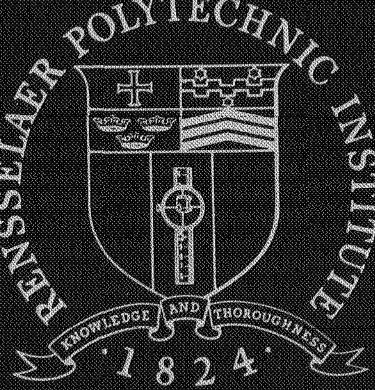

Rensselaer Polytechnic Institute

Troy, New York

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CHROMATOGRAPHIC SYSTEMS ANALYSIS: MOMENT ANALYSIS OF THE EQUILIBRIUM ADSORPTION MODEL

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

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ABSTRACT

A moment analysis of the equilibrium adsorption model is developed. The tools developed in this paper are dependent only on a knowledge of the system transport and thermodynamic parameters and on the Laplace transform of the system equations. Correlations are developed to predict the time of appearance of chromatograms for the equilibrium model and for its spread. The applicability of this method to the non-equilibrium model is discussed . The work is aimed at design of chromatographs, but most directly at the design of a chromatograph for a Mars Voyager.

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 the Chromatographic Systems Analysis program 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.

Because of the varity of mixtures to be separated and the complexity of the fractionating process, a system analysis based on the mathematical simulation of the chromatograph is being under taken. The technique will use mathematical models, which will incorporate fundamental parameters evaluated from reported experiments and analyses, to explore various concepts and to direct further experimental research.

PART II

SUMMARY

Due to the lack of an available mathematical solution to the non-equilibrium diffusion equations, several approaches have been used to describe chromatographic systems. Height of theoretical plate theories are widely used in the field (4); however they are analysis tools rather that design criteria. Approximations have also been made to allow solution of the system equations. The first order, non-diffusional model, fails to adequately characterize spreading (11). The equilibrium adsorption model is studied in this paper. However, although it is a reasonable approximation to reality for very long columns, the purpose here is not to propose it as an approximation, but rather to use it to develop tools which will be applied to the non-equilibrium case.

The "tools" are the methods of moment analysis. They are developed with the intention of designing chromatographic systems rather than analyzing them, as has been the case in previous work (5,7). The moment analysis approach requires a knowledge only of the system parameters and the Laplace transform solution of the system equations. Since the transform solution is available for both the equilibrium and non-equilibrium diffusion models, the methods developed in this paper may be applicable to the actual chromatographic systems.

The first moment about the origin, $\bar{\theta}$, calculates the time of appearance of the mean or center of gravity of the chromatogram. By a knowledge of the second (μ_2) and third (μ_3) moments about this mean, a correlation is developed such that the appearance of the maximum in the time domain can be calculated as a function of the system parameters. The variance, μ_2, allows one to determine a characteristic spread about the mode (maximum) on the time scale within which one can expect to find at least 90% of the area of the chromatogram.

Thus through a knowledge of the moments of the chromatographic system equations it appears possible to predict when a chromatogram of a substance will appear in the time domain, and to characterize its shape by the skewness of the maximum from the mean and by the spreading of the curve about this maximum. These results if obtained for the non-equilibrium case will aid preliminary design for an optimum chromatograph for a Mars Voyage.

PART III

BACKGROUND

The concern of scientists and engineers involved in chromatographic work has been and still remains the solution in the time domain of the diffusion controlled non-equilibrium model equations. The equations expressed in dimensionless form are:

$$\frac{\partial y}{\partial \theta} = \frac{1}{Pe}\left(\frac{\partial^2 y}{\partial z^2}\right) - \frac{\partial y}{\partial z} - N_{toG}\,(y-y^*) \qquad (1)$$

$$\frac{1}{R_o}\left(\frac{\partial x_L}{\partial \theta}\right) = N_{toG}\,(y-y^*) \qquad (2)$$

$$y = m\,x_L \qquad (3)$$

They have not been solved in convenient form. Lapidus and Amundson (8) have given a solution in the form of integrals of Green's functions, and it requires numerical integration. With the extended use of computers this solution may be given more attention.

At this time the majority of the work has been done under a philosophy different from that of this task. The workers have been interested in optimization of existing columns, that is, analysis on how to improve performance of equipment, and in determining value for the various rate constants. Theories such as those concerning theoretical plate height (HETP), and random walk models (4) became the objects of concern.

When the Chromatographic Systems Analysis was undertaken, it was decided that a new approach was necessary because the emphasis was to be on design of systems. In this approach it was desired to predict the time domain behavior of any column given the characteristics of the substances to be separated. This could allow the design of an "optimum" column for a Mars voyage.

Initial work was concerned with examining the suitability of using a non-diffusional first order model (11). It was assumed that in Equation 1 the term

$$\frac{1}{Pe}\left(\frac{\partial^2 y}{\partial z^2}\right)$$

was very small, that is, the effect of longitudinal diffusion was negligible as compared to the bulk flow transport. However, it was determined experimentally that this model was inadequate to descibe an actual chromatogram.(11) Figure 1. shows an experimental curve and the prediction of the first order model. It was decided that there might be two contributing factors to the extra spreading of the actual curve. One was the fact that injection time was finite rather that zero as assumed by the use of a Dirac delta function for input. This was examined by Krum (6). The second factor was assumed to be the fact that longitudinal diffusion does indeed have a significant effect upon mass transport.

Thus it was decided that a diffusion model should be examined. The work in this area in recent years had been in developing the use of statistical time moments to analyze chromatographic systems (5,7,16). However, the moments were again used in analyzing chromatograms rather than in predicting their time behavior, the real design problem. Nevertheless, it appeared that the moments technique might be applicable to this design problem, an approach which was unique. This task, then, was concerned with developing the moments as a semiquantitative tool for use in the design of chromatographic systems.

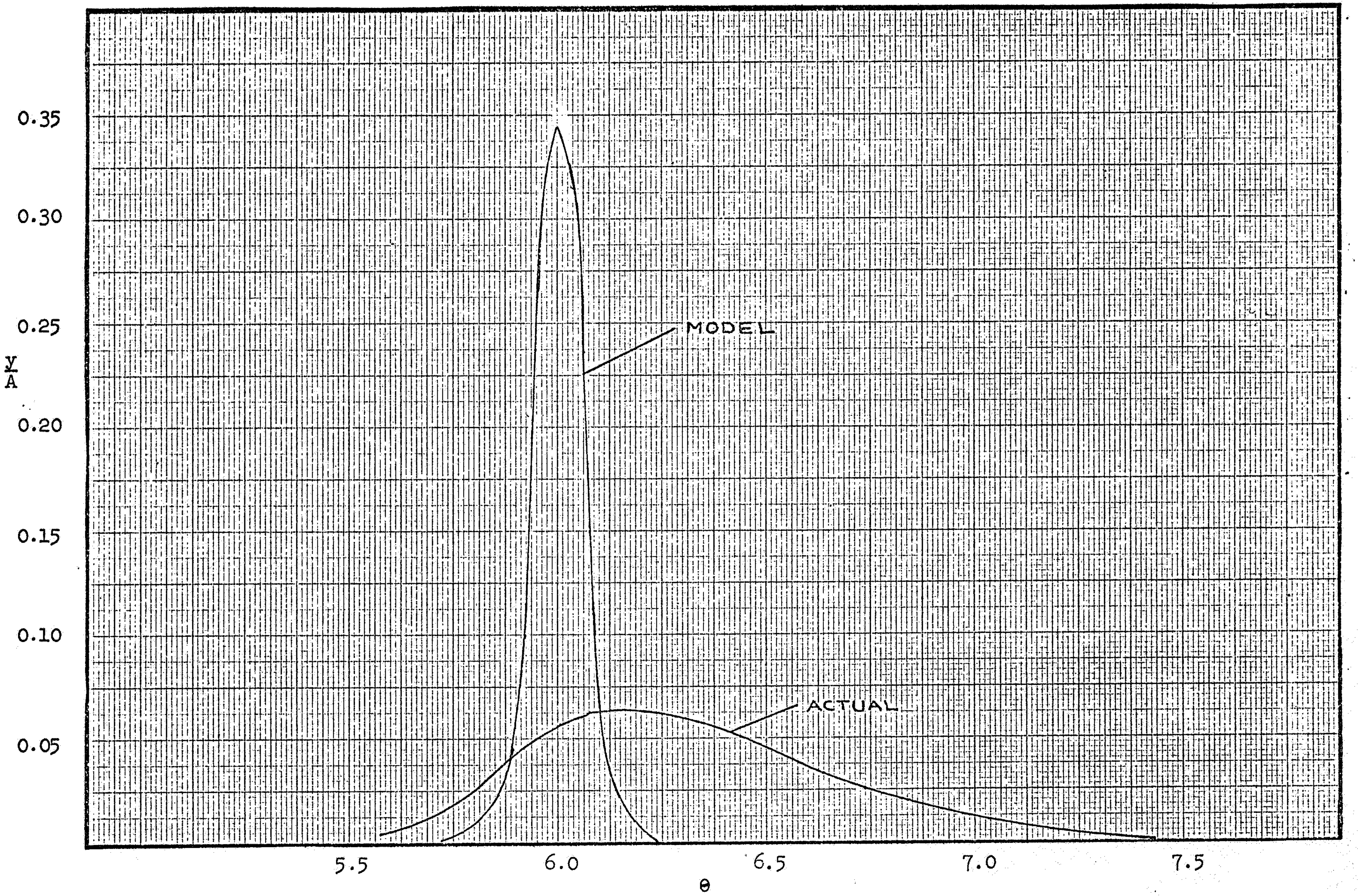

Figure 1.

Comparison of First Order Model to Actual
Chromatogram

PART IV

THEORY

A. Equilibrium Adsorbtion Model:

In order to be able to develop the tools to be used in a moment analysis, it was necessary to have a chromatographic model which exhibited characteristics similar to those of an actual chromatograph. Ideally if the solution of the non-equilibrium diffusion model would have been available, it would have served as a testing medium. However, at the time this task began, it was not available in a usable form.

The choice of the equilibrium adsorption model was made on the basis of its approximation to a real chromatograph. It has a considerable amount of characteristic skew and asymmetry, and actually for very long columns is a reasonably good approximation to reality (6).

The basis of the model can be seen if we consider the case where the adsorbed phase is always in equilibrium with the gas phase. Equations 1, 2, and 3 reduce to:

$$\frac{\partial y}{\partial \theta} + \frac{1}{R_o}\left(\frac{\partial x_L}{\partial \theta}\right) = -\frac{\partial y}{\partial z} + \frac{1}{Pe}\left(\frac{\partial^2 y}{\partial z^2}\right)$$

$$y = m\,x_L$$

Notice that this can also be obtained by letting N_{toG} become infinite. Under this condition, y approaches the equilibrium value y^*. This is true because a very long column allows the system to approach equilibrium conditions.

It was now necessary to solve the system equations so that chromatograms could be obtained for use in the analysis. The equation requires three boundary conditions for its solution. Although there is some question as to the validity of the conditions used, the ones chosen are those generally used in all chromatographic analysis, and are the ones that will be applied to the non-equilibrium model (3,14):

1. $y(0,z) = 0 \; ; \; x_L(0,z) = 0$

2. $y(\theta,0) \;=\; A\,\delta(t)$
3. $\lim\limits_{z\to\infty} y(\theta,z) \;=\; \text{finite}$

The first states that at time equal to zero, only carrier gas is flowing in the system , and no material is adsorbed on the substrate. The second states the input takes the form of an impulse, although studies are also being conducted to study the effect of pulse injection, that is finite injection time (6). The last is the questionable condition (3), but has been shown to be realistic for most practical purposes (2).

Using these boundary conditions one can obtain an analytic solution to the system equations of the form (8):

$$y(\theta,z) = A\left(\frac{z}{2}\right)\sqrt{\frac{\beta\ Pe}{\pi\ \theta^3}}\cdot\exp\left(\frac{Pe\ z}{2}\right)\cdot\exp\left(\frac{Pe\ \theta}{4\beta} - \frac{Pe\ z^2\ \beta}{4\theta}\right) \qquad (4)$$

By setting z = 1, that is, considering the exit of the column, one is able to generate time domain "curves" for the model. One is now prepared to undertake a moment analysis of the system.

B. Moments:

In order to carry out the analysis it is necessary to obtain the moments of the system. The definitions of the moments have appeared elsewhere (1,9). The mean is defined as

$$\bar{\theta} = \frac{\int_0^\infty \theta\ y d\theta}{\int_0^\infty y d\theta} \qquad (5)$$

and represents the center of gravity of the time/composition curve. The succeeding moments are found by taking moments about this mean:

$$\mu_k = \frac{\int_0^\infty (\theta-\bar{\theta})^k\ y d\theta}{\int_0^\infty y\ d\theta} \qquad (6)$$

In both cases the integral

$$\int_0^\infty y \, d\theta$$

fulfills the necessity of having the area under the curve equal unity, that is, it normalizes the moment. For this system the integral is equal to A.

The moments of interest for this paper are the mean, and the second and third moments about the mean.

The second moment about the mean, μ_2 , is commonly called the variance, and is often designated as σ^2 . It measures the spreading or dispersion about the mean, and may be computed either from Equation 6 or from the following:

$$\mu_2 = \frac{\int_0^\infty \theta^2 \, y d\theta}{A} - \bar{\theta}^2 \qquad (7)$$

The third moment about the mean, μ_3, is generally called skew, and it has been used as a qualitative measure of how much the curve is skewed from the mean. It may be calculated either from Equation 6 or from the following:

$$\mu_3 = \frac{\int_0^\infty \theta^3 \, y d\theta}{A} - 3\bar{\theta}\mu_2 - \bar{\theta}^3 \qquad (8)$$

The values of the various integrals in Equations 5,7, and8 may be obtained directly from time/composition data or by direct integration of the solution to the mathematical model. Since the mathematical models do not have simple time domain solutions, it is more convenient to obtain values for the integrals:

$$\int_0^\infty \theta^k \, y \, d\theta$$

by means other than direct insertion of values for y. Fortunately it can be shown (7), that if one has the Laplace transform of the solution, Y(s) then:

$$\int_0^\infty \theta^k \, y \, d\theta = (-1)^k \lim_{s \to 0} \frac{d^k \, Y(s)}{d \, s^k}$$

Thus only the transformed solution is necessary to obtain all needed information for the moment analysis. This transform solution is available for both equilibrium and non-equilibrium diffusion models.

PART V

RESULTS AND DISCUSSION

The purpose of the moment analysis is to characterize approximately the location and shape of a chromatographic curve, without using the time domain solution, by having a knowledge of the system parameters, Pe, mR_o, and N_{toG}. It has been shown that these parameters are predictable for any given chemical system and column (10). Thus one has the necessary tools, along with the moments, to characterize the curves. Relating quantitatively these moments to the time domain, however, is the major task.

It was shown in the previous section that by the use of the Laplace transform solution of system equations one can obtain the moments necessary for analysis. The first is the mean of the function. With this moment one can determine exactly when the mean of the chromatographic curve will appear. For the equilibrium adsorption model the mean, $\bar{\theta}$, is given as

$$\bar{\theta} = \beta = 1 + \frac{1}{mR_o}$$

The result is significant in several respects. First it is a function of a predictable system parameter, and secondly it is a function only of the thermodynamic parameter, and independent of the diffusion, 1/Pe. This result was also noted by Kucera (7).

Now that it is possible to determine where the center of gravity of the peak occurs, by use of the variance, σ^2, one should be able to characterize the spreading of the curve. The variance for the equilibrium adsorption model is

$$\mu_2 = \sigma^2 = \beta^2\left(\frac{2}{Pe}\right) \tag{9}$$

Again the result is a function of predictable parameters, and is easily calculated. However, at this point it was advantageous to examine the curves more closely. Figure 2. shows the effect of Peclet number on the location of the maximum point and the shape of the curve. If the variance about the mean, Equation 7 or 9, is used one would be characterizing curves whose maximums occur at distinctly different points by dispersion about the same point, the mean. It, therefore, appears that it would be more characteristic of the chromatogram if the spread could be taken about the maximum point,

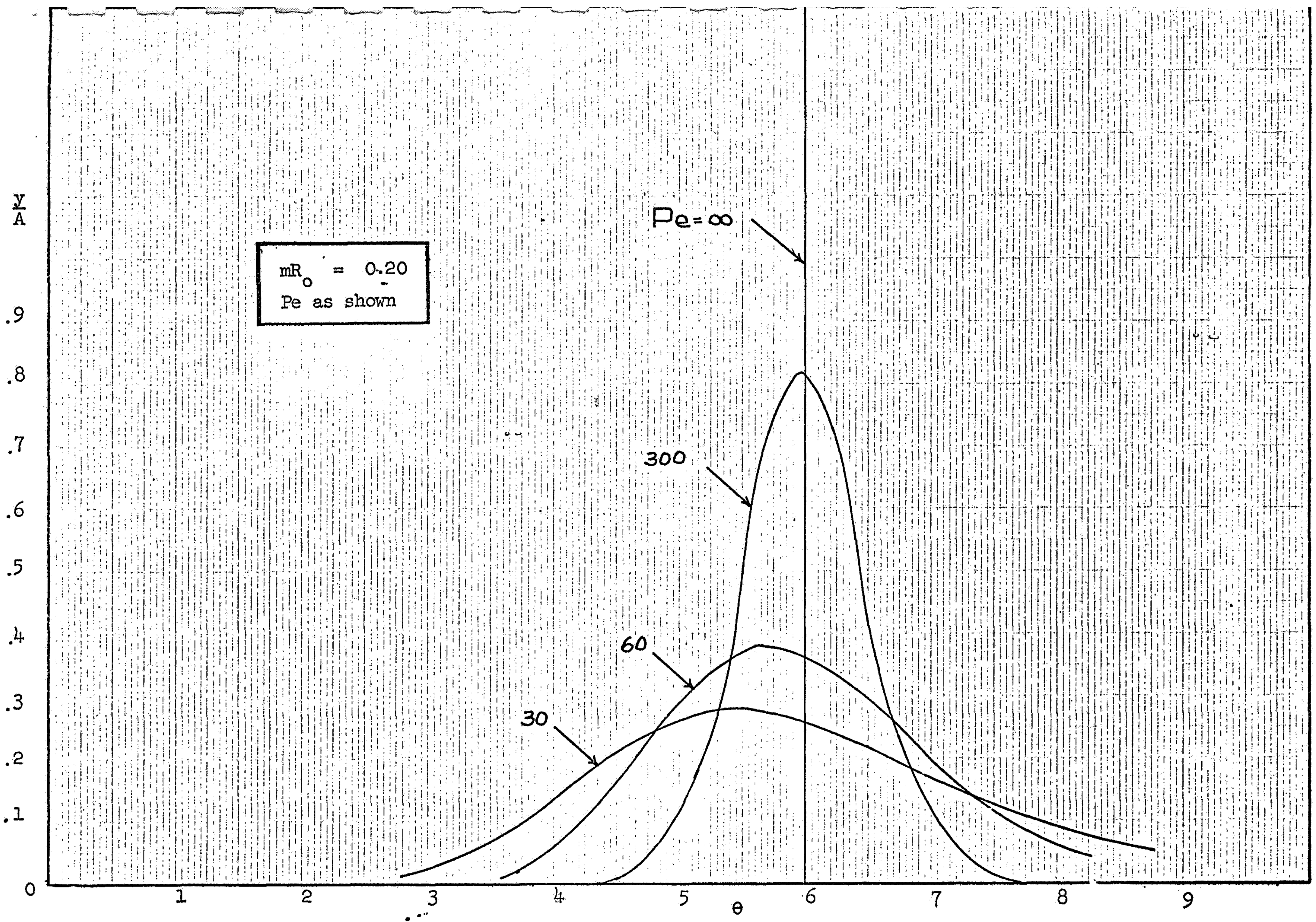

Figure 2.

Effect of Peclet Number on Chromatogram of Equilibrium Adsorption Model

θ_{max}, instead of the mean. The variance or second moment can be taken about any point by the use of the moment integral, Equation 6. If this is done for θ_{max}, the result in terms of the spread about the mean is given as

$$\sigma^2_{max} = \sigma^2 + (\bar{\theta}\Delta)^2$$

where

$$\Delta \equiv \frac{\bar{\theta} - \theta_{max}}{\bar{\theta}}$$

This would be the solution to the problem if one could estimate $\bar{\theta} - \theta_{max}$ from the various moments. Pearson (13) suggested that the deviation defined as skewness

$$\alpha \equiv \frac{\text{mean } (\bar{\theta}) - \text{mode } (\theta_{max})}{\mu^{1/2}}$$

Therefore if one could calculate the α, it would be possible to determine the time of appearance of the maximum value of y. It has been suggested (12) that for small skew

$$\alpha \sim \frac{1}{2} \mu_3 / \mu_2^{3/2}$$

or using the relation between the standard deviation and the variance, μ_2,

$$\frac{\bar{\theta}-\theta_{max}}{\sigma} = \frac{\mu_3}{2\sigma^3} \tag{10}$$

Rearrangement of Equation 10 yields

$$\frac{\bar{\theta} - \theta_{max}}{\bar{\theta}} \equiv \Delta = \frac{\mu_3}{2\bar{\theta}\mu_2} \tag{11}$$

where

$$\mu_3 = 12\,\beta^3 / \mathrm{Pe}^2$$

for the equilibrium adsorption model. This relation, however, is expected to be valid only for small degrees of skew. Empirically, one can extend the concept by stating

$$\Delta = f\left[\frac{\mu_3}{2\,\bar{\theta}\,\mu_2}\right]$$

where the functional relationship is determined experimentally. Figure 3 shows a plot of Δ, calculated for the equilibrium adsorbtion model with Pe. Notice that for values of Pe greater than 60 the linear relation represents the data extremely well. Even at a Peclet number of 30 the deviation from the linear relation is only 5%. The question now becomes whether or not the linear relation is valid in a practical range. Table I characterizes two typical chromatographic columns. One is the one used for the results of Sliva's report (11), a typical commercial column; the other is a micro column similar to that expected to be on a Mars Voyager (15). Note the worst condition appears to be a Peclet number equal to 140.

TABLE I
Characteristics of Two Typical
Chromatographic Columns

	Commercial column	Micro column
Length (cm)	61.0	2.5
Diameter (cm)	0.46	0.025
Particle diameter (cm)	0.0214	0.00265
Velocity of carrier gas (cm/sec)	15.23	16.92
Peclet number	2860.	140.

It appears that the above definition of skew is adequate for estimating the location of the maximum point, so it is possible to characterize the spreading of the curve about this. By use of σ_{max}, the deviation, it is possible to determine a certain characteristic distance on the time axis within which a certain percentage of the area will be contained. Figure 4 shows the area contained within 2 σ_{max} spread for Peclet numbers of 30 and 300. It is

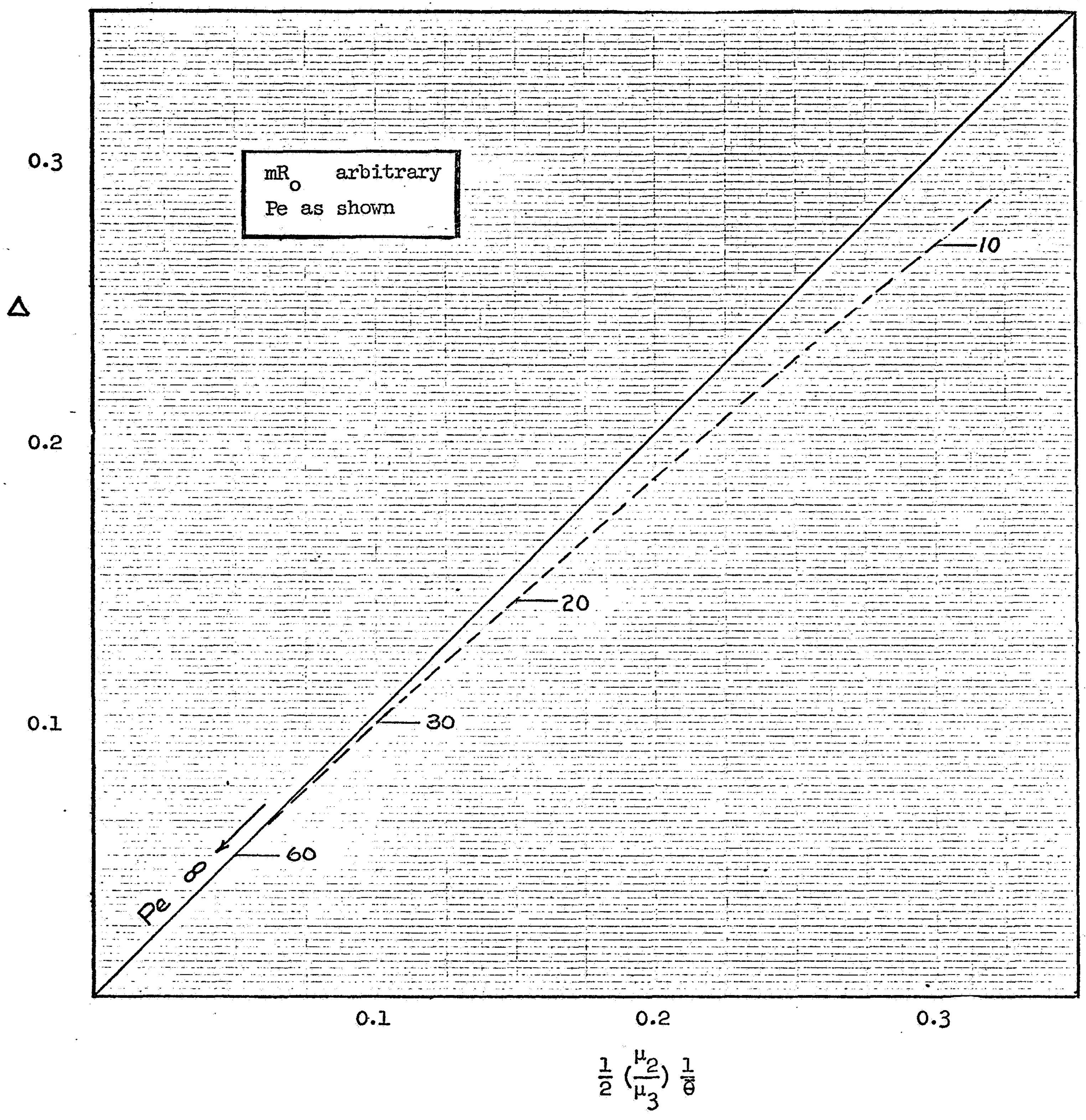

Figure 3.

Correlation of Chromatogram Peak

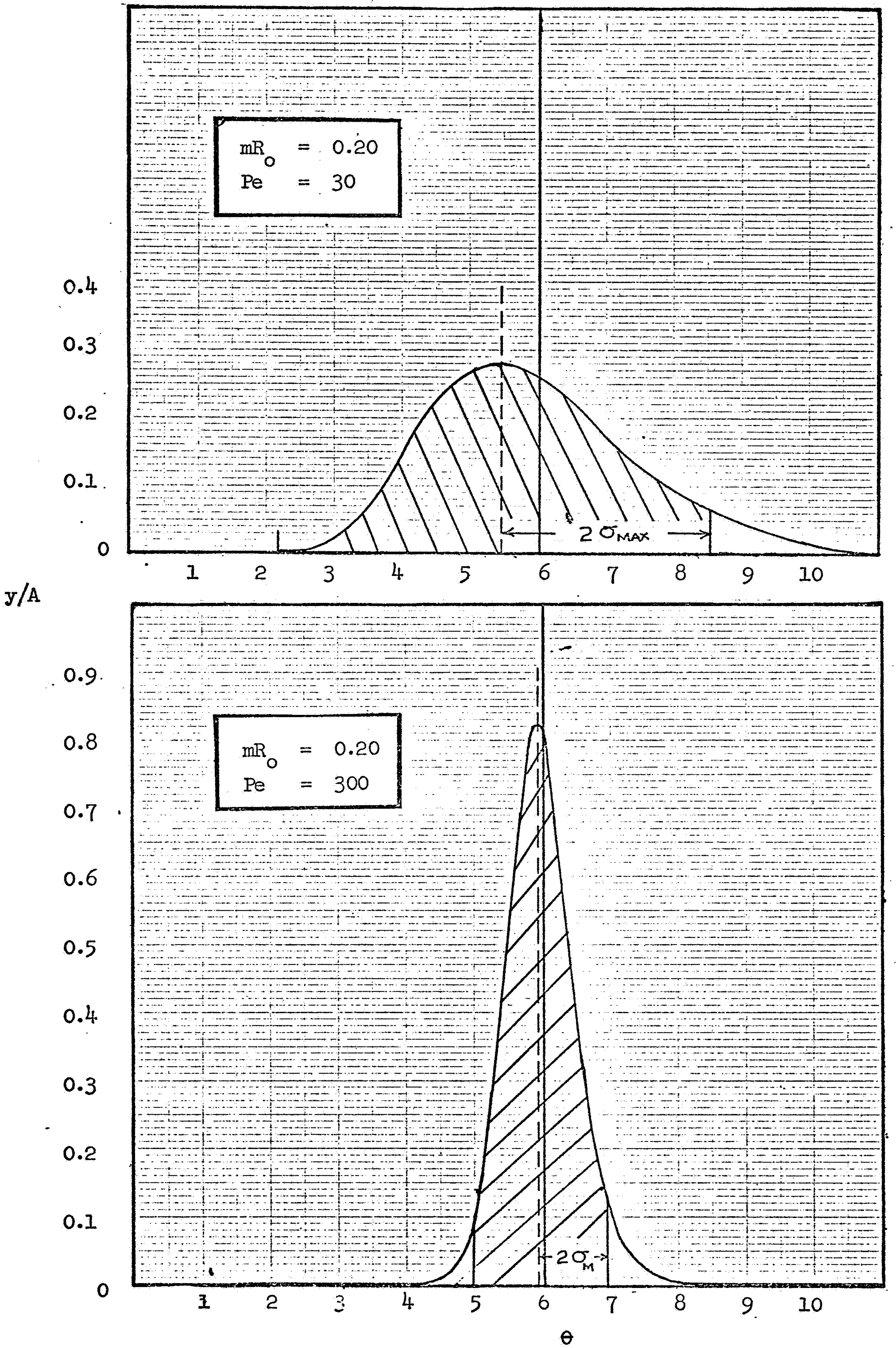

Figure 4.
Typical Spread of a Chromatogram
About the Mode

easily seen that a $2\sigma_{max}$ will yield a spread that will characterize almost the total area of the curve. Table II summarizes the exact fractions of area for various values of the column transport parameters. A great deal of the lack of a set pattern in the numbers is due to the fact that the numerical integration that was used to detremine the area was not the most accurate available. Notice that in the range under consideration at least 94% of the area is contained inside of the $2\sigma_{max}$ spread.

TABLE II

Summary of Area Correlation

Pe	mR_o	σ	σ_{max}	Area(σ_{max})	Area($2\sigma_{max}$)
30	.02	13.190	14.12	.724	.960
	.20	1.550	1.650	.738	.960
	.50	.775	.821	.736	.965
	4.0	.323	.346	.718	.980
60	.02	9.320	9.620	.728	.945
	.20	1.096	1.130	.730	.940
	.50	.548	.565	.735	.920
	4.0	.228	.236	.713	.930
100	.02	7.210	7.211		.950
	.20	.849	.850	.710	.943
	.50	.424	.425		.949
	4.0	.177	.177	.715	.960
300	.02	4.160	4.190		.942
	.20	.490	.493	.689	.944
	.50	.245	.247		.948
	4.0	.102	.103	.690	.960
1000	.02	2.280	2.280		.950
	.20	.268	.268	.685	.970
	.50	.134	.134		
	4.0	.0559	.0559	.684	

In summary, it appears that by a knowledge of the system transport parameters and only the transform solution of the system equations, it is possible to determine where the peak will occur and how wide the curve will be through the use of a moment analysis, at least for the equilibrium adsorption model. Because the model represents the characteristics of realistic chromatograms fairly well, the above moment analysis can be used to approximately characterize the chromatograph even though more complicated mathematical models may be required to represent the process. In other words, knowledge of the moments will yield the mean of the peak, the mode or maximum of the curve (Equation 11 or Figure 3), and the value of the standard deviation, σ_{max}. The time within $2\sigma_{max}$ of the maximum of the peak should encompass at least 90% of the chromatogram.

This information is useful for two purposes. It will allow preliminary evaluation of a column for the separation of known substances by providing estimates of the degree of overlapping of the component chromatograms. The moments are easily obtained and preliminary evaluation of column parameter changes can be made. The second application involves its use in the evaluation of more complicated mathematical models for the chromatograph.

It appears that a solution in the time domain may be obtained by use of numerical integration of equations developed by Lapidus and Amundson (8). The implimentation of this integration on the computer will greatly be aided by a knowledge of the moment analysis, for it will be possible to predict where the peak occurs and how much it is spread.

PART VI

CONCLUSIONS AND FUTURE WORK

This paper has presented an approach to chromatographic system analysis. It has been implemented on an equilibrium adsorption model. The philosophy of the approach is somewhat different than previous work done in the area because of its "design of column approach" rather than analysis of existing column.

It allows one to determine in the time domain the appearance of the center of gravity (mean), and the maximum of the peak (mode) merely through a knowledge of predictable system transport parameters, and the transform solution of the system equations. The method also yields a characteristic distance on the time scale, the variance (σ^2_{max}), which is a measure of the area, and therefore the amount of sample, under the chromatographic curve. A knowledge of these characteristics will allow a design analysis of the specific separation problems which may occur on a Mars voyage.

What has been done, however, has been a development of tools. It still remains to relate these tools to the non-equilibrium system model, whose transform solution and moments do exist (5,7,8,16). Testing will have to be done on actual chromatogrphic curves, as the model as of now does not have a time domain solution.

Perhaps a more direct use of the moments is in the development of a series solution for the non-equilibrium model. By the use of orthogonal polynomials, such as those of Hermite (7), or Laguerre, one may possibly generate a series solution whose coefficients are expressed only in terms of the moments of the system equations.

In a broader sense, perhaps this type of moment analysis can be extended to the analysis of other distributed processes which have complicated mathematical models and transfer functions. The development of distributed parameter model representations in control has been hampered by a lack of techniques for easily obtaining time domain solutions. Moment analysis may provide a useful tool for approximation purposes.

PART VII

NOMENCLATURE

A - dimensionless value characteristic of the total amount of material injected into the column.

$\mathcal{D}$ - diffusional constant, longitudinal.

D - diameter of column.

D_p - diameter of particles used in bed packing.

L - total length of column.

m - thermodynamic constant which characterizes the equilibrium between sample in gaseous phase and adsorbed phase.

N_{tog} - mass transfer controlling parameter, function of equilibrium between species and column length.

Pe - Peclet number, dimensionless diffusion constant, $\mathcal{D}/Lv$

R_o - ratio of moles of gas in bed to the moles of liquid in bed.

s - Laplace transform variable.

v - carrier gas velocity.

x_L - composition of sample in adsorbed phase.

$Y(s)$ - transform of y.

y - composition gaseous phase.

y^* - equilibrium gas composition.

z - dimensionless distance down the column.

α - skewness.

β - thermodynamic parameter, $1 + 1/mR_o$

Δ - defined variable,

δ - Dirac delta function.

θ - dimensionless time

$\bar{\theta}$ - mean of chromatographic curve, or time of appearance of center of gravity.

θ_{max} - mode, or time of appearance of the maximum point of chromatograhic curve.

μ_2 - second statistical moment about the mean.

μ_3 - third statistical moment about the mean.

σ - standard deviation of curve about the mean.

σ_{max} - standard deviation of the curve about the mode.

PART VIII

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PART IX

APPENDIX

SOME MATHEMATICAL CHARACTERISTICS OF THE EQUILIBRIUM ADSORPTION MODEL

i) Transfer function

$$Y(s,z) = A \exp\left((-z) \frac{Pe}{2} \left(\frac{4\beta}{Pe}\right)^{1/2} \left(\left(\frac{4\beta}{Pe}\right) + s\right)^{1/2}\right) \exp\left(\frac{Pe\ z}{2}\right)$$

ii) Mode Equation:

$$\theta_{max} = \frac{\beta}{\left(1 + \left(\frac{3}{Pe}\right)^2\right)^{1/2} + \frac{3}{Pe}}$$

iii) Moments about origin (obtained from derivatives of transfer function):

$$\int_0^\infty \theta^0 y d\theta = A$$

$$\int_0^\infty \theta^1 y d\theta = A\beta$$

$$\int_0^\infty \theta^2 y d\theta = A\beta^2 \left(1 + \frac{2}{Pe}\right)$$

$$\int_0^\infty \theta^3 y d\theta = A\beta^3 \left(1 + \frac{6}{Pe} + \frac{12}{Pe^2}\right)$$