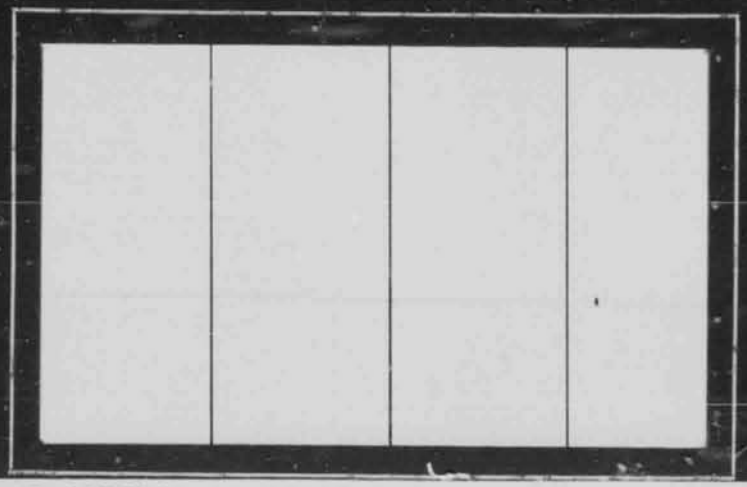

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August 5, 1975

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College Park, Maryland 20740

Dear Sirs:

Enclosed you will find five copies of RPI Technical Report MP-47 covering work being performed under NASA Grant NGL 33-018-091.

Sincerely,

Stephen Yerazunis
Associate Dean

Encls.

R.P.I. Technical Report MP-47

A NONLINEAR MODEL FOR GAS CHROMATOGRAPH SYSTEMS

Martin P. Feinberg

National Aeronautics and Space Administration

Grant NGL 33-018-091

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

Rensselaer Polytechnic Institute
Troy, New York

June 1975

ABSTRACT

Current research at Rensselaer is generating fundamental engineering design techniques and concepts for the optimization of a gas chromatograph-mass spectrometer chemical analysis system suitable for use on an unmanned, martian roving vehicle. Previously developed mathematical models of the gas chromatograph are inadequate for predicting peak heights and spreading for some experimental conditions and chemical systems. Consequently, a modification to the existing equilibrium adsorption model is required. The Langmuir isotherm replaces the linear isotherm. A closed-form analytical solution to the model is not available so the numerical technique of Crank-Nicolson is studied. Initial work considers the linear isotherm to determine the utility of the method. Modifications are made to the method to eliminate unnecessary calculations. These modifications result in an overall reduction of the computation time of about 42%.

After successful utilization of the Crank-Nicolson method to the linear isotherm, interest is shifted to the Langmuir isotherm which takes into account the composition-dependent effects on the thermodynamic parameter, mRo.

This model shows the sharp rise of the peak and the spreading of the tail generally observed in experimental

data. A secant method is incorporated into the model to determine the Langmuir constant by matching the simulated peak time with the experimental output peak time. This secant scheme coupled with the use of an mRo corresponding to a dilute sample, simulates the actual data quite well. A problem is encountered with oscillations of some of the simulations. This is due to the difficulties in using a cubic spline interpolation scheme capable for handling a limited number of input data points. These oscillations also produce problems when the secant method is used in determining the Langmuir constant. Convergence, if it occurs, is often slow. In fact, for a system which has a large number of input data points, no convergence was achieved.

An area of future research would be to find a better interpolation scheme to handle a large set of input data points. Further research could be incorporating a numerical scheme to vary mRo which in turn determines the Langmuir constant. In this way the simulation curve is fit to the actual data by varying two constants, mRo and K.

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PART 1

INTRODUCTION AND SUMMARY

One important phase of the unmanned martian roving vehicle is the search for and analysis of organic matter and living organisms on the Martian surface. The overall task is to provide design criteria and engineering techniques for use in optimizimg the design of a system. The plan is to use a gas chromatograph-mass spectrometer system, the gas chromatograph being used to separate the mixtures and the mass spectrometer to analyze the chemical compounds. There must be some flexibility in the system in order to perform a diversity of experiments, including analysis of the atmosphere and samples from incubation tests of soil and atmosphere. However, the most stringent design requirement for the system is that it be small and light enough to fit in the payload of the vehicle. This report describes the recent work done on developing a nonlinear simulation model to better represent the gas chromatograph.

Gas chromatography is a way of separating a mixture of different chemical species by utilizing the mechanism of adsorption-desorption. Owing to the different characteristics of various chemicals, each species will adsorb and desorb at different rates when exposed to a packed bed of granular particles with or without a liquid

substrate. The more strongly a species is adsorbed the longer its elution time will be. Because of the unique behavior of each chemical, a multicomponent sample may be injected into a chromatograph and elute as a series of pulses each containing one of the components.

Since gas chromatography is a complex process with many dynamic mechanisms continually taking place, mathematical models are being developed to predict system behavior for varying degrees of complexity. These predictions are then compared to actual data and if deviations from the experimental results occur then there is a flaw in the model. For an exact model which incorporates all observed phenomena, there would be no deviations; however, the complexity of such a model would make its numerical solution impractical even with present day computers.

One must be satisfied with models describing only the significant phenomena affecting the behavior of the column. If consistent deviations occur from the actual data then an important mechanism has been neglected. The model then must be amended.

Prior to this investigation, chromatographic models have been developed which have simulated successfully many systems well. However, in a few instances, model predictions have deviated consistently from the actual data. For dilute samples the model simulates the

system well but for some chemical species deviations occurred as the sample was increased. It is the objective of this report to develop and evaluate a practical nonlinear adsorption model to account for composition-dependent effects observed in previous research.

Two versions of the equilibrium adsorption model have been investigated. The first version, Equation IIIa of Figure 1, uses a linear isotherm. With the linear isotherm analytical techniques can be used to find the solution of the resulting second-order equation. The second version, Equation IIIb of Figure 1, incorporates the Langmuir isotherm into the model as a means of accounting for the observed composition-dependent effects. Analytical techniques are not available for solving the resulting nonlinear equation so numerical methods are being used. Because of instabilities with an orthogonal collocation procedure used previously (Lavoie, 1974), the simple, finite difference scheme of Crank-Nicolson is being used. This method was first applied to the linear version and the results were compared with the available analytical results. Considerable effort was made in coding to eliminate calculations involving multiplication by zero in order to reduce computation time. This additional coding reduced the computing time by about 35%. Good comparison between the numerical and analytical results gave confidence in the method.

I. Material Balance for the Equilibrium Adsorption Model

$$\frac{\partial y}{\partial \theta} + \left[\frac{1}{R_o}\right]\frac{\partial \phi}{\partial \theta} = \left[\frac{1}{Pe}\right]\frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z}$$

- $\frac{\partial y}{\partial z}$ — bulk flow
- $\left[\frac{1}{Pe}\right]\frac{\partial^2 y}{\partial z^2}$ — axial dispersion
- $\left[\frac{1}{R_o}\right]\frac{\partial \phi}{\partial \theta}$ — adsorbent accumulation
- $\frac{\partial y}{\partial \theta}$ — fluid-phase accumulation

II. Adsorption Isotherm

a. Linear: $\phi = Ky$

b. Langmuir: $\phi = \frac{Ky}{1+Ky}$

III. System Equation

a. Linear: $\frac{\partial y}{\partial \theta}\left[1 + \frac{1}{mR_o}\right] = \left[\frac{1}{Pe}\right]\frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z}$

b. Langmuir: $\frac{\partial y}{\partial \theta}\left[1 + \frac{1/mR_o}{(1 + Ky)^2}\right] = \left[\frac{1}{Pe}\right]\frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z}$

Figure 1 Equations for the Equilibrium Adsorption Model

In applying the method to the nonlinear version, a modification was required because of the nonlinear term. A predictor-corrector technique was used. Initial work with this model used the value of the thermodynamic parameter, mRo, obtained by a curve fitting technique between the simulated output and the actual output. The peak times of the simulation output was compared with the actual peak time and there was fairly close agreement. However, when the Langmuir constant, K, was increased the peak times occurred earlier. The peaks for the simulated output were much larger than the actual peaks (about 90% greater). Qualitatively, as the Langmuir constant, K, was increased the peaks became smaller approaching the actual value. More importantly, the shape of the simulated output appeared more like the actual shape for higher values of K. The curves rose more sharply and exhibited more tailing as K was increased.

Something had to be done to alleviate the problem of the early occurrence of the peaks. One possibility substantiated by the fact that mRo was composition-dependent was to correct for the fact that the sample is not dilute. Extrapolate the value of mRo to a very dilute sample and use this for the larger sample. In this way the Langmuir constant can be varied until the peak times are closely matched. After these peak times are matched, a comparison of their peak heights can be made. A sim-

ulation peak height greater than the actual peak height suggests that a smaller mRo should be attempted next. A simulation peak height smaller than the actual peak height would indicate a larger value of mRo be used. This procedure is in fact a two constant curve fitting technique to obtain a simulation curve similar to the experimental data.

When this procedure was incorporated into the program close agreement resulted between the simulated chromatograph and the actual chromatograph. Especially for a nondilute sample, the Langmuir isotherm with this two constant curve fitting simulates the actual data quite well.

This procedure of matching the peak times of the simulation with the actual data was then applied to the system of n-heptane on the Chromosorb-102 at 175°C. This system's input had a large set of data points so that oscillations in the peak occurred. Due to these oscillations the program had difficulties converging.

PART 2

BACKGROUND

One area of the overall gas chromatograph systems investigation has been the mathematical modeling of the chromatograph system. Many previous investigators have contributed to the development of mathematical models (Keba and Woodrow,1972; Meisch,1973; Sliva,1968; Taylor, 1970; Voytus, 1969). A course has been pursued wherein successively more complex models have been considered. These models have all yielded analytical expressions from which a simulation chromatograph could be computed directly. Comparison of predicted system behavior with actual system data has directed modeling efforts to consider more adequate and hence more complicated models.

A system of three coupled partial differential equations was derived earlier to model the gas chromatograph (Woodrow, 1974). Excessive computation time due to the complexity of the system of equations indicated a simplification of the model was required. Voytus(1969) derived a simplification of the model which considered axial diffusion, convection, and equilibrium adsorption/desorption using the linear isotherm. Assumptions for the model, designated the equilibrium adsorption model, included negligible mass transport effects between the carrier gas and the adsorbent phase and no intra-particle diffusion effects. In its mathematical form, the model is represented by the following second-order, linear partial differential equation

which was derived from the mass balance for the injected species in the fluid and solid phases of the column:

$$(1+1/mRo)\partial y/\partial\theta = (1/Pe)\partial^2 y/\partial z^2 - \partial y/\partial z$$

Boundary conditions:

$y(0,\theta)$ = input pulse

$\lim_{z\to\infty} y(z,\theta)$ = finite

The final solution of this equation is the following convolution integral:

$$y(z,\theta) = \int_0^\theta y(0,t-\tau)\cdot y_\ell(\tau)\cdot d\tau$$

where $y(0,\theta)$ = the input pulse

$y_\ell(\tau)$ = the unit impulse response at the end of the column

$$= \frac{1}{2}\sqrt{\frac{\beta Pe}{\pi\tau^3}}\exp\left\{\frac{-Pe}{4\beta\tau}(\tau-\beta)^2\right\}$$

and $\beta = (1+1/mRo)$

The Peclet number is a measure of the dispersion of the sample component due to the axial diffusion in the column. Smaller values of Pe indicate greater dispersion. The thermodynamic parameter, mRo, determines the elution time of the injected component. Larger values of mRo indicate that the species are not strongly adsorbed and hence they will elute at an earlier time. A study of the nonequilibrium adsorption model has shown that mass transport between the carrier gas and the adsorbent is too

fast to have any limiting effects on systems studied thus far (Keba and Woodrow, 1972).

For many systems the equilibrium adsorption model with the linear isotherm predicted quite well the results obtained experimentally. In general, these cases were dilute sample sizes and particular chemical species. For other chemical species, the model predictions deviated consistently from actual data as the sample size was increased. Figure 2 compares the actual output data to the model simulation for n-heptane on Chromosorb-102 at 175°C and there is little resemblance between the two. The actual data is very spread with much tailing, while the modeled response is a relatively sharp peak with little tailing.

Meisch (1973) found that the parameter, mRo, was a significant function of composition. This was further substantiated by Lavoie (1974) with experiments with n-heptane and a variety of sample sizes. Figure 3 shows results of those experiments. The parameter, mRo, decreased linearly with a decrease in sample size.

The equilibrium adsorption model with the linear isotherm obviously does not represent all of the physical behavior that is occurring in the column. There are many possibilities to consider. The variation of mRo with composition supports the idea that a nonlinear isotherm

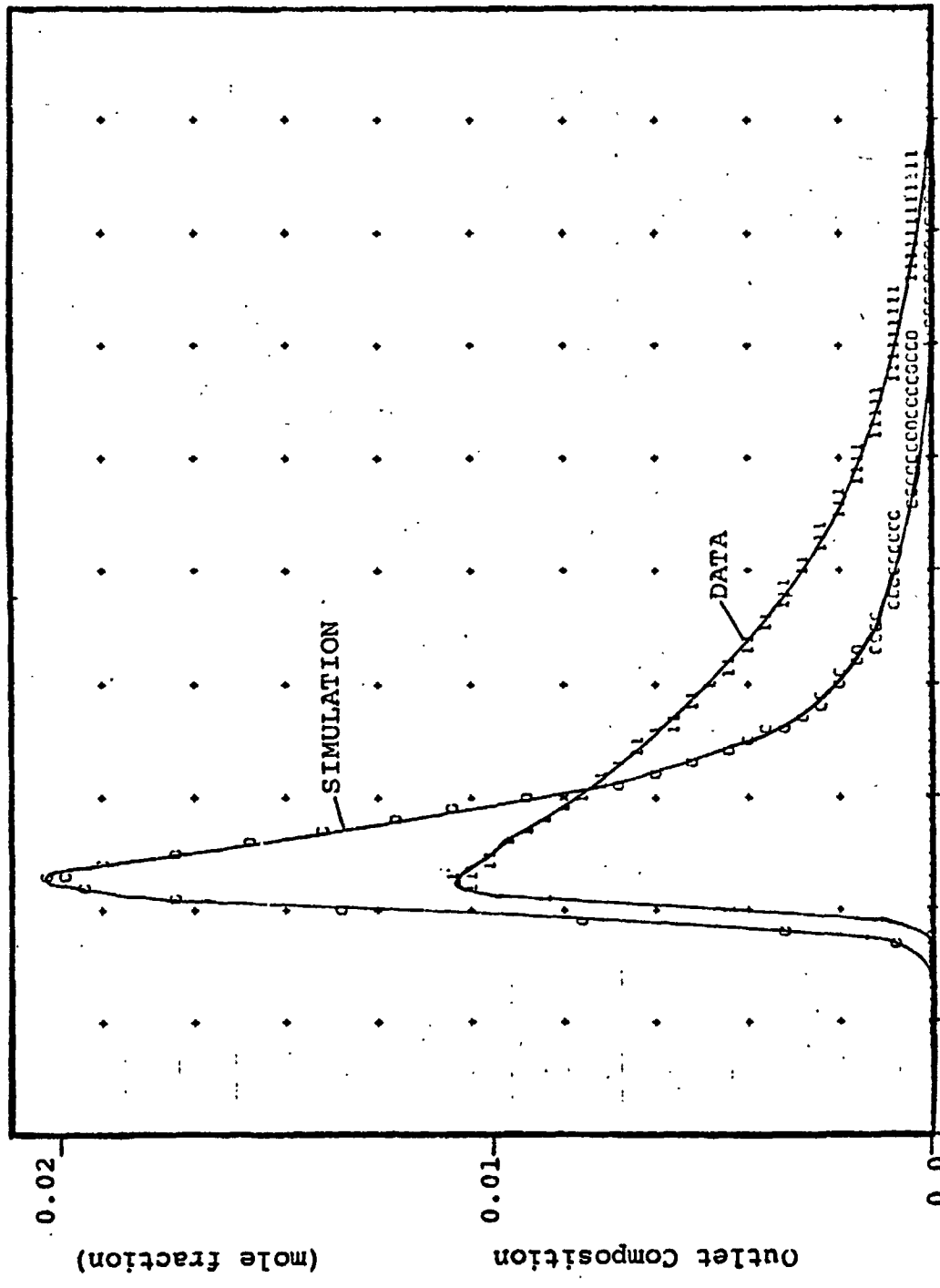

Figure 2 Comparison of Actual Chromatograph and Equilibrium Adsorption Model (Linear Isotherm) for n-Heptane on C-102 at 175°C

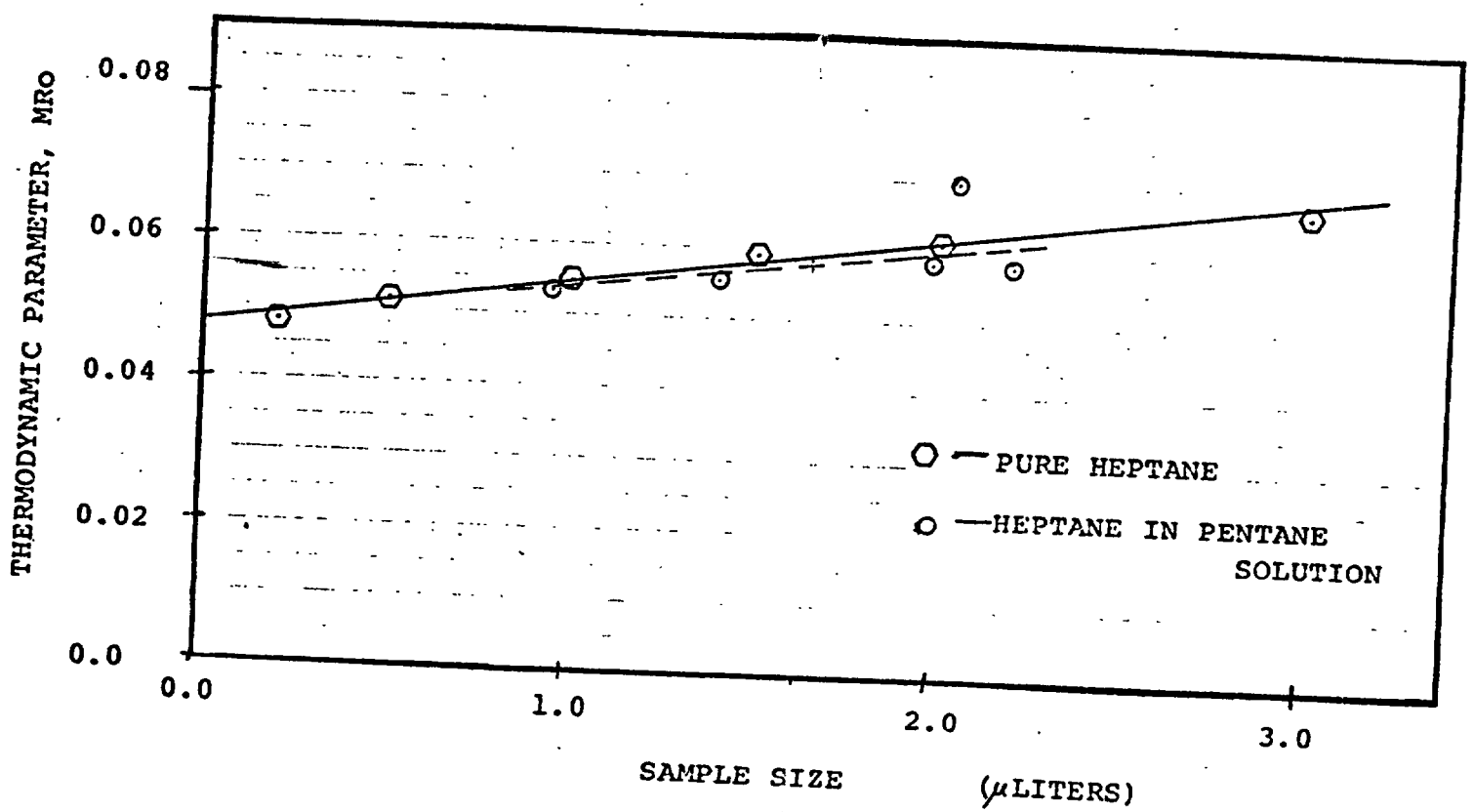

Figure 3 Effect of Sample Size on MRo for n-Heptane on Chromosorb-102

should be used in the model. Preliminary work (Lavoie, 1974) has already begun using orthogonal collocation to solve the resulting nonlinear equation but due to the instabilities in the results, a new different numerical scheme is being proposed, Crank-Nicolson. This idea is investigated in this paper.

PART 3

RESULTS AND DISCUSSION

A. Formulation of the Crank-Nicolson Algorithm to the Equilibrium Adsorption Model Using the Linear Isotherm

One mathematical model that has already been developed is the equilibrium adsorption model* using the linear isotherm to describe the adsorption kinetics. This model considers interparticle axial diffusion, convection and equilibrium adsorption/desorption. Diffusion of the chemicals in the direction of the carrier gas flow in the interparticle region is represented by the dimensionless parameter, Pe, which is determined by the system fluid mechanics. Adsorption-desorption on the particle is represented by mRo, a thermodynamic parameter peculiar to each species. This parameter contains an equilibrium constant, m, and the quantity, Ro. Ro is the ratio of the moles of fluid within the total bed to the moles of adsorptive sites within the bed.

With the above concepts in mind, the following dimensionless equation results:

$$\left[\frac{1}{Pe}\right]\frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} = \left[1 + \frac{1}{mRo}\right]\frac{\partial y}{\partial \theta} \qquad (1)$$

With boundary conditions:

$$y(0,\theta) = \text{input pulse} \qquad (2)$$

* For the details of the derivation see Appendix A

$$\lim_{z \to \infty} y(z,\theta) = \text{finite} \qquad (3)$$

and initial condition:

$$y(z,0) = 0 \qquad (4)$$

This initial condition states that initially the column has only inert carrier gas flowing through it.

An alternate terminal boundary condition that could be used instead of the finite composition at an infinite distance down the column [equation (3)] is the following proposed by Woodrow (1974):

$$\frac{\partial y(1,\theta)}{\partial z} = 0 \quad \text{for } \theta > 0 \qquad (3a)$$

Use of the infinite boundary condition [equation (3)] in analytical work yields a great deal of mathematical simplification and is consistent with the theory which has been developed. However, when numerical techniques must be applied to solve equation (1), the terminal boundary condition given by equation (3) must be replaced by a terminal boundary condition which is both computationally expedient and physically meaningful. The boundary condition proposed is given by equation (3a).

To obtain numerical solutions to partial differential equations, continuous variables are replaced by discrete variables. The relations between these discrete variables in the method of finite differences are finite difference equations which are based on Taylor series

representations of the dependent variable. The domain of the independent variable that is discretized form a system of grid points. Figure 4 shows a grid representation for the transient analysis of a system. The spatial dimension, z, is shown as being bounded and normalized and the time domain, θ, is shown with no particular bound. The grid is fixed; i.e., spatial discretizations and time discretizations are uniform for each domain. The value of z, the continuous space dimension is given by:

$$z = i \cdot (\Delta z)$$

where i refers to a particular spatial grid point and Δz is the spacing between grid points. Similarly, the value of θ, the continuous time dimension is given by:

$$\theta = n \cdot (\Delta \theta)$$

where n refers to a particular time grid point and $\Delta\theta$ is the interval between grid points.

For the parabolic system of the second order chromatograph system model, equation (1), the two-level implicit method known as the Crank-Nicolson method of solution is probably most popular and is well documented (Lapidus, 1962; von Rosenberg, 1969). The Crank-Nicolson method replaces the partial derivatives which are evaluated at the position (space i, time n+½) with their finite difference counterparts. These approximations are

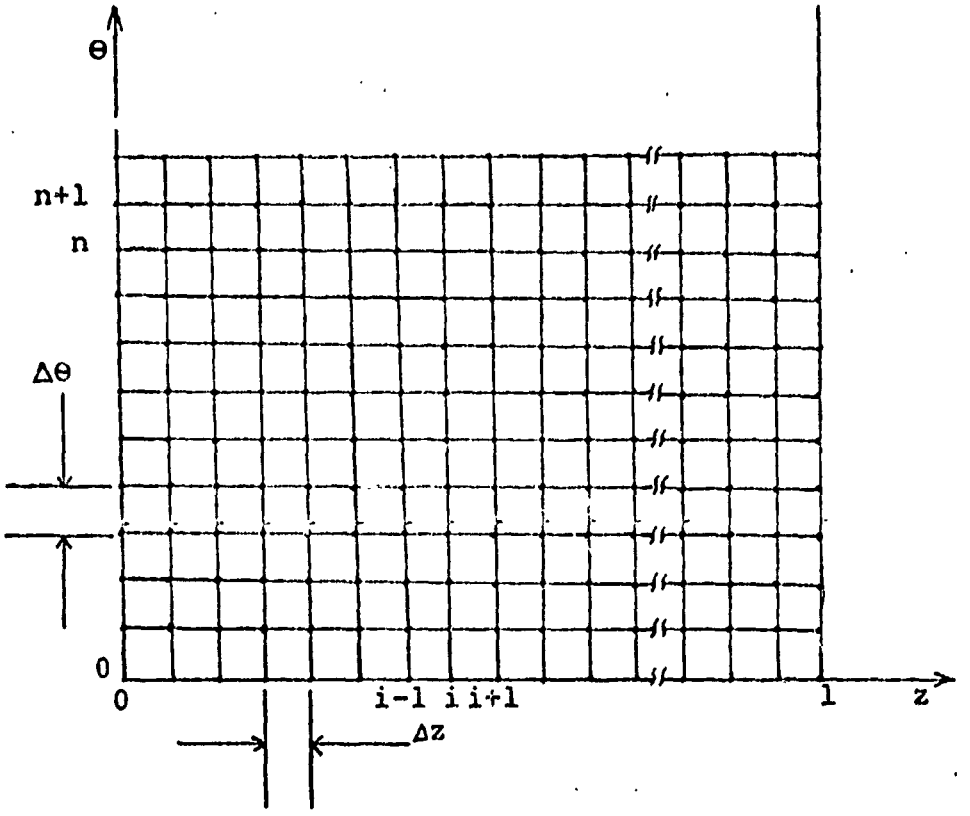

Figure 4 Grid Representation for the Finite Difference Scheme (Crank-Nicolson Method)

an arithmetic average of the finite difference analogs at the points z_i, θ_n and z_i, θ_{n+1}. The approximations at each of these points can be viewed also as as arithmetic average so that the resulting analog takes on the form of a double average of the compositions surrounding the point, $y_{i,n+\frac{1}{2}}$. In this method, the following approximations are made for the first and second spatial derivatives and the first time derivative:

$$\left(\frac{\partial y}{\partial z}\right)_{i,n+\frac{1}{2}} \approx \frac{1}{2}\left\{\frac{y_{i+1,n} - y_{i-1,n}}{2(\Delta z)} + \frac{y_{i+1,n+1} - y_{i-1,n+1}}{2(\Delta z)}\right\} \quad (5)$$

$$\left(\frac{\partial^2 y}{\partial z^2}\right)_{i,n+\frac{1}{2}} \approx \frac{1}{2}\left\{\frac{y_{i+1,n} - 2y_{i,n} + y_{i-1,n}}{(\Delta z)^2} + \frac{y_{i+1,n+1} - 2y_{i,n+1} + y_{i-1,n+1}}{(\Delta z)^2}\right\} \quad (6)$$

$$\left(\frac{\partial y}{\partial \theta}\right)_{i,n+\frac{1}{2}} \approx \left\{\frac{y_{i,n+1} - y_{i,n}}{(\Delta\theta)}\right\} \quad (7)$$

These finite differences are substituted into the partial differential equation, giving a system of algebraic equations having a tridiagonal system matrix.* This system of equations is solved using the Thomas algorithm (von Rosenberg, 1969).

Preliminary studies were done with this procedure to determine the appropriate choice of the incremental variables, $\Delta\theta$ and Δz. Von Rosenberg (1969) has determined that the Crank-Nicolson method becomes unstable (oscillatory

* For details of derivation see Appendix B

about the true curve) if the coefficient of the second space derivative is small compared to the coefficient of the first space derivative. There will be no oscillations when

$$\frac{\text{coeff. of first space der.}}{\text{coeff. of second space der.}} \times \frac{\Delta z}{2} < 1$$

For the equilibrium adsorption model, equation (1) reduces to

$$\frac{Pe \cdot \Delta z}{2} < 1$$

For practical chromatography, the Peclet numbers are in the order of 10,000. Initial computer simulations for Δz less than the values specified by von Rosenberg exhibited oscillations. For a $z = 0.001$ no oscillations were found. All of the remaining simulations were obtained with this value of the incremental space dimension.

For the Crank-Nicolson algorithm there is no stability criterion for the ratio of the incremental variables. Having determined the value of Δz needed, theoretically any time increment could be used. The effect of time step size was investigated. Table 1 shows the computation time needed for each value of $\Delta\theta$. For small values of $\Delta\theta$ the computation time is excessive. (Note the computation times in the table are for equal partial simulation runs.) For $\Delta\theta$ smaller than 0.04 the decrease in computation

TABLE 1

COMPUTATION TIME FOR VARIOUS
DIMENSIONLESS TIME INCREMENTS

Dimensionless Time Increment, Θ	Computation Time for Equivalent Partial Run (sec.)
0.0004	1840
0.004	334
0.008	204
0.01	171
0.04	87
0.05	87

time was almost negligible while the magnitude of the differences from the values calculated for smaller $\Delta\theta$ increased. As a result of this study the value of 0.04 was used for the incremental time dimension.

B. Modification of the Crank-Nicolson Method

When the decision was made on the incremental variables, modifications were necessary to further reduce the computation time. The modifications were made to the Thomas algorithm (von Rosenberg, 1969). This algorithm is used to solve a tridiagonal system of algebraic equations of the form:

$$a_i y_{i-1} + b_i y_i + c_i y_{i+1} = d_i \qquad (8)$$

for $1 \leq i \leq R$

with $a_1 = c_R = 0$

The algorithm is as follows:

First, compute

$$\beta_i = b_i - \frac{a_i c_{i-1}}{\beta_{i-1}} \qquad \text{with } \beta_1 = b_1 \qquad (9)$$

and

$$\gamma_i = \frac{d_i - a_i \gamma_{i-1}}{\beta_i} \qquad \text{with } \gamma_1 = \frac{d_1}{b_1} \qquad (10)$$

The values of the compositions (y) are then computed from

$$y_R = \gamma_R \text{ and } y_i = \gamma_i - \frac{c_i y_{i+1}}{\beta_i} \qquad (11)$$

For early times in the simulation, the pulse has not had an opportunity to spread out throughout the column. Since the 'd' vector [equation (8)] is a linear combination of the compositions at the spatial points (i-1, i, and i+1) for the previous time step (n), many of its elements are zero. The trend of thought is why do all the multiplications by zero when this will just result in zero compositions for the next time step (n+1). Because values of 'd' are either very small or zero, they may produce very small values for an intermediate calculation vector, 'δ' of equation (10). When the ith element of the 'd' vector coupled with the ith element of the 'δ' vector are both small, then the corresponding ith element of the composition vector is set equal to zero.

A numerical scheme was developed to determine when to eliminate unnecessary calculations. Between the indices, I1 and I2, are the positions at any one time step in the column where the pulse is located. The compositions are set equal to zero to the left of I1 and to the right of I2. This feature also eliminates many of the underflows previously encountered.

With this modification the computation time was reduced by about 35% for an entire simulation. The time is saved during the early part of the simulation before the pulse has propagated far down the column where there is no fluid in the late sections of the column.

Time is also conserved at the end of the simulation when there is no fluid in the beginning parts of the column.

A program has been written to solve the equilibrium adsorption model with the linear isotherm using the Crank-Nicolson finite difference scheme. Figure 5 shows the organization of the program. After the coding of the equilibrium adsorption model by the Crank-Nicolson method was completed, results obtained from the method were compared with the analytical solution. Figures 6, 7, and 8 show the actual data, the analytical solution, and the simulation by the Crank-Nicolson method. There is very little difference between the Crank-Nicolson simulation and the analytical solution and these two methods are compared for various points in Table 2. Even-though these two curves are in close agreement with themselves they do not model actual experimental data so the incorporation of the Langmuir isotherm into the equilibrium adsorption model was investigated.

C. Incorporation of the Langmuir Isotherm into the Equilibrium Adsorption Model

A nonlinear isotherm of the Langmuir type may possibly explain the deviations mentioned previously. The Langmuir isotherm gives the following relation between the adsorbed phase and mobile gas phase mole fractions (x and y respectively):

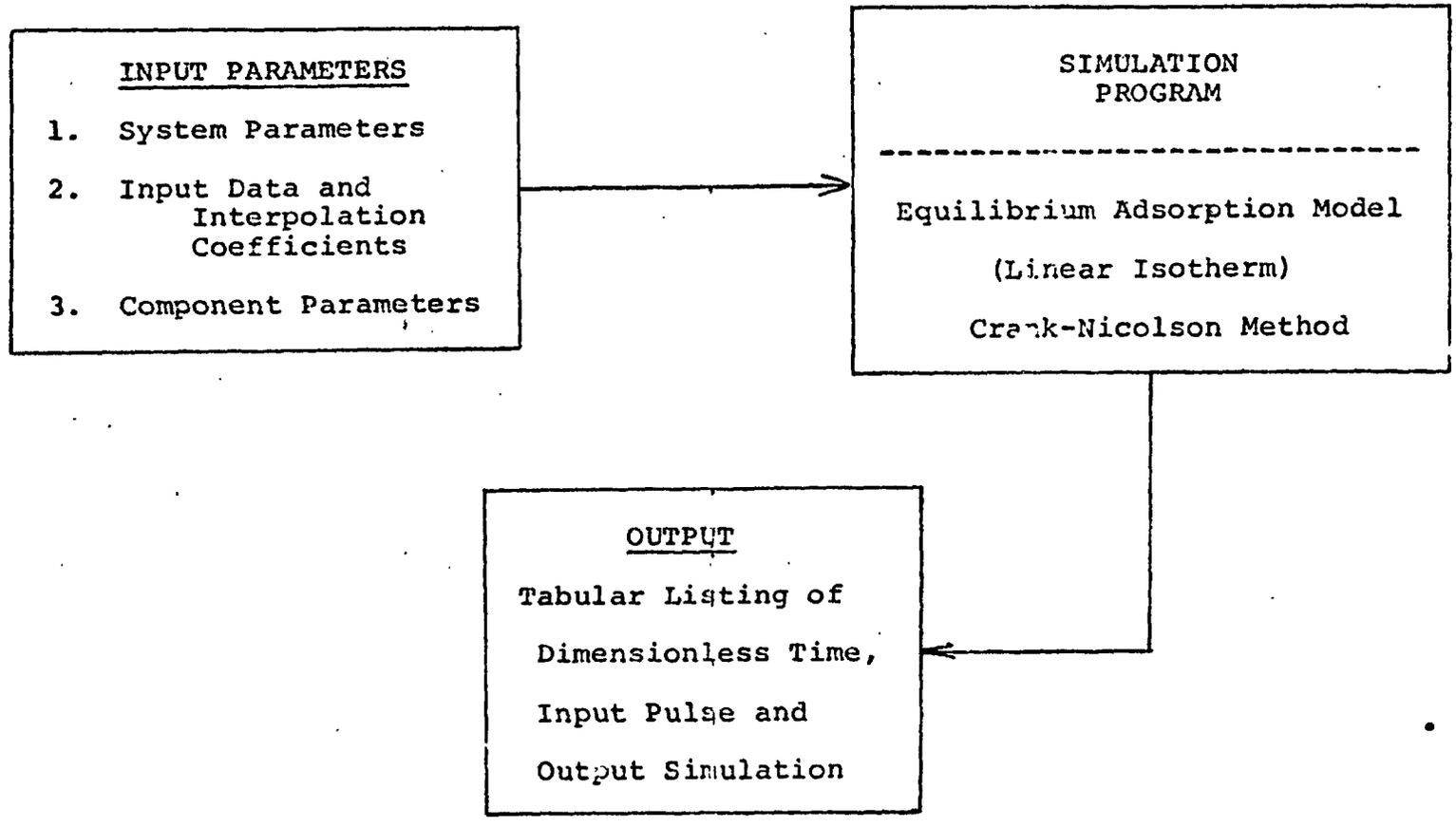

Figure 5 Crank-Nicolson Method Program for the Equilibrium Adsorption Model (Linear Isotherm)

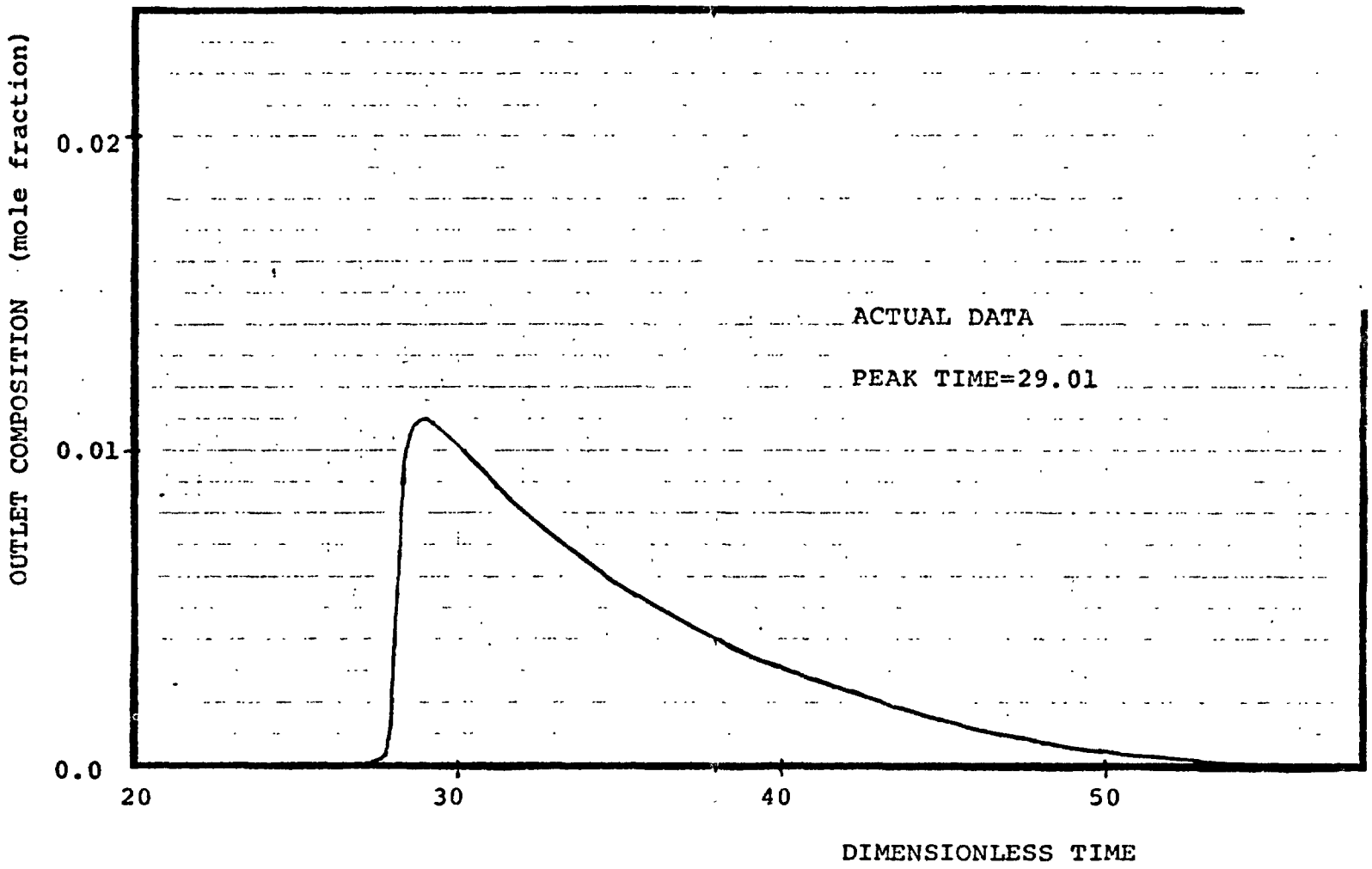

Figure 6 The Actual Chromatograph Data for n-Heptane on Chromosorb-102 at 175°C

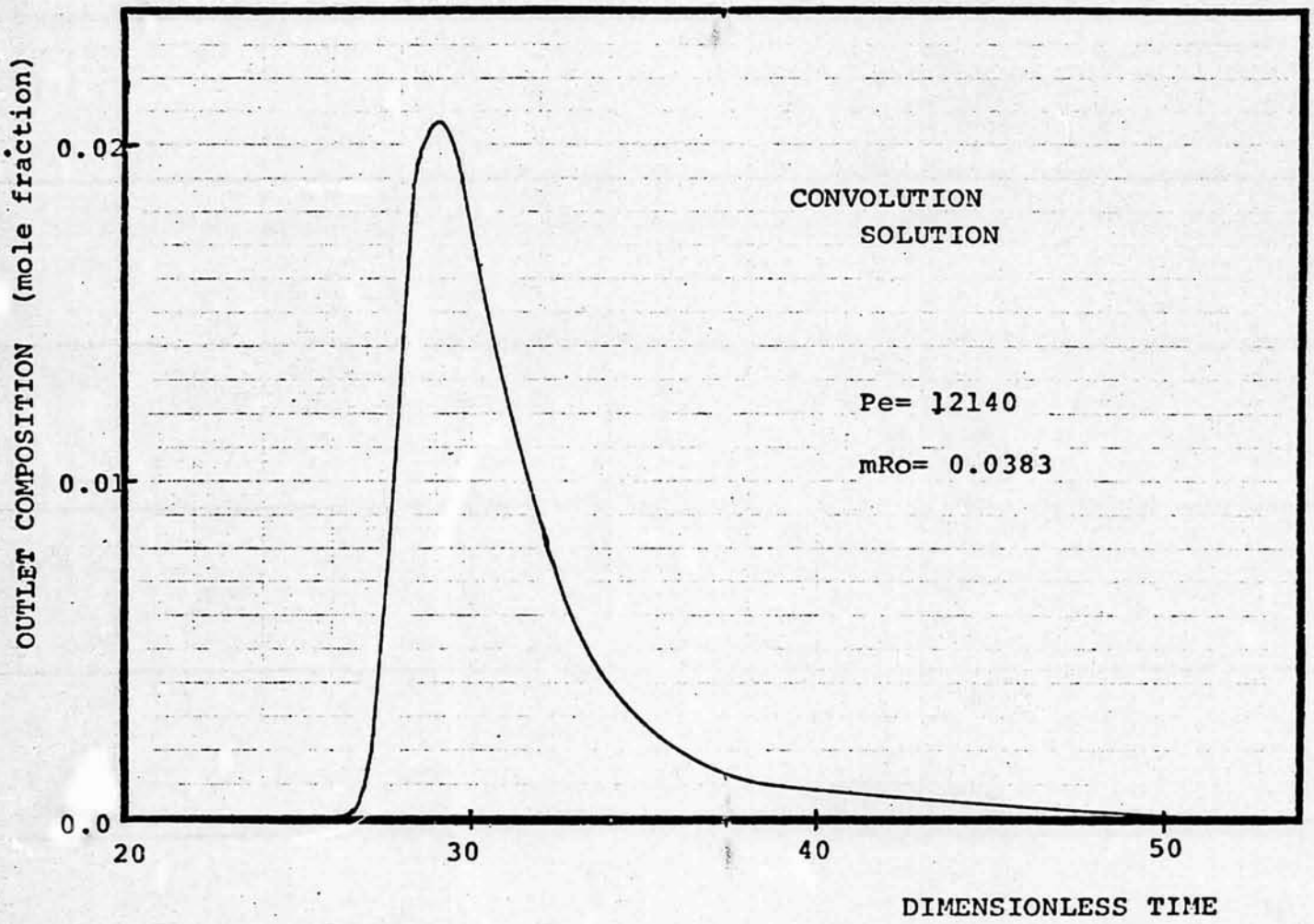

Figure 7 Analytical Chromatograph for n-Heptane on Chromosorb-102 at 175°C

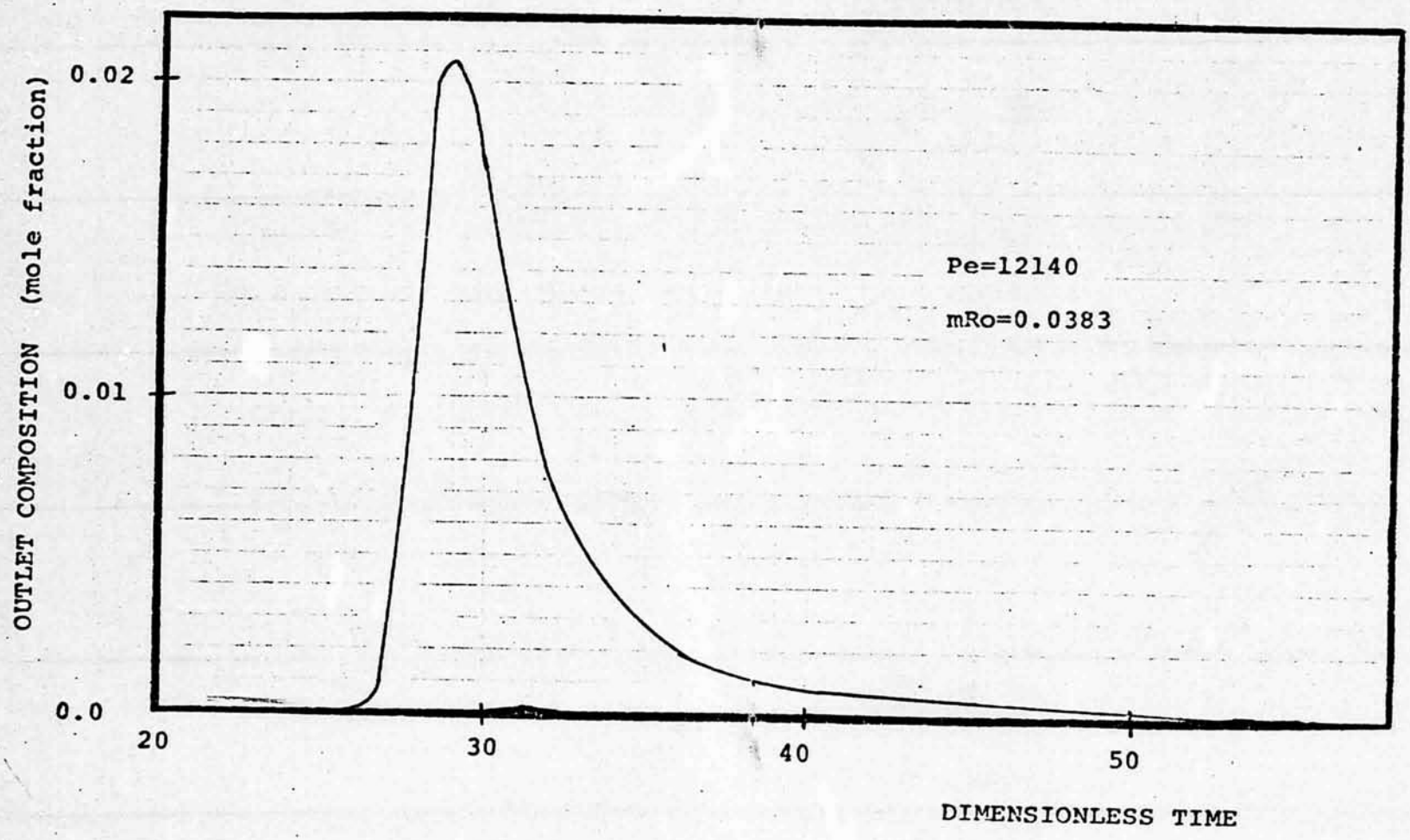

Figure 8 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 175°C (Crank-Nicolson Method)

TABLE 2

COMPARISON OF
THE CRANK-NICOLSON METHOD (LINEAR ISOTHERM)
WITH
THE CONVOLUTION (ANALYTICAL) SOLUTION

Dimensionless Time	Crank-Nicolson	Convolved (Analytic)	Relative Error
28.3058	0.018971	0.0180004	5.38%
29.0047	0.020664	0.020698	0.16%
30.1696	0.01646	0.016995	3.15%
33.8971	0.0042437	0.0042442	0.012%
38.5565	0.0010353	0.0010643	2.73%

$$x = \frac{Ky}{1 + Ky}$$

This equation is compared to the linear isotherm in Figure 9. For small concentrations the Langmuir isotherm has nearly linear behavior. For large concentrations, the amount that can be adsorbed becomes proportionately less and finally approaches a maximum value. At high concentrations the adsorbent sites become saturated so that an increase in the gas phase concentration has little effect on the adsorbent phase concentration. Larger values of K make the isotherm nonlinear at lower mobile gas phase concentrations.

The nonlinearity would have the following effect on the behavior of the column. Large samples entering the column would be adsorbed proportionately less in zones of high concentration than in low concentration. As a result large samples would begin to elute sooner than small samples and would be more spread. The quantitative effects on elution time, which is related to mRo and spreading can be found only by solving the model.

This model takes on the form*

$$\left[1 + \frac{1}{mRo(1+Ky)^2}\right]\frac{\partial y}{\partial \theta} = \left[\frac{1}{Pe}\right]\frac{\partial^2 y}{\partial z^2} - \frac{\partial y}{\partial z} \qquad (12)$$

* See Appendix A for derivation

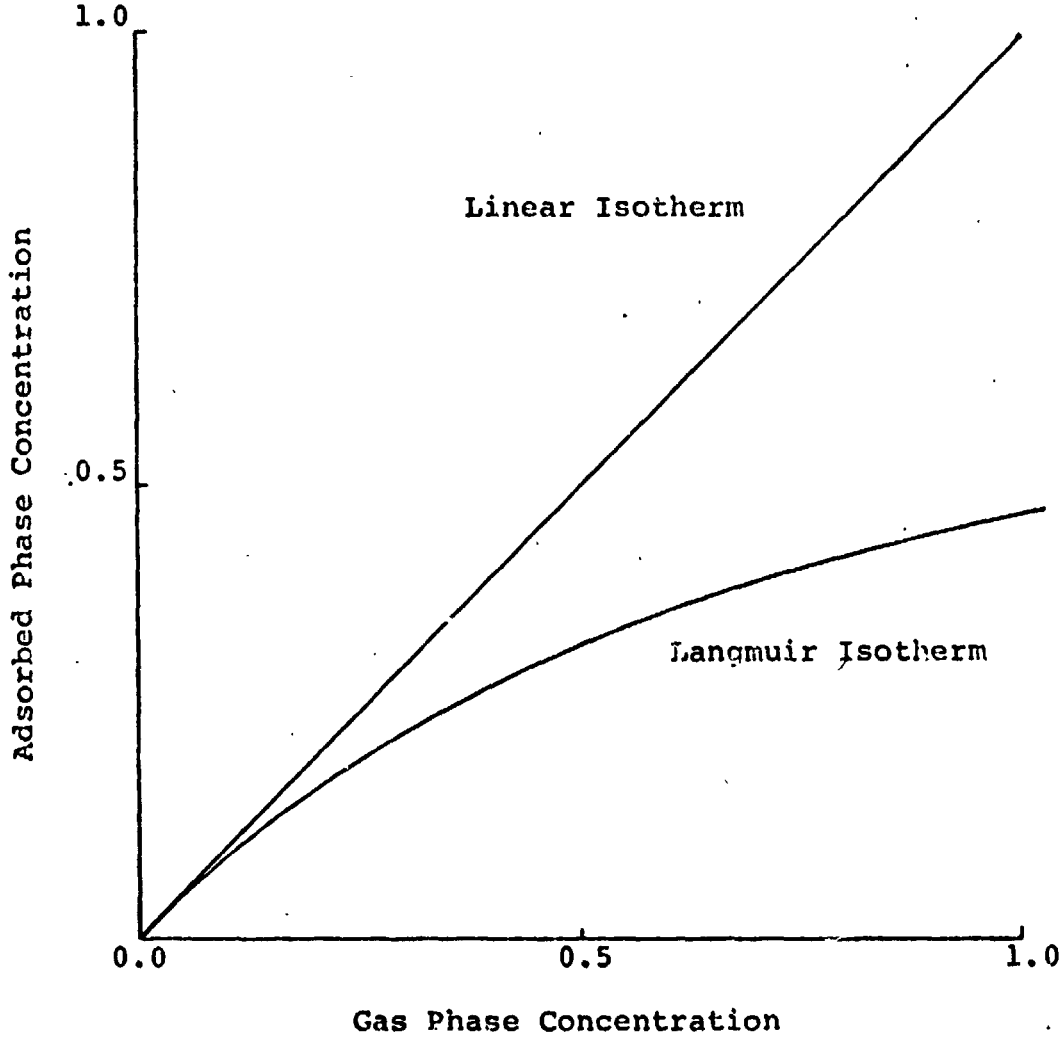

Figure 9 Comparison of the Linear and Langmuir Isotherms

Comparing this equation to the equilibrium adsorption model [equation (1)], the only difference is the term, $(1+Ky)^2$ multiplying mRo. In effect, the parameter, mRo, becomes a variable dependent on composition, y. This dependence becomes stronger for increasing K. The average value of $mRo(1+Ky)^2$ increases with sample concentration. This is the observed behavior in experimental data.

The equation must be solved numerically because of the nonlinear coefficient. Based on prior research (Lavoie, 1974), the Crank-Nicolson method will be used instead of orthogonal collocation since orthogonal collocation produced instabilities.

In applying the method to the nonlinear equation, a modification is required because of the nonlinear term. A predictor-corrector technique is used. Initially the partial derivatives are replaced by the finite differences as in the linear version. The composition-dependent coefficient of the time derivative is treated by a method developed by Douglas (1958). The composition in the nonlinear term has to be evaluated at the position (space i, time n+½). This value, $y_{i,n+½}$, is approximated by its value at the previous time step, $y_{i,n}$, and a correction factor, $(\Delta\theta/2)(\partial y/\partial\theta)_{i,n}$ where θ is time. This derivative is approximated by its value from the differential equation in which the derivatives and compositions are evaluated at the previous time step. The mathematical equations

for this approximation of $y_{i,n+½}$ are:

$$y_{i,n+½} \simeq y_{i,n} + \frac{\Delta\theta}{2}\left(\frac{\partial y}{\partial \theta}\right)_{i,n} \tag{13}$$

where

$$\left(\frac{\partial y}{\partial \theta}\right)_{i,n} = \frac{1}{1+\frac{1}{mRo(1+Ky_{i,n})^2}}\left[\frac{1}{Pe}\left(\frac{\partial^2 y}{\partial z^2}\right)_{i,n} - \left(\frac{\partial y}{\partial \theta}\right)_{i,n}\right] \tag{14}$$

This approximation for the nonlinear term is substituted into the differential equation and the resulting system of algebraic equations is solved by the Thomas algorithm. The modification incorporated into the Thomas algorithm for the linear isotherm is again used shorter computation times resulting. After the first determination of the compositions in the column, another iteration has to be done. During these subsequent iterations a new estimate is made for the nonlinear term. This is done by averaging the compositions.

$$y_{i,n+½} \simeq \frac{y_{i,n} + y_{i,n+1}}{2}$$

The program iterates at the same time step until the compositions in the column have converged. The details of the formulation of the Langmuir isotherm appears in Appendix B.

On preliminary studies done with this program, it was noticed that the indices, I1 and I2*, did not

* See program listing, Appendix C

change during the iterations. It was decided to perform calculations only from I1 to I2 for the subsequent iterations, hence eliminating unnecessary computation time without losing accuracy. This simple modification resulted in approximately a further 10% savings of computation time. Thus, with both modifications, an overall reduction of about 42% of the computation time is achieved.

For the n-heptane system on the Chromosorb-102 at 175°C (Meisch, 1973), three different values of the Langmuir constant, K (0, 5, and 10) were studied. These simulations are depicted in Figures 10, 11, and 12 respectively. For this system, n-heptane on the Chromosorb-102 at 175°C, the input pulse was not as narrow as one would like. Because of this wide input, many data points (over two hundred) are needed to describe it. With the discreteness of the input data points, an interpolation routine is needed to obtain input compositions at intermediate values. The cubic spline interpolation routine is used. With so many data points, the determination of the cubic spline coefficients becomes a problem. The subroutine, ICSICE (IMSL, 1973) can only handle a limited number of data points. When this number is exceeded, underflows are the result. The subroutine, ICSICE, will determine the cubic spline coefficients but when they are used oscillations appear in the interpolations. These oscillations then appear in the output of the simulation

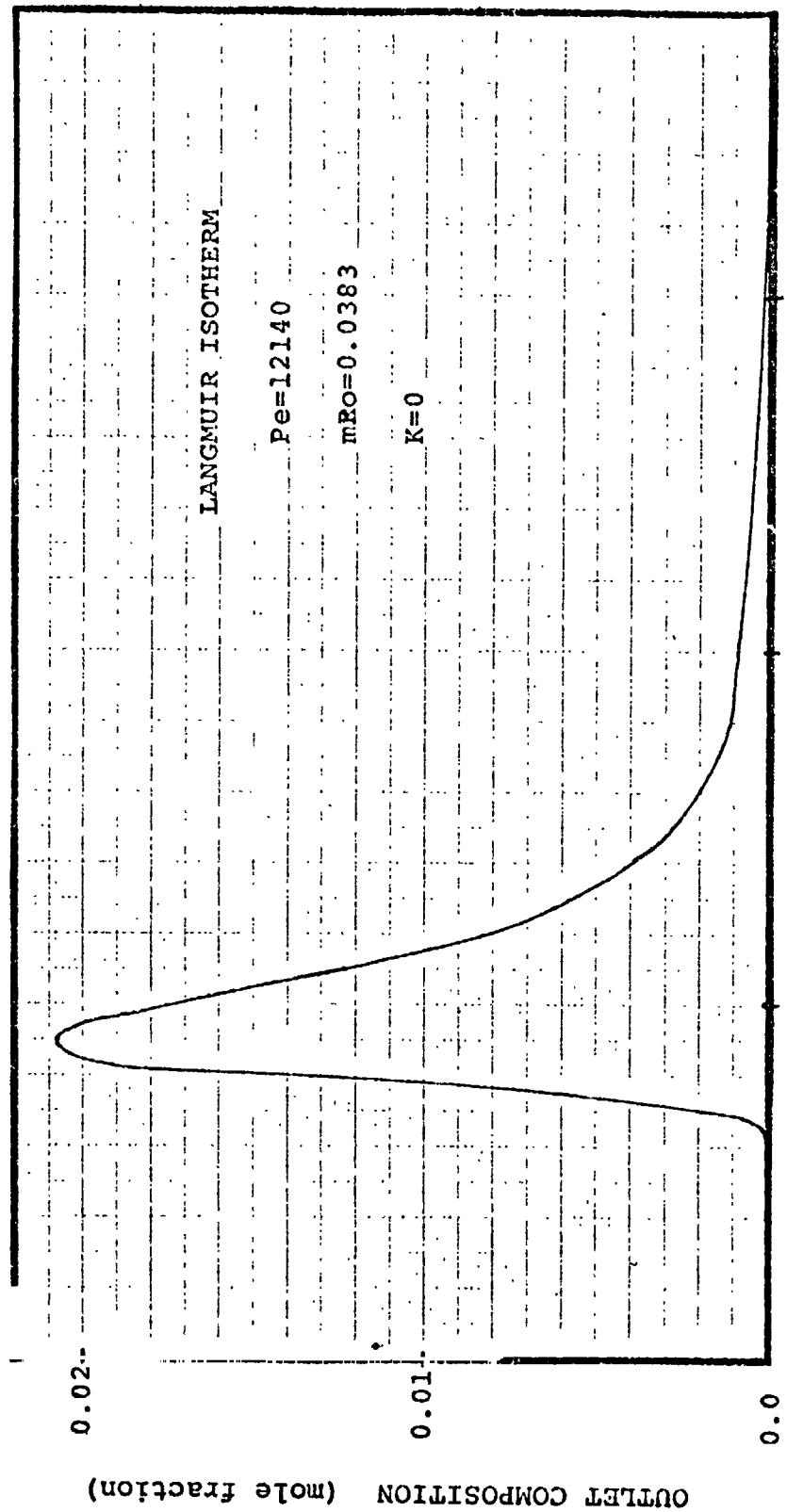

Figure 10 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 175°C for K=0

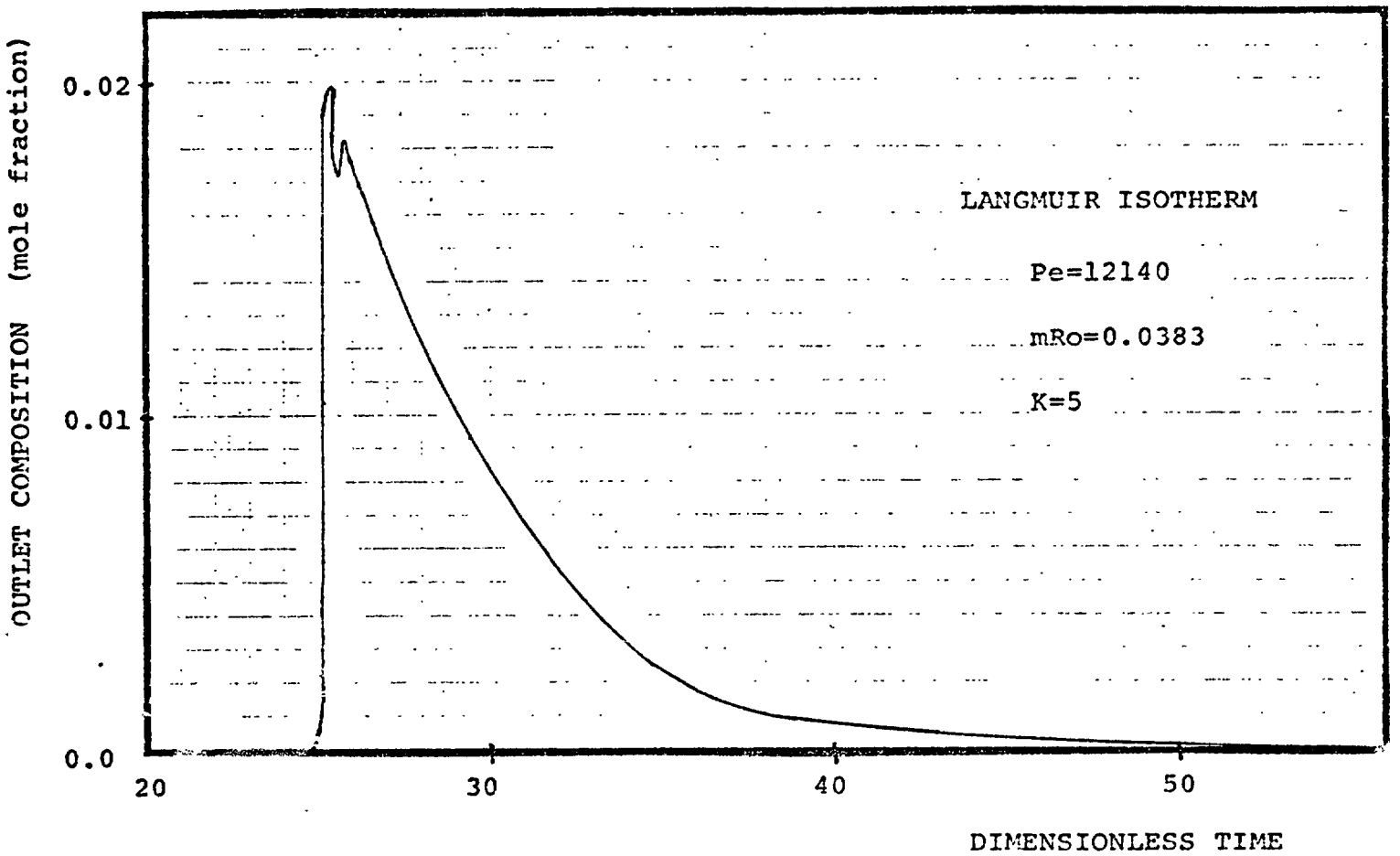

Figure 11 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 175°C for K=5

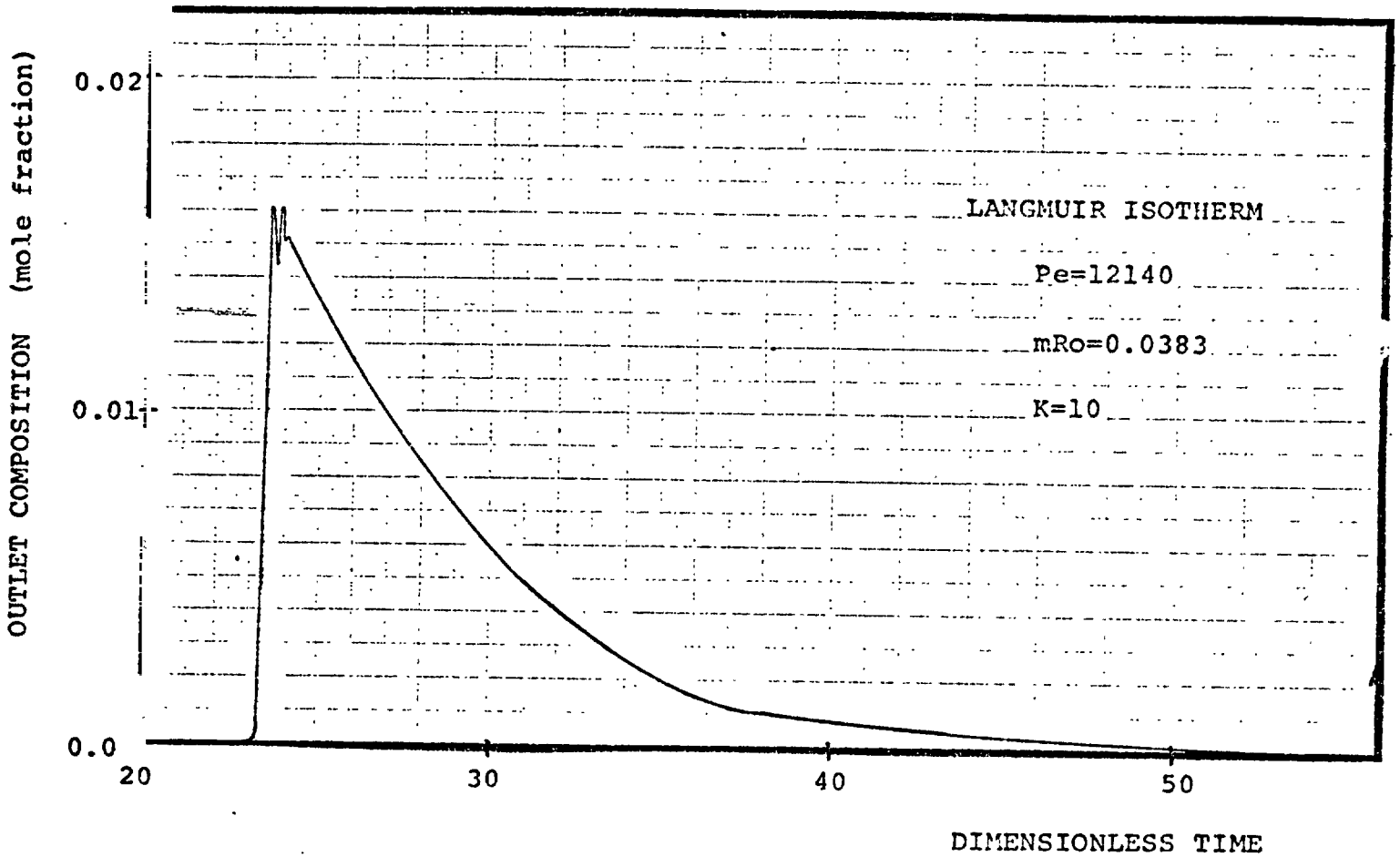

Figure 12 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 175°C for K=10

as can be seen by the oscillations at the peaks of the simulation. For smaller sets of data points, no oscillations appear at the peaks of the simulation. However, when using a large set of data points to represent the input, another interpolation scheme should be considered.

The value of K equal to zero corresponds to the linear model and the simulated results from both programs match identically. The three simulations of Figures 10, 11, and 12 can be compared with the actual data in Figure 6. For the Langmuir constant equal to zero the peak is not as sharp and there is not much spreading in the tail. As K is increased the rise of the peak is sharper and approximates the actual peak well. There is also more spreading in the tail. Unfortunately, the peak times of the simulations deviate more from the observed data peak time. Table 3 shows this trend. This indicates that the initial estimate of the thermodynamic parameter, mRo, is wrong. This suggested that another way of determining the parameter, mRo, had to have been found. This concept is discussed in the next section.

TABLE 3

COMPARISON OF THE SIMULATION PEAK TIMES OF THE OUTPUT FOR VARIOUS VALUES OF THE LANGMUIR CONSTANT, K
(N-HEPTANE ON CHROMOSORB-102 AT 175°C)

K	Peak Time (Dimensionless Time)
0	28.920
5	25.400
10	23.800
ACTUAL	29.005

D. Determination of the Langmuir Constant by Curve Fitting

Previous research done by Lavoie (1974) and Meisch (1969) have shown that the parameter, mRo, is dependent on composition. Lavoie ran experiments with n-heptane at 200°C on the Chromosorb-102 by varying the sample size. He obtained an mRo for each experiment. In the current studies, it was assumed that the mRo corresponding to the dilute sample applied for all sample sizes. The Langmuir constant could then be varied until the peak times of the actual data and of the simulation match.

A numerical scheme is needed todetermine the Langmuir constant. The secant method (Conte and de Boor, 1972) is used. Coding problems had to be dealt with when this secant method was implemented into the program. These problems arose from the oscillations produced by the interpolation of the input data at the entrance of the column. Fortunately, these oscillations damped out well before the peak of the output occurred. To determine the peak times of the simulation, the pulse maximum was required. With the early oscillations of the simulation, one would not get the true maximum of the pulse so that a level, TEST2, was introduced into the program. Nothing was done below this level. As soon as the compositions

became greater than this level, a search was made for the maximum peak. In this way the true peak time of the simulation could be obtained. Figure 13 shows this general procedure.

Another serious problem occurred due to these oscillations produced by the cubic spline interpolation of the input data. The pulse should always be propagating down the column. Consequently, it should never back track. In terms of the nomenclature of the program the indices, I1 and I2, should never decrease. This was not the case for small values of mRo, so that a new feature was required to avoid the divide checks (division by zero) that occurred due to this back tracking. The values of I1 and I2 after a successful set of iterations are stored as I1OLD and I2OLD, respectively. During the course of the program, a check is constantly being made so that the new valuesof I1 and I2 be atleast equal to their old values. This would eliminate any reversing of the indices and avoid any computer divide checks.

In Figure 14 an organization chart is presented to show the input and output of the Langmuir program.

A second n-heptane system was studied. This is one of the sample size mRo dependence experiments run by Lavoie. The actual chromatograph for n-heptane on the Chromosorb-102 column operating at 200°C is shown in Figure 15 and the equilibrium adsorption model chromatograph is presented in Figure 16. The equilibrium adsorption

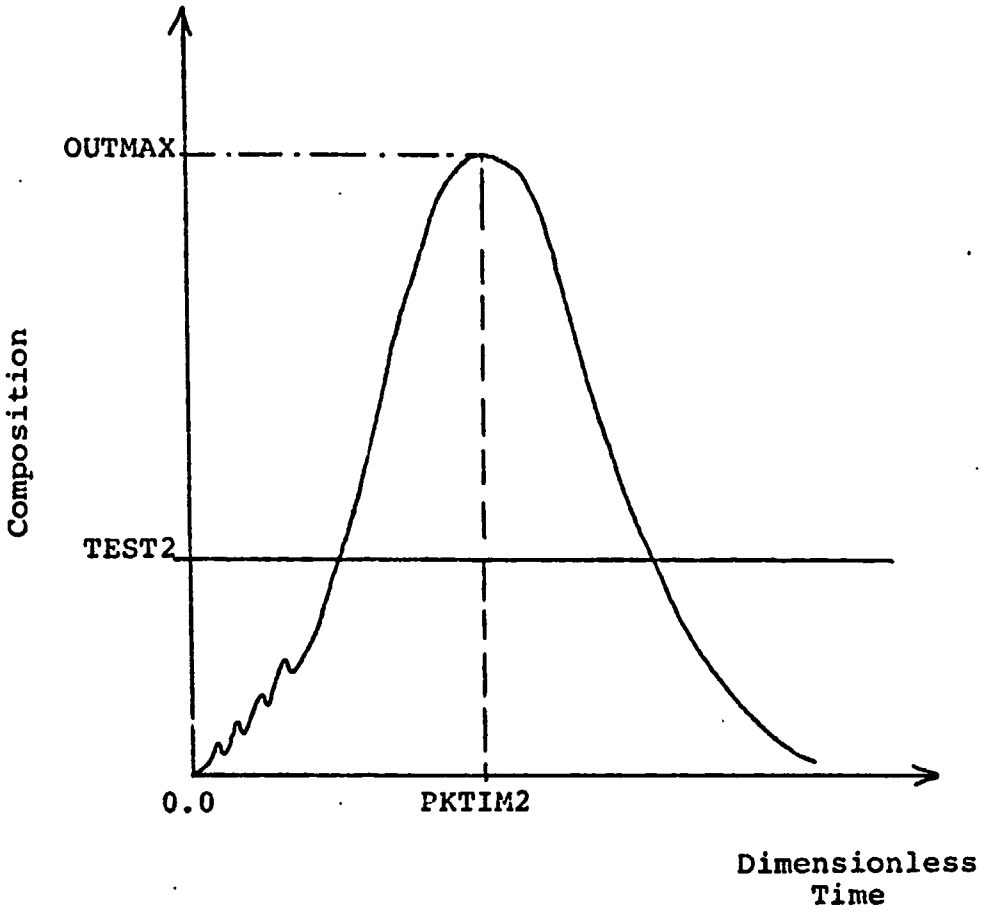

Figure 13 Determination of Peak Time for Langmuir Program

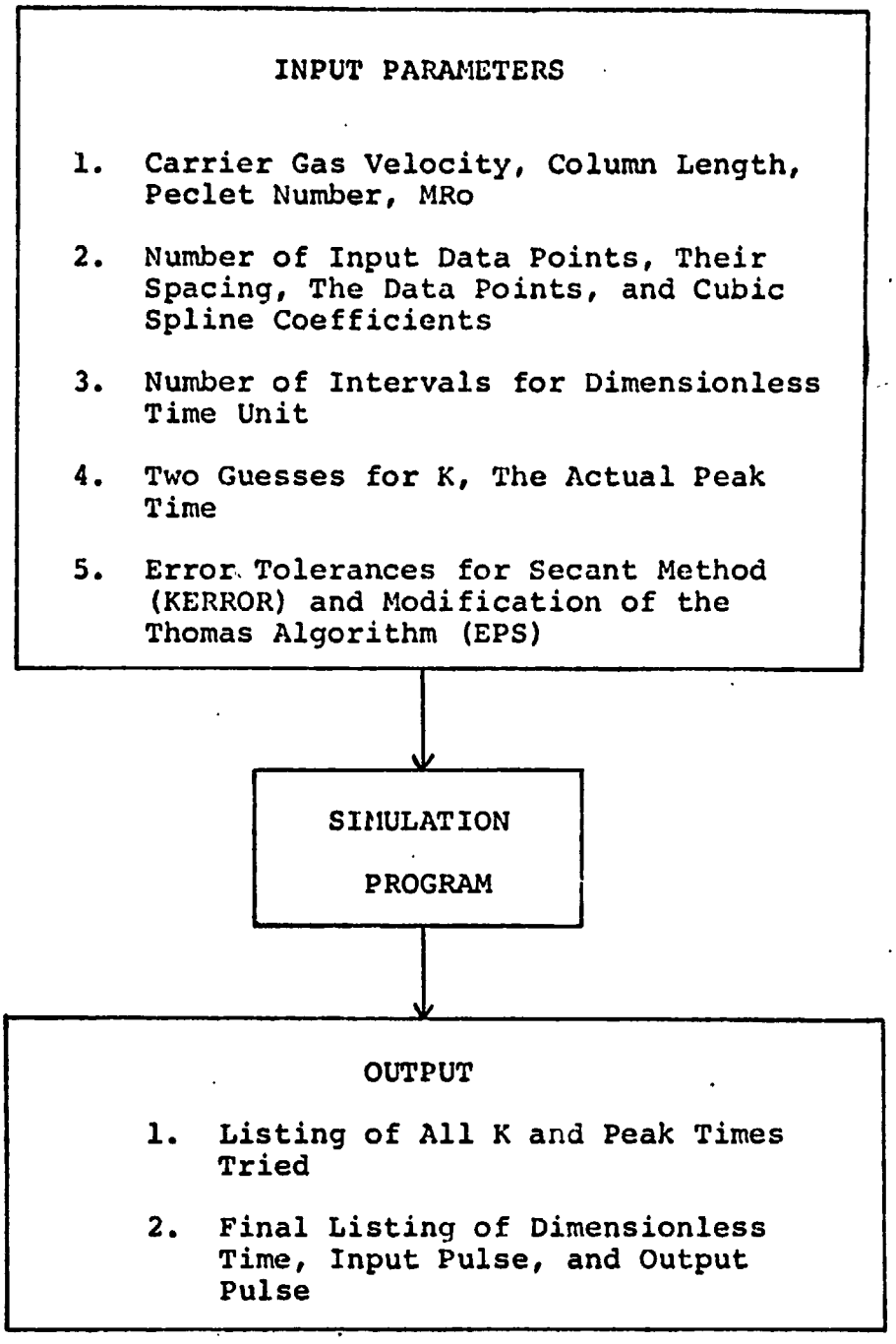

Figure 14 Organization of Langmuir Isotherm Program

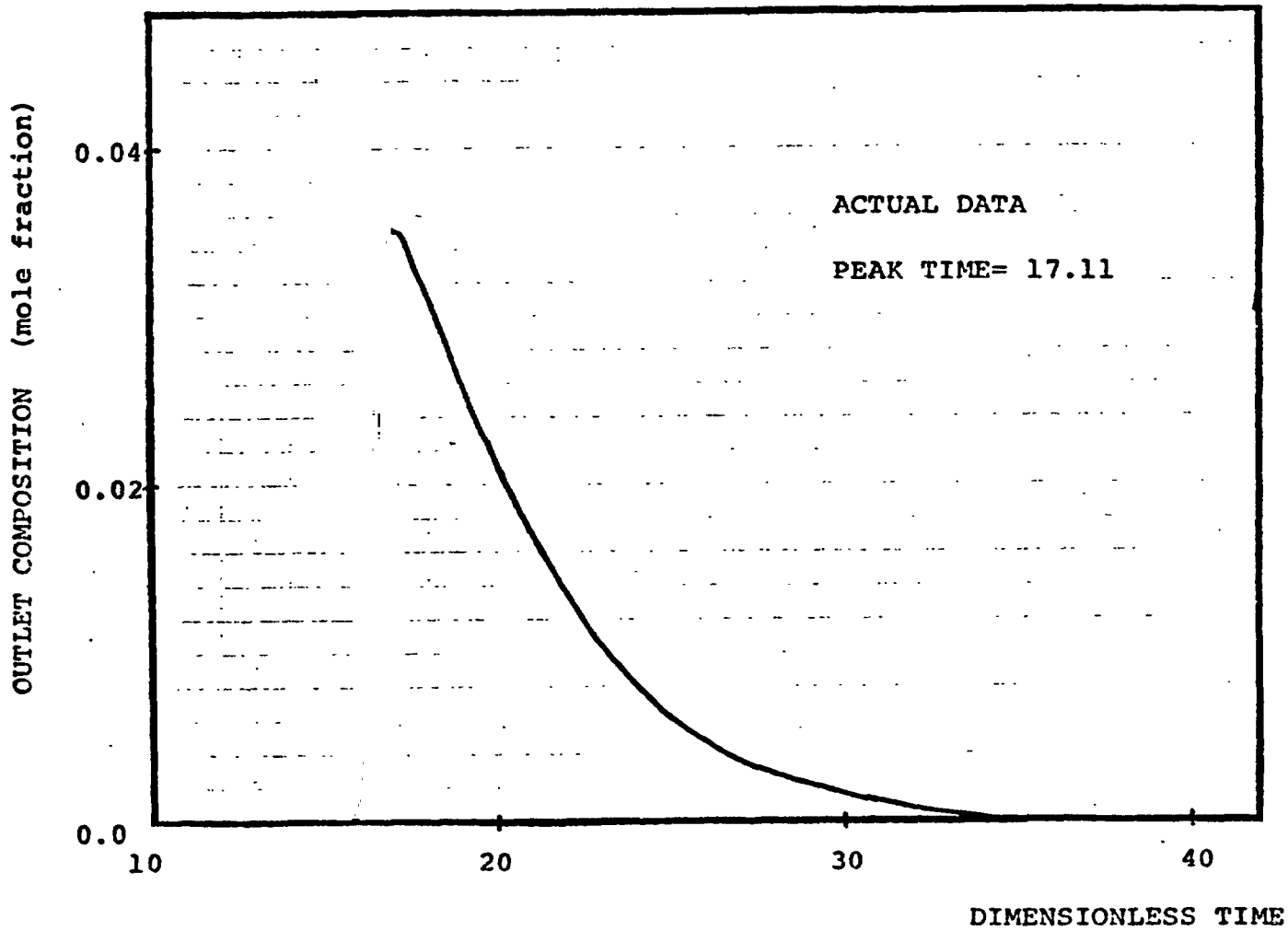

Figure 15 Actual Chromatograph for n-Heptane on Chromosorb-102 at 200°C

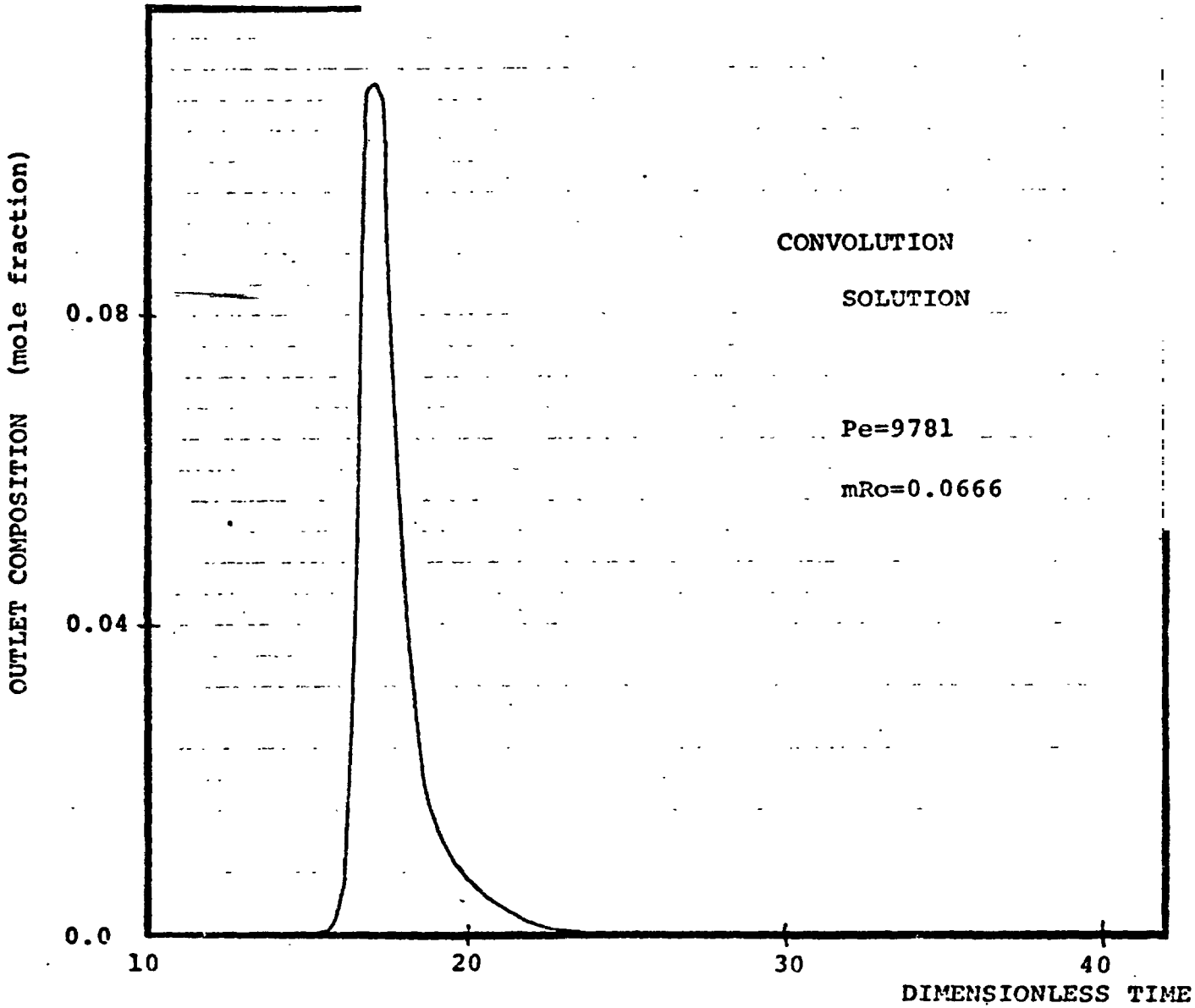

Figure 16 Chromatograph for n-Heptane on Chromosorb-102 Using the Equilibrium Adsorption Model

model curve is very sharp and the peak is about three times as great as the actual data. The simulation curve exhibits almost no spreading as opposed to the high degree of tailing in the experimental data. The compositions for this system are much larger than encountered before and the equilibrium adsorption model poorly predicts the output as expected.

For the simulation using the Langmuir isotherm, the parameter, mRo, correspoding to the sample size of 0.2 microliters was used to simulate data for the system having the larger sample size of 3.0 microliters. The Langmuir simulation for n-heptane on the Chromosorb-102 at 200°C with an mRo = 0.0482 and the Langmuir constant of 4.8 is shown in Figure 17. This simulation approximates the actual data quite well. It rises quite sharply like the actual output peak and exhibits similar tailing. The peak height is still slightly higher than the actual data but nowhere near as great as the linear isotherm prediction. To further improve the peak height, a slightly smaller mRo would seem appropriate. A value of mRo equal to 0.0382 (K=12.2) produced a simulation with a slightly smaller maximum. This simulation chromatograph is shown in Figure 18. A third and final simulation was made with an intermediate value of mRo equal to 0.0426 (K=8.6) and its simulation is presented in Figure 19. These three simulation peak heights are compared in Table 4.

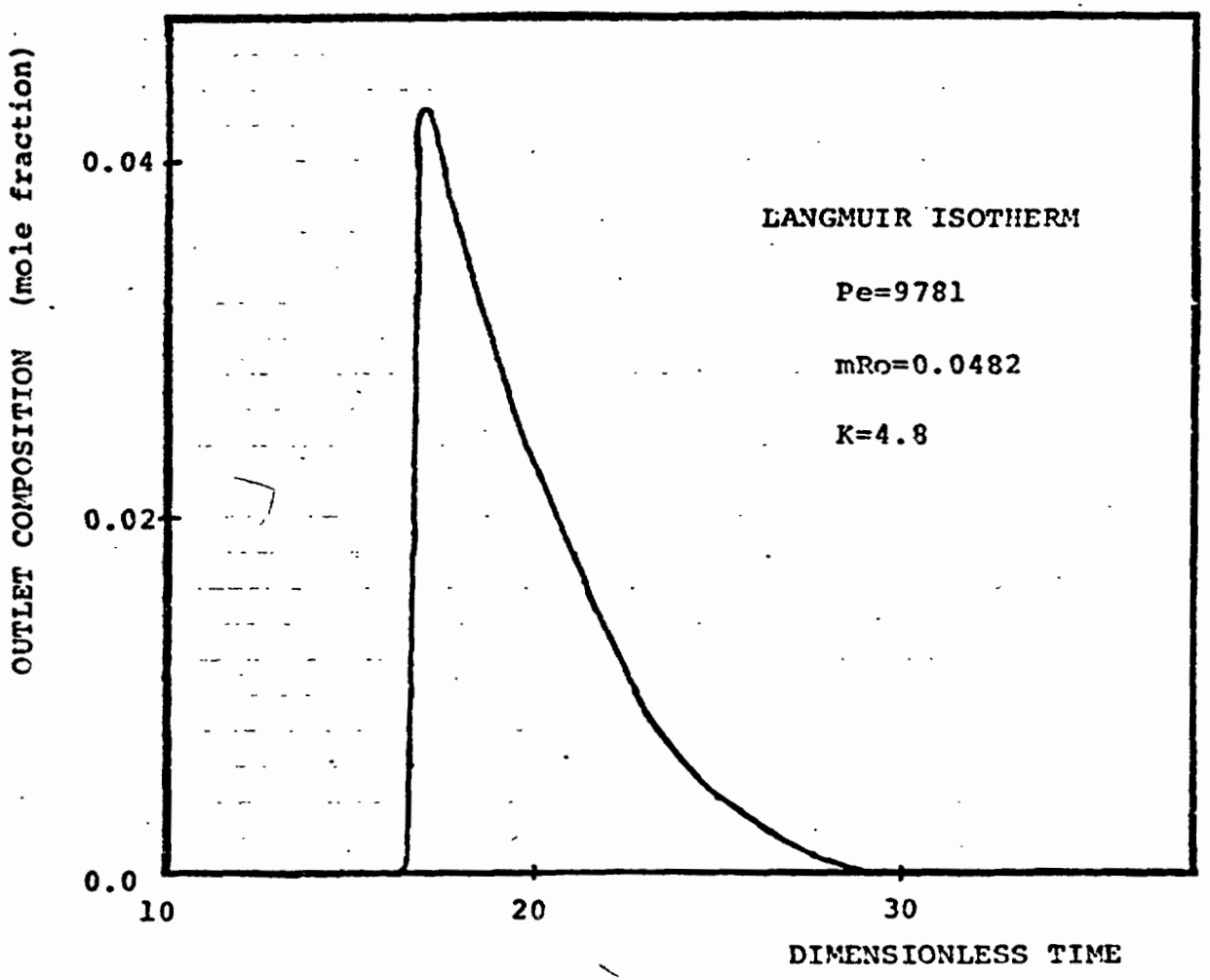

Figure 17 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 200°C for mR_o=0.0482

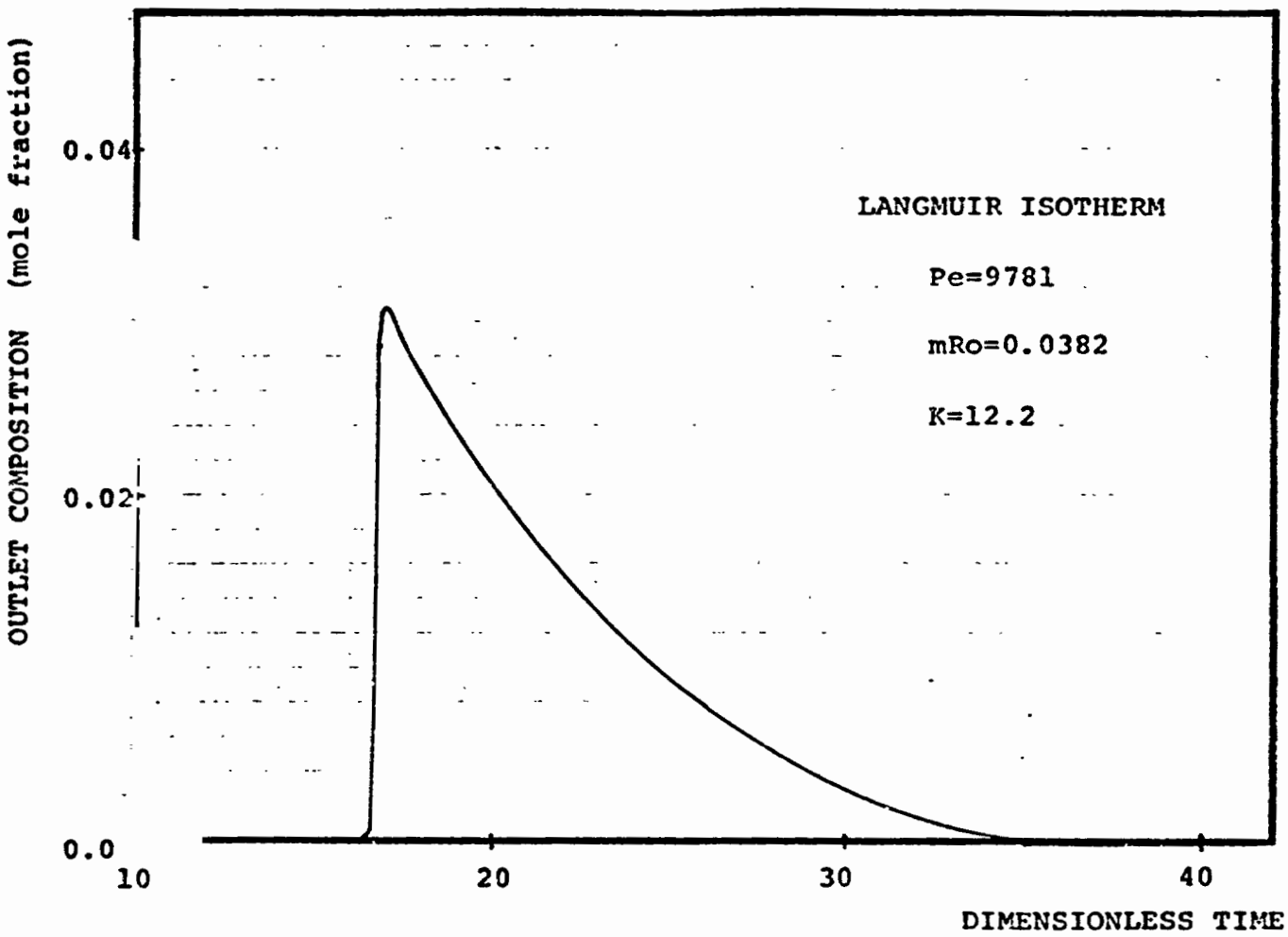

Figure 18 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 200°C for mR_o=0.0382

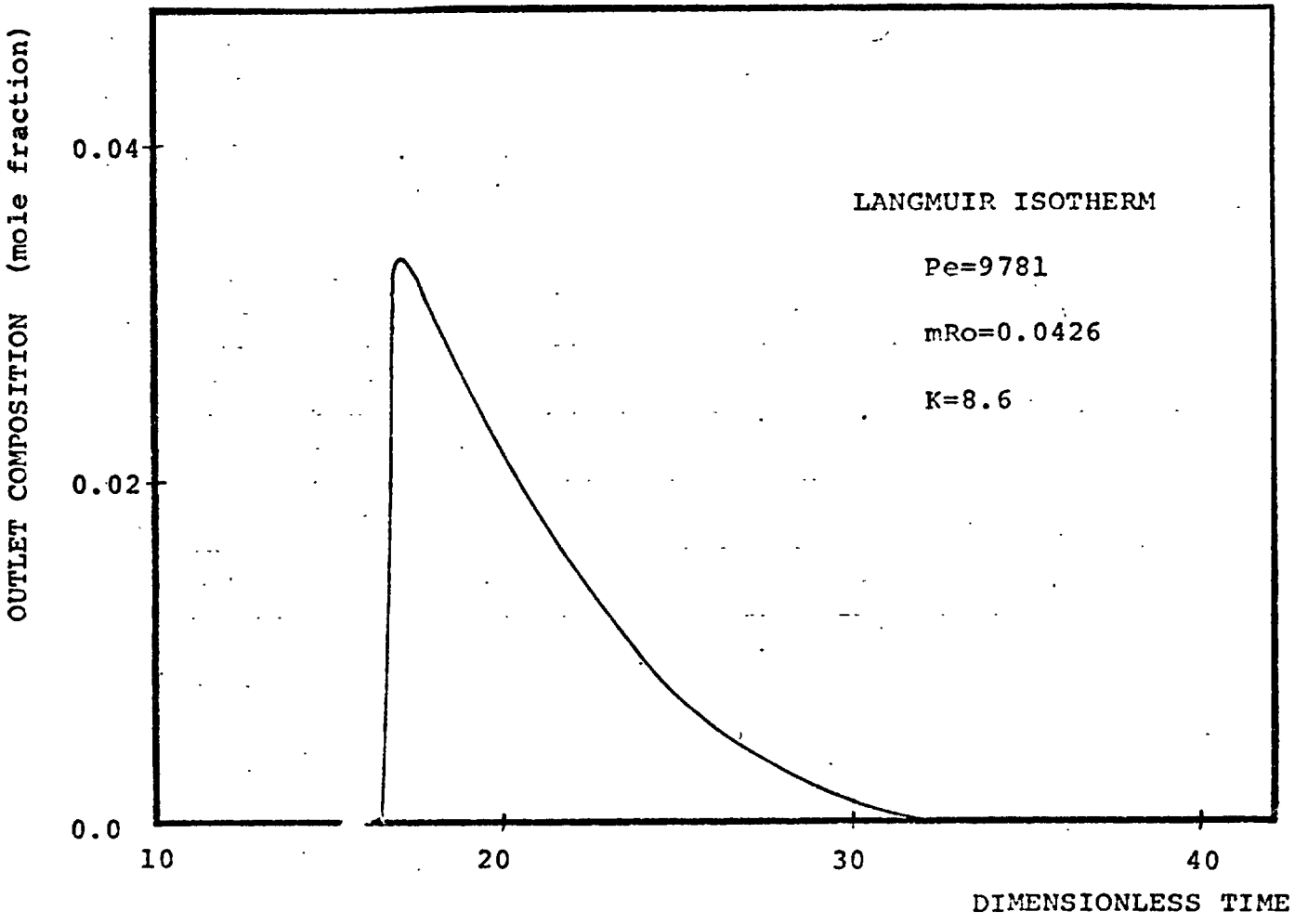

Figure 19 Simulation Chromatograph for n-Heptane on Chromosorb-102 at 200°C for mR_o=0.0426

TABLE 4

COMPARISON OF THE SIMULATION PEAK HEIGHTS FOR VARIOUS MRO'S WITH THE ACTUAL PEAK HEIGHT (N-HEPTANE ON CHROMOSORB-102 AT 200°C)

Thermodynamic Parameter, mRo	Langmuir Constant, K	Peak Height (mole fraction)
0.0382	12.2	0.0308
0.0426	8.6	0.0333
0.0482	4.8	0.0430
ACTUAL DATA	—	0.0353

With successful simulation of the n-heptane system on the Chromosorb-102 column at 200°C, attention was directed to the n-heptane system on the Chromosorb-102 column at 175°C. Since there are no data for a dilute sample, an estimate of the parameter, mRo, was made. With this approximate value of the parameter, difficulties in convergence of the Langmuir constant were encountered. The oscillations from interpolation are causing the convergence problems of K. No convergence was obtained for this system. These problems were a result of the problems of the cubic spline interpolation. Another interpolation scheme should be investigated. A different numerical scheme might be studied which would converge faster to the appropriate Langmuir constant.

PART 4

CONCLUSIONS AND RECOMMENDATIONS

This investigation has been conducted in conjunction with the group effort to define fundamental design criteria necessary for an optimal design of a combination gas chromatograph-mass spectrometer. Specifically, this report has dealt with the formulation of a modification of the equilibrium adsorption model with the incorporation of the Langmuir isotherm and subsequent efforts to ascertain the merits of the numerical technique known as Crank-Nicolson as a technique worthy of use in the simulation of a nonlinear gas chromatograph model.

Previous work suggested the formulation of a model which took into account the variation of the thermodynamic parameter, mRo, with composition. The Langmuir isotherm has been used to account for the fact that there is a saturation of adsorbent sites at higher concentrations. The analysis of the equilibrium adsorption model using the Langmuir isotherm indicates the characteristics of the actual data are more adequately predicted than with previous models.

The finite difference method of Crank-Nicolson has shown to have less instabilities than the orthogonal collocation method studied earlier. The Crank-Nicolson method can be modified to shorten computation time with no significant loss in precision. With the two modifications

implemented into the algorithm the computation time was reduced approximately 42%.

The interpolation method used on the discrete set of input points exhibited the property that for a large set of data points (a wide pulse) underflows in calculating the cubic spline coefficients resulted. These underflows manifested themselves later in the simulation by producing oscillations at the peak of the output. For a case with few data points no oscillations occurred. Therefore, an attempt should be made in the future to find a better interpolation scheme.

The incorporation of the secant method into the simulation model to match the peak times of the simulation for a given mRo with the actual peak time resulted in good approximations to the actual data. For a better approximation to the tailing and the steep rise of the peak an mRo corresponding to a dilute sample was used. The parameter, mRo, could be further varied to better fit the actual data. Future work could incorporate another secant method or least squares fit to vary mRo which in turn would determine the Langmuir constant, K, to match the peak heights and peak occurrences of the simulation with those of the actual data. This results in what amounts to as a two constant curve fitting scheme.

When the numerical scheme was applied to the

first system studied there was no convergence for the Langmuir constant. This problem was the result of the oscillations produced from the interpolation of the input using the cubic spline coefficients. This suggests again the importance of finding a better numerical scheme for interpolating the input data. A better convergent numerical technique not as dependent on the oscillatons of the peak should be investigated.

The Crank-Nicolson method solves the nonlinear equation quite well but even with the modifications made to it an excessive amount of computation time is needed. Depending on the system, between 25 and 60 minutes of computation time is needed. Another area of future work could be to go back to the method of orthogonal collocation and try new trial functions and new orthogonal functions which would result in shorter simulations. Other numerical techniques might be studied also.

PART 5

ACKNOWLEDGEMENT

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PART 6

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PART 7

APPENDICES

A. Derivation of the Equilibrium Adsorption Model

B. Formulation of the Crank-Nicolson Algorithm for the Langmuir Isotherm

C. Listing of the Crank-Nicolson Method for the Langmuir Isotherm

The appendices are not included in this report because of their length. Copies may be obtained upon request from:

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