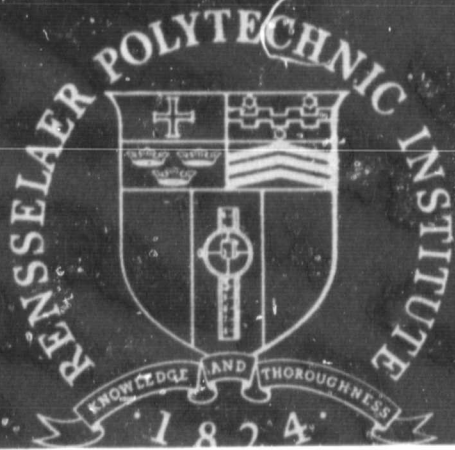


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(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

Rensselaer Polytechnic Institute
Troy, New York

R.P.I. Technical Report - MP 1

CHROMATOGRAPHIC SYSTEMS ANALYSIS:
FIRST-ORDER MODEL EVALUATION

Thomas F. Sliva

NASA Grant NGL 33-018-091

Analysis and Design of a Capsule Landing System
and Surface Vehicle Control System for Mars Exploration

SEPTEMBER 1968

Rensselaer Polytechnic Institute
Troy, New York

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ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Professor Peter K. Lashmet for suggesting the project topic, for his assistance and guidance in the preparation of this project, and for contributing a great deal of the material in Part III.

ABSTRACT

Many of the chemical/biochemical/biological experiments proposed for the unmanned Mars Voyager missions require a general-duty, chromatographic separator for fractionating complex chemical mixtures prior to chemical analysis by a mass spectrometer or other device. Review of the current literature and applicable reports has revealed that present experimental efforts involve fractionations of specific chemicals using diverse chromatographic equipment. Few significant studies have been reported on the concepts of chromatographic systems suitable for the missions. A program to investigate system concepts through the use of mathematical models of the chromatograph is being undertaken. A model for an isothermal, packed chromatograph column for use with a single component system has been derived. Neglecting second order diffusional effects, a solution to the first order mathematical model has been obtained by classical techniques. Although this solution predicts the general trends of an actual chromatogram, it does not exactly predict the entire curve. It appears from the results that the second order neglected, longitudinal diffusion and

possibly other mechanisms, must be considered if an accurate representation of the process is to be obtained.

PART I

INTRODUCTION

One important phase of the initial Voyager missions to Mars is the search for organic matter and living organisms on the martian surface. The present concept for attaining this objective consists of subjecting samples of the atmosphere and surface matter to certain chemical and biologically related reactions and thereafter analyzing the products produced. The most likely system for a general chemical analysis appears to be a combination gas chromatograph/mass spectrometer. This unit would be a major component in the biological and chemical laboratory of an unmanned, remotely controlled roving lander for Mars. It is the objective of this task to generate fundamental engineering design techniques and system concepts for use in optimizing the design of such a chromatograph separation system. Such a system should provide maximum resolution with minimum retention times and minimum carrier gas usage and should be capable of separating components evolving from many different kinds of experiments.

PART II

SUMMARY

Analysis of available literature has shown a diversity of chromatographic techniques being used for analysis in probable Voyager experiments. Samples range from gases to inorganic and organic constituents in organic and aqueous solutions. Chromatographic columns range from capillary columns to packed columns, are of a variety of dimensions, operate under a variety of temperatures, and use a number of carrier gases. Because of the variety of the mixtures to be separated and the complexity of the fractionating process, a system analysis based on the mathematical simulation of the chromatograph is being undertaken. This technique will use mathematical models, which will incorporate fundamental parameters evaluated from reported experiments, to explore various concepts and to direct further experimental research.

A mathematical model describing an isothermal chromatograph has been developed from the basic differential equations which govern rates of mass transport in packed columns. Neglecting second order diffusional effects, a solution to the single component case has been obtained by

classical techniques. This solution predicts the gas composition at any position within the column at any time.

Utilizing this solution, a computer program was used to find thermodynamic parameters to predict a chromatogram. These predicted curves follow the general trend of actual chromatographic experiments and match the retention time data for the compounds used. However, the first order model does not account for the observed pulse spreading. This additional spreading may be attributed to longitudinal diffusion which was neglected in derivation of the first order model or to other effects such as imperfect injection of the sample.

Although the first order model is adequate to predict retention times, it can not be used with confidence in a parameter study to design a column with the best resolution characteristics. Hence further work in model development is required.

PART III

SURVEY OF BACKGROUND MATERIAL

The Voyager missions to Mars have, as one purpose, the search for organic matter and living organisms on the martian surface. Much effort has been expended in developing chemical, biochemical and biological experiments for accomplishing this task (1, 17, 18, 22, 24, 26). A recent conceptual study (9) has proposed the incorporation of thirteen biochemical and life detecting experiments on the initial unmanned Voyager missions:

1. Analysis of the atmosphere
2. Analysis of surface liquids and gases
3. Determination of surface carbon content
4. Analysis of inorganic constituents of organic compounds.
5. Detection of amino acids
6. Detection of sugars
7. Detection of porphyrins
8. Detection of nitrogenous bases
9. Detection of hydrocarbons
10. Analysis of products from pyrolyzing soil samples
11. Detection of photosynthetic activity
12. Detection of metabolic activity
13. Detection of enzymic activity

It is hoped that data obtained from these or similar experiments now under investigation will be sufficient to characterize the chemical, biochemical, and biological condition of the martian surface and will provide a basis

for establishing a probability for life existence on the planet.

Of the thirteen experiments proposed, at least nine require a technique for analyzing chemically a product stream. Because of the diversity of the proposed experiments, the analytical technique must function under a wide variety of conditions:

1. Analyze light gases, organic as well as inorganic, in a gas composed principally of nitrogen and/or argon (Experiment No. 1, 11, 12) or in an atmosphere of helium (Experiment No. 2, 3).
2. Analyze heavy organics in the presence of helium or other inert gases (Experiment No. 10).
3. Analyze complex organics in the presence of organic solvents (Experiment No. 5, 6, 9) or in the presence of water and polar organics (Experiment No. 5, 6, 9, 11, 12).

Except for analysis of the martian atmosphere, the materials sought will possibly occur as minute constituents of a gas or liquid solution.

The use of a gas chromatograph/mass spectrometer (GC/MS) combination for performing these chemical analyses has been the subject of many investigations (2, 25, 27, 28, 32). In this concept, the chromatograph fractionates the gas or liquid mixtures into various compounds or groups of

compounds. The molecular weights of these species or their fragments are then determined with the mass spectrometer. Besides fractionating the mixtures, the chromatograph can provide an estimate of the mixture composition if a concentration-sensitive detector is placed at the chromatograph outlet and the detector output monitored.

In numerous investigations for demonstrating the feasibility of separating substances expected in the Mars experiments, researchers have used a diversity of chromatographic techniques and operating conditions to accomplish specific separations. Table I summarizes some representative experiments. Tubing packed with granular substances, often coated with various high molecular weight liquids, has been successful for certain separations. In other experiments, coated capillary tubes have been successfully used (8, 10, 11, 13, 14, 15, 27, 28, 34). In general, most of the work has been concerned with specific chemical systems of interest to the particular investigator.

The motivation behind these researches was the establishment of the feasibility of the basic GC/MS concept. Hence little effort was expended in determining the fundamental parameters involved in chromatographic separation. Except for studies concerning the simplest analysis - that

of the atmosphere (4, 23, 33, 35) - no significant effort has been reported on the concepts for a chromatographic system suitable for use with the many biochemical and life detecting experiments proposed for the mission and noted above. Such a system, in addition to performing many different fractionations, must meet weight, power, reliability, and data processing requirements imposed by the Mars lander. Because of the variety of the mixtures to be separated and the complexity of the fractionation process, it appears that mathematical simulations of the chromatographic system will be the most fruitful approach to the system design. Mathematical models, which can use, for parameter evaluation, data reported in specific experiments such as those shown in Table I can be used to explore various concepts such as the use of multiple columns in series or in parallel, and to direct further experimental research and development in a systematic and efficient manner.

Table I

**Representative Gas Chromatographic Separations
of Compounds Related to Exobiology and to Planetary Environments**

Compounds	Column	Sample	Carrier	Temperature	Detector*	Reference
CO ₂ , N ₂ , Ar	0.01-in. x 1-in. packed w/1% diglycerol on 0.0010/0.0011-in. silica gel; in series with 0.01-in. x 1-in. packed w/0.0010/0.0011 in. molecular sieve 5A	141 (gas)	He 0.5ml/min	room	T.C.	(34,35)
CO ₂ in (wet soil air)	?-in. x 15-in. packed w/0.0035/0.0041-in. silica gel	2541 (gas)	He 55ml/min	room	T.C.	(3)
H ₂ , N ₂ , NO, CH ₄ , CO ₂ , N ₂ O, CH ₃ F, NH ₃ , H ₂ S, NO ₂ , CH ₃ Cl, SO ₂ , CH ₃ OH, HCHO, (HCOOH, H ₂ O), (O ₂ , Ar, CO)	0.10-in x 8-ft. packed w/0.0070/ 0.0117-in. Porapak Q; in series with 0.10-in. x 8-ft. packed w/ 0.0070/0.0117-in. Porapak R	100 l (gas)	He 40ml/min	25-150°C 12 deg/min	T.C.	(36)
High molecular weight alkanes extracted from sediment; in heptane solution	0.16-in. x 5.9-ft. packed w/1% F-60 silicone oil on 0.0059/0.0070-in. Gas Chrom P	(liquid)	He	90-250°C 3.5 deg/min	M.S.	(20)

Table I

(Continued)

Compounds	Column	Sample	Carrier	Temperature	Detector*	Reference
	0.003-in. x 246-ft. capillary coated w/Polysev.		N ₂	132-200°C 5.8 deg/min	F.I.	
	0.0012-in. x ? capillary coated w/ Apiezon L		N ₂	125-300°C 5.8 deg/min	F.I.	
High molecular weight alkanes extracted from leaves; in heptane solution	0.16 in. x 5.9-ft. packed w/0.6% SE-30 silicone oil and 0.2% cyclohexanediethanol succinate on 0.0059/0.0070-in. Gas Chrom P	5 l (liquid)	He	190-260°C 1.5 deg/min	M.S.	(19)
CH ₃ CHO, acetone, MeOH, EtOH, CH ₃ Cl, (CH ₃) ₂ S, CCl ₃ F, CCl ₂ F ₂ , CHClF ₂ and others condensed from air	0.24-in. x 6.5-ft. packed w/7% Carbowax 1540 and 8% polyglycol E-300 on 0.0165/0.0197-in. Chromosorb P	40 l (gas)	He 60ml/min	40°C	T.C.	(16)
	0.24-in. x 6.5-ft. packed w/20% DC 550 silicone oil on 0.0165/0.0197-in. Chromosorb P					
	0.24-in. x 6.5-ft. packed w/15% Carbowax 1500 and 10% DC-200 silicone oil on 0.0117/0.0197-in. Chromosorb P					

Table I

(Continued)

Compounds	Column	Sample	Carrier	Temperature	Detector*	Reference
Organics evolved on pyrolysis of microorganisms	0.12-in. x 12-ft. packed w/15% SE-30 silicone oil on 0.0070/0.0098-in. Chromasorb W 0.010-in. x 300-ft. capillary coated w/diethylene glycol succinate polyester	(gas)	He 80ml/min	200°C	F.I.	(21)
Organics evolved on pyrolysis of igneous rocks and alanine	0.31-in. x 12-ft. packed w/5% Carbowax 20M on Fluoropak F	(gas)	He 50ml/min		T.C.	(23)
Amino acid esters in methanol, and cholesteryl haloacetates	0.125-in. x 3-ft. packed w/2-3% X-E60 silicone oil, neopentyl adipate polyester, or neopentyl sebacate polyester on 0.0059/0.0070-in. Anakron	1 l (liquid)	Ar 200ml/min	220°C	E.C.	(10,11)
Ester derivatives of amino acids in an inert organic solvent	? x 5-ft. packed w/5% SE-30 silicone oil on Chromosorb W	(liquid)	N ₂ 28ml/min	176-220°C 3 deg/min	F.I.	(6)

Table I

(Continued)

Compounds	Column	Sample	Carrier	Temperature	Detector*	Reference
CO ₂ , SH ₂ , H ₂ , (O ₂ + Ar), N ₂ , CH ₄ , CO	1/4-in. x 0.3-ft. packed w/0.0070/ 0.0331-in. silica gel in series w/ 1/4 in. x 6.6-ft. packed w/0.0098/ 0.0232-in. molecular sieve 5A	20 l ⁺ (gas)	He 58ml/min	28°C	T.C.	(33)
Aldehydes de- rived from amino acids. Methane from cracked alde- hydes detected	0.25-in. x 10-ft. packed w/5% ethylene carbonate and 5% propylene carbonate on 0.0098/0.0232-in. C-22 firebrick	(gas)	H ₂ 100ml/min	25°C	T.C.	(37)
Esters derived from amino acids in tri- fluoroacetic anhydride or acetonitrile	0.059-in. x 2-ft. packed w/5% neopentyl glycol succinate on 0.0059/0.0070-in. Gas Chrom P	2 l (liquid)	Ar 18ml/min	65-210°C 1.5, 2, 4 deg/min	A.I.	(5)
Heavy fatty acid esters in acetone	0.01-in. x 90-ft. capillary coated w/diethyleneglycolsuccinate	0.1 to 0. 5 l (liquid)	He 0.5ml/min		M.S.	(28)

*Types of detectors used: T.C.-thermal conductivity; M.S.-mass spectrometer ion current;
F.I.-hydrogen flame ionization; E.C.-electron capture; A.I.-argon ionization.

PART IV

DERIVATION OF THE CHROMATOGRAPHIC EQUATIONS

The packed column has been selected as the arrangement for the chromatograph model because it is perhaps the most efficient chromatographic separator. In this concept, shown schematically in Figure 1, a tube is packed with a granular solid having dimensions much smaller than the tube diameter. For the purposes of deriving the model equations, it is assumed that the granular solid is coated with a high molecular weight, non-volatile liquid which acts as the adsorbent. A carrier gas, such as helium, which is not adsorbed by the liquid, flows continuously through the column. At some instant, a trace of the materials to be separated is injected into the carrier gas stream. As this pulse flows down the column, the pulse materials diffuse to the adsorbent layer. When the pure carrier gas upstream of the pulse passes the adsorbed materials, they are desorbed. Because different materials adsorb and desorb at different rates depending upon the thermodynamic characteristics of the system, separation between the various components is possible. Thus, the output of a composition detector mounted at the chromatograph

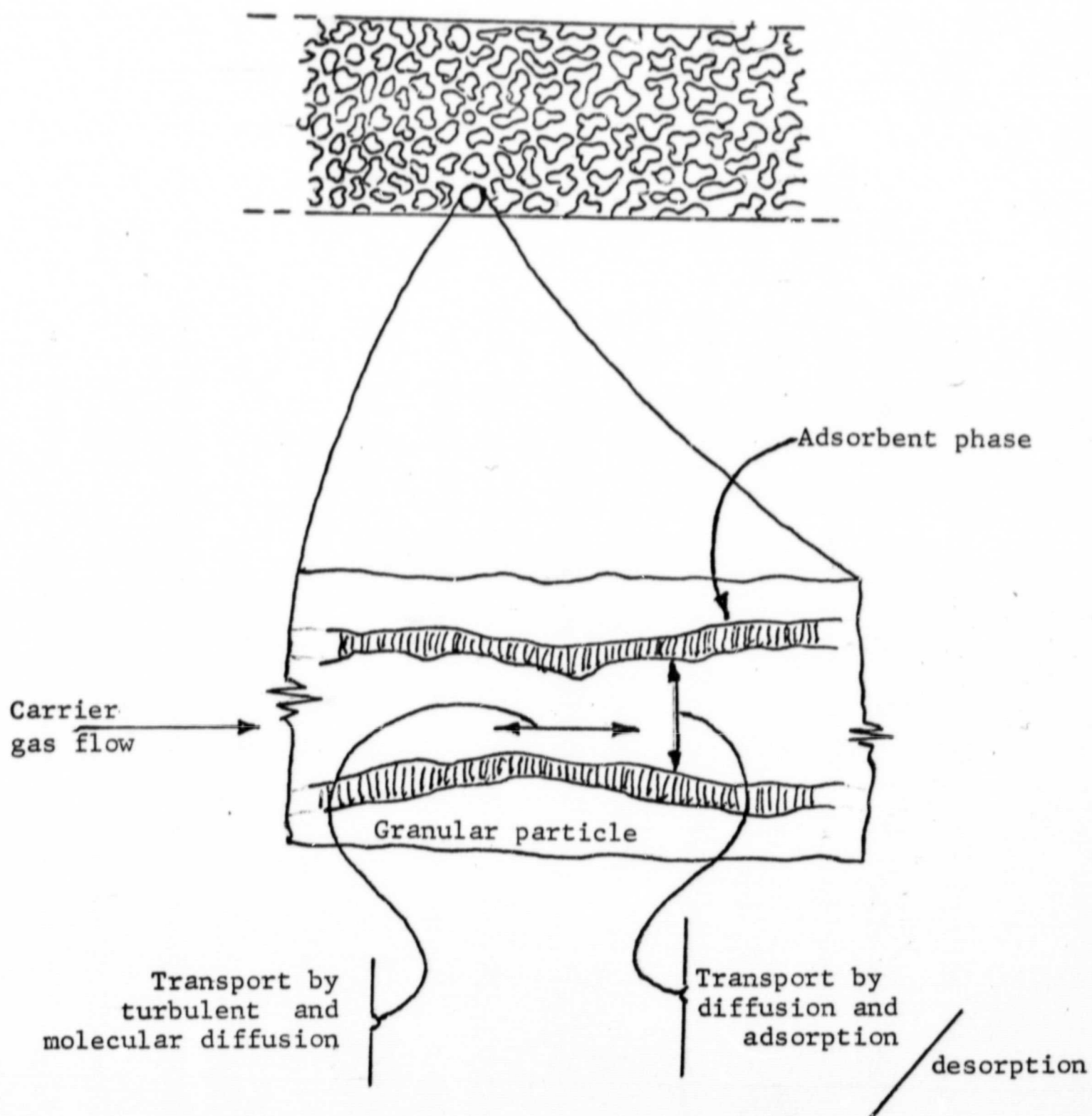


Figure 1 Concept of the Chromatograph Column

outlet will show a peak for each component (Figure 2).

The relations which govern the unsteady state mass transport of a single component in a carrier gas/adsorbent system have been derived in detail in Section X. It is believed that the behavior of the component in the gas phase can be represented by the following equation:*

$$\frac{P}{RT} \frac{D}{G_s} \frac{\partial^2 y}{\partial x^2} - \frac{1}{(1-y)^2} \frac{\partial y}{\partial x} - \frac{K_y a}{\epsilon G_s} (y-y^*) = \frac{P}{RT} \frac{1}{G_s} \frac{\partial y}{\partial t} \quad (\text{IV-1})$$

The component in the liquid or adsorbed phase is believed to behave according to

$$\rho_L (1-\epsilon) F \frac{\partial X_L}{\partial t} = K_y a (y-y^*) \quad (\text{IV-2})$$

Because the concentration of the component which is adsorbed is very small, the thermodynamic equation relating y^* and X_L is assumed to be of the following form:

$$y^* = m X_L \quad (\text{IV-3})$$

These equations are subject to the following boundary conditions:

$$y(x,t) = 0 \quad x > 0, t = 0 \quad (\text{IV-4a})$$

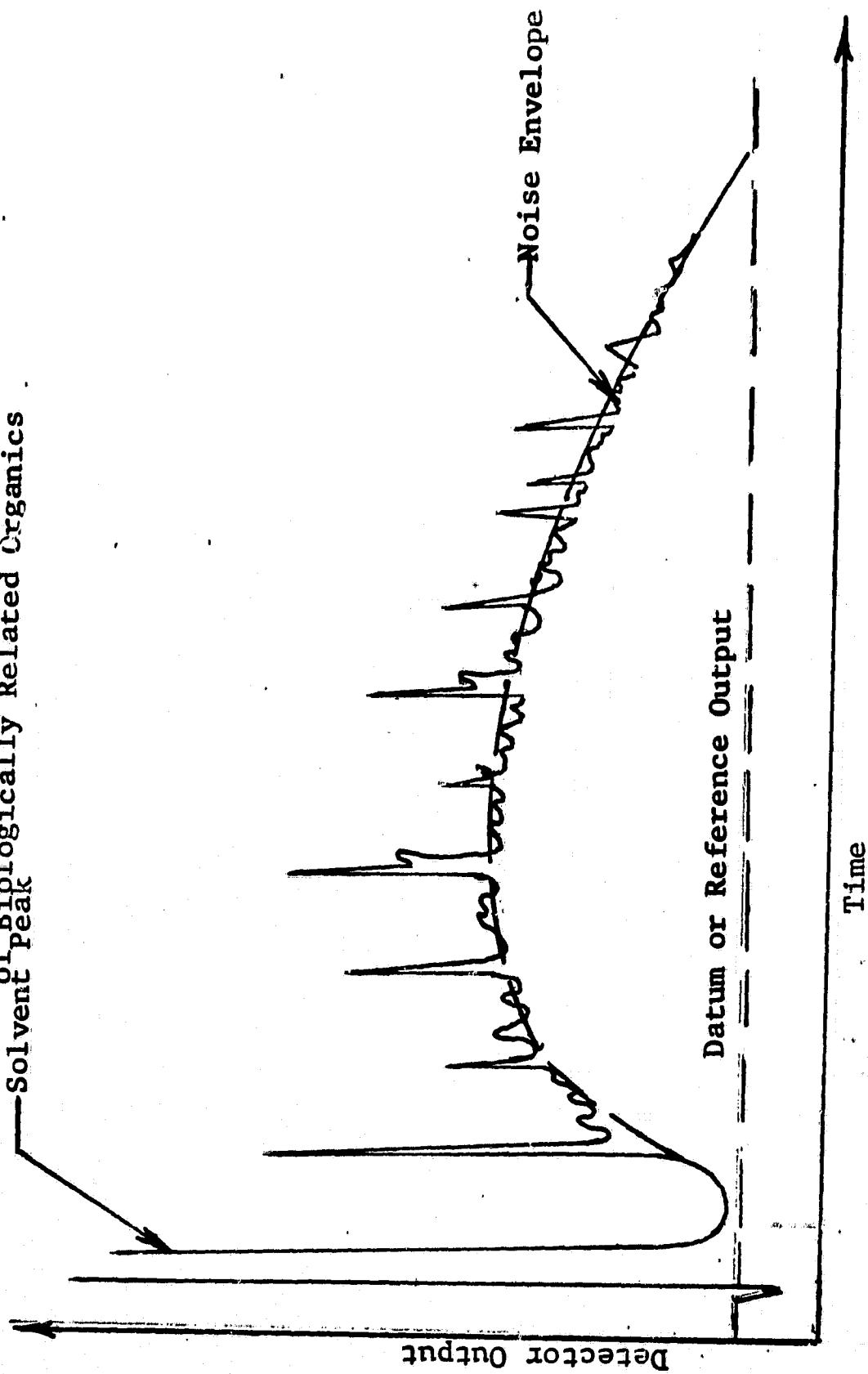
$$y(x,t) = f(t) \quad x = 0 \quad (\text{IV-4b})$$

*See Section VIII for nomenclature.

Figure 2

Typical Chromatogram for Separation

Solvent Peak
of Biologically Related Organics



The function $f(t)$ accounts for the injection of the sample into the carrier gas, and as an approximation it will be represented by the impulse function. The assumptions involved in the derivation of these equations are as follows:

1. The column is isothermal.
2. The carrier gas velocity profile is flat.
3. The axial diffusion coefficient, D is a composite factor which may or may not have a turbulent component.
4. The gas composition is approximately constant in the direction normal to flow, and the concentration gradient occurs only in a thin boundary layer near the adsorbent; i.e., mass transfer coefficients can be used.
5. The adsorbent layer is so thin that there is no diffusional resistance within the layer in the direction normal to the surface.
6. The diffusivity in the layer is so large that there is no diffusion in the direction parallel to the surface (in the axial direction).
7. The net rate of adsorption for the carrier gas is negligible.
8. Only one component is adsorbed and its gaseous phase composition is very small.
9. The carrier gas behaves as an ideal gas.

Through the use of dimensionless variables,

Equations (IV -1,2) become more general:

$$\frac{1}{Pe} \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} - N_t \log(y-y^*) = \frac{\partial y}{\partial \theta} \quad (IV-5)$$

for the gas phase, and

$$\frac{1}{R_o} \frac{\partial X_L}{\partial \theta} = N_{tog} (y-y^*) \quad (\text{IV-6})$$

for the liquid phase. An additional assumption of the gas phase composition of the adsorbing component being very small, or

$$(1 - y) \cong 1 \quad (\text{IV-7})$$

is required to obtain the form of Eqn. (IV-5). Furthermore, with this assumption, the coefficients Pe and N_{tog} become constant. Hence it is believed that the behavior of the chromatographic column can be represented reliably with the set of linear equations with constant coefficients (IV-5, 6, 3) subject to the boundary conditions (IV-4).

The second derivative appearing in (Eqn. IV-5) represents gaseous diffusion of the adsorbing compound in the direction of carrier gas flow. The appearance of the second derivative requires an additional composition-distance boundary condition to completely define the mathematical system. Several different boundary conditions have been used in studies of similar mathematical systems (7, 12, 30), but it is uncertain which form most correctly represents the column behavior. However, in many cases, especially when the diameter/length ratio of the column is

small, as it is in most chromatographic columns, this term is of second order. Hence, for the preliminary exploratory studies, Eqn. (IV-5) simplifies to

$$-\frac{\partial y}{\partial z} - N_{\text{tog}}(y-y^*) = \frac{\partial y}{\partial \theta} \quad (\text{IV-8})$$

Simultaneous solution of Eqns. (IV-8,6,3,4a,4b) in the Laplace transform domain yields

$$y'(z,s) + y(z,s) \left[N_{\text{tog}} + s - \frac{N_{\text{tog}}}{s+1} \right] = 0$$

This equation is solved in Section X and it is found that the following equation must be inverted to give y as a function of position and time:

$$y(z,s) = \frac{N(V/L)}{W} \exp[-N_{\text{tog}}z] \exp[-sz] \exp\left[\frac{N_{\text{tog}}z}{s+1}\right]$$

The coefficient

$$\frac{N(V/L)}{W}$$

results from the injection of the sample of size N in the form of an impulse. The inversion, carried out in Section X, gives the following relation between gas composition, time, and position in the column:

$$y(z, \theta) = 0 \quad \theta < z$$

$$= \frac{N(V/L)}{W} \exp \left\{ -N_{\text{tog}} Z \right\} \exp \left\{ \frac{-(\Theta - Z)}{\tau_L} \right\} \cdot \left\{ \frac{2 N_{\text{tog}} Z}{\tau_L} \cdot \frac{I_1 \left(2 \sqrt{\frac{N_{\text{tog}} Z (\Theta - Z)}{\tau_L}} \right)}{2 \sqrt{\frac{N_{\text{tog}} Z (\Theta - Z)}{\tau_L}}} + \delta(\Theta - Z) \right\}$$

or

$$= \frac{N(V/L)}{W} \exp \left\{ -N_{\text{tog}} Z \right\} \exp \left\{ - \frac{(\Theta - Z)}{\tau_L} \right\} \left\{ \delta(\Theta - Z) + \frac{N_{\text{tog}} Z}{\tau_L} \sum_{n=0}^{\infty} \left(\frac{N_{\text{tog}} Z}{\tau_L} \right)^n \frac{(\Theta - Z)^n}{n!(n+1)!} \right\} \quad \Theta > Z \quad (\text{IV-9})$$

Time is expressed as dimensionless Θ or (tv/L) , and Z is the fraction of the way down the column.

This equation, which is the mathematical representation of the first order chromatograph model, must be verified with experimental data prior to use in system studies. Hence, techniques must be devised for estimating the various parameters.

PART V

ESTIMATION OF COLUMN PARAMETERS

Any numerical evaluation of Eqn. (IV-9) requires an estimate of two parameters. One, N_{tog} , the number of overall adsorption transfer units, is independent of the adsorption thermodynamics of the column, but is, dependent upon the fluid mechanics of the chromatographic column. Therefore, in principle, once the column dimensions and the carrier gas characteristics have been defined, N_{tog} can be calculated. The other term, mR_0 , which is contained in the dimensionless time constant ,

$$\tau_L = 1/(mR_0 N_{tog})$$

is related to the chemical or thermodynamic properties of the particular chemical system under consideration. This parameter is not easily calculated or estimated. However, knowing the other parameters of the equation, mR_0 may be found by fitting the peak of Eqn. (IV-9) to the peak of the experimental data by a trial and error procedure.

N_{tog} , which is dimensionless, can be estimated through the use of other dimensionless parameters which characterize the column, and various data correlations. The most general way to accomplish this is through the use

of the Sherwood number (Sh), which corresponds to a Nusselt number for mass transfer.

$$Sh = \frac{k_y dp}{D \rho_g} \quad (V-1)$$

To convert the Sh No. to N_{tog} , which is defined as:

$$N_{tog} = \frac{k_y aL}{G} \quad (V-2)$$

the following relationship is used:

$$N_{tog} = \frac{(Sh)}{(Sc)(Re)} (aL) \quad (V-3)$$

The Schmidt number (Sc) and the Reynolds number (Re) which are functions of the system chemical properties and fluid mechanic characteristics, are known once the column dimensions, carrier gas flow rate, and gas physical properties are defined. The Sherwood number may be estimated from empirical correlations reported in the literature (31):

$$Sh = Sh_0 + 0.347(Re Sc^{0.5})^{0.62}$$

$$Sh_0 = 2.0 + 0.569 (Gr Sc)^{0.25}$$

$$Gr = \frac{g L^3 \Delta \rho}{\rho \mu} (\rho/\mu)$$

Because the column will be operated isothermally, therefore, all physical properties will be constant. The

Grashof number (Gr) will be approximately zero and the Sherwood number will be dependent only on known parameters already available. However, if temperature programming is used on the column, the Grashof number will be non-zero and must be taken into account for calculation of the Sherwood number and N_{tog} . In any event, it is possible to estimate a value of N_{tog} with an accuracy of $\pm 20\%$ using Eqns. (V-1, 2, 3).

It should be noted that while the above technique essentially predicts the gas-film mass transfer coefficient, k_y , the chromatograph model equations use an overall mass transfer coefficient, K_y . These two coefficients are equal if the transport resistance in the adsorbed layer is small (31). This is consistent with the fifth assumption used in Section X in deriving the model.

A value for mR_0 is very difficult to estimate because vapour-liquid equilibrium data for adsorbing substrates used in chromatographs is meager and is generally for simple systems. This data could be obtained directly from experiment but the process would be time consuming and costly. Also the accuracy of any such data would be questionable because of analytical problems. There is, however, another manner in which mR_0 may be determined. Since

all other parameters of Eqn. (IV-9) are known, the only unknown is mR_0 . From experiments run with a certain component in a given column, a value of the retention time (time of occurrence of the maximum in a composition time curve) can be obtained. A value of mR_0 can be found by fitting the peak of Eqn. (IV-9) to the peak in the experimental data by a trial and error procedure. Once a value of mR_0 is found, it can be used to estimate the behavior of the chemical system in columns having other configurations and flow rates, providing the temperature remains the same. Also these values of mR_0 , may possibly be used for a multicomponent mixture. At the dilute solutions used in chromatographic columns the value of mR_0 should not depend appreciably on the other components in solution.

Because of the complexity of Eqn. (IV-9) a trial and error fitting-technique is accomplished using a computer program outlined in Section XI.

In case the second order equation will be required to represent the chromatograph, techniques will be required to estimate the extent of longitudinal diffusion, i.e., the Peclet number (Pe). The longitudinal diffusion problem has been studied (e.g., ref. 7), and the Peclet number can be

predicted, although with less certainty than the value of N_{tog} .

PART VI
EVALUATION OF MODEL AND DISCUSSION

Before evaluating the model, it would be beneficial to look at the transport parameters of a few typical gas chromatography columns. Table II presents these parameters for three different columns. Columns A and B are two commercially available columns which differ primarily in length. Column C is extremely small and is of the type that would possibly be used on the Mars Lander (35). It uses very little carrier gas, weighs very little, and would require little space on the Lander.

From the values presented in Table II it is apparent that most columns will have large numbers of transfer units. Therefore, it would be of interest to determine what effect N_{tog} has on a chromatogram. To show this Figs. 3, 4, and 5 were prepared. Three different values of mR_0 were used to give a range of values for the adsorbance of a component. The values, 0.197, 0.09, and 0.038, are those for pentane, hexane, and heptane being adsorbed on a silicone grease substrate. The values of N_{tog} used in these figures are infinity, 14,300, 5000, 1000, 100 and 10. The curves were obtained in the following

TABLE II
Parameters for Three Representative
Chromatographic Columns

Reference	A (1)	B Scholly and Brenner (29)	C Wilhite (35)
Length, cm.	61.0	400.0	2.5
Diameter, cm	0.46	0.46	0.025
Particle diameter, cm	0.0214	0.0214	0.00265
Temperature, °C	50.0	50.0	25.0
Pressure	Atmos.	Atmos.	Atmos.
Carrier gas flow rate, cu cm/sec	1.0	0.767	0.00833
Carrier gas velocity, cm/sec	15.23	11.68	16.92
Void fraction	0.4	0.4	0.4
Surface area, $\frac{\text{cm}^2}{\text{cm}^3}$	168	168	1360
Reynolds number (Re)	0.28	0.24	0.041
Schmidt number (Sc)	5.77(2)	5.77(2)	3.67(3)
Sherwood number (Sh)	2.27	2.25	2.02
Number of transfer units (N_{tog})	14,300	109,600	47,100

(1) Used in obtaining chromatograms for evaluating model.

(2) Light hydrocarbon in helium carrier gas.

(3) Carbon dioxide in helium carrier gas.

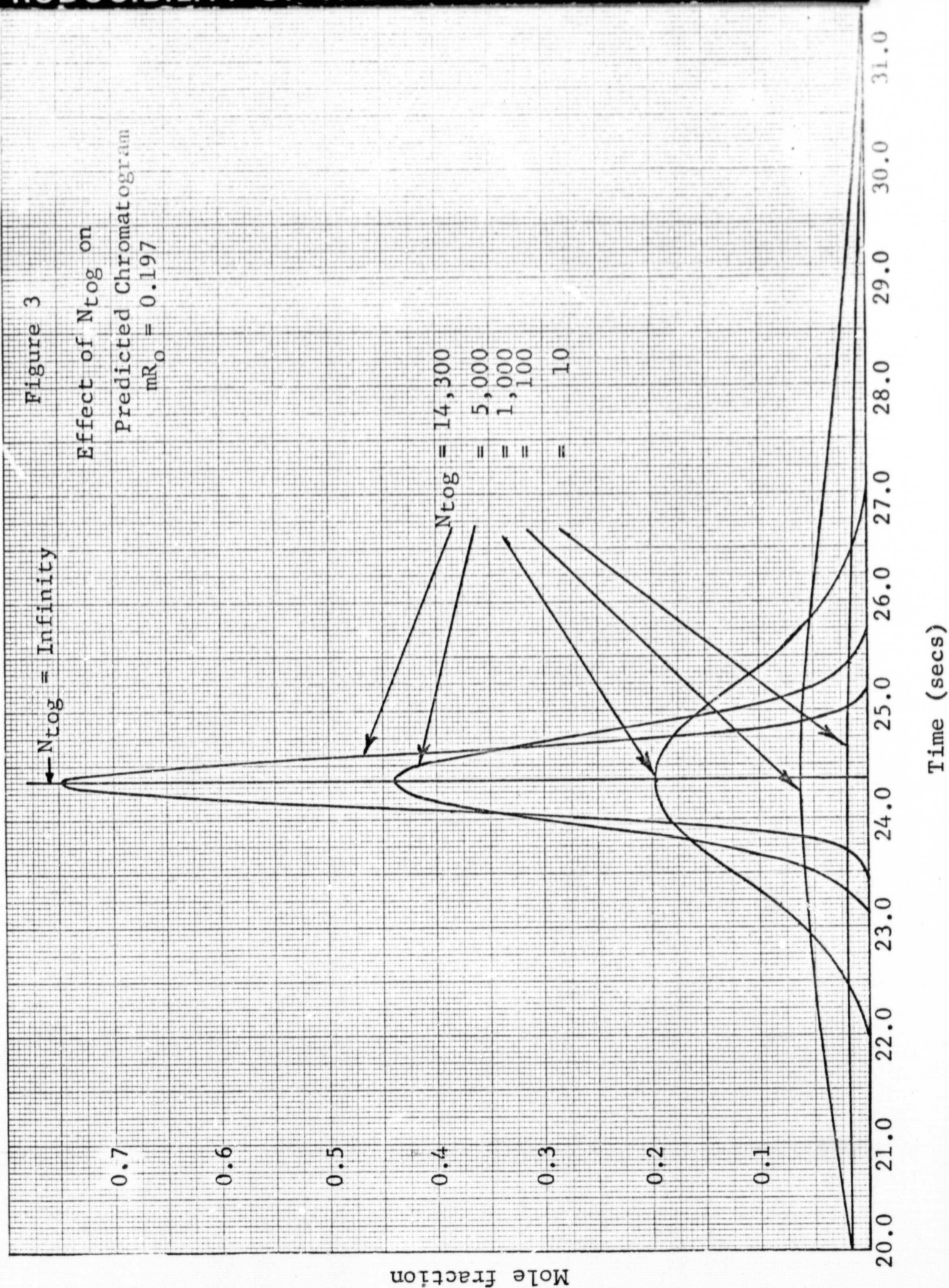
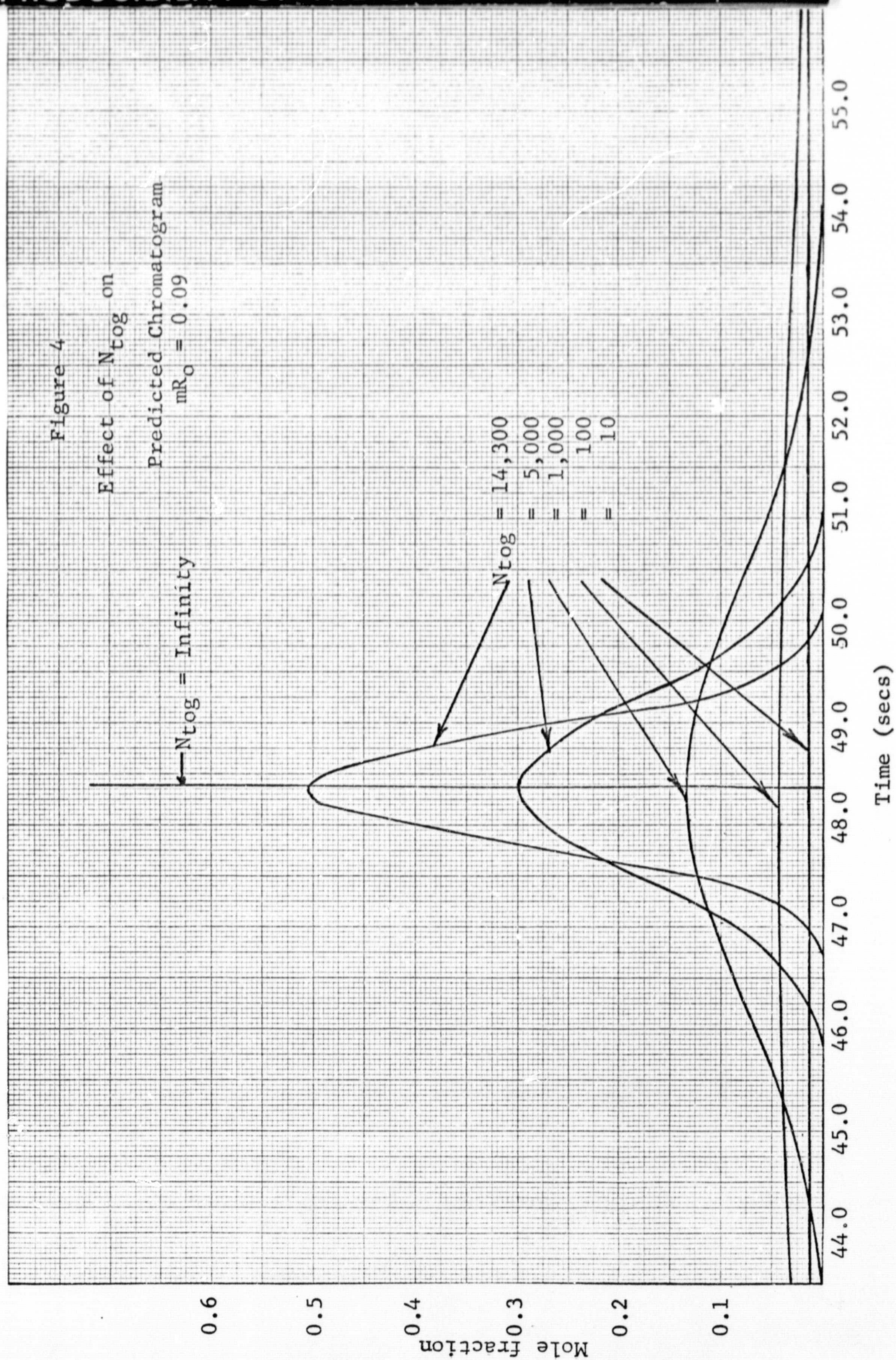
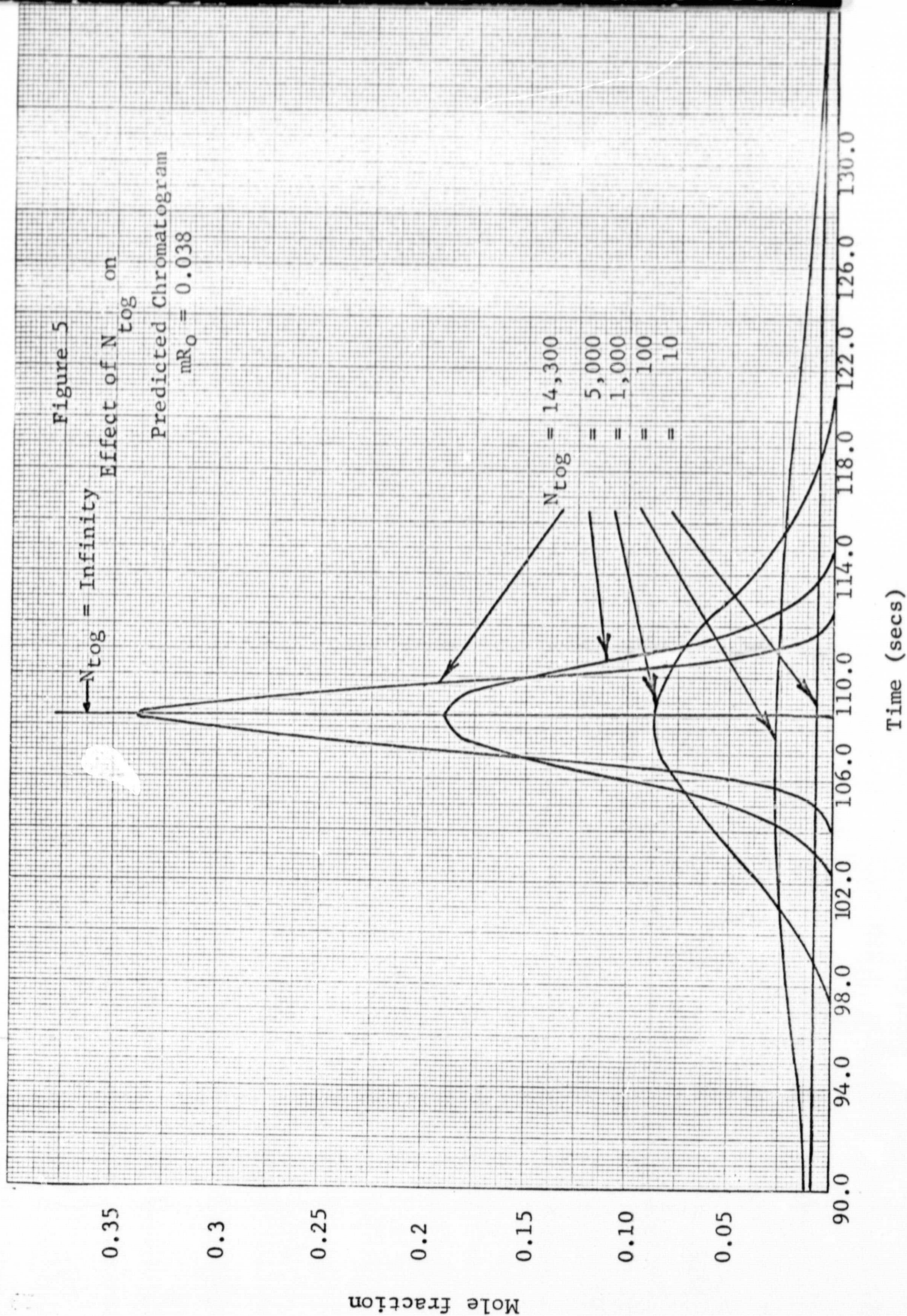


Figure 4
Effect of N_{tog} on
Predicted Chromatogram
 $mR_0 = 0.09$





manner.

For the limiting case of $N_{tog} = \text{infinity}$, the chromatogram was found from Eqn. (X-24), the solution in transform variables, by determining the limit of the equation as N_{tog} approaches infinity and for a value of $Z = 1$ (the end of the column)

$$y(1,s) = A(s) \exp \{ -N_{tog} \} \exp \{ -s \} \exp \left\{ \frac{N_{tog}}{\tau_L s + 1} \right\}$$

at the limit ($N_{tog} = \infty$), this became

$$y(1,s) = A(s) \exp \left\{ -s \left(1 + \frac{1}{mR_0} \right) \right\}$$

This equation shows that for $N_{tog} = \infty$, whatever is put into the column as a forcing function, $A(s)$, an impulse in this case, comes out exactly the same, only delayed the amount $(1 + \frac{1}{mR_0})$. Therefore an estimate of mR_0 can be found using this fact.

$$\theta_m = 1 + \frac{1}{mR_0}$$

in which θ_m is the occurrence of the peak on the actual chromatogram expressed as a dimensionless variable. As it turns out this method gives an excellent estimate, as the position of the peak is shifted very little by changing N_{tog} (Figs. 3, 4, 5).

To compute the chromatogram for the other values of N_{tog} , PROGRAM A, described in Section XI, was used

with the column parameters of Column A given in Table II. The forcing function was an impulse equivalent to a sample of one microliter (liquid) each of pentane, hexane, and heptane.

mR_0 is a measure of how much a component is adsorbed into the liquid substrate. The higher the value of mR_0 the less a component is adsorbed. This fact leads to longer retention times for small values of mR_0 . From the figures it is apparent that the smaller the value of mR_0 the longer the retention time, the smaller the peak height, and the broader the pulse. The peak for $N_{tog} = \infty$ is infinitely sharp (an impulse) for all three cases. However, as N_{tog} is decreased, the peak height is decreased and the pulse is broadened. It can be seen that if a column were to have a small value of N_{tog} it would be difficult to determine peaks and therefore difficult to determine which compounds were present in a mixture. To obtain the best separation of peaks (distance between them) it is desirable to have widely separated values of mR_0 . However, mR_0 depends primarily upon the liquid substrate for a column and is essentially fixed for a given system. On the other hand, N_{tog} determines the height and

sharpness of a peak. For a chromatogram to be of most use, it is desirable for the peaks to be as high and as sharp as possible. From Figs. 3, 4, and 5, it is noted that the larger the value of N_{tog} the higher and sharper the peak is.

Because the resolving ability of a column (the chromatogram produced allows for easy identification of components by having distinct peaks) is strongly influenced by N_{tog} , it is desirable to know what parameters affect N_{tog} and how they affect it. In Figs. 6, 7, and 8 the effect of three different parameters; carrier gas velocity, particle diameter, and column length, on N_{tog} is shown for column A of Table II. Only one parameter was varied at a time, all other parameters being kept constant. The most pronounced effect on N_{tog} is accomplished by changing the particle size of the packing. Decreasing the particle diameter by a factor of 20, from 0.02 cm to 0.001cm. has increased N_{tog} by a factor of 100, from 15,000 to 1,500,000. Of course this effect is even more pronounced at still smaller particle sizes as shown in Fig. 6. Decreasing the velocity (volume flow rate) increases N_{tog} , though not as sharply as particle diameter. Increasing the length of a column also increases N_{tog} .

10^7

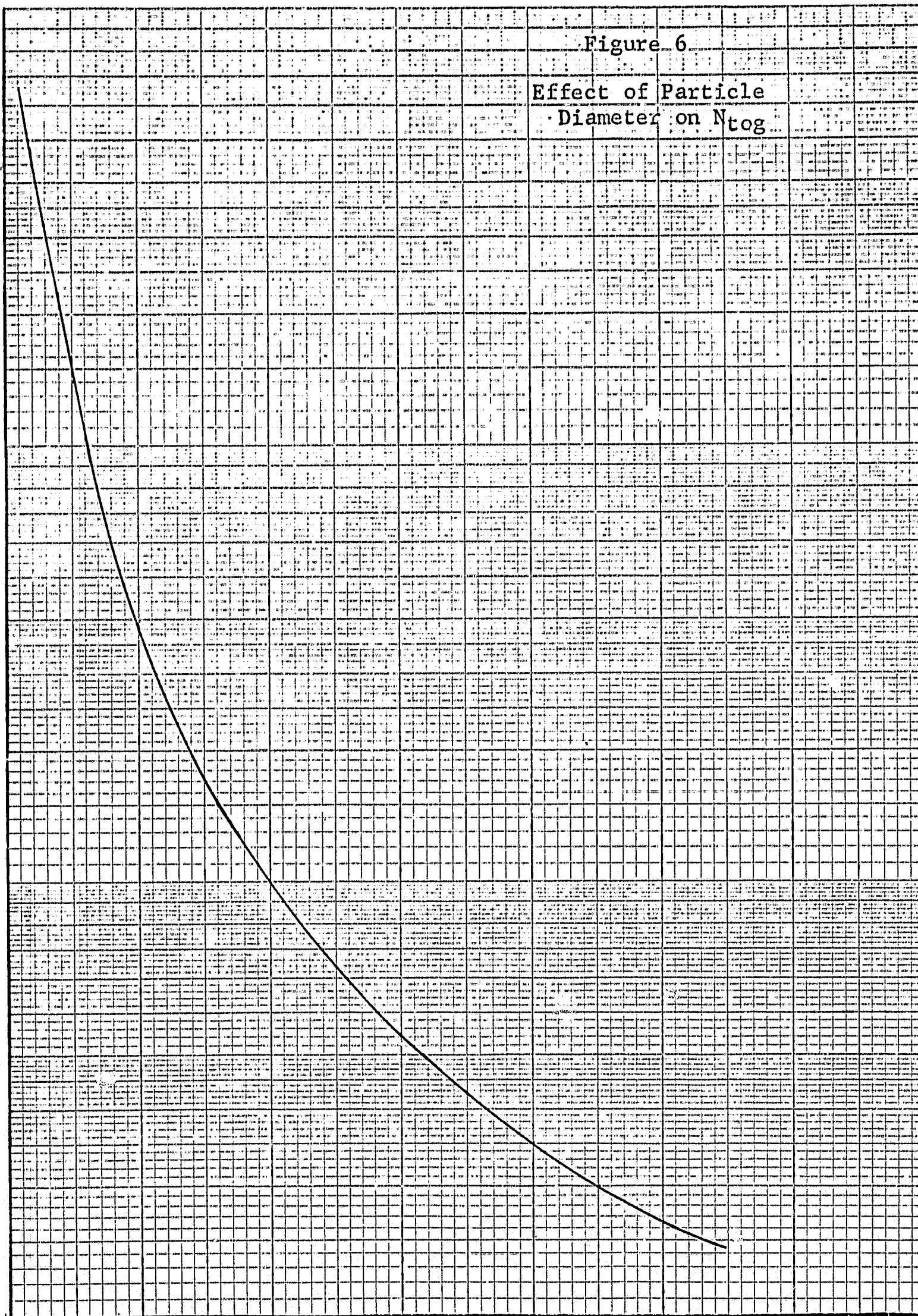
Figure 6

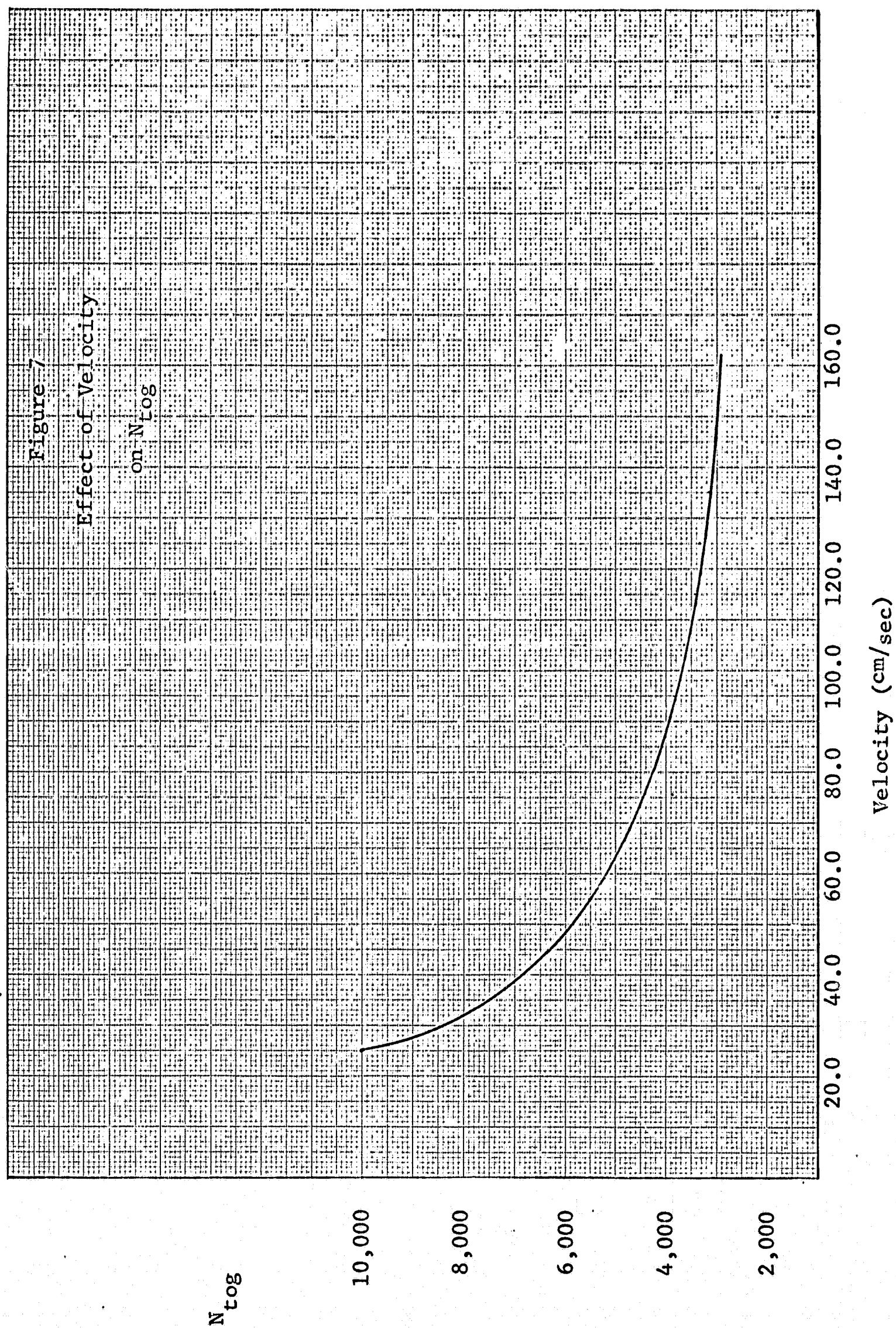
Effect of Particle
Diameter on $N_{t\log}$ 10^6 $N_{t\log}$ 10^5

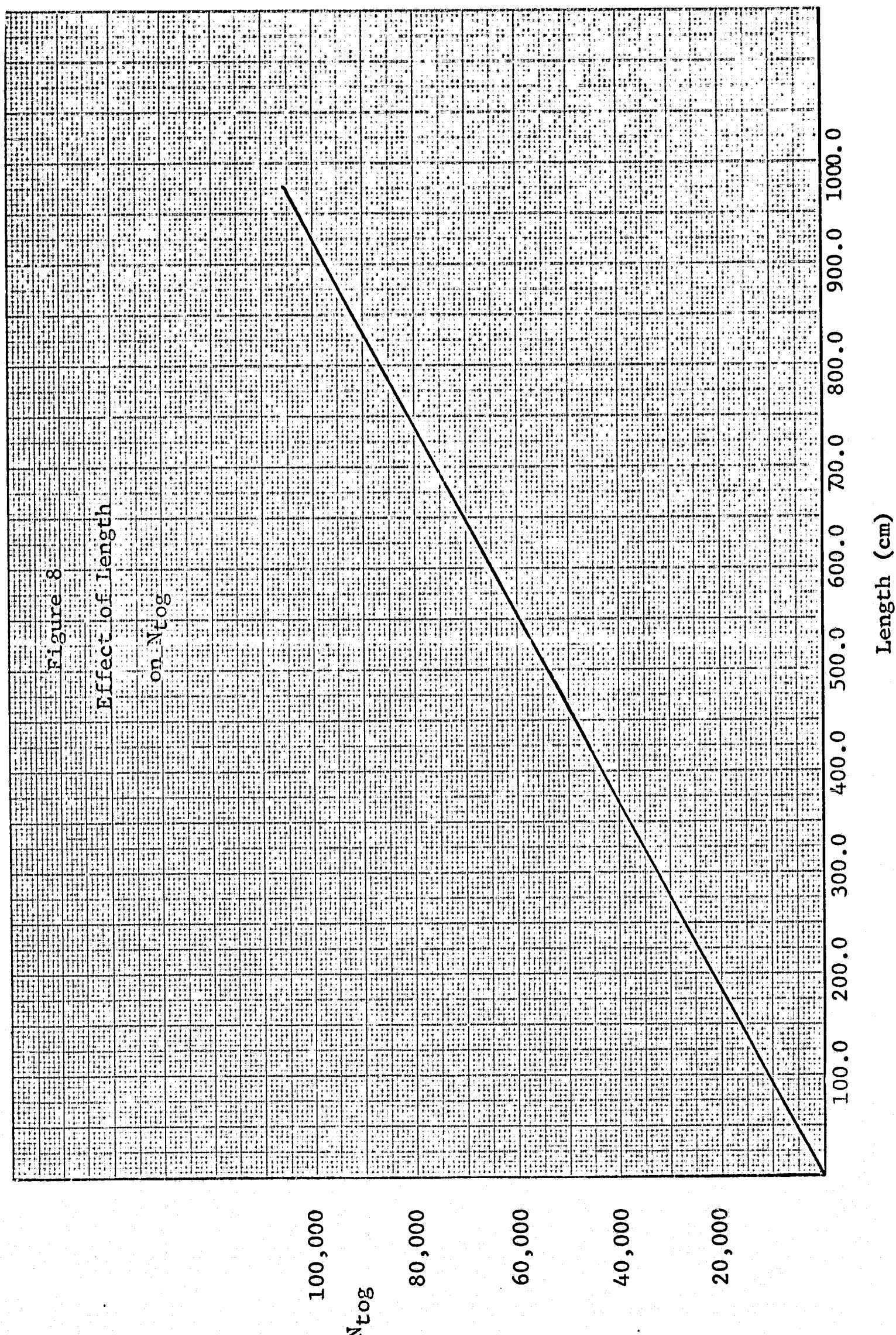
0.01

 D_p (cm)

0.02







However, this affect is not as important as particle diameter and velocity. The effects shown are for varying only one parameter at a time. If two are changed simultaneously the changes might reinforce or might counteract each other. These effects will have to be investigated before the actual choice of a column or columns for the Mars Lander is made.

The effects of these parameters are not simple. Although decreasing the particle diameter increases N_{tog} it also produces many practical problems. Working with ultra small particles is difficult and requires extreme care in packing of the columns. Channeling can occur very easily and will decrease the efficiency of the column. Smaller particles also increase the difficulty of coating them with the liquid substrate. The coating should be homogeneous and of approximately uniform thickness. Also, smaller particles increase the pressure drop across the column. Velocity changes too have disadvantages. As the velocity becomes lower, it begins to fall into the range of diffusional velocity. Once this is the case the pulses will spread greatly and will counteract the sharpness effect of large N_{tog} . Low velocities, although using little carrier gas, increase the probability that the (1-y)

term in the mathematical equation will no longer be close to one. This fact arises because the sample may become significant compared to the volume of gas in column. If this term is not close to one, the equation is no longer linear and the model is no longer valid. Decreasing the velocity also requires a longer time for analysis of a mixture. Increasing the length of a column, increases the space required, the weight of the column, and the time of analysis. Thus an optimization will be involved in the final system design.

Once these characteristics of the first order model were determined it was necessary to evaluate how well the model predicted an actual chromatogram. To do this an entire chromatogram along with sufficient information about the column was necessary. Although there are many articles in the literature reporting on gas chromatographs, very few, if any, have published the actual chromatogram. Also, most of the literature gives insufficient descriptions of the column for use in a model evaluation. The greatest part of the data in the literature is given as retention times, retention volumes, or relative retention fraction. Representative of such literature is the compilation by Scholly and Brenner (29) which provides

retention time data for many different compounds on eight different columns. It contains sufficient information to completely characterize the columns, but no chromatograms. This data although not useful for model evaluation, will be useful to determine values of mR_0 for many different compounds, and will also be of use in any parameter study to be done.

Because of this lack of required data, a chromatogram was obtained experimentally; Column A of Table II was used. This column is a commercially available column consisting of a liquid substrate of silicone grease on a packing of 60-80 mesh chromosorb. The detector for the column is a thermal conductivity cell. A three-microliter sample (liquid) composed of equal amounts of pentane, hexane, and heptane was analyzed. The sample was injected into the sample block by means of a syringe. It was then vaporized immediately and pumped into the column. The value for the forcing function, $N(V/L)/W$, of 0.05 was computed from the operating data. Values of mR_0 which would give predicted peaks at the time of appearance of the actual peaks were determined by solving Eqn. (IV-9) by trial and error using computer PROGRAM A. The actual and predicted curves for pentane, hexane, and heptane are

compared in Figs. 9, 10, and 11. Because calibration facilities for the chromatograph detector were not available, the composition of the gas at the detector was unknown although the detector output signal was proportional to it. Hence, for the purposes of comparing the predicted and observed curves in this initial investigation, the chromatogram compositions were estimated. By a material balance at the detector,

$$\int_0^{\infty} (Wy) dt = N$$

or

$$\int_0^{\infty} y dt = N/W$$

Since the detector output is proportional to concentration

$$\text{Output} = ky \quad (\text{VI-1})$$

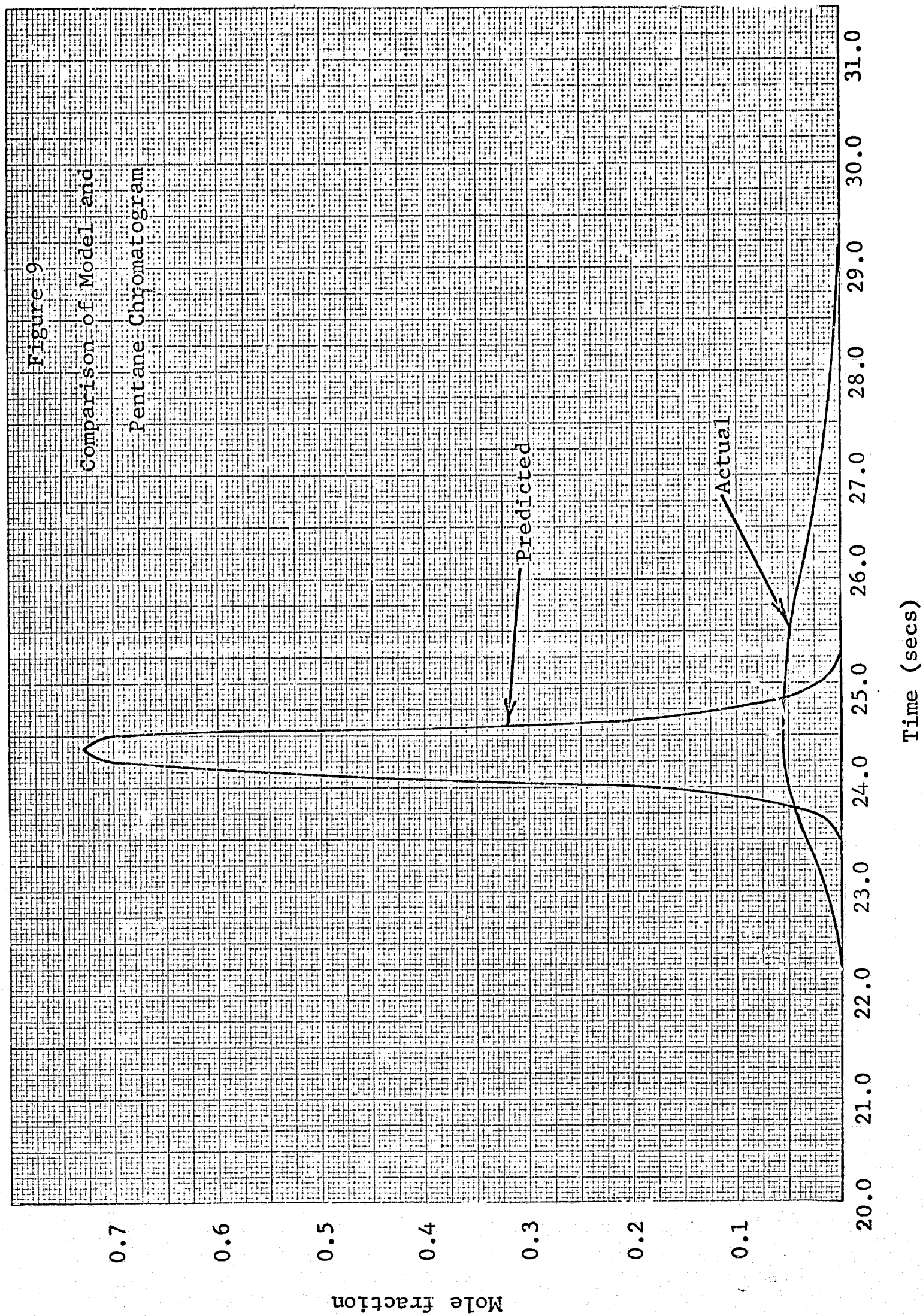
then

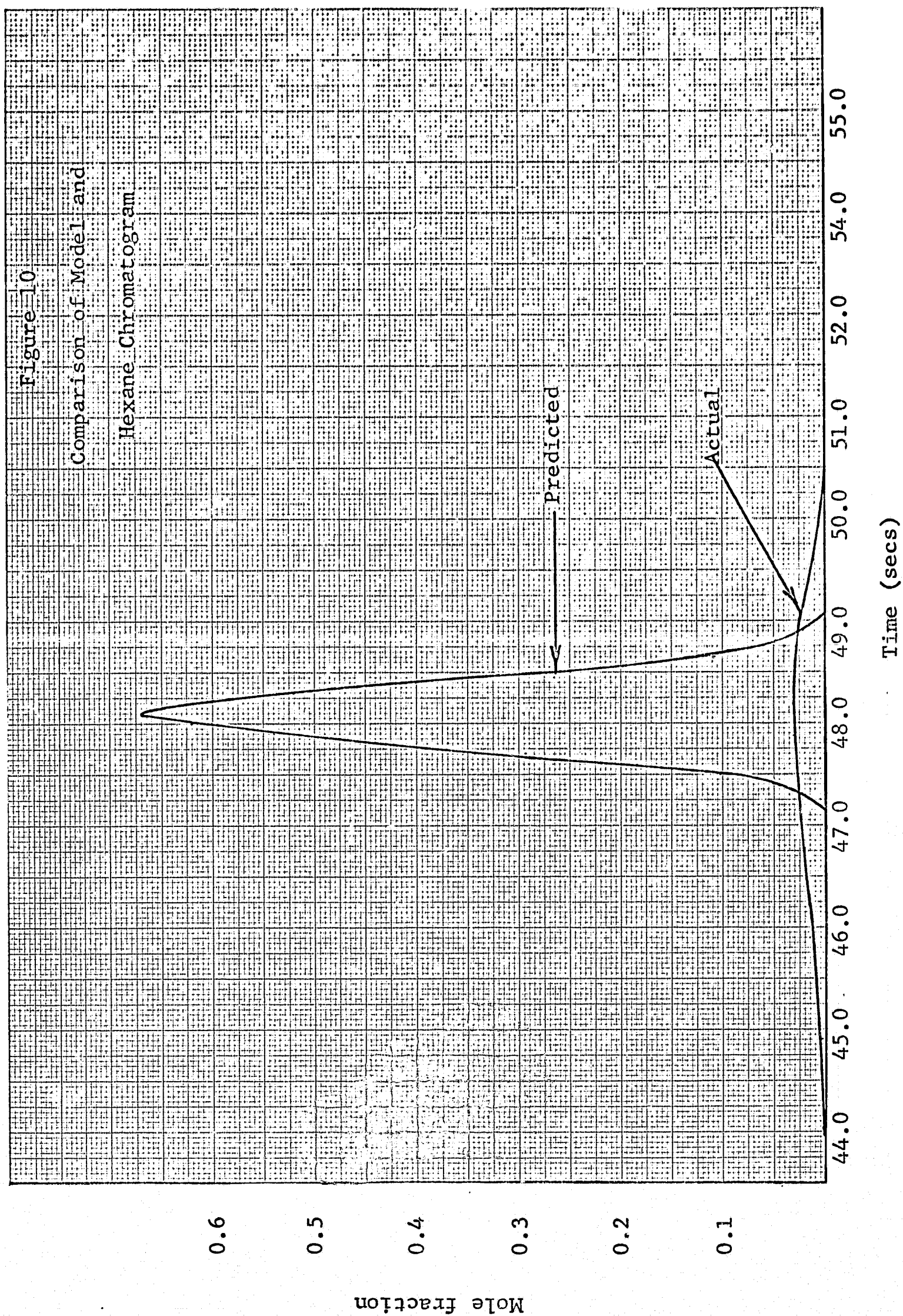
$$\int_0^{\infty} \frac{\text{Output}}{k} dt = \frac{N}{W} \quad (\text{VI-2})$$

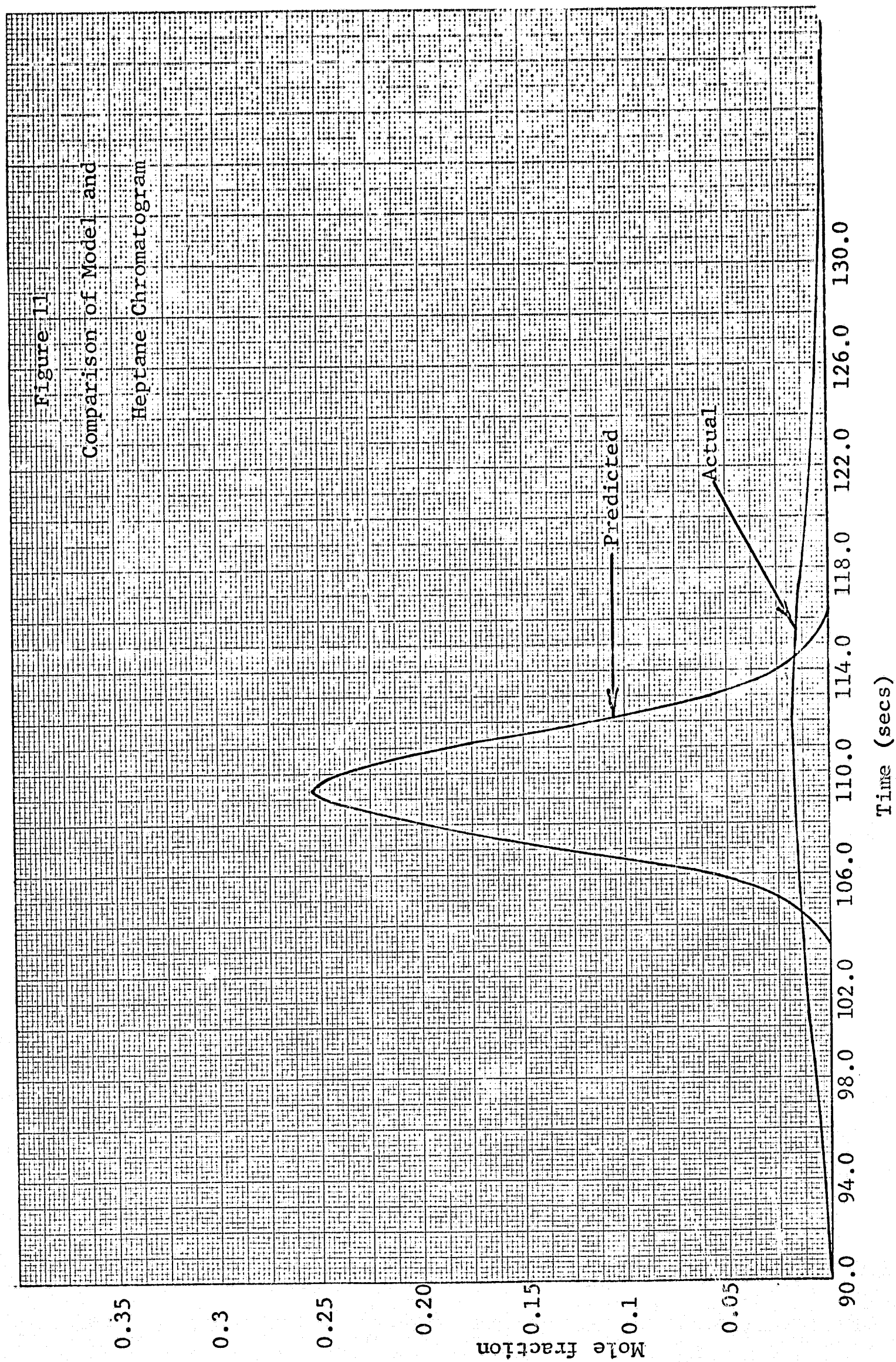
Substitution of k from Eqn (VI-2) into Eqn (VI-1) gives an estimate of the composition for any point on the chromatogram:

$$y = \frac{\text{Output} (N/W)}{\int_0^{\infty} (\text{Output}) dt}$$

The computed values of mR_0 are as follows:







pentane	0.197
hexane	0.090
heptane	0.038

An examination of Figs. 9, 10 and 11 shows that, while the first order model follows the general trends presented by the actual data, the equation does not predict the entire chromatogram very well. The predicted chromatogram in all cases is much sharper than the actual chromatogram. This discrepancy may be attributed to several factors. Other transport mechanisms, such as longitudinal diffusion or intraparticle diffusion, which were neglected, may be important. These will cause a delay in the desorption process with a consequent broadening of the output pulse. The input pulse may in fact not be represented accurately by the impulse used in the model derivation. Any deviation from the impulse representation will cause the observed peak broadening. It should be noted, however, that if the peak broadening mechanisms can be reduced or eliminated in the design of the column, it should be possible to approach the predicted curves. In this case, however, the compositions of the computed curve may be inconsistent with the assumption

$$1-y \approx 1$$

used in the model derivation, and some means for solving the equations with this nonlinearity must be developed.

In summary, the model in its present form represents the behavior of this particular chromatograph only qualitatively, and additional model development is required if the projected system studies are to have value.

PART VII

CONCLUSIONS AND FUTURE WORK

Under the set of conditions analyzed, the first order model does not represent the data obtained on a specific chromatograph. The first order model does, however, follow the general trend of the data and may be useful in predicting retention times. Because the model does not predict the spreading of the peaks it is apparent other mechanisms should be taken into account in the next model.

It was found that mR_0 and N_{tog} will be major factors to consider when choosing a column system for the Mars Lander. The smaller mR_0 , the more a component is adsorbed, the longer the time required for analysis, and the broader the peak is for that component. The larger the value of N_{tog} , the sharper and higher a peak is for a given component. For these reasons it is desirable to obtain the largest values of mR_0 and N_{tog} for a component. This will mean that the peak occurs quickly and is sharp and distinct. It may then be possible to make easy identification of the components.

Since mR_0 is essentially constant for a given

system, it is necessary to know how N_{tog} may be increased. This may be done by decreasing the particle size of the packing, decreasing the carrier gas velocity, or increasing the column length. All three have disadvantages associated with them when used to increase N_{tog} :

Particle Diameter

1. Difficulty in packing
2. Channeling
3. Difficulty in coating with liquid substrate
4. Increased pressure drop across column

Velocity

1. Diffusion takes precedence - peaks spread greatly
2. Increases non-linearity
3. Longer analysis time required

Length

1. Size is larger - more room is required
2. Weight is increased
3. Longer analysis time required

These effects are apparent only from considering one parameter at a time. If more than one is varied simultaneously the considerations are more involved. Considerations of mR_0 , N_{tog} , particle diameter, velocity and column length will have to be analyzed before the column or columns for the Lander are chosen.

All the work done here is preliminary to obtain some ideas about chromatographic columns and to guide future effort. Although not immediately applicable, it

has led to areas of study which will provide the desired design information.

Because spreading of the peak is a problem, it will be necessary to consider other transport mechanisms. The second order model, which allows for longitudinal diffusion, should be considered. Spreading will also result if the sample injection is not close to an impulse, as assumed in the derived model. The degree to which this affects the chromatogram, must be evaluated.

Parallel to these analytical analysis an experimental program should be carried out to obtain sufficient data to evaluate the model. This program should provide values of mR_0 and data for complete chromatograms to study the model. Although the column or columns should be operated isothermally, data should be obtained at various temperatures to be used in future modifications. Because the experimental system must be completely characterized if the data are to be useful in validating the models, it will be necessary to monitor the input to the column as well as the output. This will provide an estimate of the forcing function, which was assumed to be a pulse in the present studies. Also, detector calibration should be attempted so the chromatograph data and model calculations can be compared on the same basis.

Once a model for a chromatographic column has been determined, more advanced techniques for improving the resolution and separation of a column can be considered. The techniques are temperature programming and flow rate programming. These techniques will further complicate choice of a column system for the Mars Lander. Because of their complexity and because they are not yet well understood, they should be considered last.

Although the technique is not yet applicable, it is apparent the mathematical (computer) simulation can yield useful information to be applied to the final choice. It can also save considerable time and money by directing experimental efforts more efficiently.

PART VIII

NOMENCLATURE

- a = ratio of interfacial area to packed volume, 1/ft
- C = concentration, lb-moles/cu ft
- D = diffusion coefficient, sq ft/hr
- d_p = diameter of particles in bed, ft
- F = fraction of stationary phase volume which is liquid
- $f(t)$ = mathematical representation of sample injection into chromatographic column
- G = molar velocity of gas stream, W/ S, lb-mole/(hr, sq ft)
- Gr = Grashof number = $\frac{gL^3 \Delta \rho}{\rho \mu}^2$
- G_S = molar velocity of carrier gas, (1-y) G (lb-mole/hr-sq ft)
- g = gravitational constant
- I_n = modified Bessel function of the first kind of order n
- k = proportionality constant for determining height of curve
- K_y = overall mass transfer coefficient, lb mole/(hr, sq ft, mole fraction)
- k_y = gas film mass transfer coefficient, lb mole/(hr, sq ft, mole fraction)
- L = length of packed bed, ft
- m = adsorption equilibrium constant, $y^* = m_{x_L}$

- N = sample size, lb-mole
 N_A = rate of diffusion of A, lb-mole/(hr, sq ft)
 N_{tog} = number of transfer units available for adsorption dimensionless
 P = pressure, lb/sq in
 Pe = Peclet number, (vL/D) , dimensionless
 R = gas constant, 1544 (lb/sq ft, cu ft)/(lb-mole, $^{\circ}R$)
 R_o = ratio of moles of gas in bed to moles of liquid in bed
 Re = Reynolds number, $d_p \epsilon v \rho / \mu$, dimensionless
 S = cross-sectional area of empty column, sq ft
 s = Laplace transform variable, dimensionless
 Sc = Schmidt number, $\mu / \rho D$, dimensionless
 Sh = Sherwood number = $\frac{kydp}{D \rho}$
 T = absolute temperature, $^{\circ}R$
 t = time, hr
 V_L = volume of liquid, cu ft
 v = true gas velocity, ft/hr
 W = molar flow rate of gas, lb mole/hr
 x = position or distance in bed, ft
 x_L = mole fraction of component in liquid
 y = mole fraction of component in gas
 y^* = mole fraction of component in gas which is in equilibrium with liquid phase

- z = dimensionless length, x/L
 δ = Dirac delta function (unit impulse)
 e = void fraction in bed
 θ = dimensionless time, $t/(L/v)$
 θ_τ = dimensionless time corresponding to τ
 μ = gas viscosity, lb/(ft-hr)
 ρ = gas density, lb/cu ft
 ρ_G = molar density of gas, lb-mole/cu ft
 ρ_L = molar density of liquid, lb-mole/cu ft
 τ = injection time for sample, hour
 τ_L = dimensionless time constant, $1/(mR_o N_{tog})$

PART IX

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PART X

APPENDIX A - CHROMATOGRAPH MODEL DEVELOPMENT

Development of a mathematical model for a chromatographic separator requires the choice of a column, packed or capillary. A packed column was selected because of its high separating efficiency, and because the configuration has been suggested (35) as being suited to the severe shocks of aerospace service.

A packed column is a tube packed with a granular solid having dimensions much smaller than the tube diameter and length. This assumption, which is generally met in practice, permits the use of a continuous rather than a discrete mathematical model.

In deriving the equations for the model, it is assumed that the granular solid is coated with a high-molecular weight, non-volatile liquid which acts as the adsorbent. Flowing continuously through the column is a carrier gas, such as helium, which is not adsorbed by the liquid. At some instant, a trace of the materials to be separated is injected into the carrier gas stream. As this pulse flows down the column, the materials diffuse to the adsorbent layer and adsorb. When the pure carrier

gas upstream of the pulse passes the adsorbed materials, they are desorbed. Because different materials adsorb and desorb at different rates depending upon the thermodynamic characteristics of the system, separation between the various components is possible.

Actual derivation of the differential equations which govern the operation of a gas chromatograph is accomplished by doing a mass balance on a differential element of the column shown schematically in Figure 1. This element has length, Δx , *cross-sectional area, S , volume, $S\Delta x$, void fraction, ϵ , and surface area available for adsorption, $aS\Delta x$. Looking at an even smaller element, the area between two particles, it is evident what transport processes are going on.

It is assumed that the bed is sufficiently homogeneous so that its behavior may be represented by the above model. Additional assumptions required to derive a mathematical model for a packed column are as follows:

1. The column is isothermal.
2. The carrier gas velocity profile is flat.
3. The axial diffusion coefficient, D , is a composite factor which may or may not have a turbulent component.

*See Section VIII for nomenclature.

4. The gas composition is approximately constant in the direction normal to flow, and the concentration gradient occurs only in a thin boundary layer near the adsorbent; i.e., mass transfer coefficients can be used.
5. The adsorbent layer is so thin that there is no diffusional resistance within the layer in the direction normal to the surface.
6. The diffusivity in the adsorbent layer is so large that there is no diffusion in the direction parallel to the surface (in the axial direction).
7. The net rate of adsorption for the carrier gas is negligible.
8. Only one component is adsorbed and its gaseous phase composition is very small.
9. The carrier gas behaves as an ideal gas.

Three equations will be required to define the behavior of the adsorbing component: a mass balance for the gas phase, a mass balance for the adsorbent (liquid) phase, and a thermodynamic function relating the gas-phase and adsorbed-phase concentrations. All balances are to be done in terms of lb-moles/hr. The simple method of

$$\text{Input} - \text{Output} = \text{Accumulation}$$

will be used to compute the balances.

The gas phase balance will be derived first. The input term in this balance has contributions from three different phenomena: bulk flow, diffusion, and desorption. The desorption effect which is taken into account by a net rate of adsorption will be discussed later. The

term arising from bulk flow of gas is:

$$\left[\frac{SG_s}{(1-y)} \right] y \quad (X-1)$$

The diffusion term is found by starting with Fick's model of diffusion:

$$N_A = -D \frac{dC}{dx} \quad (X-2)$$

This equation gives the lb.moles/hr.ft.² diffused across a cross-sectional area. It is necessary to convert this equation to mole fractions and lb.moles/hr. The term for diffusion becomes

$$-D \left(\frac{P \epsilon S}{RT} \right) \frac{\partial y}{\partial x} \quad (X-3)$$

The sum of (X-1) and (X-3) gives the total input for the gas phase

$$\epsilon S \left[\frac{G_s y}{(1-y)} - D \left(\frac{P}{RT} \right) \frac{\partial y}{\partial x} \right] \quad (X-4)$$

The output term has contributions from the same three effects as the input term. The bulk flow effect must take into account the change in composition of the gas as it moves from one end of the element to the other. This term is:

$$\frac{\epsilon SG_s}{(1-y)} y + \frac{\partial}{\partial x} \left[\frac{SG_s}{(1-y)} \right] \Delta x = \epsilon SG_s \left(\frac{y}{(1-y)} + \frac{1}{(1-y)^2} \left(\frac{\partial y}{\partial x} \right) \Delta x \right) \quad (X-5)$$

The term for diffusion which must allow for the same effect becomes:

$$- \epsilon S \left(\frac{P}{RT} \right) D \frac{\partial}{\partial x} \left[y + \frac{\partial y}{\partial x} \Delta x \right] = - \epsilon S \left(\frac{P}{RT} \right) D \left(\frac{\partial y}{\partial x} + \frac{\partial^2 y}{\partial x^2} \Delta x \right) \quad (X-6)$$

The rate of adsorption may be expressed in terms of the rate at which the adsorbing material diffuses from the gas phase to the gas/solid interface. The concept of the mass transfer coefficient yields the rate of disappearance of the material from the gas phase

$$K_y a S (y - y^*) \Delta x \quad (X-7)$$

If the material is desorbing, the driving force will be negative and the term will behave as an input term. Hence the expression as written will represent both the adsorption and desorption processes.

This term may also be represented as the rate of removal by the condensed phase in which case the term becomes

$$\left(\frac{\text{adsorbent amount}}{\text{length}} \right) \Delta x \frac{\partial n}{\partial t}$$

the rate $\frac{\partial n}{\partial t}$ is the amount of material removed per unit

time, per unit of adsorbent. The unit of adsorbent may be either surface area, volume, or other useful unit.

Summing the terms of (X-5, X-6, X-7)

$$\epsilon SG_s \left[\frac{y}{(1-y)} + \frac{1}{(1-y)^2} \left(\frac{\partial y}{\partial x} \right) \Delta x \right] - \epsilon S \frac{P}{RT} D \left[\frac{\partial y}{\partial x} + \frac{\partial^2 y}{\partial x^2} \right] + K_y a S (y - y^*) \Delta x \quad (X-8)$$

The accumulation term is equal to the rate of change in the amount of adsorbing material in the element. It may be expressed as the product of the amount of gas in the element and the change in composition with time:

$$(\epsilon S \Delta x) \rho_g \frac{\partial y}{\partial t} \quad (X-9)$$

This term assumes ρ_g is constant, which is true as long as the pressure and temperature are constant.

Summing terms (X-4, X-8, X-9) gives the gas phase mass balance:

$$\left[\frac{\epsilon SG_s}{(1-y)} y - \epsilon S \frac{P}{RT} D \frac{\partial y}{\partial x} \right] - \left[\frac{\epsilon SG_s}{(1-y)} y + \frac{\epsilon SG_s}{(1-y)^2} \frac{\partial y}{\partial x} \Delta x - \epsilon S \frac{P}{RT} D \left(\frac{\partial y}{\partial x} + \frac{\partial^2 y}{\partial x^2} \Delta x \right) + K_y a S (y - y^*) \Delta x \right] = \epsilon S \Delta x \rho_g \frac{\partial y}{\partial t} \quad (X-10)$$

This equation may be simplified by canceling like terms and dividing through by $(\epsilon SG_s \Delta x)$. It then becomes

$$\frac{P}{RT} \frac{D}{G_s} \left(\frac{\partial^2 y}{\partial x^2} \right) - \frac{1}{(1-y)^2} \left(\frac{\partial y}{\partial x} \right) - \frac{K_y a}{\epsilon G_s} (y-y^*) = \rho_g \frac{1}{G_s} \left(\frac{\partial y}{\partial t} \right) \quad (X-11)$$

The liquid phase mass balance may be found in a similar manner. However, because there is no diffusion or bulk flow within the liquid, only two terms will result, one for the net rate of adsorption and one for the accumulation.

The net rate of adsorption is the same as in the gas phase, term (X-7), however, the accumulation term is:

$$\Delta V_L \rho_L \frac{\partial x_L}{\partial t} \quad (X-12)$$

where ΔV_L is defined by:

$$\Delta V_L = (S \Delta x) (1 - \epsilon) F$$

The mass balance for the liquid phase is:

$$\rho_L (1 - \epsilon) F \left(\frac{\partial x}{\partial t} \right) = K_y a (y - y^*) \quad (X-13)$$

The third equation necessary for each component is a thermodynamic relationship between the composition of the gas y^* , in equilibrium with the liquid composition x_L . For the dilute concentrations under consideration a linear relationship will be assumed:

$$y^* = m x_L$$

Equations (X-11, X-13, X-14) are the three

equations necessary for each component to describe a chromatographic column. They are subject to the following boundary conditions:

$$\left. \begin{array}{l} y(x,0) = 0 \\ x \quad (x,0) = 0 \end{array} \right\} \quad x > 0 \quad (X-15a)$$

$$y(0,t) = f(t) \quad (X-15b)$$

$$\frac{\partial y(L,t)}{\partial x} = 0 \quad (X-15c)$$

Condition (X-15a) states that prior to the injection of the trace, there is no adsorbing material within the column, in either the gas or liquid phases. Condition (X-15b) represents the injection of the trace. It will in general be a pulse and perhaps an impulse. An additional boundary condition is required because of the second order derivative in x . Condition (X-15c) has generally been used in similar diffusional processes, (e.g. ref. 7) but there is some doubt about its validity in this particular application. Since axial diffusion may be a second order effect especially in columns having large length/diameter ratios, study of this boundary condition will be deferred until the basic characteristics of the column model have been determined.

To make the equations more general, dimensionless variables and coefficients are used. Using definitions of G

$$G = G_s / (1-y) = v \rho_G = \frac{vP}{RT}$$

Equation (X-11) becomes

$$\frac{D}{v} \left(\frac{\partial^2 y}{\partial x^2} \right) - \frac{1}{(1-y)} \left(\frac{\partial y}{\partial x} \right) - \frac{K_y a}{\epsilon G} (y-y^*) = \frac{1}{v} \left(\frac{\partial y}{\partial t} \right) \quad (X-16)$$

A dimensionless length, Z , time, Θ , and two dimensionless transport parameters, the Peclet number, Pe , and N_{tog} , the number of transfer units available for adsorption, simplify the equation:

$$\left. \begin{aligned} Z &= x/L \\ dx &= L dz \\ dx^2 &= L^2 dz^2 \end{aligned} \right\} 0 \leq z \leq 1$$

$$\left. \begin{aligned} \Theta &= \frac{vt}{L} \\ dt &= \frac{L}{v} d\Theta \end{aligned} \right\}$$

$$Pe = D/Lv$$

$$N_{tog} = \frac{K_y a L}{G}$$

The gas phase equation becomes

$$\frac{1}{Pe} \frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} - N_{tog} (y - y^*) = \frac{\partial y}{\partial \Theta} \quad (X-17)$$

Use of the same techniques on the liquid phase equation and introduction of a new parameter

$$R_0 = \frac{\epsilon \rho_g}{F(1-\epsilon) \rho_L}$$

in which R_0 is the ratio of moles of gas present to moles of liquid present in an element of the bed, yields dimensionless form of the liquid phase mass balance:

$$\frac{1}{R_0} \frac{\partial \chi_L}{\partial \Theta} = N_{tog} (y - y^*) \quad (X-18)$$

The boundary conditions now take the form

$$\left. \begin{aligned} y(z, 0) &= 0 \\ \chi_L(z, 0) &= 0 \end{aligned} \right\} z > 0 \quad (X-19a)$$

$$y(0, \Theta) = f(\Theta L/v) \quad (X-19b)$$

$$\frac{\partial y(1, \Theta)}{\partial z} = 0 \quad (X-19c)$$

The system of equations which must be solved for a single adsorbing component is comprised of (X-17, X-18, X-14) and the boundary conditions (X-19a, b, c).

The systems of equations will be solved using Laplace transformations. Because of doubts in the validity of boundary condition (X-19c) and because the axial diffusion effects given by the second derivative term of Equation (X-17) may be second order terms, the equation may be simplified to

$$-\frac{\partial y}{\partial z} - N_{tog} (y - y^*) = \frac{\partial y}{\partial \Theta} \quad (X-20)$$

for preliminary model studies. Transformation with respect to Θ and use of (X-19a) yields

$$-y'(z,s) - (N_{tog} + s)y(z,s) = -N_{tog} y^*(z,s) \quad (X-21)$$

Transformation of (X-18) with respect to Θ and use of (X-19a) yields

$$\left(\frac{1}{R_0 N_{tog}} \right) s x_L(z,s) = y(z,s) - y^*(z,s) \quad (X-22)$$

Transformation of (X-14) yields

$$y^*(z,s) = m x_L(z,s) \quad (X-23)$$

Simultaneous solution of (X-21, X-22, X-23) yields for the gas phase composition

$$y'(z,s) + y(z,s) \left(N_{tog} + s - \frac{N_{tog}}{\tau_L s + 1} \right) = 0$$

in which the dimensionless time constant

$$\tau_L = \frac{1}{m R_0 N_{tog}}$$

appears. The solution to this equation is

$$y(z,s) = A(s) \exp \left\{ - \left(N_{tog} + s - \frac{N_{tog}}{\tau_L s + 1} \right) z \right\} \quad (X-24)$$

The arbitrary function $A(s)$ is derived from boundary condition (X-19b)

$$A(s) = y(0,s)$$

or it is the Laplace transform of the forcing function

$$f\left(\frac{\phi L}{v}\right)$$

which describes how the sample is injected into the column.

If the sample is injected at a constant rate up to a time τ , the rate of injection is

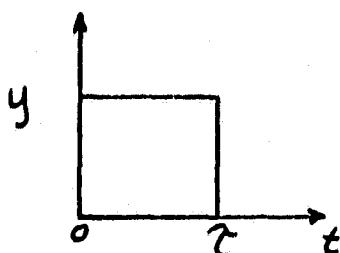
$$N/\tau$$

and the gas composition (or forcing function) becomes

$$y(o,t) = \frac{N}{\tau} / (W + \frac{N}{\tau}) \cong \frac{N}{\tau W} \quad 0 < t < \tau$$

$$= 0 \quad t > \tau$$

This function looks as follows:



The area under the curve is a constant (the total amount of sample):

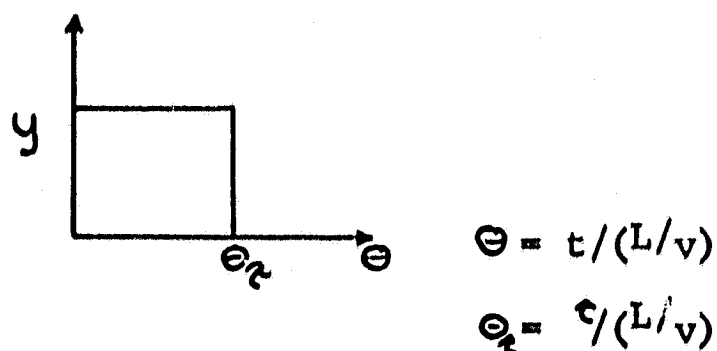
$$\int_0^{\tau} w y(t) dt = N$$

or

$$\int_0^{\tau} y(t) dt = \frac{N}{W}$$

which depends only on

the amount of sample and the carrier gas flow rate expressing the forcing function in dimensionless time



$y(0, \Theta)$ becomes

$$y(0, \Theta) = \frac{N(V/L)}{\Theta_r W} \quad 0 < \Theta < \Theta_r$$

$$= 0 \quad \Theta > \Theta_r$$

This function must now be transformed with respect to Θ for use in obtaining the solution to Eqn. (X-24).

The transform of this function is:

$$y(s) = \frac{N(V/L)}{\Theta_r W} \left(\frac{1}{s} \right) \left[1 - \exp \{ -\Theta_r s \} \right]$$

This expression contains the injection time Θ_r which depends upon the design of the injection device and which is generally not known when conducting conceptual studies. Because the injection time can be made very small by controlling the sample size and injection rate, it will be convenient to investigate system behavior as the injection time approaches zero (the forcing function becomes an impulse). Hence, the limit of this equation taken as Θ_r approaches zero (very small injection time). v

becomes the boundary condition at $Z = 0$:

$$y(s) = \frac{N(V/L)}{W} \quad (X-25)$$

Substitution of (X-25) into (X-24) yields the solution:

$$y(z,s) = \frac{N(V/L)}{W} \cdot \exp \{ -N_{\text{tog}} z \} \exp \{ -sz \} \exp \left\{ \frac{N_{\text{tog}} z}{\tau_L s + 1} \right\} \quad (X-26)$$

Equation (X-26) may be inverted by classical techniques with the following result:

$$\begin{aligned} y(z, \theta) &= 0 & z > \theta \\ &= \frac{N(V/L)}{W} \cdot \exp \{ -N_{\text{tog}} z \} \cdot \exp \left\{ -\frac{(\theta - z)}{\tau_L} \right\} \\ &\quad \left[\frac{2N_{\text{tog}} z}{\tau_L} \cdot \frac{I_1(x)}{x} + \delta(\theta - z) \right] \end{aligned} \quad (X-27)$$

in which

$$x \equiv 2 \sqrt{\frac{N_{\text{tog}} z (\theta - z)}{\tau_L}} \quad (X-28)$$

These equations may also be expressed as follows:

$$\begin{aligned} y(z, \theta) &= 0 & \theta < z \\ &= \frac{N(V/L)}{W} \exp \{ -N_{\text{tog}} z \} \exp \left\{ -\frac{(\theta - z)}{\tau_L} \right\} \\ &\quad \left[\delta(\theta - z) + \frac{N_{\text{tog}} z}{\tau_L} \sum_{n=0}^{\infty} \left(\frac{N_{\text{tog}} z}{\tau_L} \right)^n \frac{(\theta - z)^n}{n! (n+1)!} \right] \end{aligned}$$

Equations (X-27), (X-28) represent the behavior of a chromatograph when adsorbing and desorbing a single component. In general, the behavior at the end of the column ($z=1$) is of most interest. The parameters N_{tog} , (v/L) and Θ are dependent on the physical design and fluid mechanics of the column, which can be predicted with some certainty. The term τ_L contains a thermodynamic function m which is a function of the particular materials used and at the present time is generally not predictable. It is this term which will be evaluated from experimental data.

It is of interest to investigate further the forcing function

$$\frac{N(v/L)}{W}$$

which appears as a coefficient to the solution Eqn. (X-27).

If the carrier gas flow rate is expressed in terms of the velocity

$$W = v \rho_G S \epsilon$$

the forcing function may be written as

$$\frac{N(v/L)}{W} = \frac{Nv}{Lv \rho_G S \epsilon} = \frac{N}{(LS \epsilon) \rho_G}$$

The term $(LS \epsilon)$ is the volume of carrier gas in the column neglecting the compounds being separated and therefore

($LS\epsilon Q_G$) is the number of moles of carrier gas within the column. The forcing function is the ratio of sample to carrier gas within the column. It would be a composition if we took the gas in the column and mixed it with the sample.

PART XI

APPENDIX B - COMPUTER PROGRAMS

In order to be able to compute a chromatograph for a given mixture, Eqn (IV-9) has to be solved as a function of time and position. In particular, we are interested in the gas composition at the end of the column where the detector will be located. Because it was also necessary to use a trial and error procedure to determine a value for mR_0 corresponding to a given chromatogram, it was desirable to solve Eqn. (IV-9) by using a computer program. Another reason for this choice is the fact that the solution of the equation requires multiplication of very large numbers by very small numbers. This procedure can be handled more efficiently on a computer. Due to the assumption that an mR_0 for a given component is independent of the other components in a mixture, two programs were written. One program, for use with a single component system, solves for a value of mR_0 which matches the experimental data. The other program uses the data from the first program to compute a chromatogram for a multi-component mixture. No trial and error procedure is necessary in the multicomponent program because it uses

values determined for the single components.

Besides computing the chromatogram and finding a value for mR_0 , the programs also compute the characteristic parameters for the column under analysis. These parameters are; velocity, interfacial surface area, a , Reynolds number, Schmidt number, Sherwood number, and N_{tog} .

Calculation of these parameters requires that various physical properties of the constituents and the physical characteristics of the column must be supplied as data to the programs. The density and viscosity of the carrier gas as well as the diffusivity in the carrier gas of the component being analyzed must be available. Carrier gas flow rate, length of the column, diameter of the column, diameter of the packing, and the void fraction must all be input data to the programs.

The first program, PROGRAM A, can be used for two different analyses depending upon the value of an instruction index, Q . The program can be used to find a value of mR_0 from a given chromatogram ($Q = 0.0$) or may be used to compute the chromatogram for a single component ($Q = 1.0$). The program may also be used to used to study how various parameters affect a chromatogram ($Q = 1.0$).

To find a value of mR_0 , the time of occurrence of the maximum in the actual chromatogram and in the predicted chromatogram must be known since a great deal of data is presented relative to an air peak or some other base component allowance was made for this fact. If there is no such base time, $AIRP = 0.0$. The program computes a value of the relative detector output at $THETA = 1.0$ for an assumed mR_0 . The next point is computed at $THETA + DELT$, where $DELT$ is a time increment read in as input data supplied by the user. When the program finds a maximum it retains the value and time of occurrence and continues to compute the chromatogram until the end of analysis time ($RUNT$). It then goes back to one time increment before the maximum, divides $DELT$ by 10.0 and recomputes the chromatogram until it again has passed the maximum by 10 of the new $DELT$. This procedure is repeated until $DELT$ is made sufficiently small to insure accuracy of the maximum, $DELT = 0.0005$. The time of the appearance of the maximum ($RETT$) is checked against the actual retention time ($ARETT$). If the calculated time is within $ERROR$, a time band around the actual peak which is specified by the user, a value of mR_0 has been found. If not, a new value of mR_0 is estimated from

$$(mR_o)_{\text{new}} = (mR_o)_{\text{old}} \frac{\text{ARETT} - \text{RETT}}{2 \times \text{ARETT}}$$

and the computation is repeated. The starting value of mR_o may be anything, the program will still find a true value, but it is more expedient to start near the actual value. A truer estimate can be found by using the value of mR_o for $N_{\text{tog}} = \infty$. The program then requires less time to find a value of mR_o .

The second program, PROGRAM B, can only be used to compute a chromatogram and to study the effects of various parameters on this chromatogram. However, this program may be used for either a single component or a multi-component mixture.

It must be emphasized that neither one of these programs is in its most efficient form. However, because more difficult and involved programs will be required to solve the second order model equations and/or the temperature programming model, it would not be beneficial to pursue optimization of these programs.

In both programs two alternate methods of solution are used. The choice between the two depends on the value of N_{tog} and arises because of the definition of a modified Bessel function for values of N_{tog} less than 10.0. The

programs use the actual series representation of a Bessel function:

$$I_0(x) = \sum_{n=0}^{\infty} \frac{x^{2n+1}}{2^{2n+1} n! (n+1)!}$$

The number of terms in this series can be specified by the user. The series converges rapidly for 10 to 15 forms for values of N_{tog} greater than 10.0, an asymptotic representation of a Bessel function is used:

$$I_0(x) \approx \exp(x) / \sqrt{2\pi x}$$

The need for two different expressions arises because the computer can not handle efficiently the numbers when the argument of the Bessel function becomes large. Since most columns will have values of N_{tog} greater than 100, the asymptotic expression will usually be used.

Following is a listing of the variables used in the programs, the input requirements for the programs, and an actual listing of each program. Although the units used in the derivation of the chromatographic model equations were engineering units (ft-lbs-hrs), the units used in preparing and writing the programs were the metric units (cm-gm-sec). The reason for this change was the fact that most experiments conducted using gas chromatographs report data in the c-g-s system. Also many columns use this system to define their dimensions. Although most of the nomenclature is the same as that presented in Section VIII, some had to be changed due to the limits of the Fortran language.

A = ratio of interfacial area to packed volume.

AIRP = time for air peak to appear.

ARETT = time for appearance of peak (maximum) in chromatograph of component being analyzed.

DAB = diffusion coefficient for component being analyzed.

DC = diameter of column.

DELM = increment used to find a value of mR_0

DELT = time increment used to designate how often the mole fraction will be found.

DIRAC = value of Dirac delta function at different points in the column.

DP = diameter of particles used for packing in the column.

EPS = void fraction

ERROR = error used in finding a value for mR_0

K = step in time from start (injection) of the sample.

NN = number of terms in infinite series used to approximate a modified Bessel function.

Q = instruction index for PROGRAM A

RE = Reynolds number

RETT = time at which program estimates the peak occurs while it is trying to find a value for mR_0 .

RHOG = density of carrier gas.

RUNT = time for duration of experiment.

SC = Schmidt number

SH = Sherwood number

TAUL = reciprocal of dimensionless time constant ($1/\tau_L$)

THETA = dimensionless time.

TIME = actual time of analysis.

TOGN = number of adsorption transfer units

T = temperature at which experiment was performed.

V = true velocity in column.

VIS = viscosity of carrier gas.

W = volume flow rate of carrier gas.

XL = length of column

$Y(K)$ = mole fraction of component being analyzed.

$Y(K,L)$ = mole fraction of single component in multi-component analysis.

$TYTOT(K)$ = sum of mole fractions of all components in a multicomponent analysis

Z = dimensionless length

INPUT FOR PROGRAM A

CARD 1

Col 1-16 Length of column (cm)
17-32 volume flow rate (cm^3/sec)
33-48 particle diameter (cm)
49-64 column diameter (cm)
65-80 void fraction

CARD 2

Col 1-20 density of carrier gas (gm/cm^3)
21-40 viscosity of carrier gas ($\text{gm}/\text{cm-sec}$)
41-60 diffusion coefficient (cm^2/sec)
61-80 temperature of column ($^{\circ}\text{C}$)

CARD 3

Col 1- 2 number of terms in infinite series used to
approximate modified Bessel function
11-20 DELT, time increment, (secs)
21-30 RUNT, time to run experiment (secs)

CARD 4

Col 1-20 starting or actual value of mR_0

CARD 5

Col 1-10 time of occurrence of air peak (secs)
11-20 actual time of appearance of maximum in
chromatograph (secs)
21-30 error in finding mR_0
31-40 Q, when this is 0.0 program finds a value of
 mR_0 , when 1.0 computes a chromatograph for
that component

INPUT FOR PROGRAM B

Cards 1 and 2 in the input deck are the same for Program B as for Program A.

CARD 3

Col. 1- 2 number of terms in infinite series used to
 estimate the modified Bessel function
 11-12 number of components
 21-40 duration of experiment (secs)
 41-60 time increment which designates number of
 points on graph to be calculated (secs)

CARD 4

Col 1-16 value of mR_0 for component 1
 17-32 value of mR_0 for component 2
 33-48 etc
 49-64 etc
 65-80 etc

PROGRAM A

```

1      DIMENSION Y(5000),FACT(5000),FA(5000),SUM(5000)
2      READ(1,1) XL,W,DP,DC,EPS
3      1 FORMAT(5F16.6)
4      READ(1,2) RHOG,VIS,DAB,T
5      2 FORMAT(4F20.8)
6      READ(1,3) NN,DELT,RUNT
7      3 FORMAT(I2,8X,2F10.3)
8      READ(1,4) ROM
9      4 FORMAT(F20.8)
10     READ(1,5) AIRP,ARETT,ERROR,Q
11     5 FORMAT (4F10.6)
12     V = (W*4.0)/(EPS*(DC**2.0)*3.14)
13     RE = (DP*V*RHOG)/VIS
14     SC = VIS/(RHOG*DAB)
15     SH = 2.0 + 0.347*((RE*(SC**0.5))**0.62)
16     A = 6.0*(1.0-EPS)/DP
17     TOGN = (SH*A*XL)/(SC*RE)
18     WRITE(3,65) XL,W,DP,DC,EPS
19     65 FORMAT(20X,5(F16.6,5X),//)
20     WRITE(3,66) RHOG,VIS,DAB,T
21     66 FORMAT(20X,4(F20.8,5X),//)
22     WRITE(3,67) NN,DELT,RUNT
23     67 FORMAT(20X,12,8X,2(F10.3,5X),//)
24     WRITE(3,68) ROM,TOGN
25     68 FORMAT(20X,F20.8,5X,F20.8,//)
26     WRITE(3,69) V,RE,SH,SC,A
27     69 FORMAT(20X,5(F16.6,5X),//)
28     WRITE(3,10)
29     10 FORMAT(20X,13HMOLE FRACTION,12X,4HTIME,13X,5HTHETA,//)
30     Z=1.0
31     K=1
32     25 THETA = 1.0
33     TAUL = 1.0/(ROM*TOGN)
34     26 TIME = THETA*(XL/V)
35     IF(THETA-Z) 77,78,79
36     77 Y(K) = 0.0
37     GO TO 1001
38     78 DIRAC = 1.0
39     IF (TOGN-100.0) 777,776,776
40     777 Y(K)=EXP(-TOGN)
41     776 Y(K)=0.0
42     GO TO 1001
43     79 DIRAC = 0.0

```

```

44      IF(TOGN-10.0) 800,801,801
45 800 N=1
46      P1 = -TOGN - (THETA-Z)/TAUL
47      P2 = ALOG(TOGN*Z/TAUL)
48      SUMK = P2
49 33 FACT(N) = 1.0
50      IF(N-1) 70,70,50
51 50 DO 49 I = 2,N
52      FA(I) = I
53 49 FACT(N) = FACT(N)*FA(I)
54      IF(N-1) 70,70,60
55 70 P3 = 2.0*ALOG(TOGN*Z/(TAUL*2.0))+ALOG(THETA/2.0-Z/2.0)
56      SUM(1) = P3
57      SUMK = SUMK + SUM(N)
58      GO TO 98
59 60 P4 = 2.0*N*ALOG(TOGN*Z/TAUL) + N*ALOG(THETA-Z) +
      1ALOG(1.0/(FACT(N) *(N+1)*FACT(N)))
60      SUM(N) = P4
61      SUMK = SUMK + SUM(N)
62 98 IF(N-NN) 99,99,100
63 99 N = N + 1
64      GO TO 33
65 100 IF((SUMK+P1)-100.0) 14,14,15
66 15 Y(K) = 0.0
67 14 Y(K) = EXP(SUMK+P1)
68      GO TO 1001
69 801 ARG=-TOGN-(THETA-1.0)*ROM*TOGN+2.0*((TOGN*TOGN*ROM*(THETA-
      11.0))**0.5)
70      IF (ABS(ARG)-L)).) 900,901,901
71 901 Y(K)=0.0
72      GO TO 1001
73 900 CONS=0.5*(ROM**0.25)*(TOGN**0.5)/((3.14**0.5)*((THETA-1.0)**
      10.25))
74      Y(K)=CONS*EXP(ARG)
75 1001 WRITE(3,7) Y(K),TIME,THETA
76 7 FORMAT(20X,E13.5,5X,F15.7,5X,F15.7)
77      IF(K-1) 101,101,102
78 101 YMAX = Y(K)
79      RETT = TIME
80 102 IF(DELT-0.005) 45,44,44
81 44 IF(YMAX-Y(K)) 112,170,170
82 45 IF(YMAX-Y(K)) 112,43,43
83 112 YMAX = Y(K)
84      RETT = TIME
85      IF(DELT-0.0005) 43,170,170

```

```

86 170 IF(TIME - RUNT) 161,110,110
87 161 THETA = THETA + DELT
88     K = K + 1
89     GO TO 26
90 110 WRITE(3,9)  YMAX,RETT
91     9 FORMAT(10X,13HMAXIMUM Y IS ,E13.5,10X,18HRETENTION TIME IS ,
      1F10.4,/)
92     WRITE(3,111)ROM
93 111 FORMAT(20X,E20.8)
94     THETA = RETT/(XL/V) - DELT
95     DELT = DELT/10.0
96     IF(DELT - 0.0005) 162,176,176
97 176 K = 1
98     GO TO 26
99     43 IF(THETA -(RETT/(XL/V) + 10.0*DELT)) 161,110,110
100 162 IF(Q) 171,171,181
101 171 IF(ABS((RETT-AIRP) - ARETT) -ERROR) 181,181,182
102 182 DELM=(RETT-(ARETT+AIRP))*0.5*ROM/(ARETT+AIRP)
103     ROM = ROM + DELM
104     K = 1
105     DELT = 0.1
106     GO TO 25
107 181 WRITE(3,23) ROM, RETT
108     23 FORMAT(10X,28HTHE EGUILIBRIUM CONSTANT IS ,E13.5,10X,22HTHE
      1RETENTION TIME IS ,F10.4,/)
109     CALL EXIT
110     END

```

PROGRAM B

```

1      DIMENSION ARG(5),CONS(5)
2      DIMENSION Y93000,5),FACT(3000),FA(3000),SIM(3000,5),EX1(5),
      1EX2(5),COEF(5),TAUL(5),SUMK(5),YTOT(3000),ROM(5),P1(5),
      2P2(5),P3(5),P4(5),TYTOT(3000)
3      READ(1,1) XL,W,DP,DC,EPS
4      1 FORMAT(5F16.6)
5      READ(1,2) RHOG,VIS,DAB,T
6      2 FORMAT(4F20.8)
7      READ(1,3) NN,LL,RUNT,DELT
8      3 FORMAT(12,8X,12,8X,F20.8,F20.8)
9      READ(1,4) (ROM(L),L=1,LL)
10     4 FORMAT(5F16.8)
11     V = (W*4.0)/(EPS*(DC**2.0)*3.14)
12     RE = (DP*V*RHOG)/VIS
13     SC = VIS/(RHOG*DAB)
14     SH = 2.0 + 0.347*((RE*(SC**0.5))**0.62)
15     A = 6.0*(1.0-EPS)/DP
16     TOGN = (SH*A*XL)/(SC*RE)
17     WRITE(3,65) XL,W,DP,DC,EPS
18     65 FORMAT(20X,5(F16.6,5X),/)
19     WRITE(3,66) RHOG,VIS,DAB,T
20     66 FORMAT(20X,4(F20.8,5X),/)
21     WRITE(3,67) NN,DELT,RUNT
22     67 FORMAT(20X,12,8X,2(F10.3,5X),/)
23     WRITE(3,68) TOGN
24     68 FORMAT(20X,F20.8,/)
25     WRITE(3,69) V,RE,SH,SC,A
26     69 FORMAT(20X,5(F16.6,5X),/)
27     WRITE(3,10)
28     10 FORMAT(20X,13HMOLE FRACTION,12X,4HTIME,13X,5HTHETA,/)
29     Z=1.0
30     K=1
31     25 THETA = 1.01
32     26 TIME = THETA*(XL/V)
33     L=1
34     IF(THETA-Z) 77,78,79
35     77 Y(K,L) = 0.0
36     GO TO 1001
37     78 DIRAC = 1.0
38     IF(TOGN-100.0) 777,776,776
39     776 Y(K,L) = 0.0
40     777 Y(K,L) = EXP(-TOGN)
41     GO TO 87

```

```

42      79 DIRAC = 0.0
43      IF(TOGN-10.0) 800,801,801
44      800 N=1
45      TAU(L) = 1.0/(ROM(L)*TOGN)
46      P1(L) = -TOGN - (THETA-Z)/TAUL(L)
47      P2(L) = ALOG(TOGN*Z/TAUL(L))
48      SUMK(L) = P2(1)
49      33 FACT(N) = 1.0
50      IF(N-1) 70,70,50
51      50 DO 49 I = 2,N
52      FA(I) = I
53      49 FACT(N) = FACT(N)*FA(I)
54      IF (N-1) 70,70,60
55      70 P3(L) = 2.0*ALOG(TOGN*Z/(TAUL(L)*2.0)) + ALOG((THETA-Z)/2.0)
56      SUM(1,L) = P3(L)
57      SUMK(L) = SUMK(L) + SUM(N,L)
58      GO TO 98
59      60 P4(L) = 2.0*N*ALOG(TOGN*Z/TAUL(L)+N*ALOG(THETA-Z) +
      1 ALOG(1.0/FACT(N)*(N+1)*FACT(N))
60      SUM(N,L) = P4(L)
61      SUMK(L) = SUMK(L) + SUM(N,L)
62      98 IF(N-NN) 99,99,100
63      99 N = N + 1
64      GO TO 33
65      100 Y(K,L) = SUMK(L) + P1(L)
66      87 YTOT(K) = 0.0
67      IF(L-11) 88,89.89
68      88 L=L+1
69      GO TO 800
70      89 DO 39 L=1,LL
71      39 YTOT(K) = YTOT(K) + Y(K,L)
72      IF(ABS(YTOT(K))-100.0) 11,12,12
73      12 TYTOT(K) = 0.0
74      11 TYTOT(K) = EXP(YTOT(K))
75      GO TO 1001
76      801 ARG(L) = -TOGN - (THETA-1.0)*ROM(L)*TOGN +2.0*((TOGN*TOGN*
      1ROM(L)*(THETA-1.0))**0.5)
77      IF(ABS(ARG(L))-100.0) 900,901,901
78      901 YTOT(K) = 0.0
79      IF(L-LL) 700,1001,1001
80      700 L= L + 1
81      GO TO 801

```

```
82 900 CONS(L)=.5*(ROM(L)**0.25)*(TOGN**0.5)/((3.14**0.5)*  
    1(THETA-1.0)**0.25)  
83 Y(K,L) = CONS(L)*EXP(ARG(L))  
84 IF(L-LL) 400,401,401  
85 400 L = L + 1  
86 GO TO 801  
87 401 TYTOT(K) = 0.0  
88 DO 402 L=1,LL  
89 402 TYTOT(K) = TYTOT(K) +Y(K,L)  
90 1001 WRITE(3,7) TYTOT(K),TIME,THETA  
91 7 FORMAT(20X,E13,5,5X,F15.7,5X,F15.7)  
92 IF(TIME-RUNT) 161,110,110  
93 161 THETA = THETA + DELT  
94 K = K+1  
95 GO TO 26  
96 110 WRITE(3,8)(L,ROM(L),L-I,LL)  
97 8 FORMAT(10Z,12,10X,F20.8)  
98 CALL EXIT  
99 END
```

PART XII
APPENDIX C

Table III

Tabulated Data for Pentane Chromatogram

Time (secs)	Mole Fraction
0.0	0.0
20.0	0.0
21.9	0.0
22.65	0.006
22.8	0.013
23.1	0.019
23.3	0.026
23.44	0.032
23.6	0.039
23.75	0.045
23.9	0.049
24.0	0.052
24.375	0.056
25.3	0.052
25.5	0.049
25.6	0.045
26.0	0.039
26.25	0.032
26.7	0.026
27.2	0.019
27.7	0.013
28.6	0.006
29.4	0.003
30.0	0.001
31.0	0.0

Table IV

Tabulated Data for Hexane Chromatogram

Time (secs)	Mole Fraction
0.0	0.0
40.0	0.0
43.75	0.003
44.4	0.006
44.7	0.01
45.0	0.013
45.6	0.016
45.9	0.019
46.25	0.022
46.6	0.025
47.2	0.029
47.5	0.032
48.75	0.034
49.4	0.032
50.0	0.029
50.5	0.025
50.8	0.022
51.25	0.019
51.6	0.016
52.0	0.013
52.5	0.01
53.1	0.006
54.4	0.003
55.6	0.001
56.0	0.0

Table V

Tabulated Data for Heptane Chromatogram

Time (secs)	Mole Fraction
0.0	0.0
50.0	0.0
90.0	0.0
91.9	0.001
95.6	0.002
96.25	0.003
98.1	0.005
99.4	0.006
100.9	0.008
101.9	0.009
103.1	0.011
104.4	0.012
106.25	0.014
107.5	0.015
108.75	0.015
110.0	0.015
110.9	0.014
111.9	0.012
112.5	0.011
113.1	0.009
114.4	0.006
115.6	0.003
116.6	0.002
116.9	0.0015