Peclet number}) \quad (\text{Eq. 3.20-a})$$

$$\zeta = \frac{r}{R_o} \quad (\text{dimensionless distance}) \quad (\text{Eq. 3.20-b})$$

$$\tau = \frac{D_{eff}\eta}{(K_s + \eta)R_o^2} t = \frac{t}{\tau_r} \quad (\text{dimensionless time}) \quad (\text{Eq. 3.20-c})$$

For a step input of magnitude C_o these variables reduce Equation 3-16 to:

$$\frac{\partial \Delta}{\partial \tau} = \frac{\partial^2 \Delta}{\partial^2 \zeta} - \left(\frac{2p-1}{\zeta} \right) \frac{\partial \Delta}{\partial \zeta} \quad (\text{Eq. 3.21})$$

where $\Delta = C - C_o$.

Boundary conditions are applied to the bed inlet, where

$$\Delta = 0 \quad @ \quad \zeta \approx 0 \quad (\text{small inner septum}) \quad (\text{Eq. 3.22-a})$$

and the bed outlet, where

$$\frac{\partial \Delta}{\partial \zeta} = 0 \quad @ \quad \zeta = 1 \quad (\text{Eq. 3.22-b})$$

The second constraint accounts for flow reversal at the outer boundary where an impermeable wall results in a zero diffusion flux.

The initial condition for a clean bed is simply

$$\Delta = -C_o \quad @ \quad \tau = 0 \quad (Eq. \ 3.22-c)$$

A separation of variables is performed such that:

$$\Delta = R(\zeta)T(\tau) \quad (Eq. \ 3.23)$$

This yields

$$R'' - \left(\frac{2p-1}{\zeta} \right) R' + \lambda^2 R = 0 \quad (Eq. \ 3.24-a)$$

and

$$T' + \lambda^2 T = 0 \quad (Eq. \ 3.24-b)$$

Equation 3.24-A can be simplified by introducing another variable change:

$$R = \zeta^p f(\zeta) \quad (Eq. \ 3.25)$$

to yield:

$$\zeta^2 f'' + \zeta f' + (\lambda^2 \zeta^2 - p^2) f = 0 \quad (Eq. \ 3.26)$$

Since Equation 3.26 is a classical Bessel equation of the first kind of order p:

$$f = AJ_p(\lambda\zeta) + BJ_{-p}(\lambda\zeta) \quad (Eq. \ 3.27)$$

and the general solution to Equation 3.23 can be written as:

$$\Delta = \zeta^p [AJ_p(\lambda\zeta) + BJ_{-p}(\lambda\zeta)] \exp(-\lambda^2 \tau) \quad (Eq. \ 3.28)$$

The boundary conditions (Equations 3.22-A and B) are of the Sturm-Liouville type, yielding $R(0) = 0$ and $R'(1) = 0$, respectively. The ODE given by Equation 3.24-A is also a Sturm-Liouville equation with a weighting function $r(\zeta) = \zeta^{1-2p}$, so that the orthogonality condition is:

$$\int_0^1 \zeta^{1-2p} R_n(\zeta) R_m(\zeta) d\zeta = 0 \quad \text{for } n \neq m \quad (Eq. \ 3.29)$$

To evaluate the constants A and B in Equation 3-28 we consider the behavior of the Bessel functions near the centerline of the adsorber. Since:

$$J_p(\lambda\zeta) = \frac{\left(\frac{\lambda\zeta}{2}\right)^p}{\Gamma(p+1)} - \frac{\left(\frac{\lambda\zeta}{2}\right)^{p+2}}{\Gamma(p+2)} + \dots \quad (\text{Eq. 3.30-a})$$

and

$$J_{-p}(\lambda\zeta) = \frac{\left(\frac{\lambda\zeta}{2}\right)^{-p}}{\Gamma(p-1)} - \frac{\left(\frac{\lambda\zeta}{2}\right)^{2-p}}{\Gamma(p-2)} + \dots \quad (\text{Eq. 3.30-b})$$

it is clear that:

$$\lim_{\zeta \rightarrow 0} [\zeta^p J_p(\lambda\zeta)] = 0 \quad (\text{Eq. 3.31-a})$$

while:

$$\lim_{\zeta \rightarrow 0} [\zeta^p J_{-p}(\lambda\zeta)] \rightarrow \frac{\left(\frac{\lambda}{2}\right)^{-p}}{\Gamma(1-p)} \quad (\text{Eq. 3.31-b})$$

Application of the boundary condition $R(0) = 0$ thus requires that $B = 0$, while the condition that $R'(1) = 0$ yields

$$2pJ_p(\lambda_n) = \lambda_n J_{p+1}(\lambda_n) \quad (\text{Eq. 3.32})$$

Equation 3.32, which defines the eigenvalues for the system, can be simplified via introduction of the following recurrence relation (J2):

$$J_{p-1}(\lambda_n) = \left(\frac{2p}{\lambda_n}\right) J_p(\lambda_n) - J_{p+1}(\lambda_n) \quad (\text{Eq. 3.33})$$

to yield a remarkably simple expression for the countably infinite eigenvalues of the system:

$$J_{p-1}(\lambda_n) = 0 \quad (\text{Eq. 3.34})$$

The step response solution to Equation 3.21 is thus given as:

$$\Delta = \sum A_n \zeta^p J_p(\lambda_n \zeta) \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.35})$$

where the constants A_n are to be defined by invoking the orthogonality requirement along with the initial condition that $\Delta = -C_o$ at $\tau = 0$, hence:

$$A_n = \frac{-C_o \int_0^1 \zeta^{1-p} J_p(\lambda_n \zeta) d\zeta}{\int_0^1 \zeta J_p^2(\lambda_n \zeta) d\zeta} \quad (\text{Eq. 3.36})$$

where the eigenfunctions $R_n(\zeta)$ are $\zeta^p J_p(\lambda_n \zeta)$, and the orthogonality weighting function is $r(\zeta) = \zeta^{1-2p}$.

The integrals defining the constants A_n were tabulated by Hildebrand (H6), so that one ultimately obtains:

$$\frac{C}{C_o} = 1 - \sum \frac{\left(\frac{1}{2}\right)^{p-2}}{\Gamma(p)} \lambda_n^{p-2} \zeta^p \frac{J_p(\lambda_n \zeta)}{J_p^2(\lambda_n)} \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.37})$$

where the eigenvalues of the system are the zeros of $J_{p-1}(\lambda_n)$.

The impulse, or chromatographic, response at the exit ($\zeta = 1$) is derived by differentiating the step response with respect to time to obtain:

$$\left(\frac{C}{C_o}\right)_I = \sum \frac{\left(\frac{1}{2}\right)^{p-2}}{\Gamma(p)} \frac{\lambda_n^p}{J_p(\lambda_n)} \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.38})$$

This expression can be normalized in the usual experimental sense by dividing out the area under the time curve to obtain

$$C_{norm} = \frac{\sum \frac{\lambda_n^p}{J_p(\lambda_n)} \exp(-\lambda_n^2 \tau)}{\sum \frac{\lambda_n^{p-2}}{J_p(\lambda_n)}} \quad (\text{Eq. 3.39})$$

Equation 3.39 reveals that when sorption equilibrium is instantaneous and fluid phase dispersion is significant, the impulse response of a radial flow adsorber is defined by two independent groups. These groups are a Peclet number based on interstitial flow quantities, $p = \frac{j_s}{2D_{eff}}$, and the system time constant, $\tau_r = \frac{R_o^2(K_s + \eta)}{D_{eff}\eta}$ (sec).

The importance of the Peclet number arises from the fact that it is a measure of competition between convective and dispersive transport (including contributions from molecular and eddy diffusion as well as any maldistribution that may be present). As the Peclet number is increased, convection dominates dispersion more thoroughly. This effect, documented in Figure 3-4, sharpens the response and decreases solute retention.

FIGURE 3-4
RADIAL FLOW CHROMATOGRAPHIC RESPONSE:
IMPACT OF PECLET NUMBER WHEN FLUID DISPERSION CONTROLS

Note that the Peclet number can be adjusted through changes in either mechanical or molecular properties. Mechanical controls include bed compression (which impacts j_v by decreasing ϵ) and mobile phase throughput. The variable molecular property is the molecular contribution to the dispersion coefficient. For a given solute this parameter can be varied by switching mobile phases or adjusting temperature.

The second dimensionless group, $\tau_r = R_o^2[(K_s + \eta)/(D_{eff}\eta)]$, dominates solute retention. It can be manipulated by two controllable mechanical properties, R_o and η , a molecular property, K_s , and another parameter, D_{eff} , that may be either molecular (if diffusivity dominates) or mechanical (if eddy dispersion or

flow maldistribution dominates) in nature. In most cases of practical interest K_s is much larger than unity, while η is ≤ 0.4 (the "less than" applies to compressed sorbent beds). Hence τ_r varies directly with both the sorption constant and the square of the bed radius, and is inversely proportional to D_{eff} .

The squared dependence of the time constant on the radius of the sorbent bed is a characteristic of radial flow configurations resulting from the proportionality between cross-sectional bed area and the square of its radius. The near linear dependence of the time constant on K_s is also anticipated. This relationship is illustrated in Figure 3-5 for an adsorber operating with a Peclet number of 4. Note that the ratio of the individual sorption and time constants, as well as the eluent times corresponding to the respective peak maxima, are all ≈ 1.50 . The response is observed to broaden with increases in K_s , as was the case for the negligible fluid phase dispersion model.

FIGURE 3-5
RADIAL FLOW CHROMATOGRAPHIC RESPONSE:
IMPACT OF THE TIME CONSTANT WHEN FLUID DISPERSION CONTROLS

The inverse dependence of τ_r on D_{eff} indicates that a parameter which does not alter solute-sorbent interactions influences retention in a more complex fashion than that anticipated from simple competition

with convective motion. This unusual relationship suggests the existence of a previously unutilized partitioning mechanism that might ultimately be exploited to enhance the performance of a radial flow chromatograph. Such possibilities are explored briefly in Figure 3-6, where increases in the system time constant and the Peclet number resulting from decreases in the dispersion coefficient are shown to increase retention time while reducing band width.

FIGURE 3-6
RADIAL FLOW CHROMATOGRAPHIC RESPONSE:
IMPACT OF THE DISPERSION COEFFICIENT ON THE IMPULSE RESPONSE

It is interesting to contrast such behavior with that predicted by the negligible dispersion model (Section 3.2.1) and that observed by Kaizuma (K1) for axial flow columns operating in the "diffusive retention" mode (see Section 2.2). The trends presented in Figure 3-6 indicate that heavy solutes - which generally have lower diffusion coefficients and are more strongly adsorbed - may be retained longer on a radial flow chromatograph with only marginal increases in band width. Such behavior runs contrary to expectations for dispersion-free systems, where increased retention times were seen to result in wider elution bands (Figure 3-2). With respect to diffusive retention, note that Kaizuma reported a positive correlation between molecular diffusivity and

retention time. If it is assumed that dispersion in the radial flow device results solely from molecular diffusion, then D_{eff} reduces to D_{ab} and, as is documented in Figure 3-6, retention is seen to decrease as the molecular diffusion coefficient is increased.

The final comment regarding the time constant of a radial flow adsorber addresses the impact of the capacity ratio η . Note that as η tends towards zero, τ_r approaches $\frac{R_o^2 K_s}{D_{eff} \eta}$, and the ratio $\frac{K_s}{D_{eff}}$ can be seen to control partitioning. The presence of η in the denominator suggests that a highly compressed radial flow bed will behave much as a very long packed tube (since $\tau_r \propto \frac{1}{\eta}$). A radial flow chromatograph with a highly compressed sorbent bed might thus be made to perform as a much larger device.

3.2.2.1 Importance of the Point Source Assumption

The analytical result derived above (Equation 3.38 or 3.39) assumed that solute introduction occurs uniformly as a point source along the centerline of the bed. The importance of this assumption was assessed by comparing the impulse response as predicted by Equation 3-39 with that obtained via numerical solution of Equation 3.16. A forward difference technique was used to evaluate the response of a radial flow adsorber over a range of finite inner septum sizes (i.e., differing inner radii). All other parameters affecting the response (K_s , D_{eff} , Q , etc.) were kept constant. The results of this comparison are presented graphically in Figure 3-7.

The integral absolute error, or IAE, between the "exact" numerical and the "approximate" analytical solution was found to be $\leq 2\%$ provided that the sample introduction channel, or inner septum, does not take up more than 1% of the total bed volume. It is therefore recommended that use of the analytical solution be restricted to such cases. The experimental work discussed in Sections 5.2 and 5.3 utilized an inner septum radius R_i of 0.3175 cm, corresponding to a channel covering 0.75% of the total bed volume. The error for this case is estimated at $\approx 0.5\%$.

FIGURE 3-7

IMPACT OF INNER SEPTUM SIZE ON ACCURACY OF ANALYTICAL SOLUTION

3.2.2.2 Eigenvalue Requirements

Implementation of the analytical solution derived in Section 3.2.2 is feasible only if convergence is achieved with a reasonable number of eigenvalues. A study of said convergence properties is summarized in Table 3-1. Two adsorbers were considered, one with a time constant of $\tau_r = 250$ seconds, the other with a time constant $\tau_r = 2500$ seconds. Both adsorbers were assumed to be operating with a Peclet number of 3. General conclusions drawn from this data include:

- Eigenvalue requirements for the two adsorbers are consistent when compared on a dimensionless time basis, i.e. equivalent $\frac{t}{\tau_r}$ ratios.
- A large number of eigenvalues (> 10) is required to accurately predict the null response preceding the initial rise of the impulse. This requirement appears to hold for small times such that $\frac{t}{\tau_r} \leq 0.02$.
- Four or fewer eigenvalues are required once the peak maximum is reached ($\frac{t}{\tau_r} \sim 0.055$).

Table 3-1
Convergence Properties of Equation 3.39

Time, sec	Adsorber #1: $p = 3, \tau_r = 250$ sec		Adsorber #2: $p = 3, \tau_r = 2500$ sec	
	$\frac{t}{\tau_r}$	Eigenvalues Required for Convergence	$\frac{t}{\tau_r}$	Eigenvalues Required for Convergence
1	0.004	>15	0.0004	>15
5 ^a	0.020	8	0.0020	>15
10	0.040	5	0.0040	>15
14 ^b	0.056	4	0.0056	14
20	0.080	3	0.0080	11
50 ^c	0.200	1	0.0200	7
100	0.400	1	0.0400	4
145 ^d	0.580	1	0.0580	3
200	0.800	1	0.0800	2

a - end of "null" response for adsorber #1

c - end of "null" response for adsorber #2

b - time of peak maxima for adsorber #1

d - time of peak maxima for adsorber #2

Response curves for the hypothetical adsorber with a time constant of 250 seconds are presented in Figure 3-8. They were generated by summing the contributions from the first 3, 5, 10 and 15 eigenvalues, respectively. The behavior is consistent with expectations based on the data in Table 3-1: the response is nonconvergent for small numbers of eigenvalues at short dimensionless times, but convergent with very few eigenvalues once the peak maximum is reached.

Figure 3-8

SOLUTION CONVERGENCE AS A FUNCTION OF THE NUMBER OF EIGENVALUES SUMMED

The variance of system eigenvalues with the Peclet number that defines the order of the Bessel functions is summarized in Table 3-2. Remember that these eigenvalues are defined as the zeros of the Bessel functions of order (p-1):

$$J_{p-1}(\lambda_n) = 0 \quad (\text{Eq. 3.34})$$

Note that for a given order the difference between successively larger eigenvalues tends towards π .

Table 3-2
System Eigenvalues as a Function of Peclet Number

p =	2	2.5	3	3.5	4
λ_1	3.8317	4.4934	5.1356	5.7635	6.3802
λ_2	7.0156	7.7253	8.4172	9.095	9.761
λ_3	10.1735	10.9041	11.6198	12.3229	13.0152
λ_4	13.3237	14.0662	14.796	15.5146	16.2235
λ_5	16.4706	17.2208	17.9598	18.689	19.4094
λ_6	19.6159	20.3713	21.117	21.8539	22.5827
λ_7	22.7601	23.5194	24.2701	25.0128	25.7482
λ_8	25.9037	26.6661	27.4206	28.1678	28.9083
λ_9	29.0468	29.8116	30.5692	31.3201	32.0649
λ_{10}	32.1897	32.9564	33.7165	34.4705	35.2187
λ_{11}	35.3323	36.1006	36.8629	37.6194	38.3705
λ_{12}	38.4748	39.2444	40.0084	40.7671	41.5207
λ_{13}	41.6171	42.3879	43.1535	43.914	44.6697
λ_{14}	44.7593	45.5311	46.298	47.0601	47.8178
λ_{15}	47.9015	48.6741	49.4422	50.2057	50.965

3.2.2.3 Inward Flow Case

An intriguing and somewhat unexpected result is obtained when the analysis of Section 3.2.2 is applied to a radial flow adsorber with flow established from its periphery towards its centerline. For such inward flow configurations the velocity vector and convective flux term, j_r , are negative (i.e., in the "anti-r" direction). The dimensionless distance equation resulting from the separation of variables in Eq. 3.23 thus becomes:

$$R'' - \frac{(-2p-1)}{\zeta} R' + \lambda^2 R = 0 \quad (\text{Eq. 3.40})$$

The corresponding time equation, Eq. 3.24-b, remains unchanged. Equation 3.40 can also be reduced to a form of Bessel's equation:

$$R = \zeta^{-p} [AJ_p(\lambda\zeta) + BJ_{-p}(\lambda\zeta)] \quad (\text{Eq. 3.41})$$

the general solution of which is:

$$\Delta = \zeta^{-p} [AJ_p(\lambda\zeta) + BJ_{-p}(\lambda\zeta)] \exp(-\lambda^2 \tau) \quad (\text{Eq. 3.42})$$

Noting that as $\zeta \rightarrow 0$:

$$\lim_{\zeta \rightarrow 0} (\zeta^{-p} J_p) = \frac{\left(\frac{1}{2}\lambda\right)^p}{\Gamma(p+1)} - \frac{\left(\frac{1}{2}\lambda\right)^{2+p}\zeta^2}{\Gamma(p+2)} + \dots \rightarrow \text{finite value} \quad (\text{Eq. 3.43-a})$$

while

$$\lim_{\zeta \rightarrow 0} (\zeta^{-p} J_{-p}) = \frac{\left(\frac{1}{2}\lambda\right)^p \zeta^{-2p}}{\Gamma(1-p)} - \frac{\left(\frac{1}{2}\lambda\right)^{2+p} \zeta^{2-2p}}{\Gamma(2-p)} + \dots \rightarrow \infty \quad (\text{Eq. 3.43-b})$$

requires that the constant "B" be set to zero. The initial condition that $\Delta = 0$ when $\zeta = 1$ is only satisfied if

$$J_p(\lambda) = 0 \quad (\text{Eq. 3.44})$$

Thus the eigenvalues for the inward flow case are found to be simply the zeros of $J_p(\lambda)$.

Combining equations 3.41 - 3.44 yields the step response for flow from the periphery:

$$\Delta = \sum A_n \zeta^{-p} J_p(\lambda_n \zeta) \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.45})$$

where the constants A_n are again found by invoking the orthogonality constraint and initial conditions. Hence:

$$A_n = \frac{-C_o \int_0^1 \zeta^{2p+1} (\zeta^{-p} J_p(\lambda_n \zeta)) \partial \zeta}{\int_0^1 \zeta J_p^2(\lambda_n \zeta) \partial \zeta} \quad (\text{Eq. 3.46})$$

The integral tables provided by Hildebrand (H6) enable considerable simplification:

$$A_n = -C_o \frac{\frac{1}{\lambda_n} J_{p+1}(\lambda_n)}{\frac{1}{2} [J_p^2(\lambda_n) - J_{p-1}(\lambda_n) J_{p+1}(\lambda_n)]} \quad (\text{Eq. 3.47})$$

which, along with the following recurrence relation (J2):

$$J_p(\lambda \zeta) = \frac{\lambda \zeta}{2p} [J_{p+1}(\lambda \zeta) + J_{p-1}(\lambda \zeta)] \quad (\text{Eq. 3.48})$$

and the fact that $J_p(\lambda_n) = 0$ yields a simple expression for the required constants:

$$A_n = -\frac{2C_o}{\lambda_n} \frac{1}{J_{p+1}(\lambda_n)} \quad (\text{Eq. 3.49})$$

The step response for the inward flow case thus becomes:

$$\frac{C}{C_o} = 1 - \sum \frac{2 \zeta^{-p} J_p(\lambda_n \zeta)}{\lambda_n J_{p+1}(\lambda_n)} \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.50})$$

where the eigenvalues are given by $J_p(\lambda_n) = 0$. Differentiation to obtain the impulse response at $\zeta = 0$ yields:

$$\left(\frac{C}{C_o} \right)_I = \sum \frac{\left(\frac{1}{2} \right)^{p-1} \lambda_n^{p+1}}{\Gamma(p+1) J_{p+1}(\lambda_n)} \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.51})$$

or, in normalized form:

$$C_{norm} = \frac{\sum_{j_{p+1}(\lambda_n)} \frac{\lambda_n^{p+1}}{j_{p+1}(\lambda_n)} \exp(-\lambda_n^2 \tau)}{\sum_{j_{p+1}(\lambda_n)} \frac{\lambda_n^{p-1}}{j_{p+1}(\lambda_n)}} \quad (Eq. 3.52)$$

Comparison of equations 3.52 and 3.39 indicates that the solution for the inward flow case can be obtained from the outward flow solution by everywhere replacing p , the Peclet number defining the order of the Bessel functions, with $p+1$. This somewhat surprising result suggests that if all other factors are kept constant the inward flow configuration will generate a sharper response than the outward flow configuration. The magnitude of this effect is depicted in Figure 3-9.

FIGURE 3-9
RADIAL FLOW CHROMATOGRAPHIC RESPONSE:
THE INFLUENCE OF FLOW DIRECTION ON THE RESPONSE

In spite of model implications, there are several practical considerations that favor implementation of the outward flow configuration. Chief among these is the simplicity of establishing flow uniformity along the bed centerline, as opposed to the much larger periphery of the bed. An observation that supports this statement is the fact that the experimental data discussed in Section 5.3.2 indicates that the effective dispersion

coefficients observed during experimentation with the inward flow configuration were consistently larger than those observed for outward flow, probably due to non-uniform injection fronts (maldistribution) for the inward flow case.

3.2.2.4 Comparison of Solution Methods

Three separate solution methods were utilized in an attempt to fit experimental data to the sorption equilibrium/mobile phase dispersion model. Each of these solutions was ultimately incorporated into a Hooke and Jeeves pattern search to find values for the Peclet number, p , and the system time constant, τ_r , that minimized the integral absolute error (IAE) between the experimental data and the response predicted by the model. Since several iterations are required to find the optimum fit, it is essential that "per-pass" calculation time (time required to determine the response for a single set of p and τ_r values) be minimized.

Initial efforts centered on numerical integration of the relevant differential equation (Equation 3.17) using an explicit, forward difference technique. The advantage of this approach was that it was simple to implement and permitted mechanical dimensions to be expressed exactly as encountered in the experimental chromatograph. Its overwhelming disadvantage was that the small space and time increments required to ensure convergence ($t \leq 0.01$ sec, $r \leq 0.04$ cm, respectively) caused computational time for a single pass through the adsorber to exceed six hours on an IBM PS-2 and two hours on a dedicated DEC MicroVax. Such excessive time requirements rendered this approach unwieldy when incorporated into the iterative search routine required to fit theory to experimental data.

The second solution technique considered involved inversion of the Laplace solution (Equation 3.18) via Zakian integration (W3). Although this approach reduced per-pass calculation time to ≈ 20 minutes, the predicted response proved to be unreliable due to error propagation at long times. Such difficulties arise from round-off errors associated with division of small number by large numbers and the subsequent summing of results. Similar difficulties have been reported by others working on a variety of equations (H7). Unfortunately, reconciliation of these difficulties via the usual rearrangement of the Laplace solution was not possible in this case.

The last solution method utilized involved determination of eigenvalues and summation of the terms in the analytical solution discussed above. This approach, though the fastest of the three (< 10 minutes per pass), has the disadvantage that its use was restricted to situations in which the inlet flow channel occupied less than 1% of the total bed volume.

A comparison of typical impulse response curves as generated by each of the solution techniques discussed above is presented in Figure 3-10. The hypothetical radial flow adsorber considered here corresponded closely with the experimental effort discussed in Chapter 5. Note the general equivalence of the numerical integration and analytical series solution techniques. The Zakian solution agreed with the others except at long times, where the tail refused to tend towards 0 and, in fact, began to increase.

The computer programs used in these analyses are attached for reference in Appendix II.

FIGURE 3-10

EQUIVALENCY OF SOLUTION TECHNIQUES

3.2.3 Comparison of the "Intraparticle Controlled" and Dispersion Models

The models considered in Sections 3.2.1 and 3.2.2 address two operating extremes for a radial flow adsorber. The negligible dispersion case ignores the effects of fluid phase mixing and assumes that the impulse response will be dictated by film and stationary phase diffusional resistances. The model discussed in Section 3.2.2 assumes that mass transfer is instantaneous and that the response is determined by molecular or mechanical dispersion in the mobile phase. It is instructive to compare the parameters applicable to each model.

The equilibrium sorption constant is a molecular parameter common to both models. In both cases K_s exerts its largest influence on retention, and a lesser impact on band spreading. Note that - as indicated in Figures 3-2 and 3-5 - larger values of K_s increase both retention times and band spreading.

The effect of the convective-diffusive ratio on the molecular dispersion-controlled response is similar to that of the combined resistance parameter ξ on dispersion-free systems: both parameters dominate band spreading. This is evident from the curves presented in Figures 3-1 and 3-4.

One characteristic of the convective-diffusive ratio (i.e., p or Peclet number) that is not shared with ξ is its impact on column retention. In addition to controlling band-spreading, the curves in Figure 3-4 indicate that p impacts solute retention. This effect is easily visualized with respect to increases in the magnitude of the convective diffusion constant (and hence p) brought about by either increased throughput or higher capacity ratios. The fact that equivalent decreases in retention can be achieved by decreasing the effective dispersion coefficient (which also causes p to increase) is less obvious.

Another interesting aspect of the fluid-phase dispersion model is the existence of a second parameter, D_{eff} , that impacts both retention and band spreading.

Key parameters for both models are summarized and compared in Table 3-3. Methods of manipulating model parameters are discussed in Table 3-4.

Table 3-3
Comparison of Model Parameters

Model	Key Parameters	Primary Impact	Secondary Impact
Negligible Dispersion	K_s $\xi = R_p \left(\frac{K_s}{3k_m} + \frac{R_p}{15D_s} \right)$	Retention Time Band Spreading	Band Spreading -
Dispersion with Local Equilibrium	$\tau_r = \frac{R_p^2(K_s + \eta)}{D_{eff}\eta}$ $p = \frac{j_v}{2D_{eff}}$	Retention Time Band Spreading	Band Spreading Retention Time

Table 3-4
Manipulation of Model Parameters

PARAMETER

CONTROLLED BY

K_s	• Changing stationary phase composition • Changing bed temperature
ξ	• Changing particle size (impacts ξ directly as multiplier and indirectly through k_m) • Changing mobile phase composition (to effect k_m and D_s) • Changing K_s (by changing stationary phase composition or bed temperature) • Changing the structure of the stationary phase (pore size affects D_s)
τ_r	• Adjusting bed compression (to adjust ϵ and hence η) • Changing stationary phase composition (to impact K_s) • Changing bed temperature (to adjust K_s and D_{eff})
p	• Adjusting volumetric flux (j_v) • Adjusting compression (and hence ϵ, η and thus j_v) • Changing carrier gas (to change D_{eff}) • Changing bed temperature (to adjust D_{eff})

CHAPTER IV

MECHANICAL DESIGN and EXPERIMENTAL PROCEDURES

4.1 Column Configurations

The heart of any chromatograph is the sorbent bed in which the desired separations are accomplished. The experimental results presented in Chapter V were generated using three distinct beds. The first radial flow bed, henceforth referred to as the Mark II-A, was a 4" square, $2\frac{1}{8}$ " high stainless steel block containing a circular depression in which the stationary phase was compressed. Single-solute impulse response data generated with this device uncovered the limitations of Rice's original film resistance model (Equation 3.13), and led to the development of the fluid dispersion model (Equation 3.39) for systems in which solute diffusivity is significant.

A second radial flow bed, the Mark II-B, was used to demonstrate chromatographic separation of methane/n-butane mixtures in a radial flow configuration. This bed resulted from improvements made to the Mark II-A to minimize dead volume.

Data was also generated in a conventional axial flow column in order to verify equilibrium sorption constants for the methane/n-butane/helium/alumina system. This data was needed to evaluate the consistency and reliability of the data collected with the Mark II-B.

4.1.1 The Mark II-A Radial Flow Chromatograph

The Mark II-A Radial Flow Chromatograph was designed for in situ compression of the stationary phase. A schematic of its primary components - including the receiver, cap, spacer plate, and porous inner and outer septums - is presented in Figure 4.1. The Mark II-A employs centripetal flow through a "Z" configuration. This is the same arrangement considered for initial model development in Chapter III.

The base of the Mark II-A was a 4-1/2" square, 1-5/8" high block constructed of 416 SS to withstand the forces generated by compaction of the bed with pressures as high as 5,000 psi. A 3" diameter circular

FIGURE 4-1

MARK II-A PROTOTYPE RADIAL FLOW CHROMATOGRAPH

depression recessed $\frac{7}{8}$ " into this solid accommodated the packing. The square sides of the receiver permitted it to be mounted in a vice while packing and compressing the bed. These operations proved to be difficult with the circular design of the Mark I that Yee employed in his studies (Y1).

A $\frac{1}{8}$ " Swagelok fitting located bottom-dead-center on the receiver permitted the Mark II-A to be connected to a standard gas chromatograph injection port. A $\frac{1}{4}$ " hole drilled through the receiver from this fitting served as an inlet passage that channelled the mobile phase to the inner septum.

The inner septum directed the mobile phase radially outward from the feed channel through the bed. It was a 1" long, $\frac{1}{4}$ " OD annular cylinder that was precision manufactured from sintered 316 stainless steel by Mott Metallurgical. The $\frac{1}{16}$ " thick permeable walls had 2 micron diameter pores distributed uniformly throughout. These pores generated sufficient pressure drop to establish a uniform fluid distribution at the interface between the bed and the septum.

The Reynolds number for axial flow through the center of the inner septum was ≈ 5 at the highest flowrates considered in the experimental program (125 cc/minute @ STP). Since this value is well below the 2000 limit established by Kaye as the maximum above which maldistribution occurs (K5), a uniform plug flow profile was expected through both the Mark II-A and the Mark II-B. However, the experimental data presented in Chapter V indicates that other factors - probably mechanical plugging of the outlet gas collection system - probably distorted the desired flow profile.

The inner septum rested within the inlet passage on a spring that held it in a 1/4" guide hole drilled 1/4" into the bottom of the spacer plate. This spring allowed the inner septum to travel vertically down towards the inlet fitting as compressive force was applied to the bed, thus ensuring that it was not damaged during the compression process.

A 3" OD, 1/16" thick porous annular filter manufactured by Thermet was employed as an outer septum. Its primary purpose was to hold the packing in place and provide a vertical flow path between the bed periphery and the outlet collection system. The outer septum was constructed of bronze (10% tin) because of an inability to locate a suitable stainless steel alternative. It was cut to the required 1" height from a 12" section of stock material. The cut end was placed against the base of the receiver to minimize the effect of any mechanical damage to the 20 micron pore openings that may have resulted from the cutting procedure.

The spacer plate was actually a plunger that contacted the bed during the compression process. It was constructed of 416 SS to withstand the stress resulting from transmission of compressive forces to the bed. This 2-7/8" diameter, 1/4" high cylinder was machined to a "slip fit" within the outer septum. A 1/4" diameter hole drilled 1/4" into the bottom center of the plunger ensured that the inner septum remained vertical during the packing and compression processes. Two 1/8" ethylene-propylene rubber (EPR) O-rings provided a seal between the spacer and the outer septum, ensuring that the mobile phase flowed vertically upward through the outer septum past the spacer.

A 1/16" bevel cut on a 45° angle around the edge of the spacer collected the gas as it eluted from the upper edge of the outer septum. This collection chamber fed the mobile phase to a series of eight 1/16" square slots that directed the gas back to a 1/8" diameter exit channel running through the center of the cap.

The cap, which was also constructed of 416 SS, was 4-1/2" square and 1/2" high. It was bolted to the top of the receiver with twelve 5/16" by 1-1/2" long machine bolts. These bolts were used to apply compressive force to the bed as the Mark II-A was assembled. The ability to torque each bolt individually in an alternating pattern allowed for gradual, uniform compression much as a head gasket might be tightened on a car. This process allowed higher compressive forces to be generated than was possible with the screw-on cap of the Mark I (Y1). The bolt-on configuration also eliminated concerns that surface irregularities might be generated from the shear stresses established by the twisting motion of the cap at the point where it contacts the bed.

A single 1/8" EPR O-ring on the receiver formed a mechanical seal with the cap as it was tightened. A circular bronze plate recessed 1/8" into the cap provided flexibility to allow for expansion during tightening, bed compression and heat-up. A 1/8" hole drilled through both this plate and the cap served as an exit channel from the Mark II-A. A 1/8" Swagelok fitting located on top of the cap permitted the Mark II-A to be connected to a standard GC detector.

An interesting innovation of the Mark II-A design was the installation of a pressure transducer mounted flush with the bottom of the depression in the receiver. This transducer (Omega part # PX 610-5KG V) measured the compressive forces on the bed up to 5000 psi. Powered by a common 6 volt battery, it produced a 0-10 mV output that was proportional to the pressure measured at that point.

4.1.2 The Mark II-B Radial Flow Chromatograph

Experimentation with the Mark II-A revealed two design flaws with the potential to negatively affect performance. These flaws were:

- excessive dead volume
- the inability of the cap to withstand the force associated with compression of the bed to 5000 psi.

As was noted in Chapter II, dead volume can be a major source of band spreading. The warping of the cap during the compression process posed two problems: the generation of additional dead volume and the possibility of alternate flow paths. Improvements made to the Mark II-A in an effort to eliminate these difficulties resulted in what is now referred to as the Mark II-B Radial Flow Chromatograph.

The problem of excessive dead volume was addressed through elimination of the bevel on the upper edge of the spacer plate, the square slots etched along its top, and the outer septum. A new spacer plate - also

constructed of 416 SS - was machined to a slip fit for the depression in the receiver. Microgrooves impressed vertically along the periphery of this spacer and laterally across the top towards its center provided a much smaller cross-sectional area for flow than did the original bevel/groove system.

The choice of microgroove depth involved several considerations. The most obvious was the need to restrict groove depth sufficiently to ensure that sorbent particles could not enter the grooves and plug them during the compression process. More subtle, but just as important, was the need to strike a balance between the desire to minimize dead volume through the use of shallow grooves and the need to minimize the pressure drop external to the sorbent bed with deep grooves.

Whereas shallow grooves decrease dead volume and, as noted in Chapter II, band spreading, they also increase the pressure drop across the gas outlet system. This necessitates operation of the Mark II-B at higher bed pressures, thereby increasing the density of the mobile phase and decreasing its interstitial velocity. As was noted during the development of the fluid phase dispersion model in Chapter III, decreases in interstitial velocities reduce the convective/molecular diffusion ratio, which broadens the chromatographic response. Note that whereas dead volume increases in direct proportion with groove depth, the pressure drop through the outlet system varies as the inverse of the groove depth to the fourth power. Hence decreases in dead volume are obtainable only with disproportionate increases in the pressure drop. Unfortunately, the experimental program discussed in Chapter V is not yet sophisticated enough to quantitatively address this trade-off.

A final consideration is the fact that as the pressure drop through the outlet collection system is increased, it begins to dominate the pressure drop across the bed. Under such conditions the error resulting from attempts to fit experimental data to Equation 3.4 in an effort to estimate bed porosity increases.

The data presented in Table 4-1 was generated to underscore the difficulty associated with choosing appropriate groove depth. It documents calculated pressure drops as a function of groove depth for typical conditions - 100 cc/min carrier gas flow @ STP and a bed temperature of 100° C - utilized during experimentation with the Mark II-B. A gas collection/outlet system with 50 grooves was assumed.

Higher bed pressures resulting from increases in pressure drop through the outlet collection system as groove depth is decreased are shown to drastically reduce the actual volumetric flowrate through the bed. The

Table 4-1
Impact of Spacer Groove Depth on Mark II-B Pressure Drop

GROOVE DEPTH (INCHES)	PRESSURE DROP THROUGH COLLECTION SYSTEM (PSI)	VOLUMETRIC FLOW THROUGH BED (ACCM)	BED PRESSURE DROP ¹ (% OF TOTAL)
0.004	1.9	121.4	51.7
0.003	9.4	83.5	17.5
0.002	29.6	44.3	6.3

1- Pressure Drop Estimated for $\epsilon = 0.2$; Particle Diameter = 0.015 cm

decrease paralleling a reduction in groove depth from 0.004" to 0.002" would reduce the convective/diffusive ratio $\left(p = \frac{j_f}{2w_{eff}} \right)$ by more than 60%! The negative effect of such a change on band spreading was discussed in Chapter III and graphically documented in Figure 3-3.

Finally, note that bed pressure drop accounts for a smaller fraction of the total system pressure drop as groove depth is decreased to reduce dead volume. This trend raises concerns about the ability to accurately estimate bed porosity from pressure drop data as groove depth is reduced.

The initial re-design effort resulted in a spacer plate with a series of fifty 0.003" deep triangular grooves impressed along its sides and top. The triangular shape and small cross-sectional area of the grooves ($\approx 6 \times 10^{-5} \text{ cm}^2$) was intended to prohibit the passage of sorbent particles (cross sectional area $\approx 3 \times 10^{-2} \text{ cm}^2$) into the grooves during bed compression. These grooves provided a much smaller cross-sectional area for flow than did the original bevel/groove system. Unfortunately, repeated plugging by fragments of the original sorbent particles during the packing procedure (see Section 4.3.2) necessitated an increase in groove depth to 0.006". To avoid a corresponding increase in dead volume, the number of grooves was reduced by nearly half to 26.

A comparison of the original spacer plate with the final version of the improved design is given in Figure 4-2. The nearly 80% reduction in dead volume achieved by the switch to the new spacer plate is summarized in Table 4-2. The calculated pressure drop for the final 26 groove (0.006" deep) system utilized in the Mark II-B was ≈ 0.75 psi for a flow of 100 cc/min @ STP.

FIGURE 4-2
COMPARISON OF SPACER PLATES

The other problem encountered with the Mark II-A, warping of the cap during the compression process, was initially addressed through the development of a sturdier, external "packing plunger" that was not part of the fully assembled Mark II-B. This device, a 3" diameter, 6" long cylinder that slipped snugly into the packing depression bored into the receiver, is illustrated in Figure 4-3.

The packing plunger was designed for an initial compression of the sorbent bed in a hydraulic press. Markings spaced 0.01" apart along its axis facilitated mechanical measurement of volume changes and provided visual verification that verticality was maintained during the compression process. The packing plunger was then removed to facilitate the installation of the improved spacer plate.

Table 4-2
Dead Volume Reduction Through Spacer Plate Redesign

<u>SOURCE OF DEAD VOLUME</u>	<u>CONTRIBUTION IN MARK II-A (cc)</u>	<u>CONTRIBUTION IN MARK II-B (cc)</u>
INLET CHANNEL	0.20	0.20
INNER SEPTUM	0.16	0.16
OUTER SEPTUM	2.48	0
BEVEL ON SPACER	0.48	0
SPACER GROOVES	0.74	0.03
OUTLET CHANNEL	0.16	0.16
INLET/OUTLET FITTINGS	<u>0.48</u>	<u>0.48</u>
TOTALS	4.70	1.03

(Net Dead Volume Reduction: 79%)

FIGURE 4-3
THE MARK II-B PACKING PLUNGER

The subsequent tightening of the cap with the spacer plate in place partially compensated for the relaxation that occurred as the packing plunger and Mark II-B were removed from the press. This procedure was monitored with the pressure transducer in the bottom of the receiver to ensure that pressures sufficient to warp the cap (> 2500 psi) were avoided.

The compression process was thus split into two-steps:

- an initial compression of the sorbent bed in a hydraulic press that achieved higher pressures than was possible with the Mark II-A but avoided the possibility of endangering the integrity of the cap.
- final compression by tightening the cap while monitoring pressure to ensure that the generated compressive stresses do not endanger the integrity of the cap.

Unfortunately, concerns regarding the consistency and repeatability of the two-step packing procedure ultimately lead to elimination of the packing plunger. In the final evolutionary step, compression of the packing was accomplished by placing a metal plate on top of the cap to reinforce it and distribute the compressive forces from the hydraulic press uniformly. This permitted compression to be undertaken with the improved spacer plate in place.

A schematic of the Mark II-B is presented in Figure 4.4. Additional details concerning packing procedures is provided in section 4.3.2.

FIGURE 4-4
MARK 11-B PROTOTYPE RADIAL FLOW CHROMATOGRAPH

4.2 Stationary Phase Sorbent Materials

F-20 grade activated alumina was employed as the stationary phase for the initial impulse response experiments performed in the Mark II-A. The F-20 grade was chosen to maintain consistency with the earlier work of Yee (Y1). However, a smaller, more uniform particle size was used in an attempt to minimize dispersion. The smaller particle size was obtained by sieving the "as bought" material used by Yee and retaining for subsequent use only those particles falling in the 120-140 (Tyler) mesh range. The particle size distribution reported by Yee (Y1) for the "as received" F-20 alumina is documented in Figure 4-5 for reference.

All methane-butane separations, including those conducted in the axial flow column in support of the separations performed in the Mark II-B, were carried out over 100-120 mesh, F-1 grade activated alumina. The F-1 sorbent was chosen because it is widely used for the separation of light hydrocarbons.

FIGURE 4-5
PARTICLE SIZE DISTRIBUTION FOR F-20 ALUMINA

The physical properties and pore structure of the F-1 alumina (as provided by the supplier, Alltech) are summarized in Tables 4-3 and 4-4. Note that the crush strength measurement indicates fully 41% of the particles will fracture to some degree when subjected to a compressive force of 2400 psi for 60 seconds! Such extensive particle degradation is the likely explanation for the repeated pluggage of the microgrooves impressed on the spacer plate during the packing of the Mark II-B (see section 4.3).

The internal porosity reported for the F-1 is also uncharacteristically high - 56% versus more typical values of $\approx 30\%$ (V1). Such high porosities may explain the relatively low crush strength of the solid. Note also that more than 40% of the internal void volume results from micropores with diameters of 35 Å or less. As will be shown in section 5.1.2, it is these micropores that control mass transfer resistances when used in an axial flow configuration.

Porosity studies of the F-1 performed as part of this effort are documented in Appendix III. The data presented there differs slightly from the physical description provided by Alltech. The discrepancies result primarily from the inability of the equipment utilized to measure pore volumes in the micropore size-range.

Table 4-3

PHYSICAL PROPERTIES of F-1 ACTIVATED ALUMINA

ABRASION LOSS	1.6 wt% ^a
CRUSH STRENGTH	59% ^b
PACKED BULK DENSITY	0.88 g/cm ³
PARTICLE DENSITY	1.40 g/cm ³
TRUE DENSITY	3.30 g/cm ³
LOSS ON IGNITION (250-1100° C)	7 wt%
BET SURFACE AREA	250 m ² /g

a - wt% sorbent two mesh increments smaller than original after 30 minutes of vibration

b- wt% remaining in original size fraction after 60 seconds @ 2400 psi

Table 4-4

PORE VOLUME ANALYSIS OF F-1 ACTIVATED ALUMINA

TOTAL PORE VOLUME	0.40 cm ³ /gm
MICROPORE VOLUME (< 35 Å)	0.17 cm ³ /gm
MACROPORE VOLUME (> 35 Å)	0.23 cm ³ /gm
PORE DIAMETER @ 50% TOTAL PORE VOLUME	177 Å
TOTAL INTERNAL POROSITY	56%

4.3 Packing of the Chromatographic Columns

4.3.1 The Axial Flow Column

The axial flow column was vibrated during the packing procedure to ensure uniform settling, and consequently packing, of the stationary phase. One end of the column was plugged with silane wool before being connected to a vacuum pump. The column was then stretched tight, with the free end held $\approx$ 3 feet above the pump. The solid sorbent was then poured slowly into the empty column through a small funnel.

The drag resulting from the air flow established by the suction of the vacuum pump assisted gravitational forces in the effort of packing the particles tightly. Vibration, provided by both vacuum pump operation and a continual "rapping" of the column against a wall during the packing process, ensured that particle re-arrangement was adequate to eliminate large voids within the column.

A silane plug was installed in the open end of the column after the packing procedure was complete. This plug prevented loosening and loss of stationary phase particles during the handling and use of the column.

4.3.2 The Radial Flow Columns

Early attempts to achieve uniform packing in the Mark II-A met with limited success. The primary problem was an inability to spread the sorbent uniformly through the receiver prior to compression. Repeated attempts to resolve this issue via vibration of the bed proved futile. Particularly frustrating was an inability to establish a uniform surface, as evidenced by the fact that one side of the cap contacted on the powder prior to the other.

The problem of initial sorbent distribution was resolved through development of the "wet pack" technique, which utilizes a liquid to lubricate and slurry the sorbent prior to placing it in the receiver. After a brief period during which settling of the sorbent bed is encouraged via vibration (through physical contact with an operating vacuum pump), excess liquid is wicked off the surface of the bed with a sorbent cloth. The compression process is then carried out on the "wet" bed.

The lubricated packing was observed to settle more uniformly when first admitted to the receiver, thus eliminating the problems of both an "uneven" surface and void pocket formation prior to compression. As noted in Section 2.6, lubrication also facilitates re-distribution of the packing particles within the bed during the compression process, while the liquid present in the interstitial pores helps distribute compressive forces uniformly throughout the compact. All of these factors work together to minimize density variations within the resultant compressed bed. Such variations may range up to 10% in a dry compact formed in a cylindrical die, with the highest densities found near the walls where the compressive forces are greatest (F1).

Three different liquids were evaluated for the wetpack technique. Water proved to be a poor choice because of the excessive conditioning required to prepare the bed for use after compression. Carbon tetrachloride (CCl_4) was observed to evaporate too quickly, with dry spots appearing on the surface of the bed prior to initiation of the compression process. Heptane proved to be the optimal choice for the wet pack procedure. It did not evaporate as rapidly as carbon tetrachloride and, being a non-polar compound, it proved relatively easy to remove from the bed during the conditioning process.

The slurried bed was compressed in the Mark II-A simply by mounting the column in a vice and tightening the bolts that held the cap to the receiver. Excess heptane was forced out of the bed through both the inner and outer septums during the compression process. The pressure transducer mounted in the receiver indicated that compressive forces on the order of 5000 psi were sustained in this fashion.

Although the wet pack procedure performed well in the Mark II-A, the tendency for the liquid squeezed from the bed during compression to carry fine sorbent particles into the microgrooves impressed on the spacer plate required that the technique be modified for use in the Mark II-B. These fine particles - probably the remnants of larger particles fragmented during compression - plugged some of the microgrooves, causing maldistribution and large pressure drops external to the sorbent bed. An expanded wet pack procedure was developed to minimize pluggage after several aborted packing attempts resulted in excessive pressure drop. The revised procedure involved:

- 1) Deposition of the packing slurry in the receiver
- 2) Insertion of the spacer plate, with sufficient pressure applied (manually) to ensure that it contacts the surface of the bed.
- 3) Rotation of the spacer plate to ensure even contact with the top of the sorbent bed.
- 4) Removal of any liquid and packing particles found to have seeped through the micro grooves with a fine brush
- 5) Hand tightening the cap to hold the spacer plate in place
- 6) Establishing helium flow (10 psi source pressure) radially outward through the bed.
- 7) Tightening the bolts in the cap to increase compressive force on the bed.
- 8) Removal of the cap and spacer plate to facilitate cleaning of the micro grooves.
- 9) Repetition of steps 2-8 until no packing particles are found in the micro grooves upon dismantling.

- 10) Installation of the Mark II-B in a hydraulic ram for final compression.
- 11) Tightening of the cap bolts while the Mark II-B is still mounted on the ram.

Compressive forces in excess of 10,000 psi were realized using a Jet hydraulic ram to compress the sorbent bed during the packing of the Mark II-B according to this procedure.

The curves presented in Figure 4.8 document the decrease in system pressure drop achieved with the modified packing technique. Curve B, representing the final packing attempt, depicts the pressure drop characteristics of the radial flow bed used to analyze the methane-butane system. As discussed in Chapter V, the large dispersion coefficients extracted from the parameter estimation routine indicate that some pluggage occurred in spite of the improved packing procedure. If the full potential of radial flow chromatography is to be realized, additional effort is needed to eliminate this difficulty so that uniform flow profiles can be established.

4.4 Conditioning the Sorbent Beds

All sorbent beds - both axial and radial - were conditioned in the oven of an HP Series II chromatograph at 150° C with a continuous flow of helium for at least 72 hours after packing. Columns were termed adequately conditioned once the baseline signal measured by the chromatograph's flame ionization detector had stabilized.

As might be expected, conditioning of the axial flow column proceeded much more rapidly than that of the wet-packed radial flow beds. Whereas the baseline registered by the axial flow column stabilized after $\approx$ 48 hours, the baseline signal from the radial flow columns generally required 72-96 hours.

CHAPTER V

EXPERIMENTAL RESULTS, MODELING and DISCUSSION

5.1 Determination of Bed Porosity

The interstitial porosity of the conventional axial flow and prototype radial flow beds was estimated by fitting theoretical expressions to pressure drop data. Since particle size and flow conditions were measured, porosity remained as the only adjustable parameter with which to match theory with experiment.

All of the pressure drop-flow data were generated at ambient conditions using helium as the mobile phase. Data for the radial flow devices were collected at much lower interstitial velocities than those utilized for subsequent mass transfer experiments. This ensured operation under conditions of nearly constant mobile phase density and permitted the use of the radial flow analogue of the Blake-Kozeny relation discussed in Section 3.1 (Y1) for porosity estimation.

5.1.1 Porosity of the Sorbent Bed Compressed in the Mark II-A

Pressure drop data for both the packed and empty Mark II-A is presented in Figure 5-1. The linearity of these curves confirms that all of the pressure drop data was collected for the laminar flow regime. The lower line quantifies pressure drop through the gas inlet, across the inner and outer septums, and through the gas outlet, while the upper curve reflects the total pressure drop across the packed device. The difference between these curves is thus the portion of the total pressure drop attributable to the compressed bed.

Interstitial porosity was determined by fitting the difference between the slopes of the curves presented in Figure 5-1 to the laminar portion of Equation 3.4. This relation:

$$\Delta P = 75 \frac{\mu}{d_p^2} \left[\frac{(1-\epsilon)^2}{\epsilon^3} \right] \ln \left(\frac{R_o}{R_i} \right) \frac{Q}{\pi h} \quad (Eq. 5.1)$$

is the radial flow analogue of the Blake-Kozeny relation developed by Yee (Y1).

FIGURE 5-1
 FLOW vs PRESSURE DROP DATA FOR THE MARK II-A
 (POROSITY ESTIMATED @ 0.12 FOR AN AVERAGE PARTICLE DIAMETER OF 0.013 CM)

The accuracy of the porosity estimate obtained from Equation 5.1 is highly dependent on the value of the particle diameter assumed for the analysis (see Section 5.1.2 for a quantitative discussion of this point). In this instance the particle diameter was approximated as that corresponding to the mean of the 120-140 mesh size fraction charged to the Mark II-A. Substitution of this 0.0128 cm average size into Equation 5.1 yielded a porosity estimate of $\epsilon = 0.116$.

At first glance this value - which is only about 1/3 of that typically reported for uncompressed beds (V1) and $\approx 1/2$ of that reported by Yee (Y1) for his compressed beds - appears to be quite low. However, it agrees remarkably well with the estimate of $\epsilon = 0.117$ generated from an independent analysis of the impulse response data discussed in Section 5.2. The consistency of these estimates suggests that the lubrication and greater initial uniformity of the wet-packed bed facilitated a greater degree of compaction than might otherwise have been expected.

5.1.2 Porosity of the Sorbent Bed Compressed in the Mark II-B

Experimentally determined pressure drop/flow relationships for the packed and unpacked Mark II-B are presented in Figure 5-2. The much larger pressure drop observed across the Mark II-B (≈ 10 times that reported in Figure 5-1 for the Mark II-A) indicates that major differences existed between the Mark II-A and II-B with respect to either their peripherals or the properties of the sorbent beds compressed within (recall F-20 alumina was used in the Mark II-A while F-1 was charged to the II-B).

FIGURE 5-2
FLOW vs PRESSURE DROP DATA FOR THE MARK II-B
(POROSITY ESTIMATED @ 0.06 FOR AN AVERAGE PARTICLE DIAMETER OF 0.015 CM)

The two additional curves included in Figure 5-2 were needed because of an inability to hold the spacer plate tightly in place prior to packing the Mark II-B. The gap remaining between the spacer plate and the cap caused erroneously low pressure drops across the unpacked device. This problem was addressed by generating pressure drop data for the unpacked Mark II-B prior to installation of the spacer plate. The resulting curve, denoted as that for the unpacked Mark II-B in Figure 5-2, reflects only the pressure drop across the gas inlet, the inner septum and the outlet fittings. A separate pressure drop curve was then calculated for the microgroove

system impressed on the spacer plate using Equation 4.1. The difference between the pressure drop curve for the packed Mark II-B and that resulting from the summation of measured and calculated peripheral effects was assumed to represent that portion of the total system pressure drop attributable to the compressed bed.

Equation 5.1 was once again fit to the pressure drop data assuming that the average particle diameter was consistent with that of the mesh size charged to the receiver (100-120 mesh F-1 Alumina with $d_p = 0.015$ cm). In this case the larger pressure drop measured across the Mark II-B resulted in a porosity estimate of $\epsilon = 0.055$. Since this value was only 1/2 of that determined for the similarly compressed bed in the Mark II-A, it was judged to be unreasonably low.

Likely causes of the high pressure drop across the Mark II-B and the resulting low porosity estimate include microgroove pluggage (such as that which necessitated revision of packing procedures as discussed in Section 4.3.2) and an inaccurate estimate of sorbent particle size. The impact of pluggage was evaluated by using Equation 4.1 to quantify the increase in pressure drop expected across the microgroove system for assumed percentages of blockage. Equation 5-1 was then re-fit to the reduced pressure drop contribution attributable to the compressed bed. This analysis, which is summarized in Table 5-1, revealed that considerable blockage would have been required to reconcile the pressure drop data with a believable porosity estimate. In fact, over 90% of the microgrooves would have to have been plugged to reduce the pressure drop contribution attributed to the packed bed sufficiently to double the interstitial porosity estimate to a believable value of ≈ 0.1 .

Table 5-1

Impact of Microgroove Pluggage on Porosity Estimates from Pressure Drop Data

% Microgroove Pluggage	Revised Porosity Estimate
0	0.055
20	0.056
50	0.057
75	0.060
90	0.080

The most likely cause of the low porosity estimate involves uncertainty in the determination of sorbent particle diameter by sieving. This procedure probably yielded an accurate value for the uncompressed particles. However, the data presented in Table 4-3 suggests that since nearly 60% of the alumina particles in a given size fraction fractured under a load of 2400 psi, a large percentage would also have fractured during compression to 10,000 psi in the Mark II-B. Table 5-2 documents variations in the porosity estimate that would result from decreases in d_p due to particle attrition. Note that a 50% decrease in particle diameter raises the porosity estimate by nearly 60%, and that a "reasonable" estimate (consistent with the 0.116 value determined for the Mark II-A) is obtained if the average diameter of the particles fractured during compression falls between 1/2 and 1/4 of the value of d_p determined by sieving.

Table 5-2

Impact of Particle Diameter on Porosity Estimation from Pressure Drop Data

d_p	COMMENTS	ϵ
d_p	assumes no breakage	0.055
1/2 d_p	assumes all particle break in half	0.086
1/4 d_p	assumes particles break in quarters	0.131

5.1.3 Porosity of the Axial Flow Bed

The larger pressure drops encountered across axial flow columns requires that the compressibility of the mobile phase be considered when fitting experimental data to theoretical relations. Hence the interstitial porosity of the 6 foot, 1/8" ID axial flow column used here was estimated by fitting pressure drop data to the following non-linear relation (B2):

$$P_1^2 - P_2^2 = \frac{2zR_g G^2 T}{g_c M} \left[\ln \left(\frac{\bar{v}_2}{\bar{v}_1} \right) + \frac{2f_m L (1 - \epsilon)^{3-n}}{\phi_s^{3-n} \epsilon^3 D_p} \right] \quad (Eq. 5.2)$$

Here the subscripts "1" and "2" denote quantities measured at upstream and downstream locations, respectively, z is the compressibility factor of the fluid, R_g is the gas constant, G is the superficial mass velocity based on the cross sectional area of the empty flow chamber, T is the absolute temperature, $\bar{v}$ is the specific volume of

the mobile phase, f_m is a friction factor, d_p is the particle diameter and L is the length of the packed bed. The shape factor, ϕ , is a correction applied to non-spherical particles, while the exponent "n" ($= 1$) is dependent on the particle Reynolds number.

Pressure drop data collected for the axial flow column used in subsequent chromatographic experiments is documented in Figure 5-3. The interstitial porosity of the stationary phase charged to this column was estimated at $\epsilon = 0.299$ by fitting the pressure drop data to Equation 5.2. This estimate is consistent with values typically reported for randomly packed beds (V1). Note that the porosity estimation procedure is somewhat simplified for axial flow columns since there is no need to compensate for peripherals or particle attrition (since the bed is uncompressed).

FIGURE 5-3
FLOW vs PRESSURE DROP DATA FOR THE AXIAL FLOW COLUMN
(POROSITY ESTIMATED @ 0.30 FOR AN AVERAGE PARTICLE DIAMETER OF 0.015 CM)

5.2 Modeling and Analysis of Impulse Response Experiments

Impulse response experiments were conducted exclusively in the Mark II-A radial flow chromatograph. Response data was generated by injecting methane into a helium carrier gas flowing radially through a

compressed bed of F-20 alumina. The Mark II-A and its peripherals were maintained at 100° C within the oven of a standard chromatograph (Bendix Model 2000). Data was collected at flowrates of 60, 80 and 100 standard cubic centimeters per minute.

The automated procedure used to record experimental data is depicted schematically in Figure 5-4. The process began with the transmission of an analogue output from the FID detector of the chromatograph to a Hewlett Packard 3392-A integrator. This device not only plotted the continuous output from the detector, but also split the signal into a series of paired data points consisting of an area "slice" and a corresponding time. Summation of these slices yielded the total area under the curve, which was actually the total system response. The data pairs were transferred in hexidecimal format to a Zenith Z-180 laptop computer and recorded on 3-1/2" floppy media for subsequent use.

FIGURE 5-4

AUTOMATED DATA COLLECTION SYSTEM

Slice width was varied between 0.5 and 1.0 seconds depending on the breadth of the response peaks. The paired data points were recalled from the floppy disks as required and converted via a Pascal program (attached in Appendix II) to decimal format. Subsequent division of each area slice by the relevant time width yielded the desired concentration vs time relationship.

A typical experimental response curve for the methane-helium-alumina system is presented in Figure 5-5. The distinguishing features of this curve include a rapid initial rise - or shock front - and a diffuse decline with a significant amount of tailing.

Efforts to fit Rice's negligible dispersion model:

$$\frac{C(X, \theta)}{C_o} = \sqrt{\frac{K_s X}{\theta \xi^2}} \exp\left[-\frac{(K_s X + \theta)}{\xi}\right] I_1\left[\sqrt{\frac{4K_s X \theta}{\xi^2}}\right] \quad (Eq. 3.13)$$

where

$$\xi = R_p \left[\frac{K_s}{3k_m} + \frac{R_p}{15D_s} \right] \quad (Eq. 3.10)$$

to such data met with limited success. The results of one such fit, generated by performing a Hooke and Jeeves pattern search to find values for the equilibrium sorption constant (K_s) and the combined resistance parameter (ξ) that minimized the integral absolute error (IAE) between theory and experiment, are presented in Figure 5-6. Note that fundamental difference between the nearly Gaussian response predicted by the negligible dispersion theory and the obviously skewed experimental data. This poor fit suggests that the negligible dispersion model does not accurately reflect the physical phenomena occurring within the adsorber. Moreover, the value of the combined resistance parameter, $\xi \approx 1.43$ seconds, is three orders of magnitude greater than the anticipated 10^{-3} seconds (see Section 3.2.1).

Giddings (G2) listed potential causes of tailing such as that observed in Figure 5-6 as excessive dead volume, the presence of non-uniform adsorption sites, and too large a sample size. Attempts to reduce this skew by decreasing solute injection size from 5 μ l to 1 μ l failed, and the effect of non-uniform adsorption sites was judged insignificant (since minimal skew is observed when separating hydrocarbons over alumina

FIGURE 5-5

EXAMPLE OF THE IMPULSE RESPONSE DATA GENERATED
FOR THE $\text{CH}_4/\text{He}/\text{Al}$ SYSTEM IN THE MARK II-A

FIGURE 5-6

TYPICAL POOR FIT FOR RICE'S NEGLIGIBLE DISPERSION MODEL

in conventional axial flow columns). The tailing problem was thus initially attributed to the excessive dead volume of the Mark II-A, and an attempt was made to add dead volume effects to Rice's original dispersion-free model.

The extension was achieved by modeling the mixing presumed to occur within the dead volume as that resulting from an ideal CSTR. Multiplication of Rice's original Laplace solution by the transfer function for an ideal CSTR allowed the negligible dispersion/dead volume model to be expressed as a convolution integral in the time domain:

$$\frac{C(X, \theta)}{C_o} = \int_0^\theta \sqrt{\frac{K_r X}{\theta \xi^2}} \exp\left[\frac{-K_r X + \theta}{\xi}\right] I_1\left[\sqrt{\frac{4K_r X \theta}{\xi^2}}\right] K_{CSTR} \exp\left(\frac{-\theta - \tau}{\tau_{CSTR}}\right) d\tau \quad (Eq. 5.3)$$

Note that Equation 5.2 retains the original relation for the impulse response along with multiplying gain (K_{CSTR}) and lag ($\exp [(-\theta - \tau)/(\tau_{CSTR})]$) terms.

Figure 5-7 confirms that a slight improvement was achieved when the dead volume addition to the negligible dispersion model was fitted to the experimental data (the IAE was reduced from 25% to 22%). However, the resistance term ξ still gave unrealistically high values with no physical meaning (see Section 3.2.1). Since neither model was able to match the experimentally observed tails or produce realistic estimates of ξ , it was concluded that the negligible dispersion model could not accurately quantify the physical phenomena occurring within the Mark II-A.

The limitations of the negligible dispersion model are best recognized through consideration of the work of Levenspiel and Smith (L2). They determined that mobile phase diffusion and related dispersion processes will skew the response of an axial flow column to an impulse input if:

$$Pe_{a,L} = \frac{v_{i,a} L}{D_{eff}} < 100 \quad (Eq. 5.4)$$

The Peclet number of interest here, $Pe_{a,L}$, is based on the length of the column under consideration. The skew results because the Gaussian distribution of solute with respect to axial position within the column exposes individual solute elements to diffusional motion for different lengths of time.

FIGURE 5-7
POOR FIT ACHIEVED WITH NEGLIGIBLE DISPERSION/GAIN-LAG MODEL

Further consideration of the operating conditions encountered in the Mark II-A suggested that since the ratio of convective to diffusive motion was quite low ($\frac{j_s}{2D_{AB}} < 5$), the effects of mobile phase diffusion might be significant. This conclusion led to the development of the Sorption Equilibria/Mobile Phase Dispersion model presented in Section 3.2.2, and its mathematical expression as:

$$\left(\frac{C}{C_o}\right)_I = \sum_n \frac{\left(\frac{1}{2}\right)^{p-2} \lambda_n^p}{\Gamma(p) J_p(\lambda_n)} \exp(-\lambda_n^2 \tau) \quad (\text{Eq. 3.38})$$

The reconciliation of theory and experiment afforded by the mobile phase dispersion model is evident in the improved curve fit of Figure 5-8. Parameter estimation was accomplished using the Hooke and Jeeves pattern search technique to find values of the Peclet number (p) and time constant (τ), that minimized the IAE between theory and experiment. It is clear from inspection of these curves that the decrease in IAE to less than 10% results from the ability of the mobile phase dispersion model to accurately predict the occurrence of both the "shock" front and the diffuse decline.

FIGURE 5-8

IMPROVED FIT ACHIEVED WITH MOBILE PHASE DISPERSION MODEL

Model parameters generated for curve fits of several impulse response experiments conducted on this same bed are summarized in Table 5-3. Curve fits for experimental runs at two lower mobile phase flowrates are presented in Figures 5-9 and 5-10. Important observations concerning these fits and optimized system parameters include:

- The optimized values for the Peclet number ($p = Q/4\pi h\epsilon D_{eff}$) reflect the required positive correlation with the mobile phase flowrate.
- Optimized values for τ_r are independent of velocity, as required by definition. With the exception one high ($\tau_r = 246.69$ sec) and one low ($\tau_r = 252.68$ sec) value, the estimates of τ_r consistently fell within a narrow range such that $175 \leq \tau_r \leq 200$.
- The consistently low IAE's confirm importance of radial dispersion for the experimental conditions considered.
- The consistency of the optimized parameters improved with increasing mobile phase flowrate.

This last observation - which is somewhat of a surprise - may simply reflect improved fluid distribution or a "dilution" of the disturbance caused by sample injection with increasing mobile phase flowrate.

FIGURE 5-9

IMPROVED FIT ACHIEVED WITH MOBILE PHASE DISPERSION MODEL

FIGURE 5-10

IMPROVED FIT ACHIEVED WITH MOBILE PHASE DISPERSION MODEL

Table 5-3

Summary of Parameter Estimation Analyses Performed on Impulse Response Data

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet # $p = \frac{j_v}{2D_{eff}}$	Time Constant $\tau_r = \left[\frac{K_s + \eta}{D_{eff}\eta} \right] R_o^2$ (sec)	IAE (%)
80829M06	1.3214	2.77	246.69	6.10
80829M07	1.3214	2.00	194.44	9.26
80829M08	1.3214	1.68	175.94	11.23
80829M09	1.7618	1.90	151.68	12.67
80829M10	1.7618	2.83	198.30	8.39
80829M11	1.7618	2.62	186.35	9.10
80829M12	2.2023	3.14	175.80	8.44
80829M13	2.2023	3.20	180.30	7.83
80829M14	2.2023	3.20	180.26	7.82

The interstitial porosity, ϵ , of the compressed bed was derived from the slope of the Peclet number vs mobile phase flowrate plot presented in Figure 5-11. The definition of the Peclet number requires that the slope, m , of this line equals:

$$m = \frac{1}{4\pi h \epsilon D_{eff}} \quad (Eq. 5.5)$$

For $m = 1.14599 \text{ sec/cm}^3$ (as determined by linear regression) and $h = 0.4763 \text{ cm}$, the product ϵD_{eff} was found to equal 0.1144. Approximation of D_{eff} as the binary diffusion coefficient of methane in helium, $D_{AB} = 0.98 \text{ cm}^2/\text{sec}$ (per the Gilliland-type relation discussed in reference L6), yielded a porosity estimate of $\epsilon = 0.117$. The consistency of this estimate and the 0.116 value determined independently from the pressure drop data discussed in Section 5.1.1 suggests that Taylor dispersion and other maldistribution effects were indeed negligible in the Mark II-A, so that D_{eff} was essentially molecular in origin.

The magnitude of the equilibrium sorption constant was determined via manipulation of the time constant definition:

$$K_s = \eta \left[\frac{\tau_r D_{eff}}{R_o^2} - 1 \right] \quad (Eq. 5.6)$$

The known value of $R_o = 3.81$ cm, calculated value of $D_{eff} = 0.98$ cm²/sec, experimental estimate of $\epsilon = 0.117$ (or $\eta = 0.113$), and average value for $\tau_r = 184.48$ (excluding previously noted high and low values) yielded an estimate for K_s of 1.52. This estimate for F-20 alumina was subsequently found to lie within 20% of that determined for methane on F-1 alumina via the axial flow chromatographic experiments discussed in Section 5.3.1.

FIGURE 5-11
IMPULSE RESPONSE EXPERIMENTS IN THE MARK II-A:
VARIATION OF PECLET NUMBER WITH Q

A statistical analysis was also performed on the impulse response data to facilitate performance comparisons via conventional measures of chromatographic performance such as the height equivalent to a theoretical plate, or HETP. The results of this analysis are summarized in Table 5-4. The mean residence time, t_m , was determined as the first moment of each peak:

$$t_m = \frac{\int_0^{\infty} C_m t dt}{\int_0^{\infty} C_m dt} \quad (\text{Eq. 5.7})$$

while the number of plates was determined by dividing the second moment by the square of the mean residence time and multiplying by the length of the flow path (R6):

$$N_p = (R_o - R_l) \frac{\sigma_t^2}{t_m^2} = (R_o - R_l) \frac{\int_0^{\infty} C_m (t - t_m)^2 dt}{t_m^2 \int_0^{\infty} C_m dt} \quad (\text{Eq. 5.8})$$

In the case of the Mark II-A, $R_o - R_l = 3.49$ cm.

Table 5-4

Statistical Analysis of Impulse Response Peaks

Run ID	Volumetric Flow, Q (cm ³ /sec)	Residence Time, t_m (sec)	HETP, cm
80829M06	1.3214	22.84	0.85
80829M07	1.3214	25.35	1.19
80829M08	1.3214	27.88	1.45
80829M09	1.7618	21.45	1.45
80829M10	1.7618	18.66	1.11
80829M11	1.7618	18.89	1.11
80829M12	2.2023	14.86	0.93
80829M13	2.2023	14.66	0.81
80829M14	2.2023	14.66	0.81

As expected, a strong positive correlation was observed between t_m and Q. Unfortunately any trend relating HETP to flowrate was less well defined. The smallest HETP values were observed at the highest mobile phase flowrate, a trend anticipated by mobile phase dispersion model predictions of decreasing band width with increased flow. Such behavior, which reflects an increase in Peclet number with increasing flowrate, was discussed in detail in Section 3.2.2. It is also interesting to note that HETP's determined for the Mark II-A, though slightly larger, were of the same order of magnitude as the HETP's reported for the axial flow column discussed below.

5.3 Modeling and Analysis of Chromatographic Separations

Chromatographic separations were performed on both a conventional axial flow column and the Mark II-B radial flow prototype that had been modified to reduce dead volume. Alcoa F-1 activated alumina, which is widely used for the separation of light hydrocarbons, served as the stationary phase on which a 25 mole% mixture of methane in n-butane was resolved. Carrier gas (He) flowrates and sorbent bed temperatures were varied in order to generate the experimental data needed to confirm theoretical trends. Specific test conditions are summarized in Table 5-5.

Table 5-5

Experimental Conditions Used for Chromatographic Experiments

Experimental Condition	Axial Flow Column	Mark II-B Radial Flow Bed
Injector Temperature, °C	200	200
Detector Temperature, °C	200	200
Bed Temperatures, °C	100, 115	100, 115
Helium Flowrates, cc/min (@ STP)	50, 75, 100	80, 100, 120

5.3.1 Chromatographic Separations in an Axial Flow Column

Figure 5-12 depicts a typical separation achieved with the 6 foot long, 1/8 inch ID axial flow column. The narrow, widely separated solute bands are characteristic of all the axial flow experiments. Such narrow peaks required that the slice width employed by the electronic data collection system be reduced to 0.2 seconds (see Section 5.2). Larger slice widths generated too few points for accurate modelling of the narrow methane peak.

The axial flow column was operated under conditions such that the column Peclet number, $Pe_{a,L}$, was always » 200. Hence convective motion was presumed to dominate dispersion (see Equation 5.4 in Section 5.2), and Rice's negligible dispersion model:

$$\frac{C(X, \theta)}{C_o} = \sqrt{\frac{K_s X}{\theta \xi^2}} \exp\left[-\frac{(K_s X + \theta)}{\xi}\right] I_1\left[\sqrt{\frac{4K_s X \theta}{\xi^2}}\right] \quad (Eq. 3.13)$$

was adopted for data analysis.

Equation 3.13 was fit to several sets of experimental data using a Hooke and Jeeves pattern search designed to locate the values of K_p and ξ that minimized the IAE between theory and experiment. Graphical presentations of the fit obtained for the peaks presented in Figure 5-12, as well as similar fits generated for data collected at a higher velocity and higher operating temperatures, are presented in Figures 5-13 through 5-16. Experimental values of K_p and ξ deduced from the search routine for these and other axial flow experiments are summarized in Tables 5-6a, 5-6b, 5-7a and 5-7b. The visually consistent curve fits and uniformly low IAE's (generally less than 3% for both peaks at all temperatures and flowrates considered) confirm the ability of the negligible dispersion model to accurately describe the phenomena occurring within the column.

FIGURE 5-12
TYPICAL CHROMATOGRAPHIC RESPONSE FROM AXIAL FLOW COLUMN

(RUN ID: AXIAL-101, VOLUMETRIC FLOW: 50.8 CC/MIN (STP), BED TEMPERATURE: 100°C)

FIGURE 5-13
 NEGLIGIBLE DISPERSION MODEL:
 FIT TO AXIAL FLOW CHROMATOGRAPHIC DATA

(RUN ID: AXIAL-101, VOLUMETRIC FLOW: 50.8 CC/MIN (STP), BED TEMPERATURE: 100°C)

FIGURE 5-14
 NEGLIGIBLE DISPERSION MODEL:
 FIT TO AXIAL FLOW CHROMATOGRAPHIC DATA

(RUN ID: AXIAL-108, VOLUMETRIC FLOW: 102.3 CC/MIN (STP), BED TEMPERATURE: 100°C)

FIGURE 5-15
NEGLIGIBLE DISPERSION MODEL:
FIT TO AXIAL FLOW CHROMATOGRAPHIC DATA

(RUN ID: AXIAL-65, VOLUMETRIC FLOW: 50.5 CC/MIN (STP), BED TEMPERATURE: 115°C)

FIGURE 5-16
NEGLIGIBLE DISPERSION MODEL:
FIT TO AXIAL FLOW CHROMATOGRAPHIC DATA

(RUN ID: AXIAL-56, VOLUMETRIC FLOW: 102.3 CC/MIN (STP), BED TEMPERATURE: 115°C)

Table 5-6a

*Experimental Results Obtained for Chromatographic Separations
on an Axial Flow Column*

Operating Temperature: 100 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /min @ STP)	K _s	ξ, sec	IAE (%)
AXIAL-100	50.8	1.3036	0.0413	2.29
AXIAL-101	50.8	1.2952	0.0405	2.07
AXIAL-102	50.8	1.2909	0.0399	1.68
AXIAL-103	76.7	1.2674	0.0426	1.92
AXIAL-104	76.7	1.2671	0.0422	1.80
AXIAL-105	76.7	1.2654	0.0417	1.58
AXIAL-106	102.3	1.2595	0.0450	1.82
AXIAL-107	102.3	1.2674	0.0452	2.55
AXIAL-108	102.3	1.2820	0.0464	2.08
AXIAL-109	102.3	1.2639	0.0445	1.71

Table 5-6.b

*Experimental Results Obtained for Chromatographic Separations
on an Axial Flow Column*

Operating Temperature: 100 °C Component: Butane

Run ID	Volumetric Flow, Q (cm ³ /min @ STP)	K _s	ξ, sec	IAE (%)
AXIAL-100	50.8	28.5042	1.0627	3.24
AXIAL-101	50.8	28.4976	1.0672	3.25
AXIAL-102	50.8	28.4696	1.0654	3.23
AXIAL-103	76.7	28.0937	1.1695	3.20
AXIAL-104	76.7	28.0957	1.1681	3.16
AXIAL-105	76.7	28.1127	1.1645	3.11
AXIAL-106	102.3	27.8434	1.2336	3.12
AXIAL-107	102.3	27.8719	1.2286	2.97
AXIAL-108	102.3	27.8982	1.2247	3.11
AXIAL-109	102.3	27.8610	1.2316	3.14

Table 5-7.a

*Experimental Results Obtained for Chromatographic Separations
on an Axial Flow Column*

Operating Temperature: 115 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /min @ STP)	K _s	ξ, sec	IAE (%)
AXIAL-34	50.5	1.2485	0.0372	1.47
AXIAL-65	50.5	1.2458	0.0370	1.81
AXIAL-66	50.5	1.2468	0.0372	2.06
AXIAL-45	76.4	1.2161	0.0397	6.03
AXIAL-47	76.4	1.2314	0.0395	1.74
AXIAL-50	76.9	1.2461	0.0387	2.02
AXIAL-54	102.3	1.2107	0.0405	2.20
AXIAL-55	102.3	1.2097	0.0398	2.24
AXIAL-56	102.3	1.2084	0.0402	1.90
AXIAL-63	102.3	1.2128	0.0408	1.56

Table 5-7.b

*Experimental Results Obtained for Chromatographic Separations
on an Axial Flow Column*

Operating Temperature: 115 °C Component: Butane

Run ID	Volumetric Flow, Q (cm ³ /min @ STP)	K _s	ξ, sec	IAE (%)
AXIAL-34	50.5	19.1563	0.6820	3.05
AXIAL-65	50.5	19.1940	0.6845	2.98
AXIAL-66	50.5	19.1962	0.6867	3.13
AXIAL-45	76.4	18.7970	0.7419	2.90
AXIAL-47	76.4	18.9373	0.7571	3.41
AXIAL-50	76.9	18.9357	0.7521	3.07
AXIAL-54	102.3	18.7436	0.7884	3.08
AXIAL-55	102.3	18.7478	0.7867	3.04
AXIAL-56	102.3	18.7556	0.7854	2.87
AXIAL-63	102.3	18.7829	0.7872	2.64

The definition of ξ :

$$\xi = R_p \left[\frac{K_s}{3k_m} + \frac{R_p}{15D_s} \right] \quad (\text{Eq. 3.10})$$

suggests that the larger sorption constant and lower diffusivity of butane relative to methane should result in larger mass transfer resistances. This expectation is borne out by the experimental values of ξ .

The contribution of the film resistance term ($R_p K_s / 3k_m$) to the total mass transfer resistance is examined in Table 5-8. The mass transfer coefficient, k_m , was estimated from the Frössling relation, which expresses the Sherwood number as a function of the Schmidt number and the Reynolds number based on particle diameter (W4):

$$Sh = \frac{k_m d_p}{D_{AB}} = 2.0 + 0.522 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad (\text{Eq. 5.9})$$

Note that calculated values of the film resistance term are $\approx$ three orders of magnitude less than the experimentally determined ξ 's. This indicates that film resistance was negligible under the conditions studied, and that diffusion within the sorbent particles controlled the response.

Table 5-8

Contribution of Film Resistance to ξ in an Axial Flow Chromatograph

Solute	Temp (°C)	Q (cc/min)	Re	Sc	k_m (cm/sec)	$\frac{R_p K_s}{3k_m}$, (sec)	ξ^a , (sec)
CH ₄	100	50.8	0.16	2.84	94.05	0.00003	0.0429
C ₄ H ₁₀	100	50.8	0.16	5.60	49.30	0.00143	1.1616
CH ₄	115	102.3	0.24	2.65	103.32	0.00006	0.0391
C ₄ H ₁₀	115	102.3	0.24	5.22	54.44	0.00087	0.7452

^a - Determined from experimental data

The possible contributors to solid phase diffusion were listed in Section 3.2 as surface, Knudsen and intrapore diffusion. Consideration of these mechanisms when performing a mass balance around a solute particle indicates that:

$$\epsilon_p \frac{\partial C}{\partial t} + (1 - \epsilon_p) \frac{\partial q}{\partial t} = D_p \epsilon_p \nabla^2 C + D_{surf} (1 - \epsilon_p) \nabla^2 q \quad (Eq. 5.10)$$

Here ϵ_p refers to intraparticle porosity, the constant D_p accounts for diffusional motion resulting from Knudsen diffusion, pore diffusion, or a combination of the two, and D_{surf} addresses surface diffusion along the pore walls. Retaining the definition of the equilibrium sorption constant outlined in Section 3.2, $K_s = q/C^* = q/C$, we have:

$$\left[\frac{\epsilon_p}{K_s} + (1 - \epsilon_p) \right] \frac{\partial q}{\partial t} = \left[\frac{D_p \epsilon_p}{K_s} + D_{surf} (1 - \epsilon_p) \right] \nabla^2 q \quad (Eq. 5.11)$$

The total solid phase diffusivity, D_s , may thus be expressed as:

$$D_s = \frac{D_p \epsilon_p + D_{surf} (1 - \epsilon_p) K_s}{\epsilon_p + (1 - \epsilon_p) K_s} \quad (Eq. 5.12-a)$$

so that Equation 5.11 simplifies to:

$$\frac{\partial q}{\partial t} = D_s \nabla^2 q \quad (Eq. 5.12-b)$$

Solute concentrations are generally too low in gas chromatographic systems to generate sufficient surface coverage for formation of the two-dimensional solute layer needed for surface diffusion. Hence D_{surf} is assumed to be ≈ 0 , and the expression for the solid phase diffusion coefficient reduces to:

$$D_s = \frac{D_p}{1 + \left(\frac{1 - \epsilon_p}{\epsilon_p} \right) K_s} \quad (Eq. 5.13)$$

Slattery (S6) indicates that the pore diffusion constant, D_p , can be estimated from the following additive resistance relationship:

$$D_p = \left[\frac{1}{D_{k,eff}} + \frac{1}{D_{AB,eff}} \right] \quad (Eq. 5.15)$$

where the effective Knudsen diffusivity through micropores is given as:

$$D_{k,eff} = \frac{\epsilon_{p,k}}{\tau_p} \frac{4}{3} r_m \left(\frac{2 RT}{\pi MW} \right)^{\frac{1}{2}} \quad (Eq. 5.16)$$

and the effective "bulk" diffusivity through larger fluid-filled pores is given as:

$$D_{AB,eff} = \frac{\epsilon_{p,AB}}{\tau_p} D_{AB} \quad (Eq. 5.17)$$

Here τ_p refers to particle tortuosity, MW is the molecular weight of the diffusing species and R is the appropriate gas constant. Note that the terms $\epsilon_{p,k}$ and $\epsilon_{p,AB}$ refer to that portion of the total intraparticle porosity applicable to Knudsen and bulk diffusion, respectively. The bulk diffusion coefficient, D_{AB} , is the binary diffusion coefficient for the solute of interest.

Assessment of the importance of Knudsen diffusion requires comparison of sorbent molecule pore diameters with the mean free path of the solute molecules. The mean free path is related to the diameter of these molecules, d_m , and their number per unit volume, n_m , is as follows (H8):

$$l_m = \frac{1}{\pi \sqrt{2} n_m d_m^2} \quad (Eq. 5.14)$$

Using the ideal gas law to estimate molecular concentrations at 100° C and an average operating pressure of 4 atmospheres, and the Lennard-Jones collision diameter to approximate d_m , the mean free paths of the methane and butane molecules are found to be 177.9 Å and 55.9 Å, respectively. Since these values are of the same order as the pore diameters reported in Table 4-4 (micropores ≤ 35 Å, macropores ≈ 177 Å), it is concluded that Knudsen effects will be significant.

Tables 5-9a and 5-9b document the favorable comparison of expected values of ξ with experiment. The calculated values were determined from Equations 3.10, 5.13 and 5.15. Alternate tortuosities of 3 and 4, consistent with the range of 2-4 reported by Slatterly (S6), were assumed. Note that $D_p \approx D_{k,eff}$, indicating that bulk diffusion contributes little to D_s , and Knudsen diffusion controls the response.

The agreement between theory and experiment is further substantiated by a sensitivity analysis. Since ξ is inversely proportional to D_s , and D_s is a function of both K_s and $D_{k,eff}$,

$$\frac{\xi_1}{\xi_2} = \frac{D_{s,2}}{D_{s,1}} = \left(\frac{D_{k,eff,2}}{1 + \left(\frac{1-e_p}{e_p} \right) K_{s,2}} \right) \left(\frac{1 + \left(\frac{1-e_p}{e_p} \right) K_{s,1}}{D_{k,eff,1}} \right) \quad (Eq. 5.18)$$

$D_{k,eff}$ has been shown to be the controlling resistance, so that according to Equation 5.16:

$$\frac{\xi_1}{\xi_2} = \frac{1 + \left(\frac{1-e_p}{e_p} \right) K_{s,1}}{1 + \left(\frac{1-e_p}{e_p} \right) K_{s,2}} \left(\frac{MW_1}{MW_2} \right)^{\frac{1}{2}} \quad (Eq. 5.19)$$

for solutes "1" and "2" at the same temperature, or:

$$\frac{\xi_{T1}}{\xi_{T2}} = \frac{1 + \left(\frac{1-e_p}{e_p} \right) K_{s,T1}}{1 + \left(\frac{1-e_p}{e_p} \right) K_{s,T2}} \left(\frac{T_2}{T_1} \right)^{\frac{1}{2}} \quad (Eq. 5.20)$$

for the same solute at two different temperatures.

A check of the experimental values summarized in Tables 5-6a through 5-7b confirms that, for the most part, these theoretical dependencies are followed. Considering the average of the first three experimental data points reported in each table, we find that the ratio of the methane resistance at 100 °C to that at 115 °C is 1.05, vs. a theoretical ratio of 1.10. A similar evaluation of the butane data contrasts an experimental ratio of 1.56 with a calculated value of 1.51. The agreement between the theory and experiment with respect to the ratio of the methane resistance to that for butane is not quite as good. The experimental ratios are 0.0369 at 100 °C and 0.0542 at 115 °C, vs. calculated ratios of 0.0293 and 0.0420.

Tables 5-9a and 5-9b
Comparison of Calculated and Experimental Values of ξ
Methane Data

Conditions	$D_{AB,eff}^a$ cm ² /sec	$D_{k,eff}^b$ cm ² /sec (x 10 ⁴)	D_p^c cm ² /sec (x 10 ⁴)	D_s^d cm ² /sec (x 10 ⁵)	Calculated ξ , sec	Measured ξ , sec	Difference %
100° C, $\tau_p = 3$	0.0521	6.49	6.41	12.58	0.0298	0.0429	30.54
100° C, $\tau_p = 4$	0.0390	4.87	4.81	9.44	0.0397	0.0429	7.46
115° C, $\tau_p = 3$	0.0558	6.62	6.55	13.26	0.0283	0.0391	27.62
115° C, $\tau_p = 4$	0.0419	4.97	4.91	9.94	0.0377	0.0391	3.58

Butane Data

Conditions	$D_{AB,eff}^a$ cm ² /sec	$D_{k,eff}^b$ cm ² /sec (x 10 ⁴)	D_p^c cm ² /sec (x 10 ⁴)	D_s^d cm ² /sec (x 10 ⁵)	Calculated ξ , sec	Measured ξ , sec	Difference %
100° C, $\tau_p = 3$	0.0265	3.41	3.37	3.70	1.0147	1.1616	12.65
100° C, $\tau_p = 4$	0.0199	2.56	2.53	2.77	1.3529	1.1616	16.47
115° C, $\tau_p = 3$	0.0284	3.48	3.44	5.58	0.6724	0.7452	9.77
115° C, $\tau_p = 4$	0.0213	2.61	2.58	4.18	0.8966	0.7452	20.32

^a - from Eq. 5.17 ^b - from Eq. 5.16 ^c - from Eq. 5.15 ^d - from Eq. 5.13

The consistency among calculated and experimental values of ξ and expected vs. actual resistance ratios are strong indications that Knudsen diffusion provides the most significant resistance to mass transfer in the axial flow column. However, the optimized values of ξ do reflect a weak positive correlation with interstitial fluid velocity that the above analysis does not predict. At this point it is unclear whether this correlation reflects an as yet unidentified resistance that is not addressed by the negligible dispersion model, or whether it simply reflects experimental error.

Finally, it is noted that a statistical analysis of the axial response peaks indicated that the HETP's for both methane and butane were lower - but of the same order - as those reported for the radial flow, impulse response experiments discussed in Section 5.2. The HETP's for methane varied between 0.5 and 0.8 cm at 115 °C, and between 0.7 and 0.9 cm at 100 °C. Plate heights for butane ranged from 0.6 to 1.0 cm at both 115 and 100 °C.

5.3.2 Chromatographic Separations in the Mark II-B

The studies discussed below are believed to be the first ever directed towards the development and modeling of gas phase, elution mode chromatographic techniques that employ a pressure differential to establish uniform radial flow through a sorbent bed. They were conducted in the Mark II-B radial flow chromatograph at bed temperatures of 100 °C and 115 °C and mobile phase flowrates of 75, 100 and 125 standard cc/min. The same 25% methane/75% n-butane mixture separated in the axial flow column served as the test case for the radial flow experiments. Both the inward and outward flow configurations were considered in an attempt to verify the performance enhancements of the inward flow configuration predicted in Section 3.2.2.3.

5.3.2.1 The Outward Flow Configuration

Sample traces of the chromatographic separations achieved with the Mark II-B while operating in the outward flow configuration are presented in Figures 5-17, 5-18, 5-19 and 5-20. The theoretical response curves superimposed upon the experimental data were generated by substituting optimized values of $\tau_r = R_o^2 \left(\frac{K_r + \eta}{\eta D_{eff}} \right)$ and $p = \frac{Q}{4\pi h e D_{eff}}$ into the mobile phase dispersion model. These parameters were located with a Hooke and Jeeves pattern search designed to minimize the IAE between theory and experiment. The Fortran programs used to conduct the search are attached in Appendix II.

Figures 5-17 and 5-18 depict operation at 115 °C, while Figures 5-19 and 5-20 were generated at 100 °C. The band broadening observed for the latter two cases reflects the larger equilibrium sorption constants, and consequently increased time constants, encountered at the lower operating temperature. Also note that, under conditions of constant temperature, the higher mobile phase flowrate generated a sharper response (contrast Figures 5-18 and 5-20 with 5-17 and 5-19). This trend results from the increased dominance of convection over dispersion as the system Peclet number was increased. Both of these observations are consistent with the performance predictions generated from the mobile phase dispersion model in Section 3.2.2 (see Figures 3-3 and 3-4).

Experimental Peclet number and time constant values are summarized in Tables 5-10a, 5-10b, 5-11a and 5-11b for all of the chromatographic separations conducted with the outward flow configuration. It is instructive to inspect the ratios of these fitted parameters, since

$$\frac{p_1}{p_2} = \left(\frac{j_v}{2D_{eff,1}} \right) \left(\frac{2D_{eff,2}}{j_v} \right) = \frac{D_{eff,2}}{D_{eff,1}} \quad (Eq. \ 5.21)$$

and

$$\frac{\tau_{r,1}}{\tau_{r,2}} = \left(\frac{K_{s,1} + \eta}{K_{s,2} + \eta} \right) \frac{D_{eff,2}}{D_{eff,1}} \quad (Eq. \ 5.22)$$

FIGURE 5-17
 MOBILE PHASE DISPERSION MODEL
 FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B

(RUN ID: FINRAD53, OUTWARD FLOW, VOLUMETRIC FLOW: 1.37 CC/SEC, BED TEMPERATURE: 115° C)

FIGURE 5-18
 MOBILE PHASE DISPERSION MODEL
 FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B

(RUN ID: FINRAD82, OUTWARD FLOW, VOLUMETRIC FLOW: 1.91 CC/SEC, BED TEMPERATURE: 115° C)

FIGURE 5-19
MOBILE PHASE DISPERSION MODEL
FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B

(RUN ID: FINRAD25, OUTWARD FLOW, VOLUMETRIC FLOW: 1.36 CC/SEC, BED TEMPERATURE: 100°C)

FIGURE 5-20
MOBILE PHASE DISPERSION MODEL
FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B

(RUN ID: FINRAD32, OUTWARD FLOW, VOLUMETRIC FLOW: 1.92 CC/SEC, BED TEMPERATURE: 100°C)

For the case of a compressed bed $K_s \gg \eta$, and Equation 5.22 reduces to:

$$\frac{\tau_{r,1}}{\tau_{r,2}} = \left(\frac{K_{s,1}}{K_{s,2}} \right) \left(\frac{D_{eff,2}}{D_{eff,1}} \right) = \left(\frac{K_{s,1}}{K_{s,2}} \right) \left(\frac{p_1}{p_2} \right) \quad (Eq. 5.23)$$

The equilibrium sorption constant ratio for any two solutes can thus be determined from fitted time constant and Peclet number values as follows:

$$\frac{K_{s,1}}{K_{s,2}} = \left(\frac{\tau_{r,1}}{\tau_{r,2}} \right) \left(\frac{p_2}{p_1} \right) \quad (Eq. 5.24)$$

Note that Equation 5.24 is essentially independent of the possibly error-prone estimate of interstitial porosity from pressure drop vs. flow data.

Tables 5-12a and 5-12b summarize values of the methane/n-butane equilibrium sorption constant ratio determined from Equation 5.24 for each of the separations performed in the Mark II-B. These ratios are seen to agree remarkably well with those determined from the axial flow experiments discussed in Section 5.3.1.

Figures 5-21 and 5-22 depict the dependence of the optimized methane Peclet number data on flowrate at temperatures of 115 °C and 100 °C, respectively. As was noted in Section 5.2 the definition of the Peclet number requires that such a curve pass through zero with a slope equal to $1/(4\pi h \epsilon D_{eff})$. Assuming that $D_{eff} \approx D_{AB}$, as was verified in the case of methane by the impulse response data discussed in Section 5.2, the slopes determined by simple linear regression are seen to yield identical porosity estimates of $\epsilon = 0.12$. This value is consistent with estimates generated for other similarly compressed beds.

Tables 5-10a, 5-10b

Experimental Results for Outward Flow Separations on the Mark II-B Radial Flow Bed

Operating Temperature: 115 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FINRAD52	1.3656	3.09	336.79	7.12
FINRAD53	1.3656	3.20	347.26	7.15
FINRAD83	1.3630	3.18	347.42	6.83
FINRAD62	1.6618	3.26	303.12	8.49
FINRAD64	1.6618	4.15	367.42	5.04
FINRAD65	1.6618	3.63	328.43	6.95
FINRAD88	1.6607	3.69	332.73	6.74
FINRAD79	1.9147	4.51	349.37	5.53
FINRAD80	1.9147	3.78	301.17	6.6
FINRAD82	1.9147	4.05	315.39	6.17
FINRAD89	1.9147	4.17	327.42	6.65
FINRAD90	1.9138	4.14	327.42	6.27

Operating Temperature: 115 °C Component: Butane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FINRAD52	1.3656	2.87	5109.76	2.32
FINRAD53	1.3656	2.90	5148.82	2.13
FINRAD83	1.3630	3.04	5377.96	1.30
FINRAD62	1.6618	3.62	5214.68	2.10
FINRAD64	1.6618	3.69	5275.78	1.71
FINRAD65	1.6618	3.34	4858.43	1.58
FINRAD88	1.6607	3.32	4868.28	1.45
FINRAD79	1.9147	4.41	5341.71	2.79
FINRAD80	1.9147	3.76	4694.13	1.35
FINRAD82	1.9147	3.73	4720.38	1.46
FINRAD89	1.9147	3.48	4476.56	1.82
FINRAD90	1.9138	3.73	4747.18	1.40

Tables 5-11a, 5-11b

Experimental Results for Outward Flow Separations on the Mark II-B Radial Flow Bed

Operating Temperature: 100 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FINRAD24	1.3603	3.16	374.22	6.85
FINRAD25	1.3603	3.18	377.42	6.80
FINRAD93	1.3630	3.02	357.42	6.72
FINRAD94	1.3630	3.16	376.01	6.75
FINRAD95	1.3630	3.15	373.98	6.59
FINRAD43	1.6706	3.93	380.78	6.19
FINRAD44	1.6684	3.94	381.25	6.00
FINRAD45	1.6662	3.88	376.14	6.18
FINRAD46	1.6673	3.97	383.28	6.09
FINRAD32	1.9165	3.97	336.09	6.53
FINRAD33	1.9165	3.90	327.73	6.36
FINRAD102	1.9156	3.88	327.42	6.56

Operating Temperature: 100 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FINRAD24	1.3603	2.97	8214.29	1.83
FINRAD25	1.3603	3.04	8368.43	1.62
FINRAD93	1.3630	3.19	8743.59	1.01
FINRAD94	1.3630	3.17	8723.82	0.79
FINRAD95	1.3630	3.05	8472.10	1.00
FINRAD43	1.6706	3.44	7703.82	1.65
FINRAD44	1.6684	3.56	7931.32	1.72
FINRAD45	1.6662	3.59	7994.95	1.77
FINRAD46	1.6673	3.52	7861.87	1.68
FINRAD32	1.9165	3.49	6935.54	1.55
FINRAD33	1.9165	3.44	6848.04	1.68
FINRAD102	1.9156	3.56	7124.00	1.15

A similar analysis performed on the butane Peclet number data is presented in Figure 5-23. Note that the slope of this fit yielded an unreasonably large porosity estimate of $\epsilon = 0.24$, suggesting that when n-butane is the solute $D_{eff} \neq D_{AB}$. This conclusion is supported by the methane/butane Peclet number ratio, which was given previously as:

$$\frac{p_1}{p_2} = \left(\frac{j_v}{2D_{eff,1}} \right) \left(\frac{2D_{eff,2}}{j_v} \right) = \frac{D_{eff,2}}{D_{eff,1}} \quad (Eq. 5.21)$$

If D_{eff} is approximated by D_{AB} , and D_{AB} by a simple Gilland-type relation (L6):

$$D_{AB} = \frac{0.001 T^{1.75} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P \left[(\sum v)_A^{\frac{1}{3}} + (\sum v)_B^{\frac{1}{3}} \right]^2} \quad (Eq. 5.25)$$

then the Peclet number ratio should vary as

$$\frac{p_1}{p_2} = \sqrt{\frac{\frac{1}{M_2} + \frac{1}{M_{He}}}{\frac{1}{M_1} + \frac{1}{M_{He}}}} \left[\frac{(\sum v)_1^{1/3} + (\sum v)_{He}^{1/3}}{(\sum v)_2^{1/3} + (\sum v)_{He}^{1/3}} \right] \quad (Eq. 5.26)$$

Here the molecular weight of the individual solutes is given as M , the atomic diffusion values, v , for each component are determined by summing the contributions of the individual groups comprising the solute (see reference L6 for a table of representative values), and the subscript He refers to the carrier gas.

Table 5-12a and 5-12b
Comparison of Equilibrium Sorption Constant Ratios @ 115 °C

Run ID	$\frac{K_{methane}}{K_{butane}}$ (Radial Flow Value)	$\frac{K_{methane}}{K_{butane}}$ (Avg Axial Flow Value)	Difference (%)
FINRAD52	0.0612	0.0649	5.70
FINRAD53	0.0611	0.0649	5.86
FINRAD83	0.0618	0.0649	4.78
FINRAD62	0.0645	0.0649	0.62
FINRAD64	0.0619	0.0649	4.62
FINRAD65	0.0622	0.0649	4.16
FINRAD88	0.0615	0.0649	5.24
FINRAD79	0.0640	0.0649	1.39
FINRAD80	0.0638	0.0649	1.69
FINRAD82	0.0615	0.0649	5.24
FINRAD89	0.0610	0.0649	6.01
FINRAD90	0.0621	0.0649	4.31

Comparison of Equilibrium Sorption Constant Ratios @ 100 °C

Run ID	$\frac{K_{methane}}{K_{butane}}$ (Radial Flow Value)	$\frac{K_{methane}}{K_{butane}}$ (Avg Axial Flow Value)	Difference (%)
FINRAD24	0.0428	0.0454	5.73
FINRAD25	0.0431	0.0454	5.07
FINRAD93	0.0432	0.0454	4.85
FINRAD94	0.0432	0.0454	4.85
FINRAD95	0.0427	0.0454	5.95
FINRAD43	0.0433	0.0454	4.63
FINRAD44	0.0434	0.0454	4.41
FINRAD45	0.0435	0.0454	4.19
FINRAD46	0.0432	0.0454	4.85
FINRAD32	0.0426	0.0454	6.17
FINRAD33	0.0422	0.0454	7.05
FINRAD102	0.0422	0.0454	7.05

FIGURE 5-21

CHROMATOGRAPHIC EXPERIMENTS IN THE MARK II-B:
VARIATION OF METHANE PECLET NUMBER WITH Q @ T = 115°C

FIGURE 5-22

CHROMATOGRAPHIC EXPERIMENTS IN THE MARK II-B:
VARIATION OF METHANE PECLET NUMBER WITH Q @ T = 100°C

FIGURE 5-23
CHROMATOGRAPHIC EXPERIMENTS IN THE MARK II-B:
VARIATION OF BUTANE PECLET NUMBER WITH Q @ T = 100°C

Equation 5.26 forecasts a methane/n-butane Peclet number ratio of 0.5082, vs. an experimentally determined value of ≈ 1.08 . Since it has already been demonstrated that $D_{eff, methane} \approx D_{AB, methane}$, the only explanation for this discrepancy is that $D_{eff, butane} \neq D_{AB, butane}$. One reason that $D_{eff, butane}$ might not equal $D_{AB, butane}$ is that Taylor dispersion and pore hold-up effects can cause D_{eff} for strongly adsorbed solutes to exceed D_{AB} . Dayan and Levenspiel performed a theoretical analysis of such effects in an axial flow column packed with porous particles (D2). They determined that D_{eff} depends on D_{AB} and U_{eff} , the average axial velocity through the column, as follows:

$$D_{eff} = D_{AB} + K_T \frac{U_{eff}^2}{D_{AB}} + C_1 \frac{U_{eff}^2}{D_{AB}} \int_0^\infty \beta(l) l^2 dl + C_2 \frac{U_{eff}^2}{D_{AB}} \int_0^\infty \beta(l) l dl \quad (Eq. 5.27)$$

The first and second terms in this relation express molecular diffusion in the direction of flow and classical Taylor dispersion, respectively. The last two terms account for diffusion and hold-up among intraparticle

pores. The constant K , is a shape factor that is necessarily different from Taylor's original constant for an empty tube since it considers pore geometry effects. The parameters C_1 and C_2 quantify the effects of pore hold-up and adsorption. They were found to be complex, non-additive polynomial functions of both pore geometry and the equilibrium sorption constant. The two integrals are pore size distribution functions.

If we assume that a similar functionality exists for the radial flow case, and that the appropriate velocity can be expressed as the product of a modified Taylor dispersion constant and the mobile phase flowrate Q , we can condense this new constant and the radial flow analogues of the individual C_i 's from Equation 5.27 into a single constant, C_r , that is a function of, among other things, K_r (and hence temperature). We thus arrive at an illustrative approximation of the Dayan relation for the radial flow configuration:

$$D_{eff} = D_{AB} + C_r \frac{Q^2}{D_{AB}} \quad (Eq. 5.28)$$

It must be emphasized that this relationship assumes an identical functionality among dispersion coefficients for radial and axial flow adsorbers with respect to both fluid velocities and sorption constants. Although this assumption has not been rigorously proven, such an extension seems logical, since the phenomena influencing D_{eff} (ie, K_r and pore geometry) act within intraparticle pores that are essentially isolated from the direct influence of the interparticle velocity profile.

Equation 5.28 suggests that the contribution of the velocity dependent term to D_{eff} will be larger for butane than it is for methane not only because of the inverse dependence of the velocity contribution on D_{AB} , but also because butane is much more strongly adsorbed (C_r varies as a polynomial function of K_r). Whereas the effective dispersion coefficient for weakly adsorbed methane is expected to approach D_{AB} (due to a negligible contribution from the velocity dependent term), it will likely exceed D_{AB} for more strongly adsorbed solutes such as butane.

Incorporation of Equation 5.28 into the definitions of p and τ , results, upon rearrangement, in the following flowrate-dependent relationships:

$$\epsilon D_{AB} + \epsilon C_r \frac{Q^2}{D_{AB}} = \frac{Q}{4\pi h p} \quad (Eq. 5.29)$$

$$\left(\frac{\eta D_{AB}}{K_s + \eta} \right) + C_t \left(\frac{\eta}{K_s + \eta} \right) \frac{Q^2}{D_{AB}} = \frac{R_o^2}{\tau_r} \quad (Eq. 5.30)$$

Figures 5-24 and 5-25 document efforts to fit Equations 5-29 and 5-30 to the butane Peclet number data first presented in Figure 5-23. The correlation coefficients obtained for these fits (≈ 0.9) are a good indication as to the applicability of the model, as are the reasonable porosity estimates determined from the calculated value of $D_{AB, butane}$ and the intercepts of these plots ($\epsilon = 0.17$ and 0.14 , respectively).

To summarize, the analyses presented above suggest that Equation 5.28 accurately quantifies mobile phase dispersion in a radial flow adsorber. The velocity-dependent contribution is negligible for weakly adsorbed solutes such as methane, and D_{eff} is seen to approach D_{AB} . Conversely, the velocity-dependent contribution is significant for strongly adsorbed solutes such as butane, and D_{eff} is seen to exceed D_{AB} .

Finally, it is noted in passing that plate heights determined from a statistical analysis of the chromatographic peaks were generally consistent with those observed for the earlier impulse response experiments ($0.7 \leq HETP \leq 1.0$). Caution must, however, be used when interpreting these values, since the HETP concept was developed for quantification of uniform, Gaussian peaks.

FIGURE 5-24

CHROMATOGRAPHIC EXPERIMENTS IN THE MARK II-B:
FIT OF EQ. 5.29 TO BUTANE PECLET NUMBER DATA @ T = 100°C

FIGURE 5-25

CHROMATOGRAPHIC EXPERIMENTS IN THE MARK II-B:
FIT OF EQ. 5.30 TO BUTANE TIME CONSTANT DATA @ T = 100°C

5.3.2.2 The Inward Flow Configuration

Chromatographic traces for four of the methane/n-butane separations performed while operating the Mark II-B in the inward flow configuration are presented in Figures 5-26 through 5-29. The same trends observed for the outward flow data - peak sharpening at both higher mobile phase flowrates and higher operating temperatures - were demonstrated during inward flow experimentation. As was noted in Section 3.2.2, these trends are consistent with performance expectations based on the mobile phase dispersion model.

Optimized Peclet numbers and time constants for the inward flow tests are summarized in Tables 5-13a through 5-14b. An interesting trend is noted when these values are compared to their outward flow counterparts: all of the optimized parameters for the inward flow case are, when compared at appropriate conditions, less than those for the outward flow case. The decrease is $\approx 12\%$ when comparing methane time constants at the same temperature, and varies from $\approx 10\%$ to $> 20\%$ (depending on flowrate) when contrasting values of τ_r for butane. The Peclet numbers of both solutes exhibit similar trends when compared at constant temperature and flowrate.

Since the dispersion coefficient is the only parameter impacting τ_r and p that is dependent on fluid mechanics, it is logical to attribute the observed decreases to an increase in D_{eff} brought on by the switch to the inward flow configuration. This increase probably resulted from maldistribution due to the difficulty inherent in establishment of a uniform injection front at the (large!) bed periphery. This problem does not exist for the outward flow configuration, since the injection front is established across the much smaller centerline of the device.

Tracer experiments performed by injecting a carbon tetrachloride solution saturated with azobenzene into the periphery of the Mark II-B support the conclusion that D_{eff} is greater for the inward flow configuration due to maldistribution. Photographs of the yellow stains that remained on the packing at the conclusion of the dye tests are included as Figures 5-30 and 5-31 for reference. The non-uniformity of the stain (its width varied by more than 20%, from a minimum of ≈ 6.4 mm to a maximum of ≈ 8.2 mm) confirms that significant maldistribution occurred during testing of the inward flow configuration.

FIGURE 5-26
MOBILE PHASE DISPERSION MODEL
FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B
 (RUN ID: FININ06, INWARD FLOW, VOLUMETRIC FLOW: 1.31 CC/SEC, BED TEMPERATURE: 100° C)

FIGURE 5-27
MOBILE PHASE DISPERSION MODEL
FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B
 (RUN ID: FININ26, INWARD FLOW, VOLUMETRIC FLOW: 1.83 CC/SEC, BED TEMPERATURE: 100° C)

FIGURE 5-28
MOBILE PHASE DISPERSION MODEL
FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B
 (RUN ID: FININ112, INWARD FLOW, VOLUMETRIC FLOW: 1.91 CC/SEC, BED TEMPERATURE: 115° C)

FIGURE 5-29
MOBILE PHASE DISPERSION MODEL
FIT TO RADIAL FLOW CHROMATOGRAPHIC DATA FROM THE MARK II-B
 (RUN ID: FININ211, INWARD FLOW, VOLUMETRIC FLOW: 1.36 CC/SEC, BED TEMPERATURE: 115° C)

Tables 5-13a, 5-13b

Experimental Results for Inward Flow Separations on a Radial Flow Bed

Operating Temperature: 100 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FININ05	1.3128	2.19	353.04	7.52
FININ06	1.3128	2.18	339.84	7.02
FININ07	1.3128	2.09	331.63	7.24
FININ08	1.3128	2.08	324.84	7.22
FININ13	1.6028	2.65	314.84	2.11
FININ14	1.6028	2.66	314.84	2.12
FININ16	1.6028	2.65	314.84	2.17
FININ21	1.8336	3.01	303.20	2.24
FININ22	1.8336	2.88	292.03	2.18
FININ24	1.8336	4.30	379.13	4.74
FININ25	1.8336	3.01	302.34	2.21
FININ26	1.8336	3.00	302.42	2.29

Operating Temperature: 115 °C Component: Butane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FININ05	1.3128	2.07	7617.88	1.08
FININ06	1.3128	2.01	7421.86	1.24
FININ07	1.3128	2.03	7437.02	1.65
FININ08	1.3128	1.98	7331.78	1.68
FININ13	1.6028	2.11	6224.36	1.74
FININ14	1.6028	2.12	6238.89	1.65
FININ16	1.6028	2.17	6322.25	1.53
FININ21	1.8336	2.24	5655.61	1.90
FININ22	1.8336	2.18	5566.71	0.83
FININ24	1.8336	4.74	9042.33	4.82
FININ25	1.8336	2.21	5619.83	1.97
FININ26	1.8336	2.29	5720.69	1.65

Tables 5-14a, 5-14b

Experimental Results for Inward Flow Separations on a Radial Flow Bed

Operating Temperature: 115 °C Component: Methane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FININ104	1.9147	2.92	277.34	8.11
FININ105	1.9147	3.13	289.84	7.53
FININ106	1.9147	3.06	284.84	7.47
FININ109	1.9147	2.76	274.84	9.14
FININ119	1.6629	2.57	294.84	8.24
FININ120	1.6629	2.71	295.15	6.53
FININ121	1.6629	2.66	290.93	6.92
FININ122	1.6629	2.70	294.13	6.55
FININ210	1.3629	1.85	294.53	9.51
FININ211	1.3629	2.11	310.54	7.24
FININ212	1.3629	2.13	312.65	7.37
FININ214	1.3629	2.15	314.84	7.31

Operating Temperature: 115 °C Component: Butane

Run ID	Volumetric Flow, Q (cm ³ /sec)	Peclet Number, p	Time Constant τ_r (sec)	IAE (%)
FININ104	1.9147	2.18	3571.47	2.58
FININ105	1.9147	2.19	3583.58	2.58
FININ106	1.9147	2.17	3564.68	2.65
FININ109	1.9147	2.30	3695.85	1.57
FININ119	1.6629	2.35	4257.88	1.16
FININ120	1.6629	2.39	4289.13	1.13
FININ121	1.6629	2.34	4223.89	1.28
FININ122	1.6629	2.44	4320.85	1.23
FININ210	1.3629	2.22	4963.11	1.89
FININ211	1.3629	2.04	4787.72	1.28
FININ212	1.3629	1.89	4633.16	1.44
FININ214	1.3629	1.91	4640.22	1.37

Tables 5-15a and 5-15b summarize values of the methane/n-butane equilibrium sorption constant ratio (as determined from Equation 5.24) for each of the separations performed with the inward flow configuration. These ratios are again seen to agree reasonably well with those determined from the axial flow experiments discussed in Section 5.3.1.

In summary, the mobile phase dispersion model has been shown to adequately describe the behavior of a radial flow adsorber in which solutes injected at the bed periphery migrate towards the centerline. Consistency amongst sorption constant ratios determined independently from axial and (inward) radial flow experimentation confirms the validity of the time constant and Peclet number values returned from the parameter estimation routine employed for data analysis. Unfortunately, performance enhancements anticipated for the inward flow configuration were not realized because of difficulties encountered with the establishment of a uniform injection front at the bed periphery.

Tables 5-15a and 5-15b

Comparison of Equilibrium Sorption Constant Ratios @ 115 °C

Run ID	$\frac{K_{methane}}{K_{butane}}$ (Radial Flow Value)	$\frac{K_{methane}}{K_{butane}}$ (Avg. Axial Flow Value)	Difference (%)
FININ104	0.0579	0.0649	10.67
FININ105	0.0565	0.0649	12.94
FININ106	0.0566	0.0649	12.79
FININ109	0.0619	0.0649	4.62
FININ119	0.0633	0.0649	2.46
FININ120	0.0606	0.0649	6.62
FININ121	0.0605	0.0649	6.78
FININ122	0.0615	0.0649	5.24
FININ210	0.0712	0.0649	9.70
FININ211	0.0627	0.0649	3.39
FININ212	0.0598	0.0649	7.86
FININ214	0.0602	0.0649	7.24

Comparison of Equilibrium Sorption Constant Ratios @ 100 °C

Run ID	$\frac{K_{methane}}{K_{butane}}$ (Radial Flow Value)	$\frac{K_{methane}}{K_{butane}}$ (Avg. Axial Flow Value)	Difference (%)
FININ05	0.0438	0.0454	3.52
FININ06	0.0422	0.0454	7.05
FININ07	0.0433	0.0454	4.62
FININ08	0.0421	0.0454	7.27
FININ13	0.0402	0.0454	11.45
FININ14	0.0402	0.0454	11.45
FININ16	0.0407	0.0454	10.35
FININ21	0.0398	0.0454	12.22
FININ22	0.0397	0.0454	12.56
FININ24	0.0462	0.0454	1.76
FININ25	0.0395	0.0454	12.99
FININ26	0.0403	0.0454	11.22

Figures 5-30 and 5-31

YELLOW (AZOBENZENE) STAINS DOCUMENTING MALDISTRIBUTION
for the INWARD FLOW CASE

Chapter VI

CONCLUSIONS and RECOMMENDATIONS for FUTURE WORK

6.1 Conclusions

The separation of a methane/n-butane mixture has been demonstrated via radial flow through compressed, pancake-shaped beds of activated alumina particles. Several mechanical improvements implemented as part of this project made the separation possible. Chief among these was the use of a compressed stationary phase to increase impedance and ensure establishment of a uniform flow profile through the adsorber. Earlier investigators (H1, H8, W1) had used the centrifugal force generated by spinning such adsorbers to achieve flow uniformity. The introduction of a compressed stationary phase eliminated the need to spin the adsorber, facilitating both operation in the elution mode and connection of prototype radial flow devices to standard gas chromatographs.

The chief dissipative effect in the prototype radial flow chromatographs studied here was shown to be mobile phase dispersion. The analytical solution developed to quantify adsorption under such conditions revealed that, in addition to simply establishing uniform flow, stationary phase compression also mitigates radial dispersion. This reduction, which results from the increasing dominance of convection over dispersion as compression increases, can be quantified in terms of a system Peclet number based on interstitial flow conditions ($Pe = Q/4\pi h\epsilon D_{eff}$).

Film transport and solid phase diffusional resistances will control if sufficient compression is employed to render dispersion insignificant with respect to convection. Under such conditions, Rice's negligible dispersion model, which was used here to successfully quantify chromatographic separations achieved with an axial flow column, can be applied to radial flow adsorbers.

One of the unfortunate implications of mobile phase dispersion is that HETP's, and consequently peak widths, are currently larger in radial flow adsorbers than conventional axial flow columns. As was noted above, such dissipative effects can be overcome through increased bed compression. Figure 6-1 compares the enhanced performance expected for a radial flow chromatograph (in which mobile phase dispersion has been negated) with that of a conventional axial flow column. The sharpened response of the radial flow device

results from reduced film and solid phase diffusion resistances (ie, reduced $\xi = R_p K_s / 3k_m + R_p^2 / 15D_s$) achieved through the use of smaller sorbent particles. The much higher pressure drop across axial flow columns (compare, for example, Figures 5-1 and 5-2) makes the use of smaller sorbent particles impractical.

FIGURE 6-1
PERFORMANCE COMPARISON:
 ANTICIPATED RESPONSE OF A HIGHLY COMPRESSED RADIAL FLOW ADSORBER
 (WITH NEGLIGIBLE DISPERSION) VS THAT OF A STANDARD AXIAL FLOW COLUMN

Figures 6-2a and 6-2b contrast the experimental response reported for the conventional, axial flow column discussed in Section 5.3.1 with the simulated response for a radial flow bed of very fine particles (so that film transport and solid phase diffusion resistances are negligible) operating with a Peclet number $p = 20$. Such operation clearly does not approach the radial flow ideal presented in Figure 6-1. However, the decrease in fluid phase dispersion predicted by the simulation does dramatically sharpen the response relative to the experimental results discussed in Section 5.3.2 (where $p \leq 5$). Since the predicted band widths are less than the experimentally observed values for the axial flow column, it is reasonable to assume that such operation (i.e., $p = 20$) is sufficient to make radial flow adsorbers competitive with packed, axial flow columns. The increase in Peclet number required to realize such performance may be achieved through either increased compression, reduced bed height, increased throughput, decreased diffusivity (through a change to a heavier carrier such as nitrogen), or some combination of these factors.

Figure 6-2a
EXPERIMENTAL DATA FROM AXIAL FLOW COLUMN
 (T = 115 C, Q = 50 CC/MIN)

Figure 6-2b
SIMULATION OF RADIAL FLOW COLUMN WITH P=20
 (T = 115 C)

Finally, it is noted here that Knudsen diffusion dominated mass transfer resistance in the axial flow column. This observation may limit future developments with highly compressed radial flow cakes - if higher compressions generate interstices that are of the same size as the pores within the sorbent particles.

In summary, the major accomplishments of this effort have included:

- Attainment of flow uniformity with high bed compressions.
- The first demonstration of a gas phase, chromatographic separation in a radial flow device using the expedient of bed compression.
- Identification of mobile phase dispersion as the primary dissipative force operating in the radial flow adsorber.
- Development of the mobile phase dispersion model to explain observed peak shapes and quantify the effects of dispersion on the system response. This model is important since it permits a-priori prediction of the sorption response. Previous efforts to model mobile phase dispersion in radial flow adsorbers have apparently been restricted to peak width and residence time prediction based on moments analyses in the Laplace domain (H3).
- Theoretical proof that the inward flow configuration is the preferred operating mode for chromatographic separations in a radial flow adsorber (although experimental problems were shown to exist when implementing this mode of operation).
- Verification of the applicability of Rice's negligible dispersion model to the description of the dissipative effects in an axial flow column.
- Knudsen diffusion within the micropores of alumina was found to be the primary dissipative effect in the axial column considered here.

6.2 Recommendations for Future Work

The next major step in the development of a truly efficient radial flow chromatograph will involve the stacking of very thin, highly compressed beds within a single shell. One concept of such a device is presented schematically in Figure 6-3. The advantages of this approach include:

- A significant increase in the number of effective stages available for separation due to the increased length of the flow path.
- Elimination of troublesome gas collection systems and the dead volume associated with them through the use of the alternating outward/inward flow configurations that facilitate both introduction and removal of solutes along the centerline of the device (see Figure 6-1).

FIGURE 6-3
SCHEMATIC OF A PROTOTYPE, MULTI-PASS
RADIAL FLOW CHROMATOGRAPH

Specific questions to be addressed as part of the program to implement multiple pass radial flow chromatography include:

- How to ensure a uniform initial distribution at the outer edge of the individual sorbent beds used for the inward flow passes.
- Whether it is best to compress the multiple beds required in situ or in a separate compaction device prior to stacking them.
- The number of passes required to match the performance of conventional axial flow columns.
- The maximum number of passes that are feasible from both a mechanical and a modeling standpoint.

As important as attempts to extend the radial flow concept to multiple passes will be the concurrent effort to mitigate mobile phase dispersion through increased compression of the stationary phase. Specific objectives of such research will include:

- Determination of minimum interstitial porosities achievable in highly compressed beds.
- Optimization of the compression process (e.g. wet compression, etc.).

- Development of techniques to determine in situ particle sizes and interstitial porosities of compressed beds.
- Determination of the effect of compression on intraparticle porosity and pore size distributions.
- Evaluation of the consequences of particle attrition on the chromatographic response.

Finally, an attempt must be made to increase our understanding of the various dissipative phenomena observed in radial flow adsorbers. Recall that the mechanistic model used to account for the velocity dependence of the dispersion coefficient assumed that concepts developed for axial flow adsorbers could be extrapolated to the radial flow configuration in a straight-forward fashion. This assumption requires verification from both a theoretical and experimental viewpoint. Investigations of such dissipative phenomena might ultimately lead to unification of the negligible and mobile phase dispersion models into a single theory capable of quantifying the contribution of each individual dissipative effect on the total system response.

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APPENDIX I

Derivation of the Pressure Drop vs Flow Relation for a Packed, Radial Flow Bed

Consider¹ a slice of height Δz and length Δr taken from a packed, radial flow bed. Such an element is pictured below for easy reference. The usual assumptions of a constant density fluid and uniform plug flow will be employed in the derivation that follows.

Application of mass continuity requirements to the differential element shown above yields:

$$\rho 2\pi r \Delta z \epsilon v_{ir} \big|_r - \rho 2\pi r \Delta z \epsilon v_{ir} \big|_{(r+\Delta r)} = 0 \quad (\text{Eq. } i-1)$$

which reduces - upon division by Δr and evaluation as the thickness of the element is reduced to zero - to:

$$\frac{\partial}{\partial r}(r v_{ir}) = 0 \quad (\text{Eq. } i-2)$$

Hence

¹ Derivation follows that of Yee in his earlier studies (Y1)

$$rv_{ir} = f(z) \quad (\text{Eq. } i-3)$$

where, for the case of an ideal plug profile, $f(z)$ is constant such that

$$rv_{ir} = f(z) = \frac{Q}{2\pi h\epsilon} = j_v \quad (\text{Eq. } i-4)$$

Note that j_v is the volumetric flux per unit bed height as discussed in Chapter III.

A mechanical energy balance on the same differential bed element yields:

$$\rho 2\pi r \Delta z \epsilon v_{ir} \left[\frac{1}{2} (\epsilon v_{ir})^2 + \frac{P}{\rho} + gz \right] \Big|_r - \rho 2\pi r \Delta z \epsilon v_{ir} \left[\frac{1}{2} (\epsilon v_{ir})^2 + \frac{P}{\rho} + gz \right] \Big|_{(r+\Delta r)} - E_v = 0 \quad (\text{Eq. } i-5)$$

where E_v represents frictional losses. The approach used by Bird, Stewart and Lightfoot to quantify E_v for axial flow beds (see page 216 in reference B3) will be adapted to the radial flow configuration as follows:

The frictional loss term is first expressed in terms of the interstitial fluid velocity, v_{ir} , and the mass flowrate through the column, w , as follows:

$$E_v = w \frac{\Delta P}{\rho} = \frac{1}{2} w v_{ir}^2 e_v \quad (\text{Eq. } i-6)$$

Here e_v is a friction loss factor expressible in terms of the length of the packed flowpath, Δr , the hydraulic radius of the interstices between the particles, $R_h = \epsilon / a_p (1 - \epsilon)$, and the friction factor, f , as:

$$e_v = f \frac{\Delta r}{R_h} \quad (\text{Eq. } i-7)$$

Note that a_p is defined as the particle surface area per unit particle volume.

The frictional loss term thus becomes:

$$E_v = w \frac{\Delta P}{\rho} = w \frac{1}{2} v_{ir}^2 \Delta r \frac{a_p (1 - \epsilon)}{\epsilon} f \quad (\text{Eq. } i-8)$$

From Equation *i-8* it is seen that with $v_{ir} = v_o / \epsilon$ and $a_p = 6/d_p$:

$$\frac{\Delta P}{\frac{1}{2}\rho v_{or}^2} = \frac{6\Delta r}{d_p} \frac{(1-\epsilon)}{\epsilon^3} f \quad (\text{Eq. } i-9)$$

The basis of the packed bed friction factor employed by Bird, Stewart and Lightfoot (B3) is:

$$\frac{\Delta P}{\frac{1}{2}\rho v_{\alpha}^2} = \frac{4L}{d_p} f_a \quad (\text{Eq. } 10)$$

where L is the length of the axial flow path and the subscript "a" emphasizes that the friction factor addresses axial flow. Comparison of this relation with Equation i-9 suggests the following connection:

$$f = \frac{2}{3} \frac{\epsilon^3}{(1-\epsilon)} f_a \quad (\text{Eq. } i-11)$$

Substitution of the Ergun equation for the friction factor in an axial flow column:

$$f_a = \frac{(1-\epsilon)^2}{\epsilon^3} \frac{75\mu}{d_p G_o} + 0.875 \frac{(1-\epsilon)}{\epsilon^3} \quad (\text{Eq. } i-12)$$

into Equation i-11 yields a relation for the friction factor applicable to a packed, radial flow bed:

$$f = \frac{50(1-\epsilon)\mu}{d_p G_o} + \frac{7}{12} \quad (\text{Eq. } i-13)$$

Note that $G_o = \rho \epsilon v_{ir} = G_o(r)$.

From the definition of the frictional loss term we find that for a differential bed element with $w =$

$\rho 2\pi r \Delta z \epsilon v_{ir}$:

$$E_v = f a_p (1-\epsilon) 2\pi r \Delta r \Delta z \frac{1}{2} \rho v_{ir}^3 \quad (\text{Eq. } i-14)$$

Substitution of this definition into Equation i-5 yields, upon division by Δr and evaluation as $\Delta r \rightarrow 0$,:

$$\frac{\partial}{\partial r} \left[r v_{ir} \left(\frac{1}{2} (\epsilon v_{ir})^2 + \frac{P}{\rho} + g z \right) \right] + \frac{1}{2} a_p \frac{(1-\epsilon)}{\epsilon} f r (v_{ir})^3 = 0 \quad (\text{Eq. } i-15)$$

This equation can be simplified somewhat by recalling from the continuity requirement that $rv_{ir} = \text{constant}$ for the case of uniform plug flow:

$$\left(\frac{1}{\rho}\right)\frac{\partial P}{\partial r} + \frac{\partial}{\partial r}\left[\frac{\varepsilon^2(rv_{ir})^2}{2r^2}\right] + \frac{1}{2\varepsilon}\left[\frac{rv_{ir}}{r}\right]^2 fa_p(1-\varepsilon) = 0 \quad (\text{Eq. } i-16)$$

The low pressure drop generated by the radial flow configuration allows the fluid density to be treated as a constant for all isothermal systems. Hence, integration of this relation from plane 1 to plane 2 yields - upon rearrangement - the desired flow vs pressure drop relation:

$$\Delta P = -\left(\frac{1}{2}\right)\rho[\varepsilon rv_{ir}]^2\left[\frac{1}{R_1^2} - \frac{1}{R_2^2}\right] - \left(\frac{1}{2}\right)[rv_{ir}]^2 a_p \left[\frac{1-\varepsilon}{\varepsilon}\right] \int_{r_2}^{r_1} \left[\frac{f}{r^2}\right] dr \quad (\text{Eq. } i-17)$$

which becomes, upon substitution of the friction factor as defined by Equation *i-13*:

$$\begin{aligned} \Delta P = & 75 \frac{\mu}{d_p^2} \left[\frac{(1-\varepsilon)^2}{\varepsilon^3} \right] \frac{Q}{\pi h} \ln\left(\frac{r_2}{r_1}\right) \\ & + \left[\frac{7}{16} \right] \frac{\rho}{d_p} \left[\frac{(1-\varepsilon)}{\varepsilon^3} \right] \frac{1}{\pi^2 h^2} \left[\frac{1}{r_1^2} - \frac{1}{r_2^2} \right] Q^2 \\ & - \left(\frac{1}{2}\right) \left[\frac{\rho}{4\pi^2 h^2} \right] \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) Q^2 \end{aligned} \quad (\text{Eq. } i-18)$$

Equation *i-18* is the radial flow analogue of the Blake Kozeny relation discussed in Section 3.1 and used for analysis of experimental data in Section 5.1.

APPENDIX II

Computer Programs


```
For i := 0 To 31 Do
Begin
  Val(Copy(Binary,32-i,1),x,j);
  Dec := Dec+BinConv[i]*x;
End;
TimeCounter := TimeCounter+SliceTime;
TextColor(Green);
GotoXY(30,12);
Write('Slice Time = ',TimeCounter:5:1,' Sec');
Writeln(Output,TimeCounter,' ',Dec);
End;
Readln(Data);
End;
End.
```

PROGRAMS for RADIAL FLOW ADSORBERS

```

C  OUTWARD IS THE MAIN PROGRAM THAT DETERMINES SYSTEM PARAMETERS
C  FOR THE RFGC AND CALLS THE SUBROUTINES NEEDED TO INVERT THE
C  SOLUTION TO THE IMPULSE PROBLEM FROM THE LAPLACE DOMAIN.
C
C  PROGRAM OUTWARD
C
C  IMPLICIT REAL*8 (A-H, O-Z)
C  COMMON IRADIUS, ORADIUS
C  REAL*8 IRADIUS, IAEMIN, LAMDA(15), MINIAE(5)
C  INTEGER PEAKSTRT(5), ITRATN(5), DIRECT
C  DIMENSION TIME(2000), PEAKS(5,2000), OPTPEAKS(5,2000), YEXP(2000),
C  * EYEGUN(5,15), CONVDIFF(5), TIMECNST(5), SCALE(5),
C  * PLATES(5), PKSKEW(5), TMEAN(5)
C
C  INITIALIZE INPUT CONSTANTS
C
C  ORADIUS = 3.81
C  IRADIUS = 0.3175
C  BEDHTE = 0.4763
C  TEMP = 373
C  PIN = 59
C  VOLFLOW = 100
C  POROSITY = 0.12
C
C  SET DIRECT = -1 FOR INWARD FLOW, 1 FOR OUTWARD FLOW
C
C  DIRECT = 1
C
C  FILE MANAGEMENT/INPUT DATA
C
C  OPEN(1,FILE = 'JUNOUT88',STATUS = 'NEW',CARRIAGECONTROL='LIST')
C  WRITE(1,*)( ' ')
C  WRITE(1,*)( ' ')
C  WRITE(1,*)( ' ANALYSIS OF RUN FINRAD88/SERIES TECHNIQUE' )
C  WRITE(1,*)( ' (NEG CONC SET TO 0 AT SMALL TIMES)' )
C  WRITE(1,*)( ' (STARTED WHEN CONC ROSE ABOVE 5% OF CMAX)' )
C  WRITE(1,*)( ' (CH4 ANALYSIS ONLY)' )
C  WRITE(1,*)( ' ')
C  WRITE(1,*)( ' ')
C  IF(DIRECT.LT.0) WRITE(1,*)( ' INWARD FLOW CONFIGURATION' )
C  IF(DIRECT.GT.0) WRITE(1,*)( ' OUTWARD FLOW CONFIGURATION' )
C  WRITE(1,*)( ' ')
C  OPEN(2,FILE='FINAL88',STATUS='OLD')
C  REWIND(2)
C  READ(2,1) TIMEDLTA
C  1  FORMAT(17X,E16.14)
C  WRITE(6,*) TIMEDLTA
C  READ(2,*)
C  READ(2,*)
C  DO 5,I=1,2000
C    NPOINTS = I
C    READ(2,2) TIME(I),YEXP(I)
C  2  FORMAT(2X,E16.14,3X,E16.14)
C    IF(YEXP(I).EQ.0) GO TO 10
C  5  CONTINUE
C  10 CONTINUE
C  CLOSE(2)
C  NPOINTS = NPOINTS - 1
C
C  GENERATE BASELINE AND NORMALIZE EXPERIMENTAL DATA
C
C  DO 15,I=1,NPOINTS
C    YEXP(I) = YEXP(I)/(120000*TIMEDLTA)
C  15 CONTINUE
C  START = (YEXP(1) + YEXP(2) + YEXP(3) + YEXP(4))/4
C  FINISH = (YEXP(NPOINTS-3) + YEXP(NPOINTS-2) + YEXP(NPOINTS-1) +
C  *YEXP(NPOINTS))/4
C  SLOPE = (FINISH-START)/TIME(NPOINTS-4)
C  SUM = 0

```

```

DO 17,I=1,NPOINTS
  YEXP(I) = YEXP(I) - (SLOPE*TIME(I) + START)
  IF(YEXP(I).LT.0) YEXP(I) = 0
  SUM = SUM + TIMEDLTA*YEXP(I)
17 CONTINUE
DO 18,I=1,NPOINTS
  YEXP(I) = YEXP(I)/SUM
C   WRITE(6,*)TIME(I), YEXP(I)
18 CONTINUE
C
C   CHECK TO ENSURE RAW DATA IS NORMALIZED
C
SUMNORM = 0
DO 19,I=1,NPOINTS
  SUMNORM = SUMNORM + YEXP(I)*TIMEDLTA
19 CONTINUE
IF(ABS(SLOPE).LT.0.1) GO TO 25
WRITE(1,20) SLOPE
20 FORMAT(2X,'WARNING - WARNING - WARNING : BASELINE SLOPE IS 'F8.4)
C   WRITE(6,21) SLOPE, SUM,SUMNORM
21 FORMAT(2X,'SLOPE = 'F6.4,' AREA = 'F8.4,' AND NORM AREA = 'F6.4)
25 IF(ABS(1-SUMNORM).LT.05) GO TO 30
WRITE(1,28)
28 FORMAT(2X,'WARNING - WARNING - WARNING : DATA NOT NORMALIZED')
WRITE(1,29)
29 FORMAT(2X,' ')
30 CONTINUE
C   WRITE(6,35)SUM,SUMNORM
35 FORMAT(5X,'AREA UNDER THE EXP & NORM CURVE IS 'F8.4,' & 'F8.4)
C
C
C   SPLIT DATA INTO INDIVIDUAL PEAKS
C
CALL RADSPLT(NPOINTS, TIME, TIMEDLTA, YEXP, NOPEAKS, PEAKS,
* PEAKSTRT, SCALE)
C
C
C   EVALUATE SYSTEM PARAMETERS
C
WRITE(1,*)(' ')
WRITE(1,*)(' ')
WRITE(1,*)('RESULTS FROM PEAKSPLT:')
WRITE(1,88)NOPEAKS
88 FORMAT(5X,'A TOTAL OF ',I3,' PEAKS WERE IDENTIFIED')
WRITE(1,*)(' ')
WRITE(1,*)(' ')
C   DO 90, I = 1,NPOINTS,1
C   WRITE(6,89) I,TIME(I), YEXP(I), (PEAKS(J,I), J = 1,NOPEAKS)
C89 FORMAT(2X,'PT ',I4,' T= ',F10.4,' EXP = ',F8.6,' OTHER = ',
C   *F8.6,5X,F8.6,5X,F8.6)
C90 CONTINUE
ETA = POROSITY/(1-POROSITY)
QACT = (VOLFLOW/60)*(14.7/((14.7+PIN)/2))*(TEMP/298)
C
C   WRITE PROBLEM OUTPUT TO FILE
C
WRITE(1,*)(' ')
WRITE(1,*)('MECHANICAL CONFIGURATION:')
WRITE(1,*)(' ')
WRITE(1,111)IRADIUS, ORADIUS
111 FORMAT(2X,' INNER AND OUTER RADII = ',F6.4' & ',F6.4' CM
* EACH RESPECTIVELY')
WRITE(1,112)BEDHTE
112 FORMAT(2X,' THE BED THICKNESS = ',F6.4)
WRITE(1,*)(' ')
WRITE(1,*)('PROCESS CONDITIONS:')
WRITE(1,*)(' ')
WRITE(1,113)VOLFLOW
113 FORMAT(2X,' VOLUMETRIC FLOW = ',F7.2' CC/SEC @ STP')
WRITE(1,114)TEMP, PIN
114 FORMAT(2X,' TEMP = ',F6.2' KELVIN AND P = ',F5.2' PSIG')
WRITE(1,115)QACT
115 FORMAT(2X,' FLOW @ BED CONDITIONS = ',F7.3' CC/SEC')
WRITE(1,*)(' ')
WRITE(1,*)('CALCULATED CONSTANTS:')
WRITE(1,*)(' ')
WRITE(1,118)POROSITY,ETA
118 FORMAT(2X,' FOR ASSUMED BED POROSITY = ',F7.4' ETA = ',F7.4)

```

```

C
C
C EXECUTE PROCEDURE TO FIND VALUES OF EQUILK AND DISPCOEFF THAT
C MINIMIZE THE IAE BETWEEN EXPT AND CALC RESPONSE
C
C DO 299, J = 1, NOPEAKS, 1
C
C CALCULATE NUMBER OF PLATES
C
TMEAN(J) = 0
VAR = 0
SKEW = 0
DO 205, I = PEAKSTRT(J), PEAKSTRT(J+1), 1
TMEAN(J) = TMEAN(J) + TIME(I)*PEAKS(J,I)*TIMEDLTA
205 CONTINUE
DO 210, I = PEAKSTRT(J), PEAKSTRT(J+1), 1
VAR = VAR + ((TIME(I) - TMEAN(J))**2)*PEAKS(J,I)*TIMEDLTA
SKEW = SKEW + ((TIME(I) - TMEAN(J))**3)*PEAKS(J,I)*TIMEDLTA
210 CONTINUE
PLATES(J) = (TMEAN(J)**2)/VAR
PKSKEW(J) = SKEW/(VAR**1.5)
C
C FIND MAXIMUM CONCENTRATION AND START POINT FOR ITERATIONS
C
CMAX = 0
DO 220, I = PEAKSTRT(J), PEAKSTRT(J+1)
IF(PEAKS(J,I).GT.CMAX) K = I
IF(PEAKS(J,I).GT.CMAX) CMAX = PEAKS(J,I)
220 CONTINUE
START = J*0.01*CMAX
DO 225, I = K, 1, -1
IF(PEAKS(J,I).LT.START) JSTART = I
IF(PEAKS(J,I).LT.START) GO TO 230
225 CONTINUE
230 CONTINUE
JSTART = JSTART - 2
JSTOP = PEAKSTRT(J+1)
C
C INVOKE OPTIMIZATION ROUTINE
C
P = ((QACT)/(3.14*BEDHITE*POROSITY)) + 1
TAUCNST = 2*ORADIUS*ORADIUS*(2*J*(10**(J-1)) + ETA)/ETA
WRITE(1,*)(' ')
WRITE(1,238) J
238 FORMAT(10X,'INITIAL GUESSES FOR PEAK ',J2)
WRITE(1,239) J, P, TAUCNST
239 FORMAT(10X,'PEAK ',J2,' : P = ',F5.2,' TIME CONSTANT = ',F8.2)
CALL SERIESMN(P, TAUCNST, NPOINTS, TIME, TIMEDLTA, J, PEAKS,
* OPTPEAKS, DEL, IAEMIN, JSTART, JSTOP, LAMDA, ITS)
IF(DIRECT.LT.0) P = P - 1
CONVDIFF(J) = P
TIMECNST(J) = TAUCNST
MINIAE(J) = IAEMIN * 100
ITRATN(J) = ITS
DO 240, I = 1, 15
EYEGUN(J,I) = LAMDA(I)
240 CONTINUE
299 CONTINUE
C
C
C OUPUT RESULTS
C
C
WRITE(1,*)(' ')
WRITE(1,*)(' ')
WRITE(1,300)
300 FORMAT(5X,'GROSS PEAK ANALYSES:')
WRITE(1,*)(' ')
WRITE(1,301)
301 FORMAT(10X,'PEAK # MEAN RES TIME # OF PLATES SKEW RATIO')
WRITE(1,*)(' ')
DO 305 I = 1, NOPEAKS
WRITE(1,303) I, TMEAN(I), PLATES(I), PKSKEW(I)
303 FORMAT(12X,I2,9X,F6.2,8X,F6.1,8X,F6.2)
305 CONTINUE
WRITE(1,*)(' ')
WRITE(1,*)(' ')
WRITE(1,*)(' RESULTS OF OPTIMIZATION ROUTINE:')

```

```

WRITE(1,*)( ' )
WRITE(1,*)( ' )
WRITE(1,306)
306 FORMAT(10X,'EIGENVALUES: ')
WRITE(1,*)( ' )
WRITE(1,*)( '          PEAK 1    PEAK2')
WRITE(1,*)( ' )
DO 308,I=1,15,1
  WRITE(1,307) I, (EYEGUN(J,I), J=1,NOPEAKS,1)
307  FORMAT(15X,I2,5X,F9.5,5X,F9.5,5X,F9.5,5X,F9.5)
308 CONTINUE
WRITE(1,*)( ' )
WRITE(1,*)( ' )
WRITE(1,310)
310 FORMAT(10X,'PEAK # P  TIME CONST  ITS   MIN IAE
*  SCALE')
WRITE(1,*)( ' )
DO 320,I=1,NOPEAKS,1
  WRITE(1,315)I, CONVDIFF(I), TIMECNST(I), ITRATN(I),
  * MINIAE(I), SCALE(I)
315  FORMAT(12X,I2,3X,F5.2,3X,F9.2,6X,I3,6X,F6.3,3X,F7.4)
320 CONTINUE
WRITE(1,*)( ' )
WRITE(1,*)( ' )
WRITE(1,325)
325 FORMAT(5X,'TIME EXP DATA ',3('PEAK 1 '))
WRITE(1,*)( ' )
DO 335 I=1,NPOINTS,1
  WRITE(1,330) TIME(I), YEXP(I), (OPTPEAKS(J,I), J=1,NOPEAKS,1)
330  FORMAT(4X,F7.2,2X,F8.6,5(2X,F8.6))
335 CONTINUE
STOP
END

```

C THIS SUBROUTINE SPLITS A MULTICOMPONENT ANALYSES INTO INDIVIDUAL
C PEAKS FOR SUBSEQUENT ANALYSES. THE SUBROUTINE RETURNS THE NUMBER
C OF PEAKS IDENTIFIED AS WELL AS NORMALIZED C/C₀ VALUES FOR EACH.

SUBROUTINE RADSPLT(NPOINTS,TIME,TIMEDLTA,CEXP,NOPEAK,PEAKS,
* PEAKSTRT,SCALE)

```
C IMPLICIT REAL*8 (A-H, O-Z)
  INTEGER BEG, FIN, PEAKSTRT(5), COUNTDN
  DIMENSION PEAKS(5,2000),SCALE(5),CEXP(2000),AREA(5),TIME(2000)
```

LOCATE LOCAL MAXIMA AND SPLIT PEAKS

```

C      CMAX = 0.0
      CMIN = 0.0
      J = 1
      COUNTDN = 0
      DO 50, I= 1, NPOINTS, 1
        PEAKS(J,I) = CEXP(I)
        AREA(J) = AREA(J) + TIMEDLTA*PEAKS(J,I)
C      WRITE(6,5) J, TIME(I), AREA(J), CEXP(I), CMAX, CMIN
C5     FORMAT(2X,'PK ',I2,' @ T = ',F7.2,' A = ',F7.4,' C = ',F9.6,
C      '* MAX = ',F9.6,' MIN = ',F9.6)
      IF(AREA(J).LT.0.01) GO TO 50

```

POSITIVE SLOPE

```

C      IF(CEXP(I).GT.CMAX) GO TO 10
      IF(CEXP(I).GT.CTEST) GO TO 50
10     GO TO 20
      CONTINUE
      CMAX = CEXP(I)
      CMIN = CEXP(I)
      CTEST = 0.04*CMIN
      GO TO 50
20     CONTINUE

```

FOR NEGATIVE SLOPE

```

C      IF(CEXP(I).LT.CMIN) GO TO 30
      COUNTDN = COUNTDN + 1
C      WRITE(6,29) COUNTDN
C29    FORMAT(15X,'CEXP > CMIN SO COUNTDN = ',I3)
      IF(COUNTDN.GT.6) CMAX = CMIN
      IF(COUNTDN.GT.6) J = J + 1
      IF(COUNTDN.GT.6) PEAKSTRT(J) = I
      GO TO 50
30    CONTINUE
      COUNTDN = 0
      CMIN = (CEXP(I-2)+CEXP(I-1)+CEXP(I))/3
50    CONTINUE
      NOPEAK = J
C      WRITE(6,60) NOPEAK
C60    FORMAT(5X,'SPLT2 INITIALLY IDENTIFIED ',I3,' PEAKS')
      PEAKSTRT(1) = 1
      PEAKSTRT(J+1) = NPOINTS
      DO 65, J = NOPEAK, 1, -1
        IF(AREA(J).LT.0.02) NOPEAK = NOPEAK - 1
65    CONTINUE
C      WRITE(6,*)(' ')
C      WRITE(6,*)('THE NUMBER OF PEAKS RETURNED FROM SP
C      WRITE(6,*) NOPEAK
C      WRITE(6,*)(' ')

```

NORMALIZE INDIVIDUAL PEAKS/ASSIGN SCALING FACTORS

```

DO 80, J=1, NOPEAK, 1
  SUMNORM = 0
  BEG = PEAKSTRT(J)
  FIN = PEAKSTRT(J+1)
  DO 70, I = BEG, FIN, 1
    SUMNORM = SUMNORM + PEAKS(J,I)*TIMEDLTA
70  CONTINUE
  SCALE(J) = SUMNORM
  DO 75, I = PEAKSTRT(J), PEAKSTRT(J+1), 1

```

```
      PEAKS(J,I) = PEAKS(J,I)/SUMNORM
75    CONTINUE
80    CONTINUE
C
C      CHECK TO ENSURE DATA IS NORMALIZED
C
      DO 90, J=1, NOPEAK, 1
        AREA(J) = 0
        DO 85, I = 1, NPOINTS, 1
          AREA(J) = AREA(J) + PEAKS(J,I)*TIMEDLTA
85      CONTINUE
90    CONTINUE
      END
```



```

C
C THIS SUBROUTINE PERFORMS A TWO-DIMENSIONAL PATTERN SEARCH
C TO DETERMINE THE PARAMETERS THAT MINIMIZES THE IAE BETWEEN
C A THERORETICAL RESULT AND A SET OF EXPERIMENTAL DATA POINTS
C
C SUBROUTINE SERIESMN(X1, X2, NPOINTS, TIME, TIMEDLTA, J,
* PEAKS, OPTPEAKS, DEL, IAEMIN, JSTART, JSTOP, LAMDA, ITS)
C
C IMPLICIT REAL*8 (A-H, O-Z)
C DIMENSION PEAKS(5,2000), OPTPEAKS(5,2000), TIME(2000)
C DIMENSION YSECND(2000), YTHIRD(2000)
C REAL*8 IAEINIT, IAEMIN, IAECSECND, IAETHIRD, IAE, LAMDA(15)
C
C DEL = 0.2
C XINIT1 = X1
C XINIT2 = X2
C CALL SRIESRCH(X1, X2, NPOINTS, TIME, TIMEDLTA, J, PEAKS,
* OPTPEAKS, DEL, IAE, JSTART, JSTOP, LAMDA)
C XSECND1 = X1
C XSECND2 = X2
C IAECSECND = IAE
C DO 5,I = JSTART,JSTOP,1
C   YSECND(I) = OPTPEAKS(J,I)
5 CONTINUE
C CHECK = ABS(XINIT1-XSECND1) + ABS(XINIT2-XSECND2)
C IF(CHECK.EQ.0) GO TO 150
C
C BEGIN ITERATIVE SEARCH
C
C DO 100,I = 1,300
C   ITS = I
C   X1 = XSECND1 + (XSECND1 - XINIT1)
C   X2 = XSECND2 + (XSECND2 - XINIT2)
C   CALL SRIESRCH(X1, X2, NPOINTS, TIME, TIMEDLTA, J, PEAKS,
* OPTPEAKS, DEL, IAE, JSTART, JSTOP, LAMDA)
C   XTHIRD1 = X1
C   XTHIRD2 = X2
C   IAETHIRD = IAE
C   WRITE(6,19) I,XTHIRD1,XTHIRD2,IAETHIRD
C19  FORMAT(5X,'IT # ',I3,' P= ',F9.4,' T = ',F12.4,' IAE = ',F7.4)
C   DO 20, K = JSTART,JSTOP
C     YTHIRD(K) = OPTPEAKS(J,K)
20  CONTINUE
C   IF(IAETHIRD.GE.IAECSECND) GO TO 50
C   XINIT1 = XSECND1
C   XINIT2 = XSECND2
C   IAEINIT = IAECSECND
C   XSECND1 = XTHIRD1
C   XSECND2 = XTHIRD2
C   IAECSECND = IAETHIRD
C   GO TO 100
50  IF(DEL.LT.0.001) GO TO 200
C   DEL = DEL/2
C   XINIT1 = XSECND1
C   XINIT2 = XSECND2
C   X1 = XINIT1
C   X2 = XINIT2
C   IAEINIT = IAECSECND
C   CALL SRIESRCH(X1, X2, NPOINTS, TIME, TIMEDLTA, J, PEAKS,
* OPTPEAKS, DEL, IAE, JSTART, JSTOP, LAMDA)
C   XSECND1 = X1
C   XSECND2 = X2
C   IAECSECND = IAE
C   IAEMIN = IAE
C   DO 60,K = JSTART,JSTOP,1
C     YSECND(K) = OPTPEAKS(J,K)
60  CONTINUE
100 CONTINUE
C   GO TO 200
150 WRITE(1,151)
151 FORMAT(2X,'INITIAL SEARCH FAILED')
200 END

```

```

C
C THIS SUBROUTINE PERFORMS A TWO-DIMENSIONAL PATTERN SEARCH
C TO DETERMINE THE PARAMETERS THAT MINIMIZES THE IAE BETWEEN
C A THERORETICAL RESULT AND A SET OF EXPERIMENTAL DATA POINTS
C
C SUBROUTINE SRIESRCH(X1,X2,NPOINTS,TIME,TIMEDLTA,J,PEAKS,
* OPTPEAKS,DEL,IAE,JSTART,JSTOP,LAMDA)
C IMPLICIT REAL*8 (A-H,O-Z)
C DIMENSION TIME(2000),PEAKS(5,2000),OPTPEAKS(5,2000),
* FRSTY(2000),SCNDY(2000),CONCOPT(2000),ALAMDA(15),
* BLAMDA(15)
C COMMON IRADIUS,ORADIUS
C REAL*8 IAE,LAMDA(15)
C
C DEFINE INITIAL CONSTANTS
C
C IAE = 0
C DO 3,I = 1,NPOINTS
C   OPTPEAKS(J,I) = 0
C   CONCOPT(I) = 0
3 CONTINUE
C
C CALCULATE IAE FOR INITIAL GUESS
C
C 4 FORMAT(15X,'IG IN SRCH P = ',F7.4,' TAU = ',F10.4)
C CALL EIGENVLU(X1,LAMDA)
C CALL OPTSRIES(X1,X2,NPOINTS,TIME,TIMEDLTA,CONCOPT,JSTART,
* JSTOP,LAMDA)
C DO 5,I = JSTART,JSTOP
C   IAE = IAE + ABS(PEAKS(J,I)-CONCOPT(I))*(TIMEDLTA)
5 CONTINUE
C WRITE(6,*)(' ')
C WRITE(6,*)(' ')
C WRITE(6,7) X1,X2,IAE
C7 FORMAT(15X,'FOR IG P = ',F7.4,' TAU = ',F10.4,' IAE = ',F7.4)
10 CONTINUE
C
C EXPLORATORY SEARCH FOR FRSTPARM
C
C POSITIVE INCREMENT
C
C FRSTIAE = 0
C FRSTX = X1 + DEL
C DO 15,I = 1,NPOINTS
C   FRSTY(I) = 0
15 CONTINUE
C CALL EIGENVLU(FRSTX,ALAMDA)
C CALL OPTSRIES(FRSTX,X2,NPOINTS,TIME,TIMEDLTA,FRSTY,JSTART,
* JSTOP,ALAMDA)
C DO 20,I = JSTART,JSTOP
C   FRSTIAE = FRSTIAE + ABS(PEAKS(J,I)-FRSTY(I))*(TIMEDLTA)
20 CONTINUE
C WRITE(6,21)FRSTX,X2,FRSTIAE
C21 FORMAT(20X,'FIRST : P = ',F7.4,' TAU = ',F10.4,' IAE = ',F7.4)
C
C NEGATIVE INCREMENT
C
C SCNDIAE = 0
C SCNDX = X1 - DEL
C DO 24,I = 1,NPOINTS
C   SCNDY(I) = 0
24 CONTINUE
C CALL EIGENVLU(SCNDX,BLAMDA)
C CALL OPTSRIES(SCNDX,X2,NPOINTS,TIME,TIMEDLTA,SCNDY,JSTART,
* JSTOP,BLAMDA)
C DO 25,I = JSTART,JSTOP
C   SCNDIAE = SCNDIAE + ABS(PEAKS(J,I)-SCNDY(I))*(TIMEDLTA)
25 CONTINUE
C WRITE(6,26)SCNDX,X2,SCNDIAE
C26 FORMAT(20X,'SECOND : P = ',F7.4,' TAU = ',F10.4,' IAE = ',F7.4)
C
C COMPARE FIRST SEARCH TO PREVIOUS (INITAL) GUESS
C
C IF(SCNDIAE.GE.FRSTIAE) GO TO 30
C FRSTIAE = SCNDIAE
C FRSTX = SCNDX
C DO 27,I = 1,NPOINTS

```

```

      FRSTY(I) = SCNDY(I)
27  CONTINUE
      DO 29,I = 1,15,1
        ALAMDA(I) = BLAMDA(I)
29  CONTINUE
30  IF(FRSTIAE.GE.IAE) GO TO 35
      X1 = FRSTX
      IAE = FRSTIAE
      DO 31,I = 1,NPOINTS
        CONCOPT(I) = FRSTY(I)
31  CONTINUE
      DO 33,I = 1,15,1
        LAMDA(I) = ALAMDA(I)
33  CONTINUE
35  CONTINUE
C
C
C      EXPLORATORY SEARCH FOR SCNDPARM
C
C
C      POSITIVE INCREMENT
C
      FRSTIAE = 0
      FRSTX2 = X2 + 100*DEL
      DO 39,I = 1,NPOINTS
        FRSTY(I) = 0
39  CONTINUE
      CALL OPTSRIES(X1, FRSTX2, NPOINTS, TIME, TIMEDLTA, FRSTY, JSTART,
        * JSTOP, LAMDA)
      DO 40,I = JSTART, JSTOP
        FRSTIAE = FRSTIAE + ABS(PEAKS(J,I)-FRSTY(I))*(TIMEDLTA)
40  CONTINUE
C      WRITE(6,41)X1,FRSTX2,FRSTIAE
C41  FORMAT(20X,'THIRD : P = ',F7.4,' TAU = ',F10.4,' IAE = ',F7.4)
C
C      NEGATIVE INCREMENT
C
      SCNDIAE = 0
      SCNDX2 = X2 - 100*DEL
      DO 44,I = 1,NPOINTS
        SCNDY(I) = 0
44  CONTINUE
      CALL OPTSRIES(X1, SCNDX2, NPOINTS, TIME, TIMEDLTA, SCNDY, JSTART,
        * JSTOP, LAMDA)
      DO 45,I = JSTART, JSTOP
        SCNDIAE = SCNDIAE + ABS(PEAKS(J,I)-SCNDY(I))*(TIMEDLTA)
45  CONTINUE
C      WRITE(6,46)X1,SCNDX2,SCNDIAE
C46  FORMAT(20X,'FOURTH : P = ',F7.4,' TAU = ',F10.4,' IAE = ',F7.4)
C
C      COMPARE TO PREVIOUS (INITIAL) GUESS
C
      IF(SCNDIAE.GE.FRSTIAE) GO TO 50
      FRSTIAE = SCNDIAE
      FRSTX2 = SCNDX2
      DO 49,I = 1,NPOINTS
        FRSTY(I) = SCNDY(I)
49  CONTINUE
50  IF(FRSTIAE.GE.IAE) GO TO 52
      X2 = FRSTX2
      IAE = FRSTIAE
      DO 51,I = 1,NPOINTS
        CONCOPT(I) = FRSTY(I)
51  CONTINUE
52  CONTINUE
      DO 53,I = 1,NPOINTS
        OPTPEAKS(J,I) = CONCOPT(I)
53  CONTINUE
      END

```

```

C  THIS SUBROUTINE DETERMINES THE RESPONSE OF A RADIAL FLOW CHROMATOGRAPH
C  TO AN IMPULSE USING RICE'S SERIES SOLUTION
C
C  SUBROUTINE OPTSRIS(P, TIMECNST, NPOINTS, TIME, TIMEDLTA, CONC,
C  * JSTART, JSTOP, LAMDA)
C  IMPLICIT REAL*8(A-H,O-Z)
C  REAL*8 CONC(2000), TIME(2000), LAMDA(15), SCND(15),
C  * IRADIUS,ORADIUS
C  COMMON IRADIUS, ORADIUS
C
C          INITIALIZATIONS
C
C  DO 2, I=1,NPOINTS,1
C    CONC(I) = 0
2  CONTINUE
C  CONCTOT = 0
C  H = 0.0001
C  NOSTEPS = 100
C
C          EVALUATION OF CNSTS FOR EACH LAMDA
C
C  G1 = GAMMA2(H,P)
C  FRST = (0.5**(P-2))/G1
C
C  PPLUS = P + 0.5
C  GPPLUS = GAMMA2(H,PPLUS)
C  DO 10,I = 1,15,1
C    G = GPPLUS
C    Z = LAMDA(I)
C    WRITE(6,*) Z
C    CALL JINTGRAL(P,Z,G,NOSTEPS,BESS1)
C    SCND(I) = (Z**P)/BESS1
10  CONTINUE
C
C          EVALUATION OF RESPONSE
C
C  DO 50, J = JSTART, JSTOP, 1
C    SUM = 0
C    TAU = TIME(J)/TIMECNST
C    DO 20, I = 1,15,1
C      EXPN = EXP(-(LAMDA(I)**2)*TAU)
C      PROD = FRST*SCND(I)*EXPN
C      SUM = SUM + PROD
20  CONTINUE
C    CONC(J) = SUM
C    IF (CONC(J).LT.0) CONC(J) = 0.0
C    CONCTOT = CONCTOT + TIMEDLTA*CONC(J)
50  CONTINUE
C  DO 60, I = 1,NPOINTS,1
C    CONC(I) = CONC(I)/CONCTOT
60  CONTINUE
C  END

```

```

C  SUBROUTINE EIGENVLU FINDS ALL LAMDA SUCH THAT:
C
C      0 = Jp(LAMDA)
C
C  SUBROUTINE EIGENVLU(P,LAMDA)
C  IMPLICIT REAL*8(A-H,O-Z)
C  REAL*8 LAMDA(15), LAMDA1, LAMDA2, LOWEND, HIGHEND, MOLDIFF
C  INTEGER IFLAG
C
C      INITIALIZE COUNTERS AND TOLERENCES
C
C      DO 10 I = 1,15,1
C          LAMDA(I) = 0
10  CONTINUE
C      K      = 0
C      NOSTEPS = 100
C      H      = 0.0001
C      XTOL   = 0.00001
C      LOWEND = 1.0
C      HIGHEND = 2.0
C      PROOT  = P - 1
C      PINTRNL = PROOT + 0.5
C      GINTRNL = GAMMA2(H,PINTRNL)
C
C      ESTABLISH LOOP TO FIND ALL VALUES OF LAMDA
C
C      DO 25 I = 1,100,1
C          IFLAG = 1
C          LAMDA1 = LOWEND
C          LAMDA2 = HIGHEND
C
C      INCREASE NUMBER OF STEPS FOR LARGE ARGUEMENT
C
C      CALL BISECT(LAMDA1,LAMDA2,PROOT,GINTRNL,NOSTEPS,XTOL,IFLAG)
C      IF (IFLAG.LT.0) GO TO 20
C      K = K + 1
C      IF(K.GT.15) GO TO 30
C      LAMDA(K) = (LAMDA1+LAMDA2)/2
C      WRITE(6,18) I,K,LAMDA(K)
C18  FORMAT(35X,'WHEN I= ',I3,' EIGENVLU ',I4,' = ',F10.6)
C      ERROR = (LAMDA1-LAMDA2)/2
20  LOWEND = HIGHEND
C      HIGHEND = HIGHEND + 1.0
25  CONTINUE
C      WRITE(6,*)('EXITING EIGEN VALUE LOOP')
30  CONTINUE
C      DO 50, I = 2,15,1
C          IF(LAMDA(I).EQ.0) LAMDA(I) = LAMDA(I-1) + 3.1416
50  CONTINUE
C      END

```

```

C  SUBROUTINE BISECT FINDS THE ZERO OF A FUNCTION (F) THAT EXISTS
C  BETWEEN THE TWO INITIAL POINTS A AND B. XTOL IS THE
C  CONVERGENCE TOLERANCE FOR THE ITERATION AND IFLAG IS A KEY
C  THAT EXPLAINS WHY THE SUBROUTINE WAS INTERRUPTED:
C
C  IFLAG = -1 INDICATES FUNCTION HAS SAME SIGN AT ENDPOINTS
C  IFLAG = 0 TERMINATION BECAUSE  $ABS(A-B)/2 < XTOL$ 
C  IFLAG = 1 TERMINATION SINCE  $ABS(A-B)/2$  IS SO SMALL THAT
C          ADDITION TO  $(A+B)/2$  HAS NO EFFECT
C
C  OPTIONS /G_FLOATING
C
C  SUBROUTINE BISECT(A,B,P1,G1,NOSTEPS,XTOL,IFLAG)
C  IMPLICIT REAL*8(A-H,O-Z)
C  INTEGER IFLAG
C
C      CHECK TO ENSURE ROOT IS BETWEEN INITIAL GUESSES
C
C      GG1 = G1
C      CALL JINTGRAL(P1,A,GG1,NOSTEPS,FA)
C      GG1 = G1
C      CALL JINTGRAL(P1,B,GG1,NOSTEPS,FB)
C      WRITE(6,2)A,B,FA,FB
C2   FORMAT(10X,'BOUNDS ',F7.4' AND ',F7.4' FX = ',E10.5' & ',E10.5)
C      WRITE(6,*)FA,FB
C      WRITE(6,*)(' ')
C      IF (FA*FB.GE.0) THEN
C          IFLAG = -1
C          WRITE(6,5) A,B
C5   FORMAT(25X,'BAD INITIAL GUESSES AT ',F10.4' AND ',F10.4)
C      RETURN
C      END IF
C
C      ESTABLISH LOOP FOR ITERATIONS
C
C      ERROR = ABS(B-A)
C10  ERROR = ERROR/2
C      IF (ERROR.LT.XTOL) RETURN
C      XM = (A+B)/2
C
C      CHECK FOR UNREASONABLE ERROR REQUIREMENT
C
C      IF (XM+ERROR.EQ.XM) THEN
C          IFLAG = 1
C          RETURN
C      END IF
C
C      ESTABLISH NEW ERROR INTERVAL WITH MIDPOINT @ XM
C
C      GG1 = G1
C      CALL JINTGRAL(P1, XM, GG1, NOSTEPS, FM)
C      IF (FA*FM.GT.0) THEN
C          A = XM
C          FA = FM
C      ELSE
C          B = XM
C      END IF
C      GO TO 10
C      END

```

```

C THIS SUBROUTINE EVALUATES AN INTEGRAL EXPRESION TO DETERMINE
C THE VALUE OF A BESSEL FUNCTION OF THE FIRST TYPE, J, FOR A GIVEN
C ORDER, P, AND ARGUMENT, Z.
C
C OPTIONS /G_FLOATING
C
C SUBROUTINE JINTGRAL(P,Z,G,NOSTEPS,JBESS)
C IMPLICIT REAL*8(A-H, O-Z)
C INTEGER EXTSTEPS
C REAL*8 JBESS
C
C DECREASE STEP SIZE IF ARGUMENT IS LARGE
C
C EXSTEPS = NOSTEPS
C IF(Z.GT.30) NOSTEPS = 500
C H = 0.0001
C SUM2 = 0
C SUM4 = 0
C STEP = 3.14159265/(NOSTEPS)
C WRITE(6,1)P,Z,G
C1 FORMAT(5X,'FOR INT METH P = ',F7.4,' Z = ',F9.4,' G = ',F9.4)
C WRITE(6,2) STEP, NOSTEPS
C2 FORMAT(5X,'THE STEP SIZE IS ',F8.6,' FOR ',I9,' STEPS.')
C
C EVALUATE CONSTANT FIRST
C
C CONST = ((Z/2)**P)/(G*1.77245385)
C WRITE(6,3) CONST
C3 FORMAT(5X,'THE VALUE OF THE CONSTANT IS ',F15.6)
C
C EVALUATE INTEGRAL BETWEEN 0 AND PI
C
C DO 10, I = 1, NOSTEPS, 2
C THETA = I*STEP
C SUM4 = SUM4 + COS(Z*COS(THETA))*((SIN(THETA))**(2*P))
C WRITE(6,8) I, THETA, SUM4
C8 FORMAT(10X,'I = ',I4,' THETA = ',F7.4,' SUM4 = ',F15.6)
C10 CONTINUE
C DO 20, I = 2, NOSTEPS-1, 2
C THETA = I*STEP
C SUM2 = SUM2 + COS(Z*COS(THETA))*((SIN(THETA))**(2*P))
C WRITE(6,9) I, THETA, SUM2
C9 FORMAT(10X,'I = ',I4,' THETA = ',F7.4,' SUM2 = ',F15.6)
C20 CONTINUE
C JBESS = CONST*(STEP/3.0)*(4.0*SUM4 + 2.0*SUM2)
C NOSTEPS = EXSTEPS
C END

```

```

C
C      This subroutine calculates the GAMMA Function for a given
C      value of n. The numerical integration of
C       $t^{(x-1)} * e^{(-t)} dt$  from 0 to b
C      will be made using Simpson's Rule
C
C      OPTIONS /G_FLOATING
C
C      Function GAMMA2(h,x)
C      IMPLICIT REAL*8 (A-H, O-Z)
C
C      Logical LessThan1
C
C      LessThan1 = .False.
C      Sum2 = 0.0
C      Sum4 = 0.0
C      ARG = X
C      PROD = 1
C      x1 = ARG
C      x2 = 1.0
C
C      If (x1 .EQ. 1.0) GO TO 100
C      If (x1 .GT. 1.0) GO TO 50
C
C      If x < 1 then GAMMA can be determined by  $G(x) = G(x+1)/x$ 
C
C      LessThan1 = .True.
C      Test = x1
C      F = x1
C
C      30 Test = Test + 1
C      If (Test .GT. 1.0) then
C          Goto 40
C      Else
C          F = F * Test
C          x2 = x2 + 1
C          Goto 30
C      EndIf
C
C      Calculate G(x+1)
C
C      40 x1 = x1 + x2
C
C      Calculate the number of even Intervals
C
C      50 NIntvl = 1/(h*2)
C      DO 5 I = 1, 20, 1
C          IF(X1-2) 6,6,4
C      4   X1 = X1-1
C          PROD = PROD*X1
C      5   CONTINUE
C
C      Do 10 i = 1, (2*NIntvl-1), 2
C      6   Sum4 = Sum4 + log(1/(i*h))**(x1-1)
C      10 Sum4 = 4*Sum4
C
C      Do 20 i = 2, (2*NIntvl-2), 2
C      20 Sum2 = Sum2 + log(1/(i*h))**(x1-1)
C
C      Sum2 = 2*Sum2
C
C      GAMMA2 = h/3*(log(1/(2*NIntvl*h))**(x1-1) + Sum4 + Sum2)
C      GAMMA2 = PROD*GAMMA2
C
C      Divide by F to correct for GAMMA < 1 cases
C
C      If (LessThan1) GAMMA2 = GAMMA2/F
C      GOTO 200
C
C      x = 1 case
C
C      100 GAMMA2 = 1
C
C      200 End

```


PROGRAMS for AXIAL FLOW ADSORBERS

```

C  AXIALRSP IS THE MAIN PROGRAM THAT DETERMINES SYSTEM PARAMETERS
C  FOR THE RFGC AND CALLS THE SUBROUTINES NEEDED TO PERFORM THE
C  SERIES SOLUTION TO THE IMPULSE PROBLEM FROM THE TIME DOMAIN.
C
C  OPTIONS /G_FLOATING
C
C  PROGRAM AXIALRSP
C
C  IMPLICIT REAL*8 (A-H, O-Z)
C  INTEGER PEAKSTRT(5), ITERRS(5)
C  REAL*8 IAEMIN, LENGTH, MOM0, MOM1, MOM2, MOMCONST, JFACT
C  DIMENSION TIME(2000), THETA(2000), YEXP(2000), PEAKS(5,2000),
C  * OPTPEAKS(5,2000), YOPT(5,2000), EQUILK(5), RESIST(5),
C  * ERRORMIN(5), HETP(5), TMEAN(5), PKSKEW(5), SCALE(5)
C
C  READ-IN EXPERIMENTAL DATA
C
C  OPEN(2,FILE='FINAX109.DAT',STATUS='OLD')
C  REWIND(2)
C  READ(2,1) TIMEDLTA
1  FORMAT(17X,E16.14)
C  WRITE(6,*) TIMEDLTA
C  READ(2,*)
C  READ(2,*)
C  DO 5,I=1,2000
C    NPOINTS = I
C    READ(2,2) TIME(I),YEXP(I)
2  FORMAT(2X,E16.14,3X,E16.14)
C    IF(YEXP(I).EQ.0) GO TO 10
5  CONTINUE
10 CONTINUE
C  CLOSE(2)
C    NPOINTS = NPOINTS - 1
C  WRITE(6,11) NPOINTS
11 FORMAT(2X,'A TOTAL OF 'J4' POINTS WAS READ IN')
C
C  GENERATE BASELINE AND NORMALIZE EXPERIMENTAL DATA
C
C  DO 15,I=1,NPOINTS
C    YEXP(I) = YEXP(I)/(120000*TIMEDLTA)
C  WRITE(6,14)TIME(I),YEXP(I)
C14  FORMAT(2X,'AT T = 'F9.4' CONC = 'F15.6)
15  CONTINUE
C  START = (YEXP(1) + YEXP(2) + YEXP(3) + YEXP(4))/4
C  FINISH = (YEXP(NPOINTS-3) + YEXP(NPOINTS-2) + YEXP(NPOINTS-1) +
C  *YEXP(NPOINTS))/4
C  SLOPE = (FINISH-START)/TIME(NPOINTS-4)
C  SUM = 0
C  DO 17,I=1,NPOINTS
C    YEXP(I) = YEXP(I) - (SLOPE*TIME(I) + START)
C    IF(YEXP(I).LT.0) YEXP(I) = 0
C    SUM = SUM + TIMEDLTA*YEXP(I)
17  CONTINUE
C  DO 18,I=1,NPOINTS
C    YEXP(I) = YEXP(I)/SUM
18  CONTINUE
C
C  CHECK TO ENSURE RAW DATA IS NORMALIZED
C
C  SUMNORM = 0
C  DO 19,I=1,NPOINTS
C    SUMNORM = SUMNORM + YEXP(I)*TIMEDLTA
19  CONTINUE
C  IF(ABS(SLOPE).LT.0.1) GO TO 25
C  WRITE(1,20) SLOPE
20  FORMAT(2X,'WARNING - WARNING - WARNING : BASELINE SLOPE IS 'F8.4)
C  WRITE(6,21) SLOPE, SUM,SUMNORM
C 21  FORMAT(2X,'SLOPE = 'F6.4,' AREA = 'F8.4,' AND NORM AREA = 'F6.4)
25  IF(ABS(1-SUMNORM).LT.05) GO TO 30

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WRITE(1,28)
28  FORMAT(2X,'WARNING - WARNING - WARNING : DATA NOT NORMALIZED')
WRITE(1,29)
29  FORMAT(2X,' ')
30  CONTINUE
C   WRITE(6,35)SUM,SUMNORM
35  FORMAT(5X,'AREA UNDER THE EXP & NORM CURVE IS 'F8.4,' & 'F8.4)
C   DO 37,I= 1, NPOINTS
C     WRITE(6,36)TIME(I),YEXP(I)
C36  FORMAT(5X,'TIME = 'F8.2,5X,'EXP CONC = 'F6.4)
C37  CONTINUE
C
C
C   SPLIT DATA INTO INDIVIDUAL PEAKS
C
C   CALL SPLT3(NPOINTS,TIME,TIMEDLTA,YEXP,NOPEAKS,PEAKS,
* PEAKSTRT,SCALE)
WRITE(6,40) NOPEAKS
40  FORMAT(15X,'THE NUMBER OF PEAKS RETURNED FROM PEAKSPLT IS ',I3)
C   DO 45 I=1,NPOINTS,1
C     WRITE(6,41) TIME(I), YEXP(I), (PEAKS(J,I), J=1,NOPEAKS)
C41  FORMAT(5X,'T = ',F8.4,' EXP = ',F8.6,3X,F8.6,3X,F8.6,3X,F8.6)
C45  CONTINUE
WRITE(6,46) (PEAKSTRT(I), I = 1,NOPEAKS)
46  FORMAT(2X,'PEAKSTRT = ',I4,5X,I4,5X,I4)
C
C
C   OPEN OUTPUT FILE AND WRITE PROBLEM STATEMENT TO IT
C
C   OPEN(1,FILE = 'AXRST109',STATUS = 'NEW',CARRIAGECONTROL='LIST')
WRITE(1,*)( ' ')
WRITE(1,35) SUM, SUMNORM
C
C   INPUT DATA:
C
RADIUS  = 0.15875
LENGTH  = 180.34
TEMP     = 373
VOLFLOW  = 107.4
POROSITY = 0.3
C
C
C   CALCULATE INLET PRESSURE FROM DP DATA
C
PSQUARE = 61.6046*VOLFLOW
PIN = SQRT(PSQUARE + (14.7**2))
C
C   EVALUATE SYSTEM PARAMETERS
C
PRATIO = PIN/14.7
JFACT = 1.5*((PRATIO**2)-1)/((PRATIO**3)-1)
AVGVEL = JFACT*(TEMP/273)*
*(VOLFLOW/60)/(3.1416*(RADIUS**2)*POROSITY)
WRITE(6,90) PRATIO, JFACT
90  FORMAT(5X,'PRESSURE RATIO = ',F7.4' J = ',F7.4)
VOIDAGE = POROSITY/(1-POROSITY)
WRITE(6,91)POROSITY, VOIDAGE
91  FORMAT(5X,'THE POROSITY OF ',F7.4' YIELDS A VOIDAGE OF ',F7.4)
COORD = LENGTH/(AVGVEL*VOIDAGE)
DO 92,I=1,NPOINTS,1
  THETA(I) = TIME(I) - VOIDAGE*COORD
92  CONTINUE
WRITE(6,93) COORD, LENGTH
93  FORMAT(5X,'COORD = ',F8.4' FOR L = ',F9.4)
WRITE(6,*)( ' ')
C
C   WRITE PROBLEM OUTPUT TO FILE
C
WRITE(1,*)( ' ')
WRITE(1,*)( ' ANALYSIS OF RUN AXIAL109/ORIGINAL RICE MODEL')
WRITE(1,*)( ' (AXIAL COLUMN - METHANE/BUTANE SEP) ')
WRITE(1,*)( ' (NEG CONC SET TO 0 AT SMALL TIMES)')
WRITE(1,*)( ' (STARTED WHEN CONC ROSE ABOVE 5% OF CMAX)')
WRITE(1,*)( ' ')
WRITE(1,*)( ' ')
WRITE(1,*)( 'MECHANICAL CONFIGURATION:')

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WRITE(1,*)(' ')
WRITE(1,100) RADIUS, LENGTH
100 FORMAT(2X,' TUBE RADIUS AND LENGTH = ',F6.4' & ',F8.4' CM
* EACH RESPECTIVELY')
WRITE(1,110) POROSITY, VOIDAGE
110 FORMAT(2X,' FOR ASSUMED BED POROSITY = ',F7.4' ETA = ',F7.4)
WRITE(1,*)(' ')
WRITE(1,*)('PROCESS CONDITIONS:')
WRITE(1,*)(' ')
WRITE(1,120) VOLFLOW
120 FORMAT(2X,' VOLUMETRIC FLOW = ',F7.2' CC/SEC @ STP')
WRITE(1,130) TEMP, PIN
130 FORMAT(2X,' TEMP = ',F6.2' KELVIN, PIN (CALC) = ',F5.2)
WRITE(1,*)(' ')
WRITE(1,*)('CALCULATED CONSTANTS:')
WRITE(1,*)(' ')
WRITE(1,140) JFACT
140 FORMAT(2X,' THE COMPRESSIBILITY FACTOR, J, WAS ',F7.4)
WRITE(1,150) AVGVEL
150 FORMAT(2X,' THE AVERAGE INTERSTITIAL VELOCITY WAS ',F10.4'
*CC/SEC')
WRITE(1,160) COORD
160 FORMAT(2X,' THE DISTANCE COORDINATE WAS ',F10.4)
C
WRITE(6,*)(' ')
WRITE(6,*)(' ')
C WRITE(6,415)
C415 FORMAT(4X,'TIME',4X,'EXP DATA',4(' PEAK 1'))
C DO 450 I = 1,NPOINTS,1
C WRITE(6,425)TIME(I),YEXP(I),(PEAKS(J,I),J = 1,NOPEAKS)
C425 FORMAT(2X,F7.2,2X,F9.6,10(2X,F9.6))
C450 CONTINUE
C
C SET UP LOOP TO DETERMINE EQUILK AND RESIST FOR EACH PEAK
C
C
C DO 299, J = 1, NOPEAKS, 1
WRITE(6,200) J
200 FORMAT(10X,'BEGINNING CALCULATIONS FOR PEAK ',I3)
C
C
C USE MOMENTS TO GENERATE IG OFR EQUILK AND RESIST
AND CALCULATE HETP & SKEW
C
C TMEAN(J) = 0
VAR = 0
SKEW = 0
DO 201, I = PEAKSTRT(J),PEAKSTRT(J+1),1
TMEAN(J) = TMEAN(J) + TIME(I)*PEAKS(J,I)*TIMEDLTA
201 CONTINUE
DO 202, I = PEAKSTRT(J),PEAKSTRT(J+1),1
VAR = VAR + ((TIME(I) - TMEAN(J))**2)*PEAKS(J,I)*TIMEDLTA
SKEW = SKEW + ((TIME(I) - TMEAN(J))**3)*PEAKS(J,I)*TIMEDLTA
202 CONTINUE
HETP(J) = (TMEAN(J)**2)/VAR
PKSKEW(J) = SKEW/(VAR**1.5)
MOM0 = 0
MOM1 = 0
MOM2 = 0
DO 205, I = PEAKSTRT(J),PEAKSTRT(J+1),1
IF(THETA(I).GT.0) GO TO 204
PEAKSTRT(J) = I
GO TO 205
204 CONTINUE
MOM0 = MOM0 + (PEAKS(J,I)*TIMEDLTA)
MOM1 = MOM1 + (PEAKS(J,I)*TIMEDLTA*THETA(I))
MOM2 = MOM2 + (PEAKS(J,I)*TIMEDLTA*(THETA(I)**2))
205 CONTINUE
WRITE(6,206) MOM0, MOM1, MOM2
206 FORMAT(5X,'THE FIRST, SCND & THIRD MOMENTS ARE ',3F15.5)
MOMCONST = ((MOM2/MOM0)-((MOM1/MOM0)**2))/(MOM1/MOM0)
RES = MOMCONST/2
CONSTK = (MOM1/MOM0)/COORD
WRITE(6,207) J,CONSTK,RES
207 FORMAT(2X,'FOR PEAK ',I3' MOMENTS YIELDS K = ',F7.4' R = ',F10.4)
C
WRITE(6,208) J, TMEAN(J), HETP(J), PKSKEW(J)
208 FORMAT(5X,'PEAK # ',I2' TMEAN = ',F10.4,' HETP = ',F10.4,
* 'SKEW = ',F12.4)

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```

C
C
C      FIND MAXIMUM CONCENTRATION AND START POINT FOR ITERATIONS
C
C      CMAX = 0
      DO 210,I=PEAKSTRT(J),PEAKSTRT(J+1)
        IF(PEAKS(J,I).GT.CMAX) K=I
        IF(PEAKS(J,I).GT.CMAX) CMAX = PEAKS(J,I)
210  CONTINUE
      START = 0.01*CMAX
      WRITE(6,215)J,CMAX
      WRITE(6,216)TIME(K),THETA(K),START
215  FORMAT(2X,'MAX CONC FOR PEAK ',I3,' IS ',F8.5)
216  FORMAT(2X,'MAX OCCURS @ T = ',F7.2,' THETA = ',F7.2)
      * START = ',F10.7)
      DO 220,I=K,1,-1
        IF(PEAKS(J,I).LT.START) JSTART=I
        IF(PEAKS(J,I).LT.START) GO TO 230
220  CONTINUE
230  CONTINUE
      WRITE(6,235)JSTART,TIME(JSTART)
235  FORMAT(5X,'THE START POINT IS ',I5,' @ T = ',F7.2)
      JSTOP = PEAKSTRT(J+1)

C
C
C      EXECUTE PROCEDURE TO FIND VALUES OF EQUILK AND RESISTANCE THAT
C      MINIMIZE THE IAE BETWEEN EXPT AND CALC RESPONSE
C
C      CALL ORIGMIN(CONSTK, RES, NPOINTS, THETA, TIMEDLTA, J, PEAKS,
      * OPTPEAKS, IAEMIN, JSTART, JSTOP, COORD, ITS)
C
C      EQUILK(J) = CONSTK
      RESIST(J) = RES
      ERRORMIN(J) = 100*IAEMIN
      ITERS(J) = ITS
      WRITE(6,250)K,EQUILK(J),RESIST(J),ERRORMIN(J)
250  FORMAT(5X,'FOR PEAK ',I3,' K= ',F7.4,' R= ',F7.4,' & IAE = ',F7.4)
299  CONTINUE

C
C
C      DATA OUTPUT
C
C
      WRITE(1,*)(' ')
      WRITE(1,*)(' ')
      WRITE(1,*)('RESULTS OF OPTIMIZATION ROUTINE:')
      WRITE(1,*)(' ')
      WRITE(1,301)
301  FORMAT(10X,'PEAK # SORPTION CNST RESISTANCE IAE ITS
      *SCALE')
      DO 310 I=1,NOPEAKS,1
        WRITE(1,305)I,EQUILK(I),RESIST(I),ERRORMIN(I),ITERS(I),
      * SCALE(I)
305  FORMAT(11X,I2,9X,F7.4,7X,F8.4,2X,F6.2,2X,I3,2X,F6.4)
310  CONTINUE
      WRITE(1,*)(' ')
      WRITE(1,*)(' PEAK # TMEAN # OF PLATES SKEW')
      DO 314 I=1,NOPEAKS,1
        WRITE(1,312) I, TMEAN(I), HETP(I), PKSKEW(I)
312  FORMAT(11X,I2,6X,F7.2,6X,F7.2,7X,F5.2)
314  CONTINUE
      WRITE(1,*)(' ')
      WRITE(1,*)(' ')
      WRITE(1,315)
315  FORMAT(4X,'TIME',4X,'EXP DATA',3(' PEAK 1'))
      WRITE(1,*)(' ')
      DO 350 I=1,NPOINTS,1
        WRITE(1,325)TIME(I),YEXP(I),(OPTPEAKS(J,I),J=1,NOPEAKS)
325  FORMAT(2X,F7.2,2X,F9.6,10(2X,F9.6))
350  CONTINUE
      DO 354 I=1,NOPEAKS,1
        WRITE(6,352) I, TMEAN(I), HETP(I), PKSKEW(I)
352  FORMAT(11X,'PEAK # ',I2,' TMEAN = ',F10.4,' PLATES = ',F10.4,
      * ' SKEW = ',F12.4)
354  CONTINUE
      STOP
      END

```



```
60  CONTINUE
100 CONTINUE
    GO TO 200
150 WRITE(1,151)
151 FORMAT(2X,'INITIAL SEARCH FAILED')
200 END
```

```

C
C THIS SUBROUTINE PERFORMS A TWO-DIMENSIONAL PATTERN SEARCH
C TO DETERMINE THE PARAMETERS THAT MINIMIZES THE IAE BETWEEN
C A THERORETICAL RESULT AND A SET OF EXPERIMENTAL DATA POINTS
C
C OPTIONS /G_FLOATING
C
C SUBROUTINE ORIGSRCH(X1, X2, NPOINTS, THETA, TIMEDLTA, J, PEAKS,
* OPTPEAKS, DEL, IAE, JSTART, JSTOP, COORD)
IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION THETA(2000), PEAKS(5,2000), OPTPEAKS(5,2000),
* FRSTY(2000), SCNDY(2000), CONCOPT(2000)
REAL*8 IAE
C
C DEFINE INITIAL CONSTANTS
C
IAE = 0
DO 3, I = 1, NPOINTS
  OPTPEAKS(J,I) = 0
  CONCOPT(I) = 0
3 CONTINUE
C
C CALCULATE IAE FOR INITIAL GUESS
C
WRITE(6,4) X1, X2
C4 FORMAT(10X, 'INITIAL GUESSES = ', F7.4, ' & ', F7.4)
CALL ORIGRICE(THETA, CONCOPT, X1, X2, JSTART, JSTOP, NPOINTS,
* COORD)
DO 7, I = JSTART, JSTOP
  IAE = IAE + ABS(PEAKS(J,I) - CONCOPT(I)) * (TIMEDLTA)
7 CONTINUE
C WRITE(6,8) IAE
C8 FORMAT(12X, 'THE IAE FOR THE IGS IS ', F10.4)
DO 10, I = 1, NPOINTS, 1
  OPTPEAKS(J,I) = CONCOPT(I)
10 CONTINUE
C
C EXPLORATORY SEARCH FOR FRSTPARM
C
C POSITIVE INCREMENT
C
FRSTIAE = 0
FRSTK = X1 + DEL
DO 15, I = 1, NPOINTS
  FRSTY(I) = 0
15 CONTINUE
C WRITE(6,16) FRSTK, X2
C16 FORMAT(10X, 'FIRST INCREMENTS XS: ', F7.4, ' & ', F7.4)
CALL ORIGRICE(THETA, FRSTY, FRSTK, X2, JSTART, JSTOP, NPOINTS,
* COORD)
DO 20, I = JSTART, JSTOP
  FRSTIAE = FRSTIAE + ABS(PEAKS(J,I) - FRSTY(I)) * (TIMEDLTA)
20 CONTINUE
C WRITE(6,21) FRSTIAE
C21 FORMAT(12X, 'IAE FOR THIS GUESS = ', F10.4)
C
C NEGATIVE INCREMENT
C
SCNDIAE = 0
SCNDK = X1 - DEL
C WRITE(6,23) SCNDK, X2
C23 FORMAT(10X, 'THE SECOND INCREMENTS : ', F7.4, ' & ', F7.4)
DO 24, I = 1, NPOINTS
  SCNDY(I) = 0
24 CONTINUE
CALL ORIGRICE(THETA, SCNDY, SCNDK, X2, JSTART, JSTOP, NPOINTS,
* COORD)
DO 26, I = JSTART, JSTOP
  SCNDIAE = SCNDIAE + ABS(PEAKS(J,I) - SCNDY(I)) * (TIMEDLTA)
26 CONTINUE
C WRITE(6,27) SCNDIAE
C27 FORMAT(12X, 'IAE FOR THIS GUESS = ', F10.4)
C
C COMPARE FIRST SEARCH TO PREVIOUS (INITAL) GUESS
C
IF(SCNDIAE.GE.FRSTIAE) GO TO 30
FRSTIAE = SCNDIAE
FRSTK = SCNDK

```

```

DO 28,I = 1,NPOINTS
  FRSTY(I) = SCNDY(I)
28  CONTINUE
30  IF(FRSTIAE.GE.IAE) GO TO 35
    X1 = FRSTK
    IAE = FRSTIAE
    DO 31,I = 1,NPOINTS
      OPTPEAKS(J,I) = FRSTY(I)
31  CONTINUE
35  CONTINUE
C
C
C      EXPLORATORY SEARCH FOR SCNDPARM
C
C  POSITIVE INCREMENT
C
  FRSTIAE = 0
  FRSTRES = X2 + 0.1*DEL
C  WRITE(6,38) X1, FRSTRES
C38  FORMAT(10X,'THE THIRD INCREMENTS : ',F7.4,' & ',F7.4)
  DO 39,I = 1,NPOINTS
    FRSTY(I) = 0
39  CONTINUE
  CALL ORIGRICE(THETA, FRSTY, X1, FRSTRES, JSTART, JSTOP, NPOINTS,
    * COORD)
  DO 41,I = JSTART,JSTOP
    FRSTIAE = FRSTIAE + ABS(PEAKS(J,I)-FRSTY(I))*(TIMEDLTA)
41  CONTINUE
C  WRITE(6,42) FRSTIAE
C42  FORMAT(12X,'THE IAE FOR THIS SET OF GUESSES = ',F10.4)
C
C  NEGATIVE INCREMENT
C
  SCNDIAE = 0
  SCNDRES = X2 - 0.1*DEL
C  WRITE(6,43) X1, SCNDRES
C43  FORMAT(10X,'THE LAST INCREMENTS ARE ',F7.4' AND ',F7.4)
  DO 44,I = 1,NPOINTS
    SCNDY(I) = 0
44  CONTINUE
  CALL ORIGRICE(THETA, SCNDY, X1, SCNDRES, JSTART, JSTOP, NPOINTS,
    * COORD)
  DO 46,I = JSTART,JSTOP
    SCNDIAE = SCNDIAE + ABS(PEAKS(J,I)-SCNDY(I))*(TIMEDLTA)
46  CONTINUE
C  WRITE(6,47)SCNDIAE
C47  FORMAT(12X,'THE FINAL IAE IS ',F10.4)
C
C      COMPARE TO PREVIOUS (INITAL) GUESS
C
  IF(SCNDIAE.GE.FRSTIAE) GO TO 50
    FRSTIAE = SCNDIAE
    FRSTRES = SCNDRES
    DO 49,I = 1,NPOINTS
      FRSTY(I) = SCNDY(I)
49  CONTINUE
50  IF(FRSTIAE.GE.IAE) GO TO 52
    X2 = FRSTRES
    IAE = FRSTIAE
    DO 51,I = 1,NPOINTS
      OPTPEAKS(J,I) = FRSTY(I)
51  CONTINUE
52  CONTINUE
55  END

```



```

C  ORIGRICE IS THE PROGRAM THAT CALCULATE THE IMPULSE RESPONSE OF
C  AN ADSORBER BASED ON RICE'S ORIGINAL MODEL IN WHICH FLUID
C  PHASE DISPERSION IS NEGLIGIBLE. THE EQUILIBRIUM SORPTION
C  CONSTANT AND MASS TRANSFER RESISTANCES DICTATE THE RESPONSE IN
C  THIS CASE.

```

```

C  OPTIONS /G_FLOATING

```

```

C  SUBROUTINE ORIGRICE(THETA,CONC,CONSTK,RES,JSTART,JSTOP,NPOINTS,
C  *COORD)

```

```

C  IMPLICIT REAL*8(A-H, O-Z)
C  REAL*8 NUMCONST
C  DIMENSION THETA(2000), CONC(2000)
C  DO 50 I = JSTART,JSTOP,1
C    S = CONSTK*COORD/RES
C    NUMCONST = 1/(2*(3.141593**0.5))
C    EXPARG = 2*((S*THETA(I)/RES)**0.5) - S - THETA(I)/RES
C    CONC(I) = 0
C    IF(EXPARG.LT.-50.0) GO TO 48
C    CONC(I) = NUMCONST * ((S/RES)**0.25) * 1/(THETA(I)**0.75)
C  ** EXP(EXPARG)
48  CONTINUE
C  WRITE(6,49)S,THETA(I),EXPARG,CONC(I)
C49  FORMAT(5X,'S= ',F9.4' THETA= ',F9.4' EXPARG= ',F9.4' C= ',F6.4)
50  CONTINUE
C  RETURN
C  END

```

PROGRAMS for LAPLACE SOLUTIONS and INVERSIONS

```

C  Needs subroutines INVLT and SYST and an INPUT FILE
C  SYST contains the function to be inverted
C  INPUT FILE must contain one line with:
C  # of time values to be evaluated, first time value, time increment
C  ie. 20,0.05,0.05 (to get 20 values from 0.05 to 1.0)
C
C  Open and read in input file
C
C  Open(1,file='LTINPUT',status='OLD')
C  Rewind(1)
C  Read(1,*) Nobs, Tinit, Tdel
C  Close(1)
C
C  Write Heading
C
C  OPEN(2,FILE='PULSE',STATUS='NEW',CARRIAGECONTROL='LIST')
C  WRITE(2,*)( ' TIME ORIGINAL WRONSKIAN' )
C  WRITE(2,*)( ' ' )
C  Write(6,86)
86  Format(4x,'Time',10x,'ZAKIAN')
C
C  Calculate Value Determined by Zakian Inversion
C
C  Z1 = 1
C  Do 12 j=1, Nobs
C    T = Tinit + (j-1)*Tdel
C    Call TESTINVT(T,FT)
C    WRITE(2,*)(T,FT)
C    Write(6,*) T, FT
12  CONTINUE
C  CLOSE(2)
C  Stop
C  End

```

```
C
C      For a given value of T, the subroutine returns the inverse of
C      the LT, Ft.
C
C      The LT must be available as a user supplied subroutine SYST
C
C      OPTIONS /G_FLOATING
C
C      Subroutine RESPINVT(T,Ft,BETA,Z1,Z1NEG,Z2,Z2NEG,GAMMA1,GAMMA2,
C      * GAMMA3,GAMMA4)
C      IMPLICIT REAL*8 (A-H, O-Z)
C      Complex*16 s, Func, Kap(5), Alph(5)
C
C      Values of constants
C
C      Alph(1) = (1.28376768e+01,1.66606344e+00)
C      Alph(2) = (1.22261321e+01,5.01271879e+00)
C      Alph(3) = (1.09343031e+01,8.40967312e+00)
C      Alph(4) = (8.77643472e+00,1.19218539e+01)
C      Alph(5) = (5.22545336e+00,1.57295290e+01)
C
C      Kap(1) = (-3.69020821e+04, 1.96990426e+05)
C      Kap(2) = ( 6.12770252e+04,-9.54086255e+04)
C      Kap(3) = (-2.89165629e+04, 1.81691853e+04)
C      Kap(4) = ( 4.65536114e+03,-1.90152864e+00)
C      Kap(5) = (-1.18741401e+02,-1.41303691e+02)
C
C      Evaluate ZAKIAN Sum
C
C      Sum = 0.0
C      Do 10 i=1,5
C      S = Alph(i)/T
C      Call SHORT(S, Func, BETA, Z1, Z1NEG, Z2, Z2NEG, GAMMA1,
C      * GAMMA2, GAMMA3, GAMMA4)
10  Sum = Sum + Real(Kap(i)*Func)
C      Ft = 2*Sum/T
C      Return
C      End
```

```

C THIS PROGRAM EVALUATES THE LAPALCE SOLUTION FOR A RADIAL FLOW
C CHROMATOGRAPH.
C
C FACT CALCULATES FACTORIALS FOR INTEGERS
C
FUNCTION FACT(N)
  SUM = 0
  IF(N.LT.2) GO TO 12
  DO 10 I = N,1,-1
    SUM = SUM + LOG(REAL(I))
  10 CONTINUE
  12 FACT = SUM
END
C
C
C POSBESS CALCULATES BESSEL FUNCTIONS OF POSITIVE ORDER Z1 AND ARG FX1
C
FUNCTION BESSPOS(Z1,FX1)
  COMPLEX FX1, SUM, SUMTOT, BESSPOS
  REAL*8 GAMMA
  SUM = 0
  SUMTOT = 0
  H = 0.0001
  G = LOG(GAMMA(H,Z1))
  DO 10 I = 0,100,1
    G = G + LOG(Z1+I)
    SUM = EXP((Z1+2*I)*LOG(FX1/2) - FACT(I) - G)
    IF (ABS(SUM).LT.0.00001) GO TO 20
    SUMTOT = SUMTOT + SUM
  10 CONTINUE
  20 BESSPOS = SUMTOT
  WRITE(6,21)
  21 FORMAT('THE VALUE OF SUMTOT/BESSPOS IS:')
  WRITE(6,*)BESSPOS
END
C
C
C NEGBESS CALCULATES BESSEL FUNCTIONS OF NEGATIVE ORDER Z2 AND ARG FX2
C
FUNCTION BESSNEG(Z2,FX2)
  COMPLEX FX2, SUM, SUMTOT, BESSNEG
  REAL*8 GAMMA, G
  SUM = 0
  SUMTOT = 0
  H = 0.0001
  G = GAMMA(H,Z2)
  5 DO 10, I=0,100,1
    G = G * (Z2 + I)
    IF(G.LT.0) GO TO 8
    SUM = EXP((2*I-Z2)*LOG(FX2/2) - FACT(I) - LOG(G))
    GO TO 9
  8 SUM = EXP((2*I-Z2)*LOG(FX2/2) - FACT(I))/G
  9 IF(ABS(SUM).LT.0.00001) GO TO 20
  SUMTOT = SUMTOT + SUM
  10 CONTINUE
  20 BESSNEG = SUMTOT
  WRITE(6,21)
  21 FORMAT(2X,'THE VALUE OF SUMTOT/BESSNEG IS:')
  WRITE(6,*)BESSNEG
END
C
C SUBROUTINE LPLSOL(S,FUNC)
C
C SPECIFY COMPLEX VARIABLES
C
COMPLEX S, FX1, FX2, BESS1, BESS2, BESS3, BESS4, BESS5,
* BESS6, BESSPOS, BESSNEG, FUNC
REAL IRADIUS, MULT
COMPLEX*16 DENOM, NUM
C
C
C CALCULATE ARGUEMENTS AND ORDERS OF BESSEL FUNCTIONS
C
C INPUT CONSTANTS ARE :
C
ORADIUS = 3.6513
IRADIUS = 0.3175
BEDHITE = 0.4763
TEMP = 373

```

```

PIN = 1
VOLFLOW = 100
EQUILK = 1.5
POROSITY = 0.12
DISPCOEF = 1.0
C
C CALCULATED PARAMETERS ARE:
C
ETA = POROSITY/(1-POROSITY)
QACT = (VOLFLOW/60)*(14.7/(14.7+PIN))*(TEMP/298)
CONVDIFF = QACT/(2*3.1416*BEDHITE*POROSITY)
BETA = SQRT((EQUILK + ETA)/(ETA*DISPCOEF))
BASEORDR = CONVDIFF/(2*DISPCOEF)
WRITE(6,5)ETA,BETA,BASEORDR
5  FORMAT(2X,'ETA = ',F8.4,' BETA = ',F8.4,' ALPHA = ',F8.4)
WRITE(6,*)S
C
C CALCULATE ORDERS AND ARGUEMENTS OF BESSEL SUNCTIONS
C
Z1 = BASEORDR
Z11 = -Z1
Z2 = BASEORDR - 1
Z22 = -Z2
FX1 = BETA*SQRT(S)*ORADIUS
FX2 = BETA*SQRT(S)*IRADIUS
WRITE(6,6)
6  FORMAT(2X,'ORDERS OF THE BESSEL FUNCTIONS:')
WRITE(6,*)Z1,Z11,Z2,Z22
WRITE(6,7)
7  FORMAT(2X,'SQRT OF S, OUTER RADIUS AND INNER RADIUS:')
WRITE(6,*)SQRT(S),ORADIUS,IRADIUS
WRITE(6,8)
8  FORMAT(2X,'ARGUEMENTS OF THE BESSEL FUNCTIONS:')
WRITE(6,*)FX1,FX2
C
C CALCULATE BESSEL FUNCTIONS:
C
BESS1 = BESSPOS(Z2,FX1)
BESS2 = BESSNEG(Z11,FX1)
BESS3 = BESSNEG(Z22,FX1)
BESS4 = BESSPOS(Z1,FX1)
BESS5 = BESSNEG(Z11,FX2)
BESS6 = BESSPOS(Z1,FX2)
C
WRITE(6,27)
WRITE(6,27)
WRITE(6,27)
WRITE(6,28)
27  FORMAT(2X,' ')
28  FORMAT(2X,'ORDER, ARGUEMENT AND VALUE OF BESSEL FUNCTS:')
WRITE(6,*)Z2,FX1,BESS1
WRITE(6,*)Z11,FX1,BESS2
WRITE(6,*)Z22,FX1,BESS3
WRITE(6,*)Z1,FX1,BESS4
WRITE(6,*)Z11,FX2,BESS5
WRITE(6,*)Z1,FX2,BESS6
C
C CALCULATE SOLUTION IN LAPLACE DOMAIN:
C
WRITE(6,29)
DENOM = BESS1*BESS5 - BESS3*BESS6
WRITE(6,*)DENOM
NUM = BESS1*BESS2 - BESS3*BESS4
WRITE(6,*)NUM
MULT = (ORADIUS/IRADIUS)**Z1
WRITE(6,*)MULT
FUNC = MULT * NUM/DENOM
WRITE(6,*)FUNC
29  FORMAT(2X,' THE DENOM, NUM, MULT, & CONCENTRATION ARE: ')
30  RETURN
END

```

```

C
C      For a given value of T, the subroutine returns the inverse of
C      the LT, Ft.
C
C      The LT must be available as a user supplied subroutine SYST
C
C      OPTIONS /G_FLOATING
C
C      Subroutine INVL(T,Ft,BETA,Z1,Z1NEG,Z2,Z2NEG,GAMMA1,GAMMA2,
C      * GAMMA3, GAMMA4)
C      IMPLICIT REAL*8 (A-H, O-Z)
C      Complex*16 s, Func, ALTFUNC, Kap(5), Alph(5)
C
C      Values of constants
C
C      Alph(1) = (1.28376768e+01,1.66606344e+00)
C      Alph(2) = (1.22261321e+01,5.01271879e+00)
C      Alph(3) = (1.09343031e+01,8.40967312e+00)
C      Alph(4) = (8.77643472e+00,1.19218539e+01)
C      Alph(5) = (5.22545336e+00,1.57295290e+01)
C
C      Kap(1) = (-3.69020821e+04, 1.96990426e+05)
C      Kap(2) = ( 6.12770252e+04,-9.54086255e+04)
C      Kap(3) = (-2.89165629e+04, 1.81691853e+04)
C      Kap(4) = ( 4.65536114e+03,-1.90152864e+00)
C      Kap(5) = (-1.18741401e+02,-1.41303691e+02)
C
C      Evaluate ZAKIAN Sum
C
C      ALTSUM = 0.0
C      Sum = 0.0
C      Do 10 i=1,5
C          s = Alph(i)/T
C          Call SHORT(s, Func, BETA, Z1, Z1NEG, Z2, Z2NEG, GAMMA1,
C      * GAMMA2, GAMMA3, GAMMA4)
10      Sum = Sum + Real(Kap(i)*Func)
C      Ft = 2*Sum/T
C      Return
C      End

```

APPENDIX III

Porosity Analysis of F-1 Alumina

AUTOCORE 11 9220 V1.07

SAMPLE NUMBER: 88 OPERATOR: SCD
 SAMPLE ID: F1 AL(8)
 SLEWITTER: RGR

LF 18:48:48 10/31/90
 RP 18:17:29 10/31/90
 REP 18:24:15 10/31/90

PRESSURE	PORE DIPHE SA	CUMULATIVE VOLUME	CUMULATIVE PORE AREA	DIFFEREN. VOL. dV/dP	ICE DIFF. VOL. dV/dP
psia	cm	cm ³	cm ² /g	ml/g-psi	ml/g
1.83	118.2528	0.0000	0.000	0.000E+00	0.000E+00
2.03	39.2020	0.0122	0.003	4.297E-04	1.020E-01
2.31	72.0650	0.0411	0.003	1.887E-03	3.082E-01
2.60	89.2012	0.1087	0.008	3.713E-03	3.873E-01
2.91	91.2534	0.1402	0.012	1.531E-03	1.387E-01
3.21	91.2481	0.1531	0.018	3.343E-04	3.117E-01
3.59	49.3217	0.4122	0.030	3.512E-03	3.512E+00
4.30	40.2347	0.5202	0.040	2.050E-03	2.017E+00
4.92	38.2232	0.5701	0.048	1.245E-03	1.037E+00
5.93	30.2123	0.6122	0.050	7.502E-03	5.712E-01
6.97	25.9213	0.6322	0.052	4.737E-03	3.057E-01
7.98	22.2741	0.6451	0.052	4.140E-03	3.217E-01
8.95	20.1992	0.6527	0.057	2.880E-03	1.311E-01
9.93	18.1751	0.6627	0.058	4.009E-03	1.789E-01
11.94	15.1422	0.6711	0.060	2.422E-03	9.222E-02
13.94	12.9727	0.6752	0.061	2.136E-03	7.102E-02
15.92	11.3592	0.6792	0.063	2.504E-03	7.004E-02
17.91	10.0325	0.6821	0.064	1.743E-03	4.302E-02
19.92	9.0202	0.6847	0.065	2.529E-03	5.577E-02
21.92	8.2229	0.6872	0.066	3.011E-03	5.932E-02
23.92	7.5436	0.6878	0.066	3.371E-04	9.746E-03
25.20	6.4223	0.6857	0.067	9.206E-04	1.272E-02
25.89	6.0217	0.6894	0.067	1.511E-03	2.746E-02
31.91	5.2274	0.6920	0.068	-3.224E-03	-2.152E-01
37.02	4.2774	0.6908	0.068	3.242E-03	3.537E-02
42.02	4.1000	0.6918	0.069	1.902E-03	1.006E-02
43.92	3.6201	0.6924	0.070	1.222E-03	1.222E-02
52.02	2.4742	0.6924	0.070	-7.300E-02	-5.131E-02
62.14	2.5107	0.6928	0.074	5.890E-03	4.222E-02
71.72	2.2192	0.6950	0.074	9.221E-04	5.720E-03
82.02	2.2041	0.6978	0.077	5.757E-03	3.142E-02
91.92	1.9672	0.6978	0.077	-2.122E-02	-1.022E-04
101.92	1.7744	0.6978	0.077	-2.712E-02	-1.122E-04
121.20	1.4222	0.6922	0.079	2.532E-03	9.422E-03
141.91	1.2742	0.7007	0.083	1.022E-02	3.242E-02
161.27	1.1194	0.7022	0.083	1.414E-02	3.221E-02
182.60	0.9902	0.7037	0.096	3.610E-03	1.361E-02
201.13	0.8993	0.7042	0.100	1.197E-02	2.602E-02
226.01	0.2002	0.7055	0.104	7.222E-03	1.422E-02
252.12	0.7172	0.7073	0.113	2.122E-02	3.221E-02
301.67	0.5992	0.7092	0.126	1.849E-02	2.792E-02
352.65	0.5129	0.7122	0.150	3.781E-02	4.222E-02
401.03	0.4210	0.7137	0.174	4.706E-02	5.212E-02
450.21	0.4017	0.7182	0.202	5.909E-02	5.792E-02
501.15	0.3609	0.7211	0.228	6.222E-02	5.462E-02

ALTOX-11 9800 V1.07

SAMPLE NUMBER: 55 OPERATOR: SPD
 SAMPLE ID: F1 AL(6)
 SUBMITTER: RGR

LP 16:45:48 10/29/90
 HP 16:17:29 10/31/90
 REP 16:24:16 10/31/90

PRESSURE PSIA	PORE DIAMETER UM	CUMULATIVE VOLUME ML/g	CUMULATIVE PORE AREA CM ² /g	DIFFEREN. VOL CM ³ /CD ML/g-UM	LOG DIFF. VOL CM ³ /logD ML/g
604.12	0.2584	0.7289	0.299	9.461E-02	7.171E-02
700.57	0.2581	0.7295	0.325	8.107E-02	3.912E-02
800.76	0.2555	0.7327	0.389	1.008E-01	5.602E-02
902.27	0.2002	0.7356	0.443	1.122E-01	5.456E-02
995.97	0.1609	0.7370	0.473	7.391E-02	3.883E-02
1213.30	0.1491	0.7391	0.790	4.121E-01	1.260E-01
1414.28	0.1279	0.7559	0.957	2.784E-01	8.668E-02
1503.25	0.1128	0.7580	1.027	1.392E-01	3.854E-02
1605.79	0.1002	0.7612	1.147	2.538E-01	5.212E-02
2002.26	0.0903	0.7625	1.305	1.392E-01	3.051E-02
2252.25	0.0803	0.7606	1.113	-1.957E-01	-3.841E-02
2393.07	0.0504	0.7872	1.488	3.322E-01	5.247E-02
3489.41	0.0518	0.7738	1.941	7.402E-01	9.648E-02
3584.59	0.0484	0.7781	2.314	7.031E-01	7.859E-02
4210.35	0.0401	0.7819	2.668	7.153E-01	7.031E-02
4355.67	0.0382	0.7875	3.250	1.448E+00	1.271E-01
5575.79	0.0302	0.7984	4.574	1.832E+00	1.358E-01
5562.62	0.0259	0.8101	2.834	2.584E+00	1.731E-01
7569.38	0.0227	0.8210	3.025	3.409E+00	1.902E-01
8571.84	0.0202	0.8201	9.725	3.591E+00	1.769E-01
9574.33	0.0181	0.8411	12.022	3.402E+00	2.331E-01
11559.12	0.0151	0.8554	15.712	3.652E+00	1.947E-01
12534.19	0.0130	0.8672	16.941	3.289E+00	1.706E-01
13527.52	0.0114	0.8751	21.521	7.002E+00	1.550E-01
17536.40	0.0101	0.8875	22.843	6.862E+00	1.542E-01
19508.77	0.0091	0.8924	29.103	7.322E+00	1.722E-01
22572.72	0.0073	0.9171	33.715	1.152E+01	2.241E-01
25624.65	0.0051	0.9417	24.440	2.023E+01	3.056E-01
34559.66	0.0032	0.9850	71.043	2.833E+01	3.400E-01
39514.34	0.0045	0.9923	51.109	3.790E+01	4.222E-01
42530.44	0.0040	1.0172	117.175	5.617E+01	5.332E-01
45783.86	0.0032	1.0491	147.334	7.226E+01	5.373E-01
54252.41	0.0033	1.0766	164.886	9.630E+01	7.679E-01
58733.01	0.0030	1.1035	219.217	9.933E+01	7.227E-01

ALTOPCORE II 9820 V1.07

SAMPLE NUMBER: 55 OPERATOR: SCS

SAMPLE ID: F1 AL(6)

SUBMITTER: RGR

LB 16:46:46 10/25/90
RP 16:17:29 10/31/90
REP 16:24:16 10/31/90

DIAMETER VS CUMULATIVE INTRUSION

AUTOPURE II 9220 V1.07

SAMPLE NUMBER: 55 OPERATOR: SJD
SAMPLE ID: F1 AL(6)
SUBMITTER: RGR

LP 16:45:48 10/29/90
HP 16:17:29 10/31/90
REP 16:24:16 10/31/90

DIAMETER VS DIFFERENTIAL INTRUSION

ALTOPORE II S220 V1.07

SAMPLE NUMBER: 55 OPERATOR: SJD
SAMPLE ID: F1 PL(6)
SUBMITTER: RSR

LS 16:45:49 10/29/90
LS 16:17:23 10/31/90
RSR 16:13:16 10/31/90

DIAMETER VS LOG DIFFERENTIAL INTRUSION

ANALYSIS 11 9220 VL07

SAMPLE NUMBER: 55 OPERATOR: SDD

SAMPLE ID: F1 PL(6)

SMPLTTER: RSR

12 12:45:43 10/29/90

13 12:17:22 10/21/90

14 12:14:12 10/21/90

DIAMETER VS CUMULATIVE PORE VOLUME

MEASURE II 9820 V1.07

SAMPLE NUMBER: 58 OPERATOR: SJD
 SAMPLE ID: FIAL(7)
 SUBMITTER: RGR

LP 16:04:28 11/07/90
 HP 17:41:13 11/07/90
 REP 17:41:19 11/07/90

PENETROMETER NUMBER: 181708	ADVANCING CONTACT ANGLE: 139.0 deg
PENETROMETER CONSTANT: 10.79 $\mu\text{L}/\text{m}^2$	RECEDING CONTACT ANGLE: 130.0 deg
PENETROMETER WEIGHT: 71.8180 g	MERCURY SURFACE TENSION: 485.0 dyne/cm
STEM VOLUME: 0.3580 mL	MERCURY DENSITY: 13.5310 g/mL
MAXIMUM HEAD PRESSURE: 4.4800 cmHg	SAMPLE WEIGHT: 0.1930 g
PENETROMETER VOLUME: 5.3920 mL	SAMPLE+PEN+H ₂ WEIGHT: 143.4397 g

LOW PRESSURE:
 EVACUATION PRESSURE: 50 μmHg
 EVACUATION TIME: 30 min
 MERCURY FILLING PRESSURE: 1.5275 cmHg
 EQUILIBRATION TIME: 30 sec

HIGH PRESSURE:
 EQUILIBRATION TIME: 30 sec

INTRUSION DATA SUMMARY

TOTAL INTRUSION VOLUME =	1.0897 mL/g
TOTAL PORE AREA =	802.838 cm^2/g
MEDIAN PORE DIAMETER (VOLUME) =	41.7147 μm
MEDIAN PORE DIAMETER (AREA) =	0.0041 μm
AVERAGE PORE DIAMETER (AV/2) =	0.0813 μm
BULK DENSITY =	1.3937 g/mL
STEM VOLUME LOSS =	54 %

ALLURE 11 9829 VL07

SAMPLE NUMBER: 53 OPERATOR: SCD
SAMPLE ID: FIAL(7)
SUBSTRATE: R04

LP 16:04:23 11/07/90
HP 17:41:13 11/07/90
RP 17:41:19 11/07/90

Pressure Psi	Pore Diameter um	EXHAUSTIVE VOLUME ML/g	CUMULATIVE PORE AREA sq-m/g	DIFFERENTIAL VOL. G/PSI	RELATIVE ML/g-um	RELATIVE ML/g
1.23	118.2772	0.0000	0.000	0.0000-00	0.0000-00	0.0000-00
2.02	29.7026	0.0229	0.001	7.5735-04	1.5552-01	1.5552-01
3.22	71.7524	0.0724	0.003	3.7543-03	3.1133-01	3.1133-01
3.01	50.1693	0.1693	0.010	1.0103-02	1.3502-00	1.3502-00
3.45	51.2727	0.3334	0.022	3.0432-02	3.5223-00	3.5223-00
3.45	51.8543	0.3703	0.025	4.5702-01	3.4532-01	3.4532-01
3.55	45.4131	0.4551	0.033	1.5232-02	3.0442-00	3.0442-00
3.55	42.4121	0.4553	0.034	0.0000-00	0.0000-00	0.0000-00
4.50	40.2303	0.5309	0.040	1.2443-02	1.5332-01	1.5332-01
4.55	39.2232	0.5993	0.043	3.7232-02	7.8732-01	7.8732-01
4.97	30.2707	0.8301	0.043	5.7613-03	4.1133-01	4.1133-01
5.55	23.5692	0.8505	0.051	4.8402-03	3.1133-01	3.1133-01
7.97	22.7015	0.8631	0.052	3.4472-03	1.5332-01	1.5332-01
8.96	20.1531	0.8710	0.054	3.3282-03	1.7432-01	1.7432-01
9.55	18.1810	0.8755	0.055	3.3052-03	3.7332-02	3.7332-02
11.95	15.1272	0.8843	0.057	2.5032-03	1.1112-01	1.1112-01
12.94	12.9712	0.8934	0.058	3.3732-03	7.8632-02	7.8632-02
15.22	11.5222	0.8945	0.060	3.3942-03	3.4532-01	3.4532-01
17.51	10.1002	0.8972	0.061	1.5532-03	4.8732-02	4.8732-02
18.99	9.0456	0.8997	0.062	3.2742-03	3.0032-02	3.0032-02
21.55	8.2252	0.7021	0.063	3.6132-03	3.7502-02	3.7502-02
23.97	7.5442	0.7034	0.064	1.5332-03	3.5132-02	3.5132-02
25.32	5.5677	0.7031	0.066	4.8742-03	7.5032-02	7.5032-02
28.18	5.4132	0.7033	0.067	3.3732-04	3.5132-02	3.5132-02
30.00	5.0132	0.7033	0.067	3.0232-03	7.1502-02	7.1502-02
34.90	4.3052	0.7035	0.068	4.1632-04	3.5332-02	3.5332-02
44.22	4.0221	0.7035	0.069	3.8432-03	3.7542-02	3.7542-02
50.27	3.8572	0.7112	0.070	7.6532-04	3.7432-02	3.7432-02
50.27	3.0002	0.7129	0.072	3.8332-03	3.1432-02	3.1432-02
70.47	3.5635	0.7143	0.074	3.5532-03	3.1342-02	3.1342-02
60.42	3.2451	0.7153	0.075	3.1032-03	1.1272-02	1.1272-02
60.35	3.0016	0.7153	0.077	4.0232-03	1.5332-02	1.5332-02
100.20	1.7557	0.7155	0.077	3.7502-03	3.5332-04	3.5332-04
115.50	1.8135	0.7150	0.084	3.4532-03	3.5332-03	3.5332-03
135.50	1.8537	0.7193	0.085	1.4232-03	4.8032-02	4.8032-02
155.55	1.1228	0.7155	0.087	4.0752-03	1.1272-02	1.1272-02
175.75	1.0061	0.7186	0.088	1.0552-03	3.7042-02	3.7042-02
200.32	0.8029	0.7193	0.087	1.5552-03	3.5442-02	3.5442-02
224.51	0.8056	0.7223	0.101	3.1242-02	3.1322-02	3.1322-02
245.14	0.7250	0.7226	0.099	4.7052-03	3.8332-03	3.8332-03
295.16	0.5046	0.7256	0.124	3.3152-02	3.0552-02	3.0552-02
345.56	0.5174	0.7305	0.152	4.6212-02	3.5572-02	3.5572-02
358.16	0.4542	0.7343	0.183	5.8412-02	3.5322-02	3.5322-02
430.90	0.4011	0.7355	0.195	3.4222-02	3.3552-02	3.3552-02

ALTITUDE IT 9880 V1.07

SAMPLE NUMBER: 58 OPERATOR: SJD
 SAMPLE ID: FIAL(7)
 SUBMITTER: RGR

LP 16:04:28 11/07/90
 HP 17:41:13 11/07/90
 REP 17:41:19 11/07/90

PRESSURE psia	PORE DIAMETER µm	CUMULATIVE VOLUME mL/g	CUMULATIVE PORE AREA sq-m/µ	DIFFEREN. VOL dv/ds mL/g-µm	LOG DIFF. VOL dv/dlogD mL/g
497.82	0.2833	0.7375	0.215	5.250E-02	4.818E-02
501.51	0.3002	0.7429	0.220	5.488E-02	5.432E-02
701.26	0.2579	0.7455	0.317	6.052E-02	3.911E-02
800.15	0.2250	0.7481	0.350	5.159E-02	4.239E-02
900.85	0.2008	0.7510	0.415	1.182E-01	5.703E-02
1002.69	0.1802	0.7533	0.462	1.103E-01	4.635E-02
1205.22	0.1501	0.7551	0.505	5.270E-02	2.525E-02
1359.71	0.1292	0.7579	0.566	1.350E-01	4.332E-02
1507.27	0.1125	0.7614	0.701	2.082E-01	5.793E-02
1798.93	0.1005	0.7632	0.763	1.497E-01	3.882E-02
2005.89	0.0905	0.7665	0.914	3.350E-01	7.352E-02
2255.79	0.0801	0.7690	1.027	2.392E-01	4.856E-02
2589.22	0.0605	0.7739	1.303	2.468E-01	3.971E-02
3488.62	0.0518	0.7794	1.694	5.348E-01	8.155E-02
3587.64	0.0454	0.7839	2.053	5.906E-01	7.718E-02
4511.58	0.0401	0.7863	2.480	5.452E-01	6.307E-02
4991.10	0.0352	0.7916	2.845	9.084E-01	7.958E-02
5583.01	0.0302	0.8022	4.094	1.722E+00	1.317E-01
6572.92	0.0235	0.8122	5.322	2.339E+00	1.510E-01
7560.53	0.0227	0.8237	7.408	3.537E+00	1.929E-01
8592.36	0.0201	0.8237	9.251	3.653E+00	1.999E-01
9571.73	0.0181	0.8425	11.112	4.453E+00	1.950E-01
11527.05	0.0151	0.8575	14.723	5.068E+00	1.911E-01
13532.41	0.0130	0.8712	18.709	5.504E+00	2.059E-01
15534.51	0.0114	0.8833	22.279	5.862E+00	1.982E-01
17532.02	0.0101	0.8902	25.335	5.410E+00	1.875E-01
19515.23	0.0091	0.8975	28.242	7.003E+00	1.543E-01
24875.55	0.0073	0.9193	38.903	1.204E+01	2.256E-01
29892.43	0.0051	0.9388	50.622	1.601E+01	2.448E-01
34822.89	0.0032	0.9585	64.550	2.302E+01	2.874E-01
39873.54	0.0045	0.9607	82.917	3.375E+01	3.773E-01
44815.55	0.0040	1.0032	104.480	4.815E+01	4.545E-01
49842.06	0.0025	1.0365	139.059	5.147E+01	7.122E-01
54845.52	0.0023	1.0841	170.481	8.201E+01	6.534E-01
59788.75	0.0020	1.0897	202.628	9.429E+01	5.838E-01

AUTOPURE II 5280 V1.07

SAMPLE NUMBER: 58
 SAMPLE ID: P14L (7)
 SLEW RATE: RGR

OPERATOR: SJD

LP 16:04:26 11/07/90
 RP 17:41:13 11/07/90
 REP 17:41:19 11/07/90

DIAMETER VS CUMULATIVE INTRUSION

PIPORE II 9280 V1.07

SAMPLE NUMBER: 28 OPERATOR: BJD
 SAMPLE ID: F14L(7)
 SUBMITTER: RGR

LP 16:04:55 11/07/90
 HP 17:41:13 11/07/90
 REP 17:41:19 11/07/90

DIAMETER VS DIFFERENTIAL INTRUSION

APR08 11 5220 V1.07

SAMPLE NUMBER: 88
 SAMPLE ID: F1AL17)
 SUBMITTER: RBR

LS 18:04:53 11/07/90
 HD 17:41:13 11/07/90
 REP 17:41:19 11/07/90

DIMETER VS LOG DIFFERENTIAL INTRUSION

AUTOPORE II 9830 V1.07

SAMPLE NUMBER: 58 OPERATOR: SJD
SAMPLE ID: F14L(7)
SUBMITTER: RGR

LP 15:04:26 11/07/90
HR 17:41:13 11/07/90
REP 17:41:15 11/07/90

DIAMETER VS CUMULATIVE PORE AREA

APPENDIX IV

Experimental Data and Analyses

(see diskettes in back pocket)

VITA

Brian Keith Heft was born in Bethlehem, Pennsylvania on the sixteenth day of May, 1958, to Doris May and Lester Kenneth Heft. He graduated from Liberty High School in Bethlehem, Pennsylvania, in June of 1976. He studied chemical engineering at Rensselaer Polytechnic Institute, and received his B. S. in May of 1980. In June of that same year he began working at the corporate headquarters of Air Products and Chemicals, Inc, in Trexlertown, Pa. He married Carolyn Shirley Steria of Lowville, N. Y., on May 15, 1982. Shortly after graduating from Lehigh University with a Master of Science Degree in May, 1983, he was transferred to Air Products' Alkylamine Facility in St. Gabriel, La., where he is currently employed as the Technical Superintendent. He has three children, Aaron, age 3, Bethany, age 2, and Joshua, age 3 months.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Brian K. Heft

Major Field: Chemical Engineering

Title of Dissertation: Radial Flow Chromatography in Compressed Pancake-Shaped Beds

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

December 17, 1990