

Equilibrium and response curve analyses on the adsorption of CaCl2 and Ca(NO3)2 using a retardation resin

by Jeffrey Edward Rehor

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering

Montana State University

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Abstract:
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Experimental response curves were also generated for CaCl2 and Ca(NO3)2 by injecting a concentrated pulse into a column packed with the resin. These response curves were analyzed using the method of weighted moments to estimate an equilibrium and rate parameter. Both of these parameters showed maximum values at 20°C.

The experimental curves were compared to curves generated from a model of the system. The best fit between the theory and the experimental data occurred at 10°C while the agreement at 20°C and 50°C was not quite as good.

The equilibrium parameter was also estimated directly from the equilibrium constant to yield a comparison.

A wide discrepancy between the two values was found.

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EQUILIBRIUM AND RESPONSE CURVE ANALYSES ON THE ADSORPTION OF $CaCl_2$ AND $Ca(NO_3)_2$ USING A RETARDATION RESIN

by

JEFFREY EDWARD REHOR

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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in

Chemical Engineering

Approved:

Robert L. Nickelson
Chairperson, Graduate Committee

J P McCandless
Head, Major Department

Michael Malone
Graduate Dean

MONTANA STATE UNIVERSITY
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ABSTRACT

Equilibrium constants were determined for the adsorption of $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$ by Bio-Rad Laboratories' AG11A8 bifunctional resin. The equilibrium constants were found to decrease with rising temperature for $CaCl_2$ but increase for $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$.

Experimental response curves were also generated for $CaCl_2$ and $Ca(NO_3)_2$ by injecting a concentrated pulse into a column packed with the resin. These response curves were analyzed using the method of weighted moments to estimate an equilibrium and rate parameter. Both of these parameters showed maximum values at 20°C.

The experimental curves were compared to curves generated from a model of the system. The best fit between the theory and the experimental data occurred at 10°C while the agreement at 20°C and 50°C was not quite as good.

The equilibrium parameter was also estimated directly from the equilibrium constant to yield a comparison. A wide discrepancy between the two values was found.

INTRODUCTION

Several recent investigations have studied the desalination of water using retardation resins (1,9,10). Very little research, however, has been done using inorganic salts other than sodium chloride. The applications of retardation resins to the removal of other ions would seem to be numerous and important.

The most significant applications may be in the area of pollution control. Concern has grown about the quantity of chemicals which have been released into our waterways. As restrictions on effluent quality increase the need for alternate methods to remove a variety of ions will be necessary. Another possible use will be the recovery of valuable products from plant effluents. There are also processes involving substances such as mercury and cadmium where such a recovery is valuable for both of these reasons (2,3).

The retardation resins have properties that make them unique when compared with the usual ion exchange resins that have been used in the past. The ion exchange resins work on the principle that an ion present on fresh resin is removed in exchange for an ion in the treated solution. For example, in the simple water softening process, sod-

ium ions on the resin are released as calcium ions are removed from the water. To reuse the ion exchange resin it must be chemically treated to replace the ions removed so it is restored to its original form.

Retardation resins, on the other hand, have both positive and negative sites that satisfy each other until some ionic substance is present. Then both anions and cations are adsorbed into the resin. Regeneration can be accomplished by contacting the resin with pure water. The rate of regeneration can usually be increased by heating the water prior to contact with the resin.

Very little information is available on the mechanism of adsorption on the retardation resin. Equilibrium and rate data are available only for sodium chloride. There are many unanswered questions about the effects the valency state of the ions, the ionic radius, and the interaction between different anions and cations have on the adsorption equilibrium and rate.

EXPERIMENTAL PROGRAM

The experimental program can be divided into two independent experiments. The first of these is an equilibrium measurement. The objective of this experiment is to estimate the equilibrium constants for the adsorption of inorganic chemicals from aqueous solutions using a specific resin.

The second part is an experimental generation of response curves from pulse injections of inorganic species into a packed column. The objective here is to obtain both an equilibrium and rate parameter. These two parameters will be estimated using the method of weighted moments to numerically integrate the experimental response curves. By substituting both of these parameters into the theoretical model of the system a theoretical response curve can be generated.

Several different chemical species at varied temperatures will be investigated. The inorganic chemicals to be used are: $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$. The operating temperatures are 10^oC, 20^oC, and 50^oC.

EXPERIMENTAL MATERIALS AND EQUIPMENT

To perform the equilibrium analysis the only required materials and equipment are the resin and the conductivity probe with its associated electronics. The pulse response experimentation requires one additional item, namely the glass column. Each of these items will now be discussed in detail.

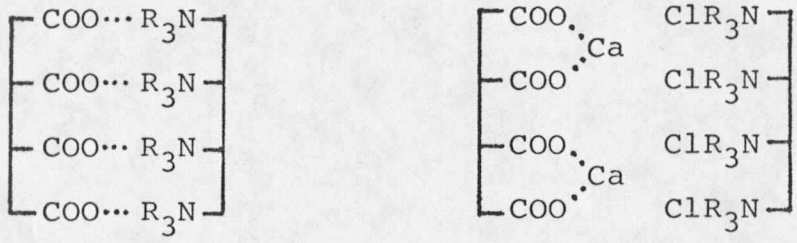
Column

The column used for this experimentation is jacketed and made by Bio-Rad Laboratories. The inside diameter is 0.7 cm and the bed length is 15.0 cm.

Resin

The resin used in this research is Bio-Rad Laboratories' AG11A8. They produce this type of resin by polymerizing acrylic acid inside another of their resins, AG-1X8 or Dowex 1. The result is a styrene divinylbenzene, cross-linked polymer lattice, with paired anion and cation exchange sites. This resin is referred to as bifunctional because of its ability to adsorb both anions and cations. A simplified structure of the resin in its completely cleansed form is shown in Figure 1a. When the resin is brought into contact with the ionic solution, the inorganic substance is adsorbed without an exchange.

This is represented in Figure 1b. The resin has a moisture content of 40% and the particle size is 50-100 mesh. (4)



(a) (b)

FIGURE 1: AG11A8 RESIN (a) BEFORE ADSORPTION
(b) AFTER ADSORPTION

Conductivity Probe

The concentrations in the liquid phase were measured using a conductivity probe. A sketch of the probe assembly is shown in Figure 2. The design is similar to a design described by Lamb et. al. (5). The probe measures the electrical conductivity of a very small volume of fluid surrounding the tip of the probe. A brief description of the principles of the conductivity probe follows:

The most important "sections" of the probe are the two electrodes. One of these is a point electrode

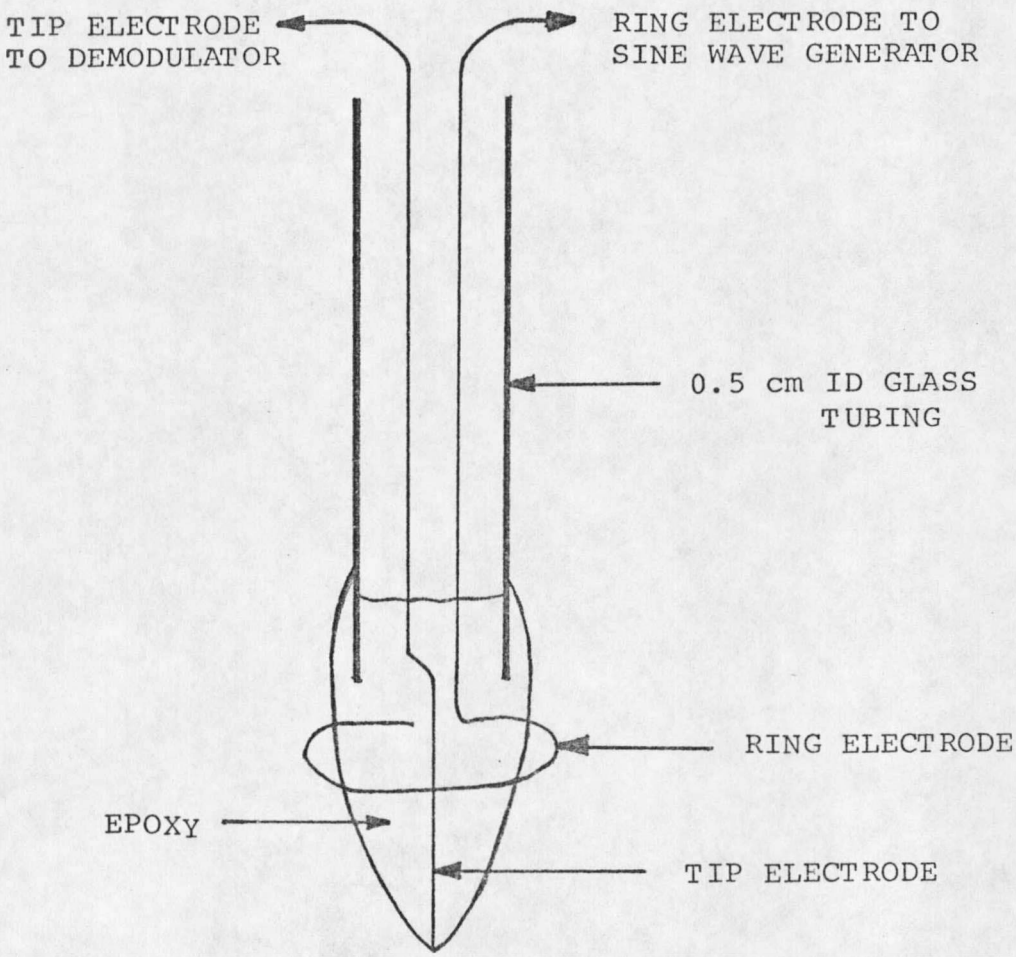


FIGURE 2: CONDUCTIVITY PROBE

located at the tip of the probe while the other is a ring electrode located approximately one centimeter above the tip. The tip consists of the cross-sectional area of an exposed face of platinum wire with a diameter of 0.01 cm. The ring electrode is approximately three centimeters of 0.015 cm platinum wire. The sizes are not important as long as the tip electrode is much smaller than the ring electrode.

An a.c. voltage source is then connected to the ring electrode. The result is an electric field in the electrolyte surrounding the ring. The current between the two electrodes is a function of the resistance of the electrolyte between them. The current that enters the tip is proportional to the conductivity of the fluid at the tip.

When the probe is placed in a nonhomogeneous fluid the changes in conductivity of the fluid alter the impedance of the probe. This causes variations in the amplitude of the input carrier wave. So the signal exiting the probe is an amplitude modulated sine wave. This signal must be processed in order to give a usable result. First the signal leaving the probe is amplified. Next it is demodulated by rectifying it. Finally the

signal is run through a low pass filter to remove the carrier wave and all other high frequencies. Figure 3 shows a block diagram of the signal processing components and a typical signal at each point.

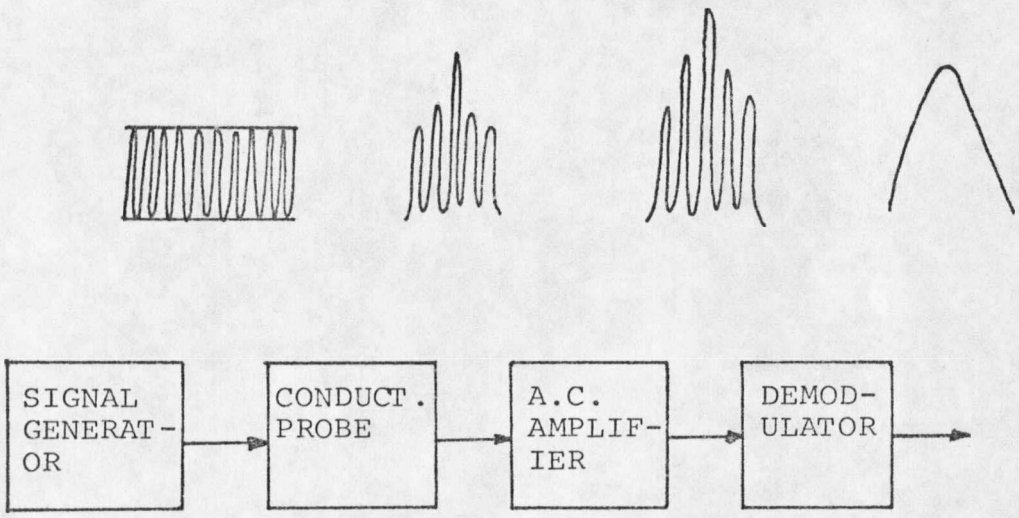


FIGURE 3: SIGNAL PROCESSING BLOCK DIAGRAM

Electronics

The sine wave generator used is the Heathkit model IG-18 Sine-Square Audio Generator. A signal of .3V with a frequency of 5 kHz was output. A Heathkit model IP-17 high voltage power supply was used to send a 25V signal to the demodulating system. The demodulator was constructed

by Arthur McCready in 1977 for use in his doctorate project. The details on the demodulator can be found in his thesis (6). The output voltages were measured using a Hewlett Packard model 3440A digital voltmeter. Finally the response curves were plotted using a Hewlett Packard 7030AM X-Y recorder.

EXPERIMENTAL PROCEDURE

Before any experimentation was done the resin was given a thorough rinsing. This was accomplished using a 2.5 cm by 70 cm glass column. The column was filled generally halfway with resin. Distilled water was then pumped through the packed bed at a flow rate of about 12.0 liters/day for 72 hours. After the rinsing cycle was completed air was blown through the column to remove any excess moisture. A small sample of the rinsed resin was then weighed and allowed to dry in order to check the moisture content. This moisture content was found to be 40%. The resin was then placed in a tightly sealed jar for use in the experimentation.

Equilibrium Analysis

The entire experimentation to determine the equilibrium constants was performed in two small beakers. Five grams of the wet resin was carefully weighed into one of the beakers. Fifty milliliters of distilled water was then added to each beaker. The beaker with only water was used to construct a calibration curve between concentration and voltage. A small volume, on the order of 0.5 ml, of the inorganic solution to be tested was added to each beaker. The concentration of this addition

was .2M. A magnetic stirrer kept the resin and solution properly mixed. The extent of the adsorption was monitored using the conductivity probe. In general thirty minutes was allowed for the adsorption to reach equilibrium. At this point a final voltage reading was taken. This procedure was repeated until a total of three milliliters of the inorganic chemical were added.

Trials were made at temperatures of 10°C, 20°C, and 50°C. The trials at 10°C and 50°C required two specializations. First a constant temperature bath was used to alleviate any temperature fluctuations. A second difference was how the final voltage reading was taken. After the adsorption reached equilibrium the liquid was drained from the resin. This liquid was then either warmed or cooled to room temperature. It was at this temperature that the final voltage reading was taken. After the reading the liquid was returned to the adsorption beaker. The calibration curve was also prepared at room temperature.

Pulse Responses

A simplified sketch of the system used to perform the pulse responses is shown in Figure 4. The first step was to pack the column. The best technique for accomplish-

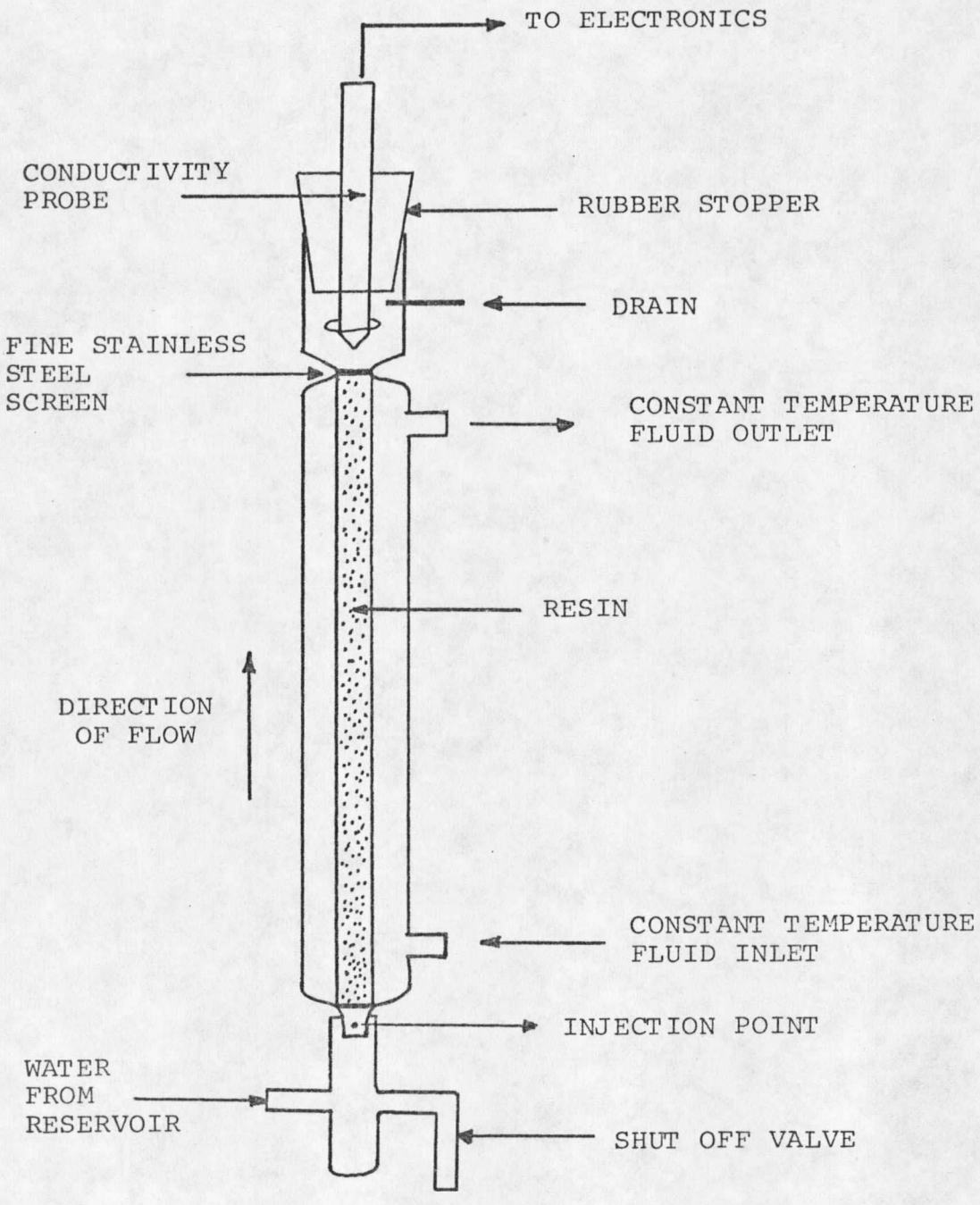


FIGURE 4: PACKED COLUMN ASSEMBLY

ing this was to form a slurry of resin and water and pour this mixture into the column. This step must be done carefully to prevent air bubbles from forming in the bed. As soon as this step was completed the valve at the base of the column was opened which allowed distilled water to flow through the system. The flow rate was kept as close to 1.0 ml/min as possible. The system was allowed to run in this manner for thirty minutes. This time allowed for the stablization of the flow rate and also the flushing out of any soluble impurities in the system.

The next step was to inject a sample of the inorganic compound. The concentration of this impulse was generally 4M. The volume of the impulse was 2 μl. The recorder was started 50 seconds after the injection. This was useful since the recorder had a maximum limit on the time axis of 20 minutes. Therefore delaying the start by 50 seconds allowed more of the tail on the response curve to be sketched.

After the run was completed the used resin was discarded. The final step was to use the conductivity probe to take voltage readings on samples of known concentrations in order to construct a calibration curve between voltage and concentration. This calibration

curve is needed to convert the response curves from voltage versus time to concentration versus time.

There is one more step that had to be done prior to each run whether it was an equilibrium analysis or a pulse response. This was an electro-treatment of the probe tip. The treatment was necessary to help alleviate the drifting of the voltage readings. The drift was caused by the formation of scale on the tip electrode. Prior to each run the following steps were performed. First the tip was rubbed with emery cloth to remove the buildup of scale. Next a voltage of approximately +2V was applied for 10 seconds to the probe. The current flowing from the ring electrode to the tip formed an oxide layer on the tip. This oxide layer is far less susceptible to drifting, thus increasing the accuracy of the readings.

A MODEL OF THE ADSORPTION SYSTEM

Solid phase diffusion is most often the rate controlling step in liquid adsorption processes. Simplifications developed recently by Liaw et. al. (7) and Rice (8) for step responses in packed columns make it possible to determine a solution for impulse responses when both film and solid phase diffusions are important. These simplifications will now be briefly discussed. Liaw et. al. solved the combined transport equation:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q}{\partial r}\right) \qquad \text{(I-1)}$$

This was paired with a non-dispersive convection equation for the fluid phase:

$$V \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} = -\left(\frac{\partial \bar{q}}{\partial t}\right)/\eta \qquad \text{(I-2)}$$

where:

$$\bar{q} = \frac{3}{R^3} \int_0^R q r^2 \, dr \qquad \text{(I-3)}$$

Next they assumed the solid phase composition profiles are always parabolic with respect to the radial coordinate, or simply:

$$q(r,z,t) = a_0(z,t) + a_2(z,t) r^2 \qquad \text{(I-4)}$$

This assumption leads to a simplified conservation relationship:

$$\frac{\partial C}{\partial x} + K\frac{\partial C}{\partial \theta} + \xi\frac{\partial C}{\partial x\,\partial \theta} = 0 \qquad \text{(I-5)}$$

where K is the equilibrium constant and ξ is the combined transfer resistance defined as:

$$\xi = R\left(\frac{K}{3k} + \frac{R}{15D_s}\right) \qquad \text{(I-6)}$$

Equation (I-5) can be solved by a LaPlace Transformation with a step change at the inlet. This solution was shown by Liaw et. al. to be:

$$\frac{C}{C_o} = \frac{1}{p}\exp\left(\frac{-Kpx}{1+\xi p}\right) \qquad \text{(I-7)}$$

where p is the LaPlace transform variable.

Rice (8) showed that equation (I-7) had a closed form inversion which is tabulated as a J function:

$$J(s,\tau) = \frac{C(x,\theta)}{C_o} = 1 - \int_0^s \exp(-\tau-\beta)\, I_o(\sqrt{4\tau\beta})\, d\beta \qquad \text{(I-8)}$$

where:

$$s = \frac{Kx}{\xi} \qquad \text{and} \qquad \tau = \frac{\theta}{\xi}$$

The impulse response is simply the derivative of the J

function with respect to time. This produces:

$$\frac{C_i(x,\theta)}{C_o} = \sqrt{\frac{s}{\theta\ell}}\ \exp(-s-\frac{\theta}{\ell})\cdot I_1(\sqrt{4s\theta/\ell}) + \delta(\theta) \qquad \text{(I-9)}$$

where C_o is taken to be the impulse strength. $\delta(\theta)$ has meaning only at the column entrance where s=0.

It is much easier to arrive at the impulse response in the LaPlace domain by directly using equation (I-7). This produces an impulse response of:

$$C_i = \exp(\frac{-Kpx}{1+\ell p}) \qquad \text{(I-10)}$$

Later when the method of weighted moments is discussed, equation (I-10) will be very important in the determination of Kx and ℓ.

EXPERIMENTAL RESULTS AND DISCUSSION

Equilibrium Analysis

The first step in processing the raw experimental data is to convert the voltage readings into concentrations using a calibration curve. A typical calibration curve is shown in Figure 5. Each voltage reading has its corresponding concentration value read off of the calibration curve. This step produces all of the liquid phase concentrations.

Next the concentration of the inorganic species in the resin must be calculated. This concentration is denoted by Q and can be shown to be:

$$Q = \frac{VC_o - (V + V_m)C}{w} \cdot \rho_p \qquad \text{(II-1)}$$

where:

$$\rho_p = \rho_s(1 - \epsilon_p) \qquad \text{(II-2)}$$

ρ_s represents the dry compressed particle density and ϵ_p is the internal void fraction. For Bio-Rad's AG11A8 resin, ρ_p was found to be 0.66 grams/ml. (9)

Values for C and Q for all the equilibrium analyses are given in Appendix A. The solid phase concentration, Q is then plotted versus the equilibrium liquid concen-

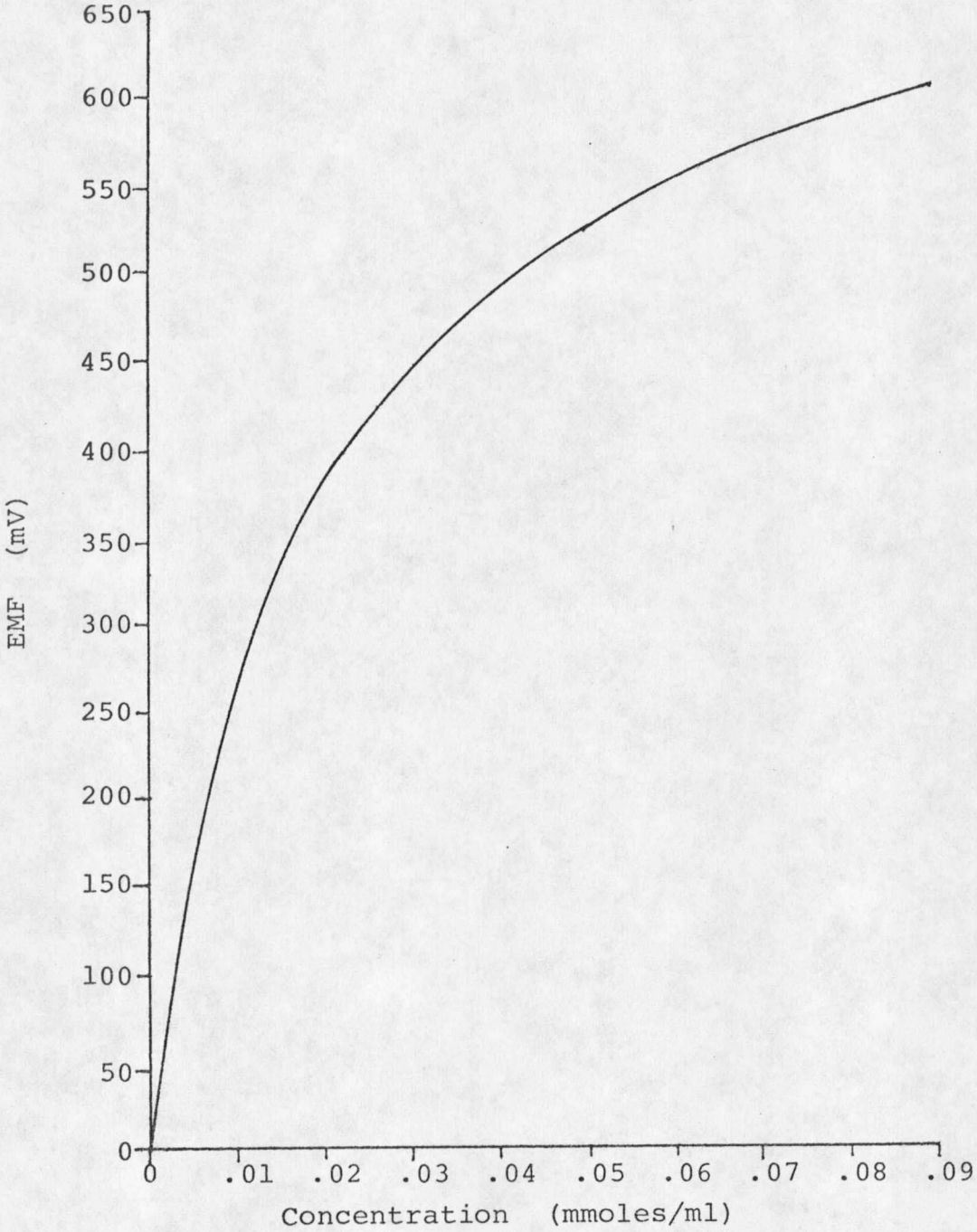


FIGURE 5: TYPICAL CALIBRATION CURVE

tration, C. The slopes on these curves is K, also known as the equilibrium constant.

The equilibrium graphs are shown for $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$ in Figures 6-9, respectively. The data points at concentrations less than 0.02 mmoles/ml are the least accurate due to fluctuating voltage measurements. The best line through the points was found simply by using a straightedge. This line was drawn so that it always included the best data point, the origin. The equilibrium constants found from these graphs are summarized in Table I.

Three equilibrium data points were also taken using NaCl. The reason for doing this was as a comparison to results from previous research. Table II summarizes the values for the equilibrium liquid and solid phase concentrations, C and Q, repectively. Also included are values of Q for both rinsed and unrinsed AG11A8 resin determined by Rice and Foo. (10)

As can be noted from Table II the experimental values for Q are somewhat lower than those suggested by Rice and Foo. Part of this difference is simply due to differences in batches of resin and the degree of rinsing.

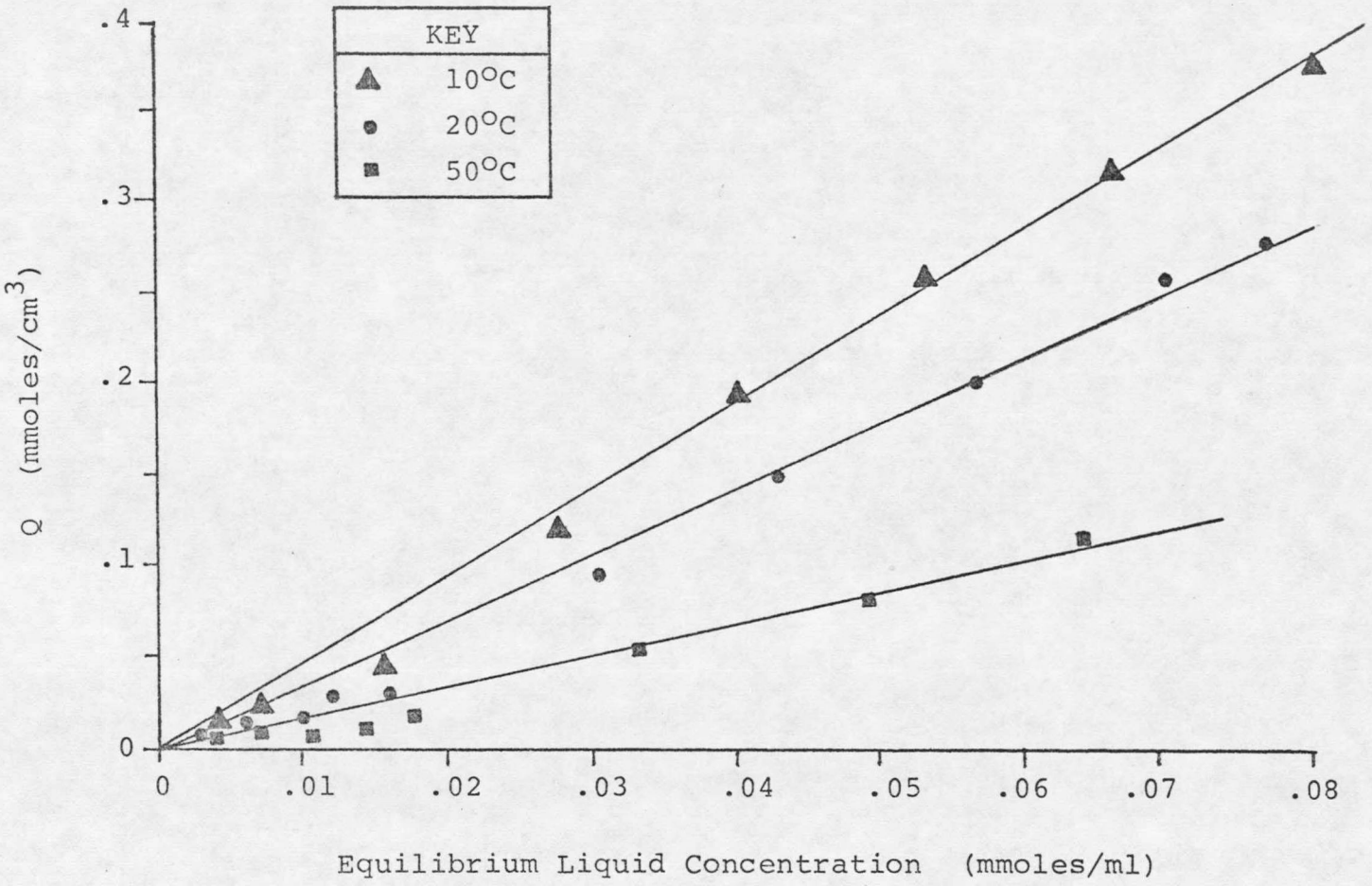


FIGURE 6: $CaCl_2$ EQUILIBRIUM CURVES

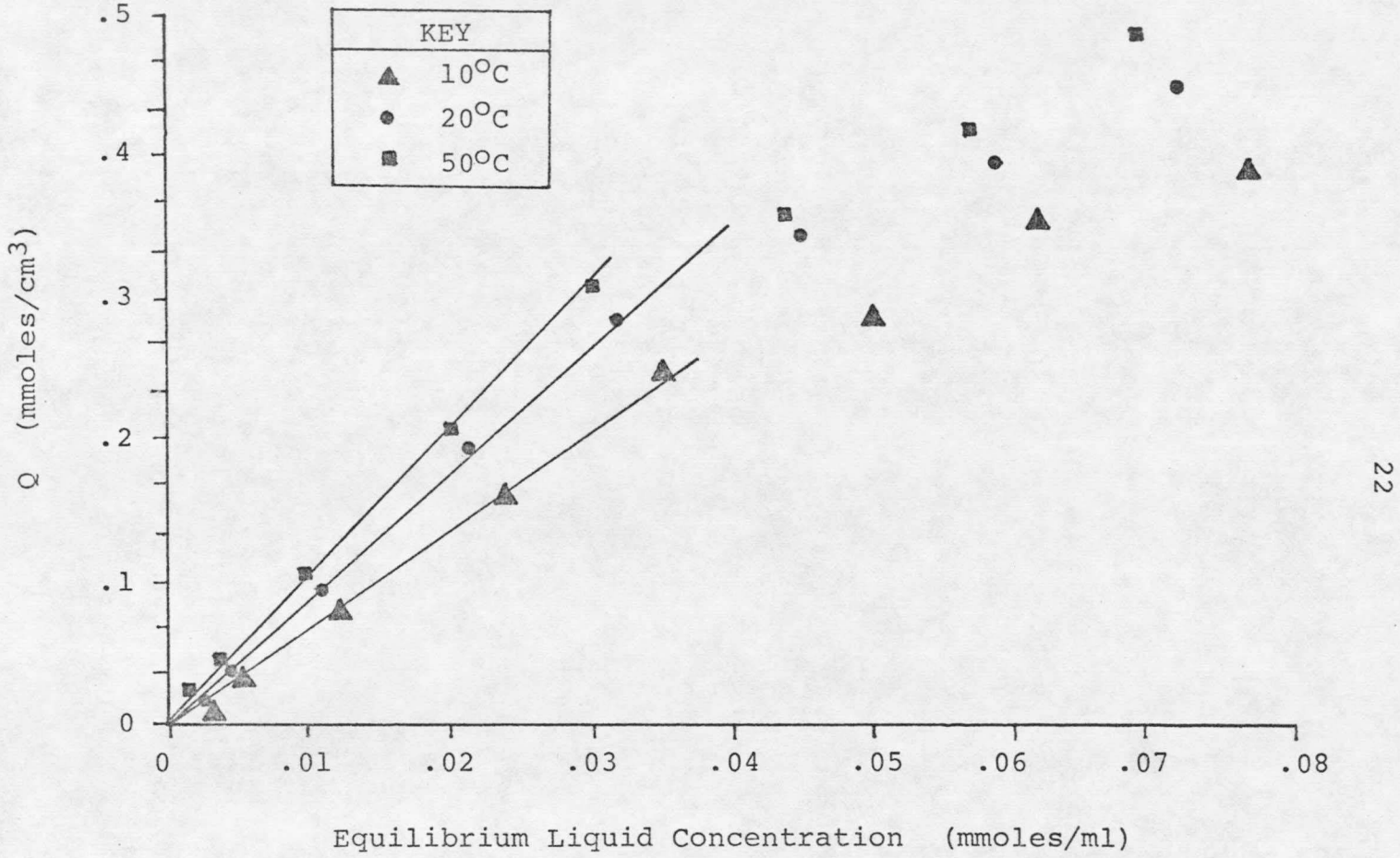


FIGURE 7 : $Ca(NO_3)_2$ EQUILIBRIUM CURVES

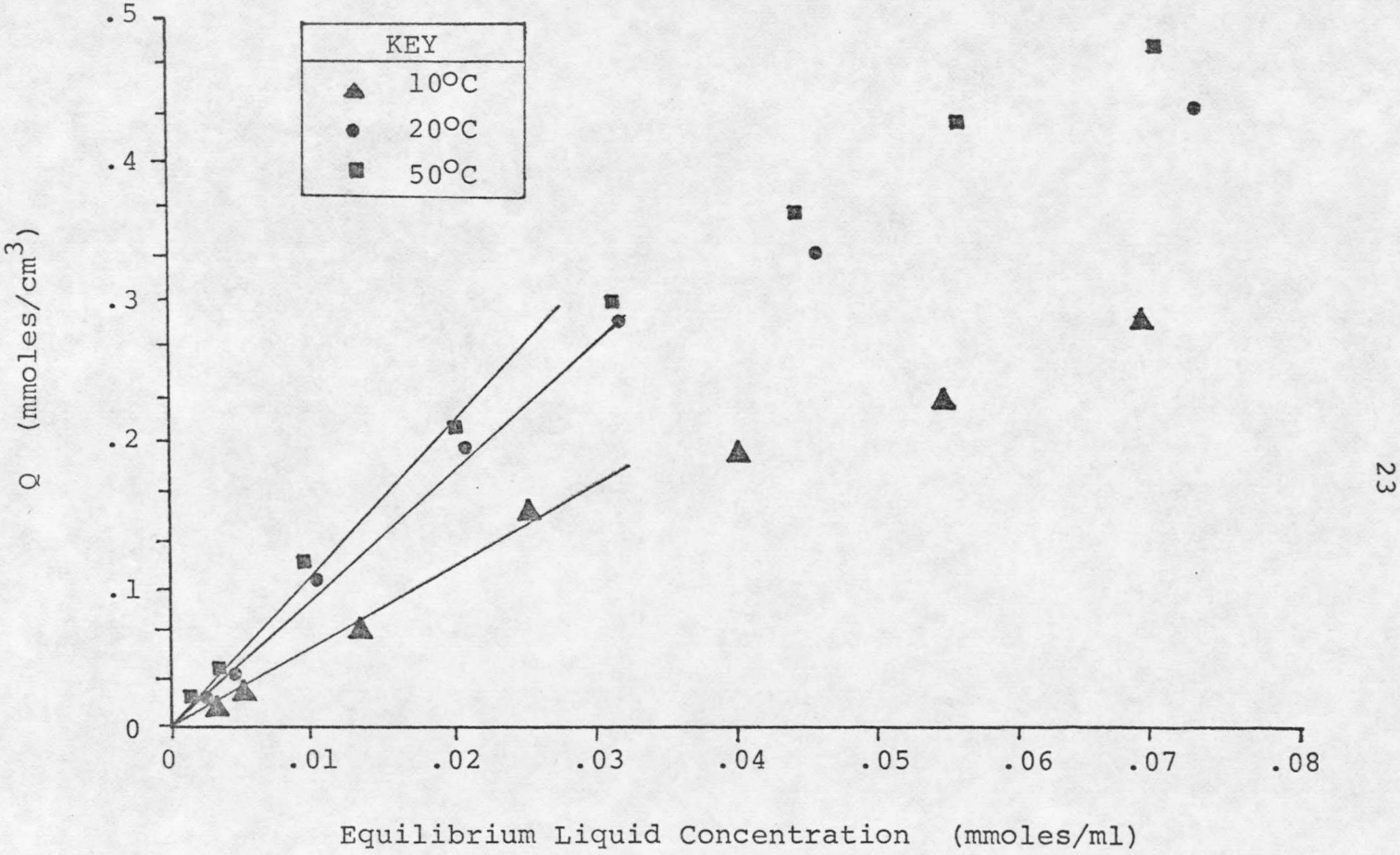


FIGURE 8: $CdCl_2$ EQUILIBRIUM CURVES

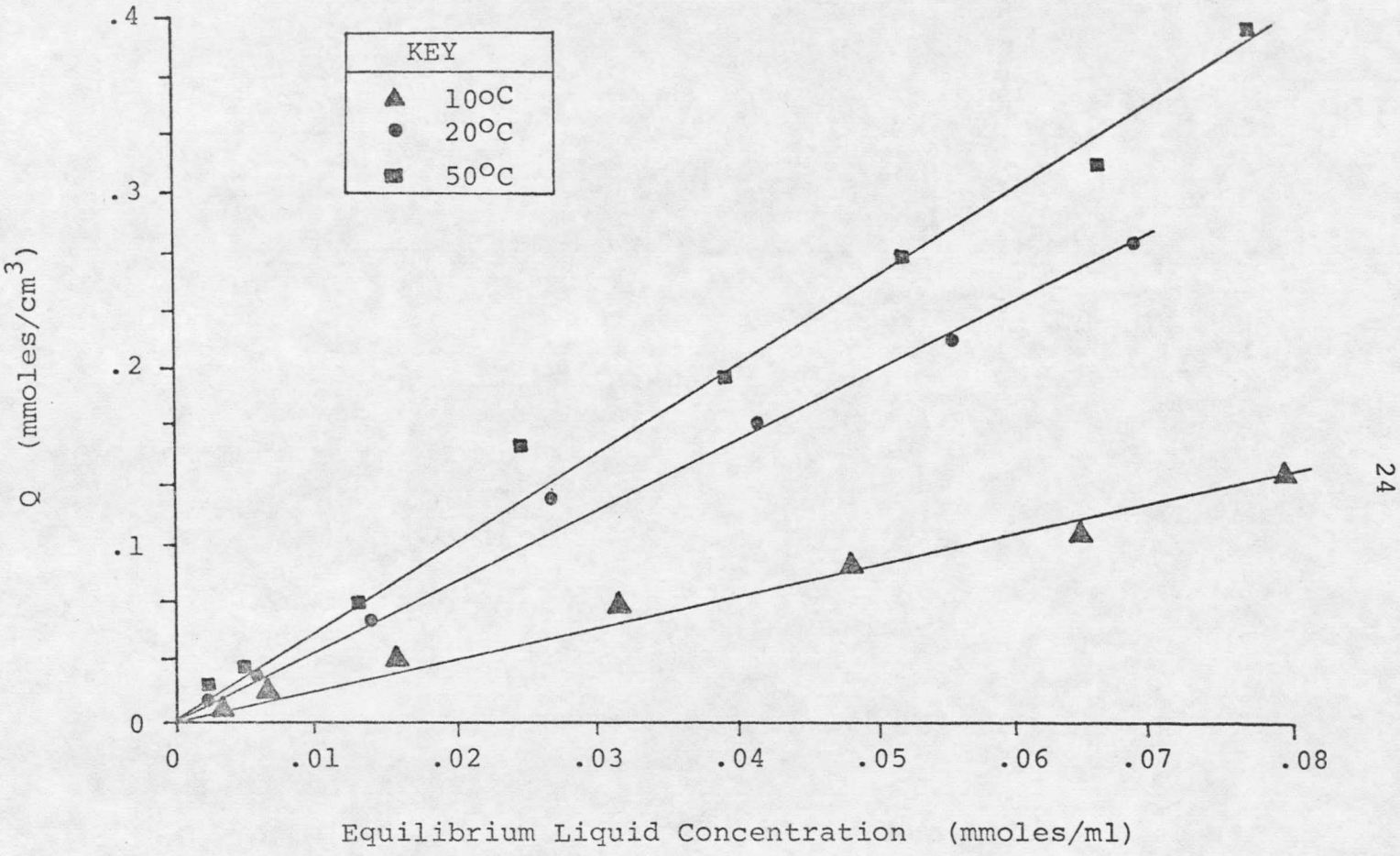


FIGURE 9: $ZnCl_2$ EQUILIBRIUM CURVES

TABLE I: EXPERIMENTAL EQUILIBRIUM CONSTANTS

CHEMICAL SPECIES	TEMPERATURE (°C)	K
$CaCl_2$	10	4.80
	20	3.50
	50	1.70
$Ca(NO_3)_2$	10	7.10
	20	9.10
	50	10.40
$CdCl_2$	10	6.00
	20	9.20
	50	10.10
$ZnCl_2$	10	1.80
	20	4.00
	50	5.10

The values of Q, however, do fall in the range experienced by Rice and Foo.

TABLE II: LIQUID AND SOLID PHASE CONCENTRATIONS FOR NaCl

EXPERIMENTAL		RICE AND FOO	
		UNRINSED	RINSED
C (mmoles/ml)	Q (mmoles/g)	Q (mmoles/g)	Q (mmoles/g)
.09	.12	.06	.19
.17	.22	.15	.31
.22	.31	.20	.38

Response Curve Analysis

In order to analyze the response curves they must be reduced to a finite series of data points. A typical raw response curve is shown in Appendix C. A total of 22 (time,voltage) coordinates are read off of each response curve. These points are generally evenly spaced except in key areas of the curve such as the start and the peak. The calibration curve is again used to convert the voltage readings into corresponding concentrations. After conversion the first 20 points are ready to be plotted.

As previously mentioned the tail of the response curve is the least accurate part. The reasons for this

include the fact that the voltage readings are changing much slower with time and at these longer times the voltage drift is more dominant. Another difficulty arises since after 20 minutes the tail has not dropped down to zero. To standardize the inaccuracies an exponential decay curve is used to predict concentration values at times greater than the first twenty data points. The equation for the exponential curve can be found by using the final two data points (Numbers 21 and 22). The equation has the form:

$$C = a \cdot \exp(-bt) \qquad \text{(II-2)}$$

By solving two equations simultaneously values of a and b can easily be calculated. Using the solved form of equation (II-2) points 21-100 can be generated. All of the data points are used to estimate the two experimental parameters. The graphs of the experimental response curves only show approximately the first 25 data points. These curves are shown later in Figures 10-20.

It has been previously shown that an equilibrium analysis was performed on $CaCl_2$, $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$. The analysis of the response curves for $CdCl_2$ and $ZnCl_2$, however, was dropped. The reason for this was the

radically different nature of their response curves. The differences included the peak height and the time to peak. A typical $CdCl_2$ or $ZnCl_2$ response curve had only 5% of the height of a normal calcium curve. This in itself was no big problem since it is possible to adjust the recorder's sensitivity. The big concern was the time necessary to reach a peak. For $CdCl_2$ and $ZnCl_2$ this peak occurred after about 30 minutes. $CaCl_2$ and $Ca(NO_3)_2$ showed peaks between 3-5 minutes. In order to obtain a good sketch of a $CdCl_2$ or $ZnCl_2$ response curve, at least an hour at a much more sensitive adjustment would be required. After an hour the drifting of the probe readings due to this high sensitivity would make the results totally useless. For these reasons it was decided to concentrate the effort on obtaining accurate response curves for $CaCl_2$ and $Ca(NO_3)_2$.

It has been mentioned several times that the method of weighted moments will be used to estimate the experimental parameters. A brief discussion of this method will now be given.

Method Of Weighted Moments

Using the method of weighted moments to estimate

parameters from response curves has been in wide use since the work of Kubin (11).

The simple ordinary k^{th} moment for a response curve describing $C(\theta,x)$ is defined as:

$$\mu_k = \int_0^\infty \theta^k \, C(\theta,x) d\theta \qquad \text{(II-3)}$$

Ordinary moments, however, lose accuracy in the tails of response curves. This problem can be lessened with the use of weighted moments. The k^{th} weighted moment is defined as:

$$M_k(p) = \int_0^\infty \theta^k \, e^{-p\theta} \, C(\theta,x) d\theta \qquad \text{(II-4)}$$

where p is the weighting factor. By letting p approach zero the weighted moment reduces to the simple ordinary moment.

By using equation (II-4) the zeroth weighted moment is found to be:

$$M_o(p) = \int_0^\infty e^{-p\theta} \, C(\theta,x) d\theta \qquad \text{(II-5)}$$

This integral is also by definition the LaPlace Transform of $C(\theta,x)$. Using the derivation in equations (I-6) through (I-10) it is easy to note the following equality:

$$M_o(p) = C_i(p,x) = \exp\left(\frac{-Kpx}{1+\zeta p}\right) \qquad \text{(II-6)}$$

Higher level moments can be constructed by using the following recurrence relationship:

$$\frac{dM_k}{dp} = -M_{k+1} \qquad \text{(II-7)}$$

So if the zeroth weighted moment is represented by equation (II-5) then the first weighted moment is:

$$M_1(p) = \left[\frac{Kx}{(1+\zeta p)^2}\right] \exp\left(\frac{-Kpx}{1+\zeta p}\right) \qquad \text{(II-8)}$$

By defining $K_1(p)$ as the ratio of the first and zeroth moments the following is obtained:

$$K_1(p) = \frac{M_1(p)}{M_o(p)} = \frac{Kx}{(1+\zeta p)^2} \qquad \text{(II-9)}$$

This has the advantage of eliminating the exponential term. The second moment can now be derived using the first weighted moment:

$$M_2(p) = \left[\frac{(Kx)^2}{(1+\zeta p)^4} + \frac{2(1+\zeta p)Kx\zeta}{(1+\zeta p)^4}\right] \exp\left(\frac{-Kpx}{1+\zeta p}\right) \qquad \text{(II-10)}$$

Again dividing through by $M_o(p)$ yields:

$$\frac{M_2(p)}{M_o(p)} = \frac{(Kx)^2 + 2(1+\xi p)Kx\xi}{(1+\xi p)^4} \qquad \text{(II-11)}$$

$K_2(p)$ is defined as:

$$K_2(p) = \frac{M_2(p)}{M_o(p)} - \left[\frac{M_1(p)}{M_o(p)}\right]^2 \qquad \text{(II-12)}$$

Dividing both sides of this equation by $K_1(p)$ produces:

$$\frac{K_2(p)}{K_1(p)} = \frac{M_2/M_o - (M_1/M_o)^2}{M_1/M_o} \qquad \text{(II-13)}$$

This can be expressed more simply as:

$$\frac{K_2(p)}{K_1(p)} = \frac{2\xi}{1+\xi p} \qquad \text{(II-14)}$$

The rate parameter, ξ, can now be solved for:

$$\xi = \frac{K_2(p)/K_1(p)}{2 - pK_2(p)/K_1(p)} \qquad \text{(II-15)}$$

By substituting the value of ξ into equation (II-9) a corresponding value of Kx can be calculated.

Sometimes a more useful approach is to use moments about the mean. The k^{th} moment about the mean is defined as:

$$M_k' = \int_0^\infty C(\theta) \left[\theta - \frac{M_1(p)}{M_o(p)}\right]^k \exp(-p\theta)d\theta \qquad \text{(II-16)}$$

It can then be shown that:

$$K_2(p) = \frac{M_2'(p)}{M_o(p)} \qquad \text{(II-17)}$$

From this point ζ and Kx can again be calculated using equations (II-15) and (II-9), respectively.

The only step left is to decide upon a value for the weighting factor, p. Anderssen and White (12) suggest that the optimum weighting is simply twice the average order moment divided by the response curve rise time. This method of finding the weighting factor is used in this research.

The average order moment is one, since the only moments used in the calculations have orders of zero, one, and two. Table III summarizes the optimum weighting factors used for each response curve.

Calculation of Kx and ζ

The calculation of Kx and ζ was done using a computer program. A listing of this program is given in Appendix E. The program can be divided into six sections. These

TABLE III: OPTIMUM WEIGHTING FACTORS

CHEMICAL SPECIES	TEMPERATURE (^{o}C)	RISE TIME (sec)	p_{opt} (sec^{-1})
$CaCl_2$	10	110	.0182
	10	138	.0145
	20	110	.0182
	20	130	.0154
	50	60	.0330
	50	65	.0310
$Ca(NO_3)_2$	10	90	.0220
	10	125	.0160
	20	135	.0148
	20	160	.0125
	50	50	.0400

are:

(1) Input data: All 22 (time,concentration) coordinates are input. Values for the column residence time and weighting factor are also required.

(2) Exponential decay: The exponential decay curve is calculated and data points 21-100 are generated.

(3) Integrate response curves: The program numerically integrates the curve to obtain the total area under it.

(4) Normalization: The area under the curve is normalized to unity.

(5) Moments: The moment equations are evaluated and equations (II-15) and (II-9) are solved.

(6) Output: Values for the moments plus Kx and ξ are printed.

Table IV summarizes the values of Kx and ξ estimated from the response curves.

The final step is to generate a theoretical curve to compare to the experimental data. This can easily be done by substituting the experimental values for Kx and ξ into

equation (I-9).

The curves which are generated by equation (I-9) are shifted to the left or simply towards t=0 by the quantity z/u, the fluid residence time. In order to compare this curve to the experimental data the residence time must be added back on.

Also from equation (I-9) it can be seen that a value of $I_1(x)$ is required. A polynomial approximation of this Bessel Function is used in the calculations (13). These calculations are carried out using another computer program. The listing is included in Appendix E. The theoretical curves are plotted on the same graphs as the experimental data. All of these curves are shown in Figures 10-20.

By inspection the fit between the experimental response curves and the curves generated from the model of the system is good. The best results appear to occur at $10^{o}C$. The correspondence is poor for the tails of the response curves. This, however, is an inherent problem when fitting experimental and theoretical response curves.

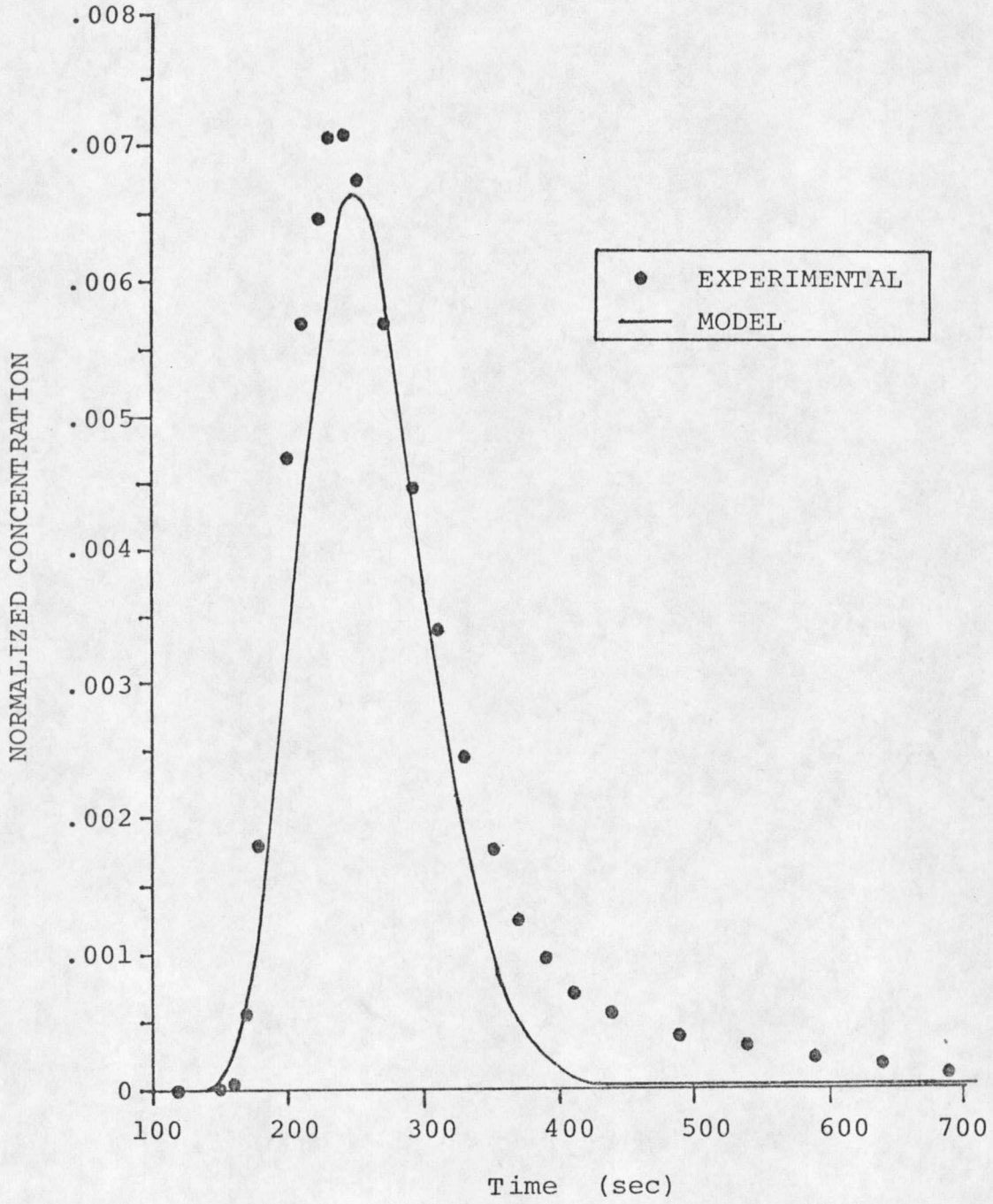


FIGURE 10: $CaCl_2$ ($10^{o}C$) RESPONSE CURVES (TRIAL 1)

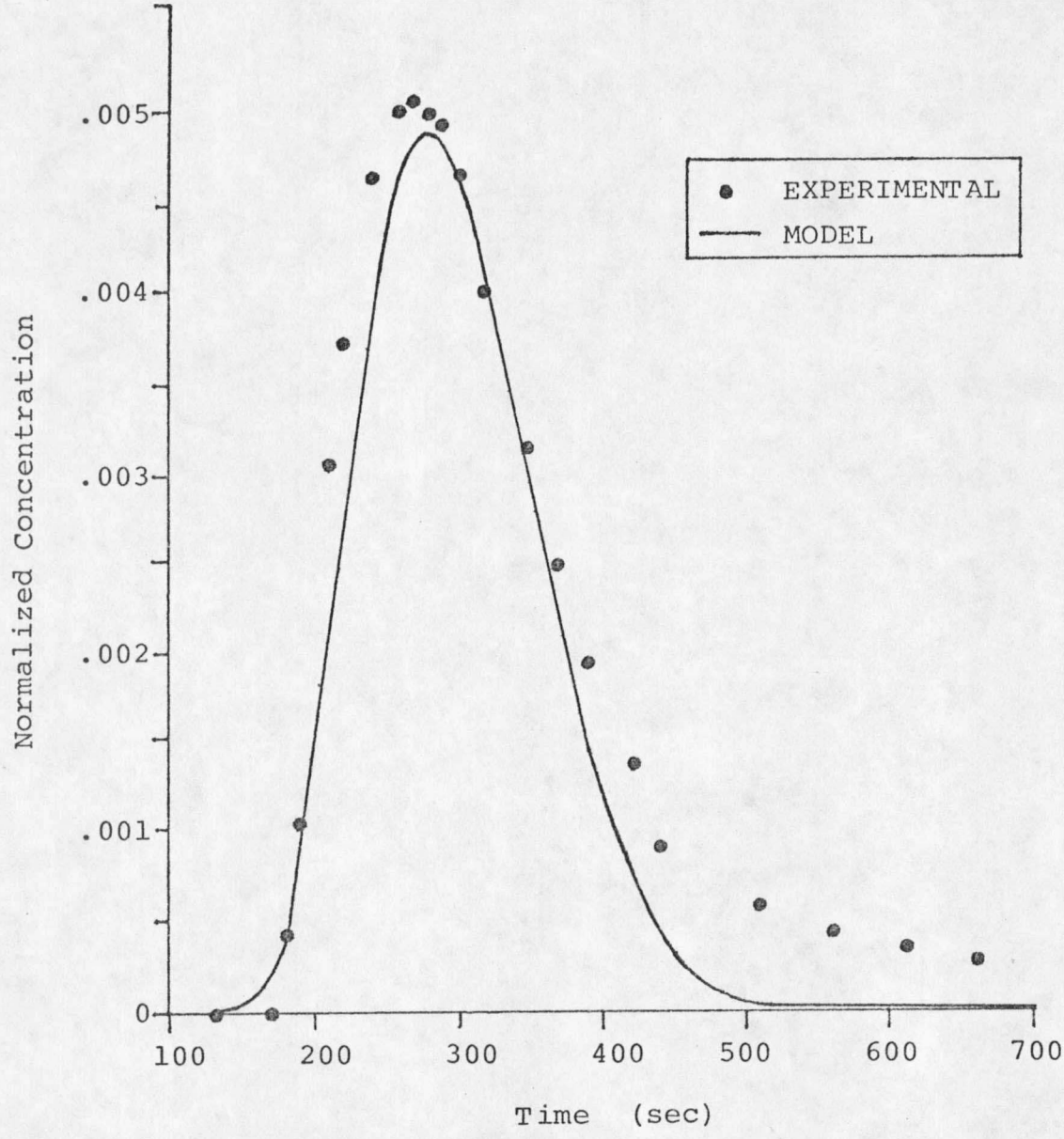


FIGURE 11: $CaCl_2$ (10°C) RESPONSE CURVES (TRIAL 2)

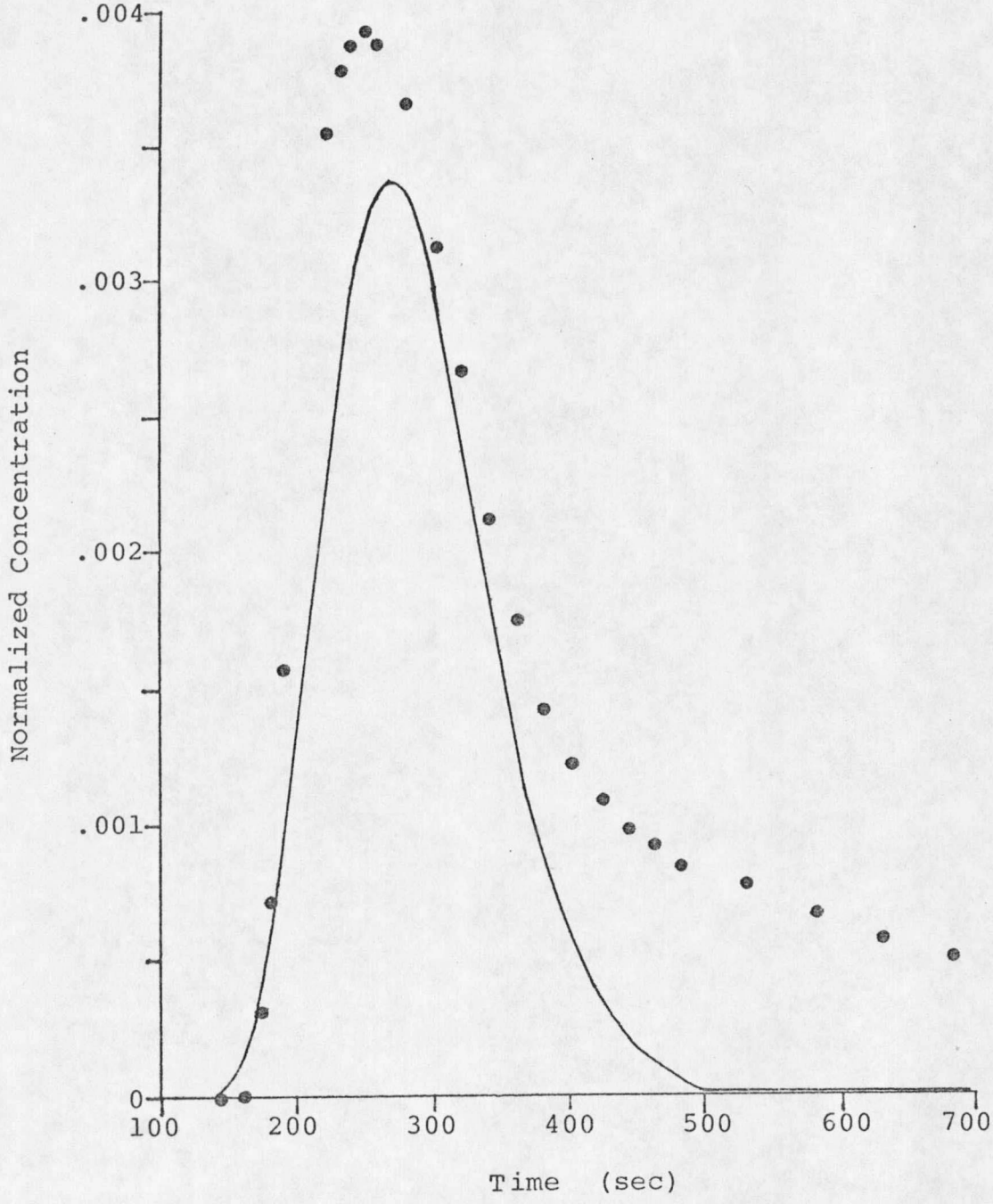


FIGURE 12: $CaCl_2$ (20°C) RESPONSE CURVES (TRIAL 1)

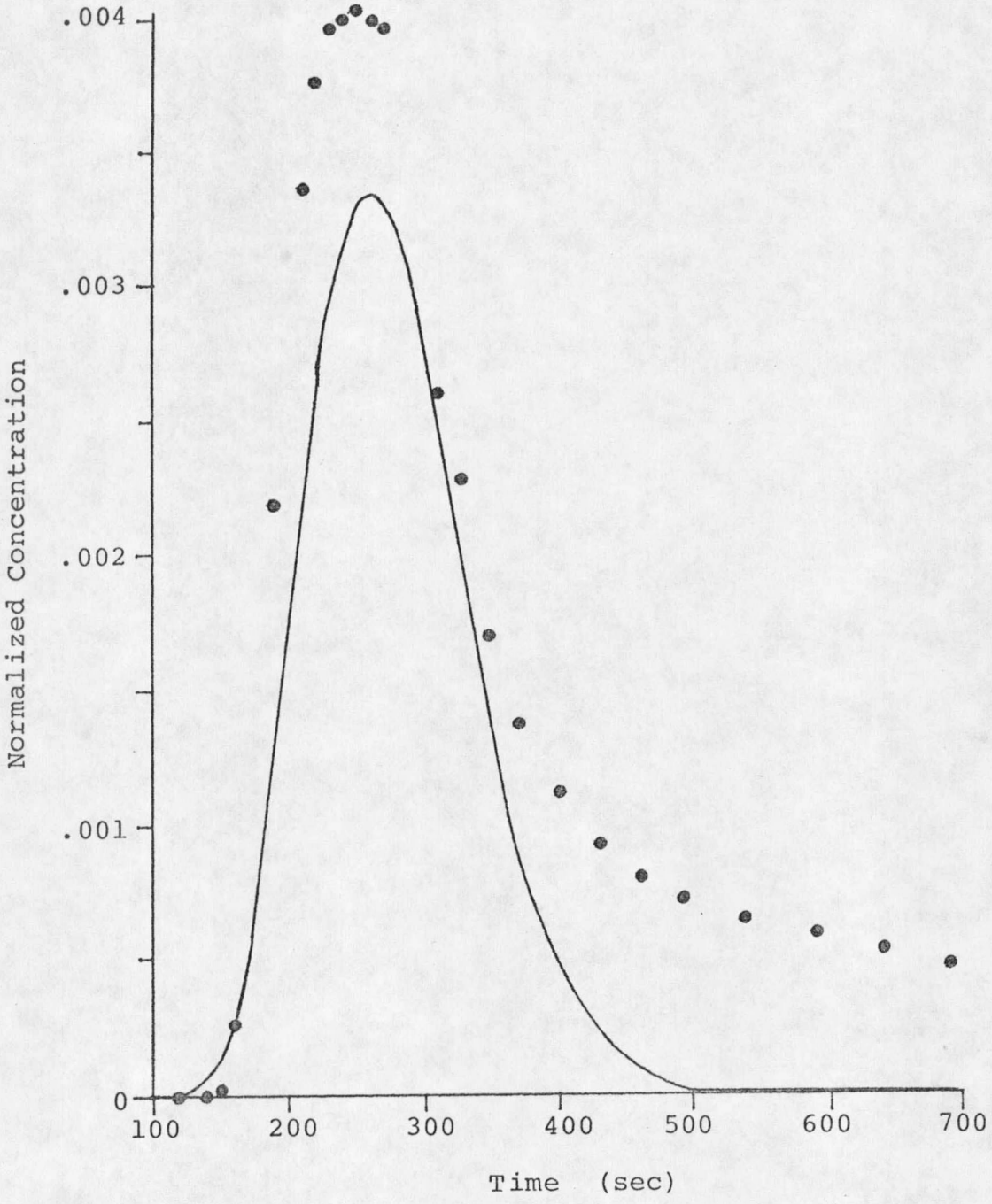


FIGURE 13: $CaCl_2$ (20°C) RESPONSE CURVES (TRIAL 2)

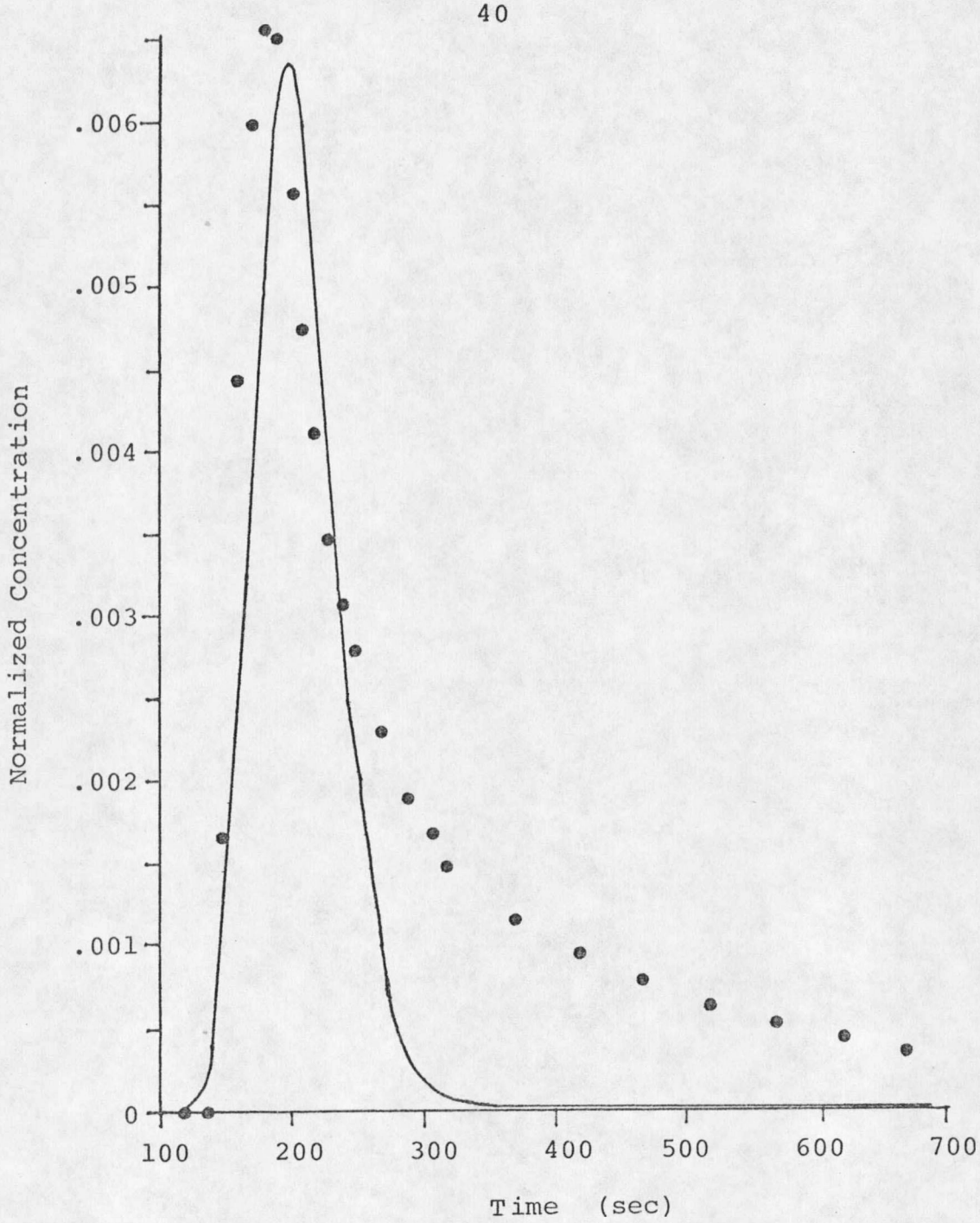


FIGURE 14: $CaCl_2$ (50°C) RESPONSE CURVES (TRIAL 1)

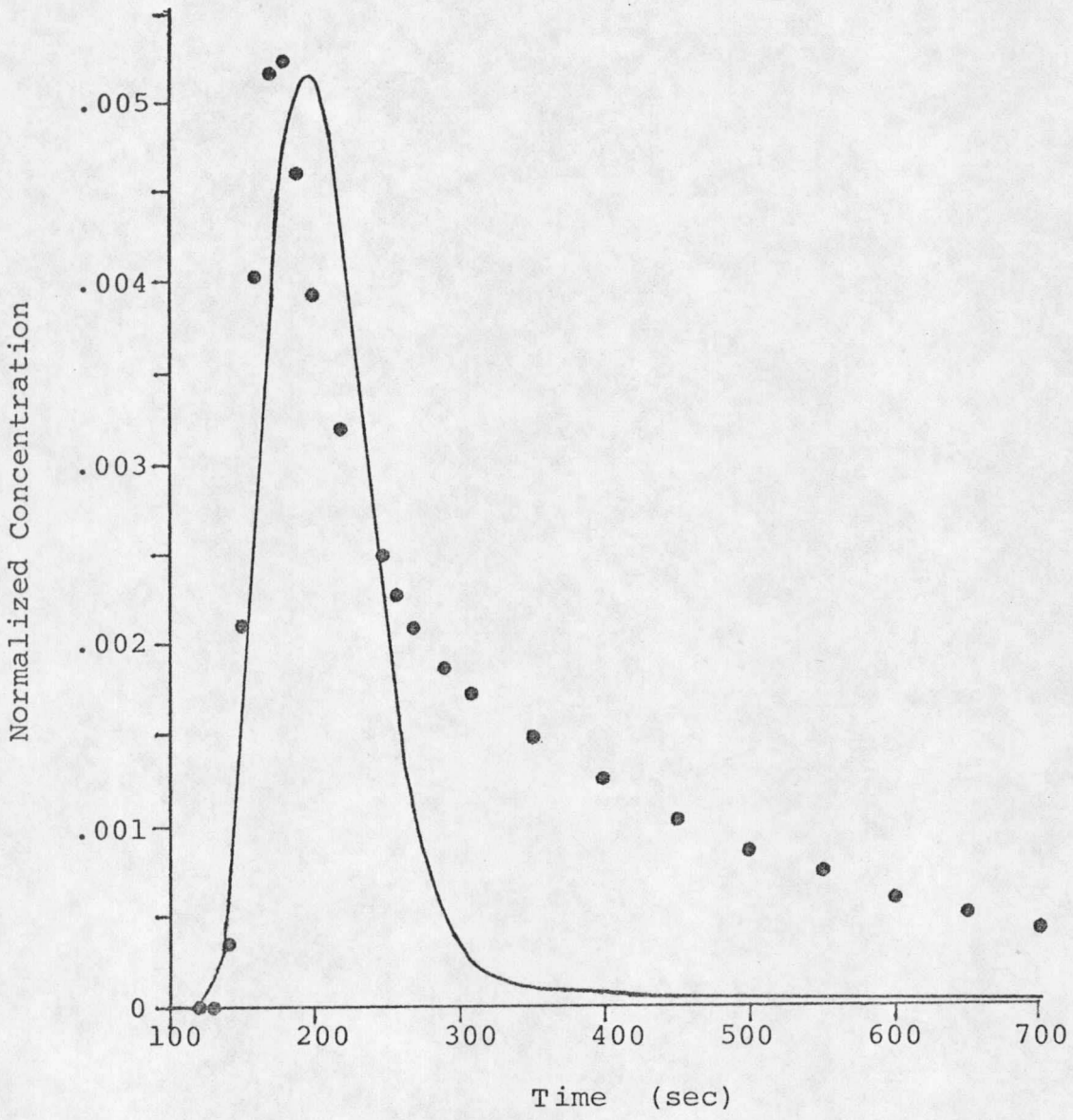


FIGURE 15: $CaCl_2$ (50°C) RESPONSE CURVES (TRIAL 2)

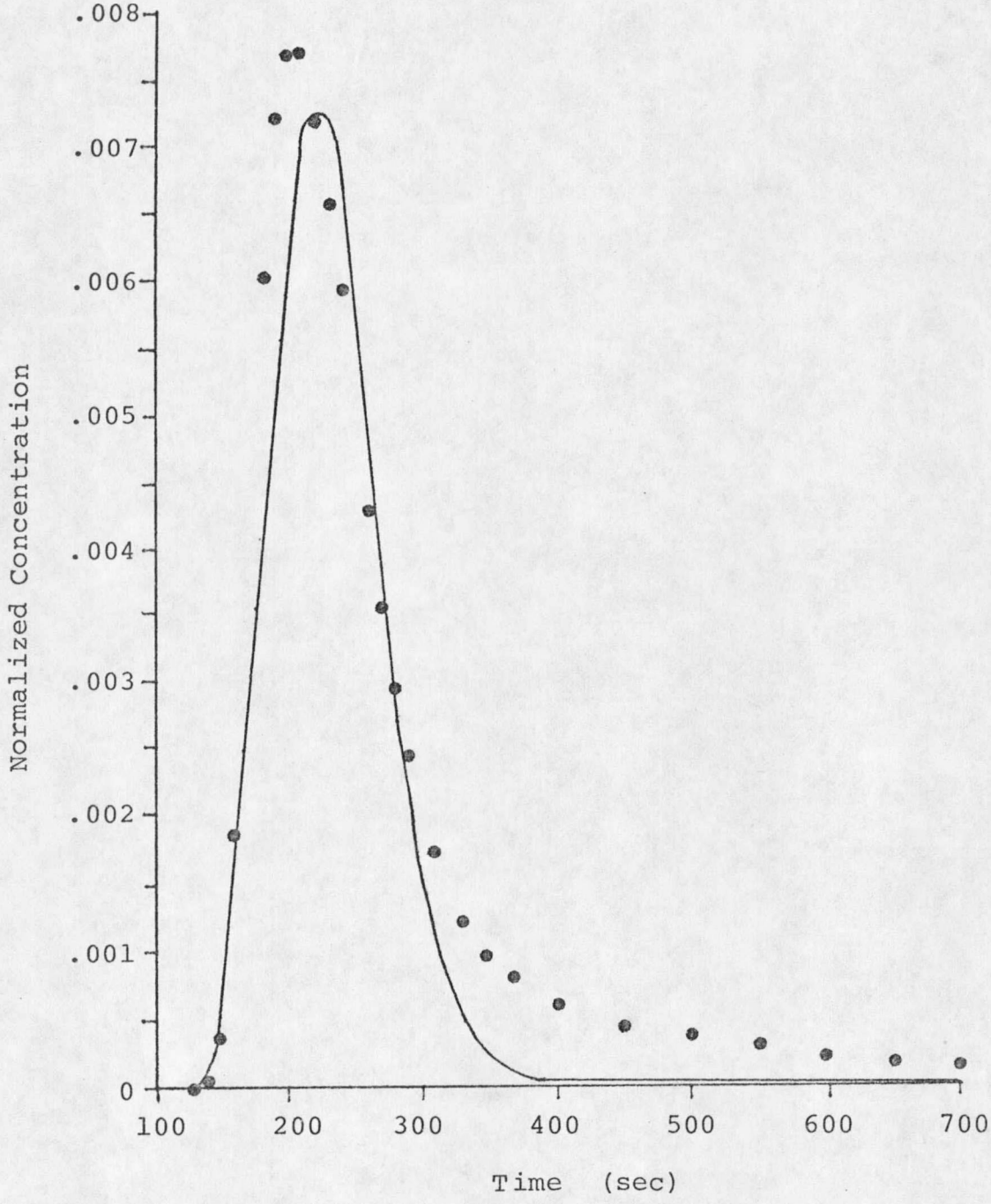


FIGURE 16: $Ca(NO_3)_2$ ($10^{o}C$) RESPONSE CURVES (TRIAL 1)

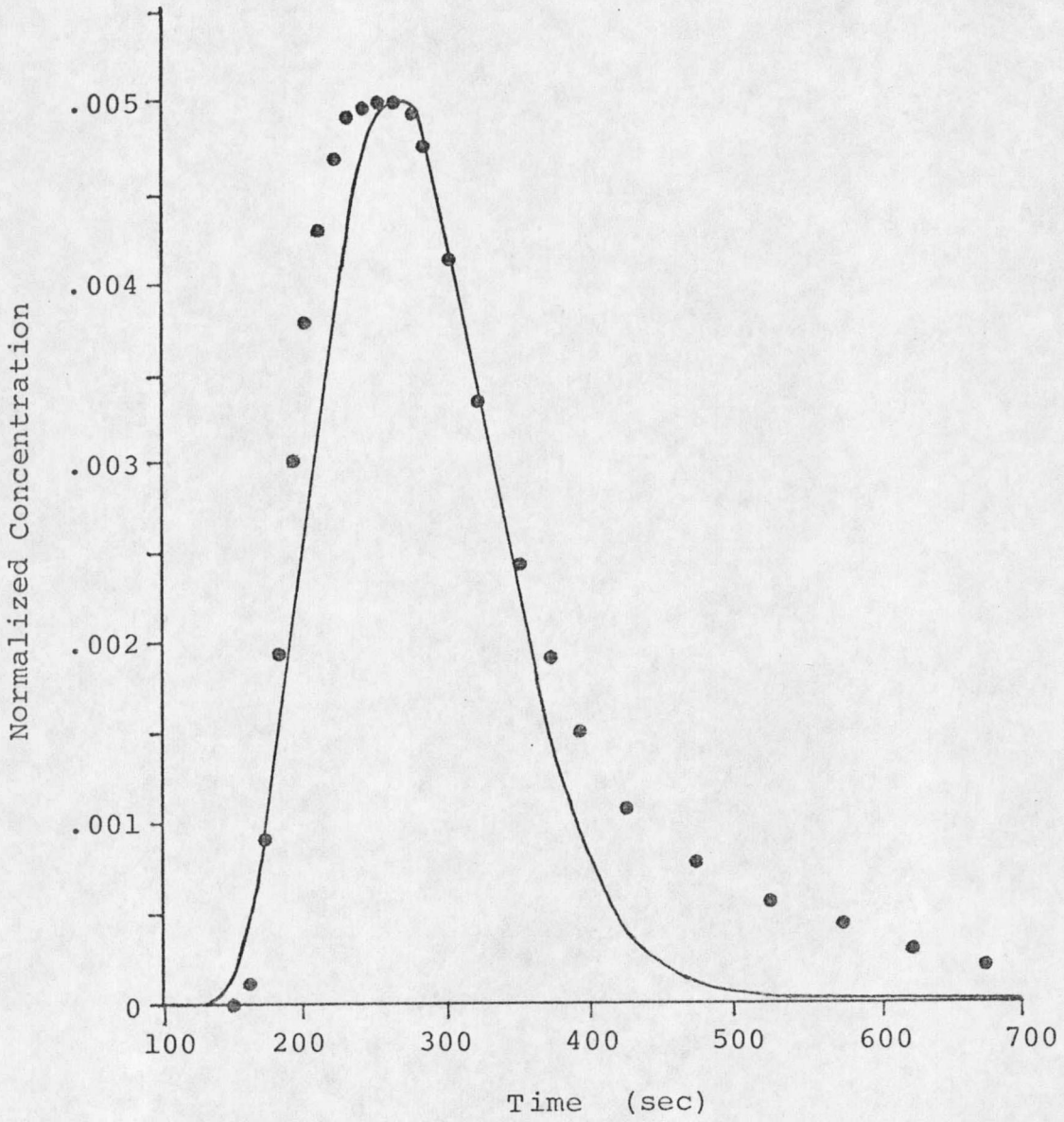


FIGURE 17: $Ca(NO_3)_2$ ($10^{o}C$) RESPONSE CURVES (TRIAL 2)

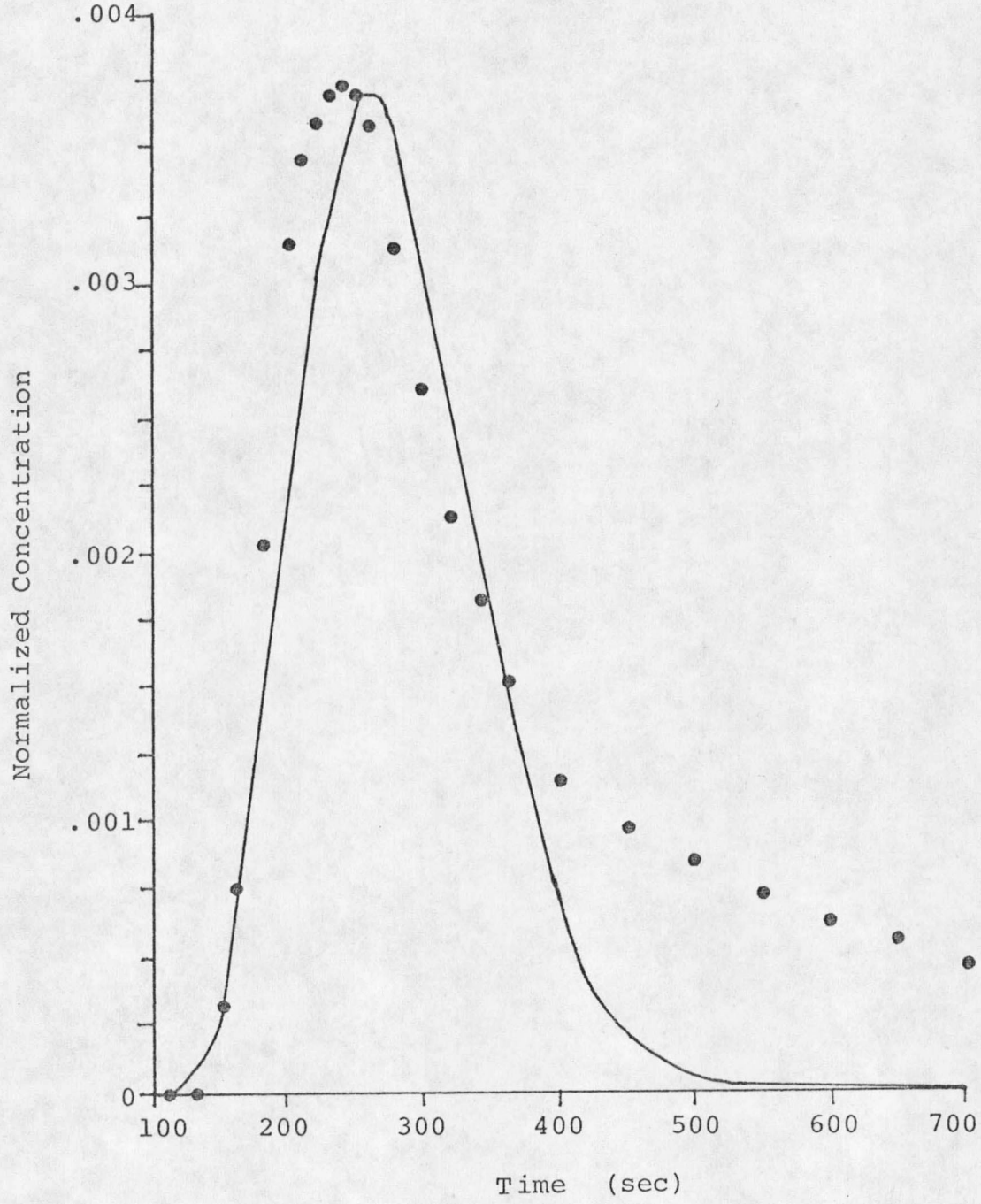


FIGURE 18: $Ca(NO_3)_2$ (20°C) RESPONSE CURVES (TRIAL 1)

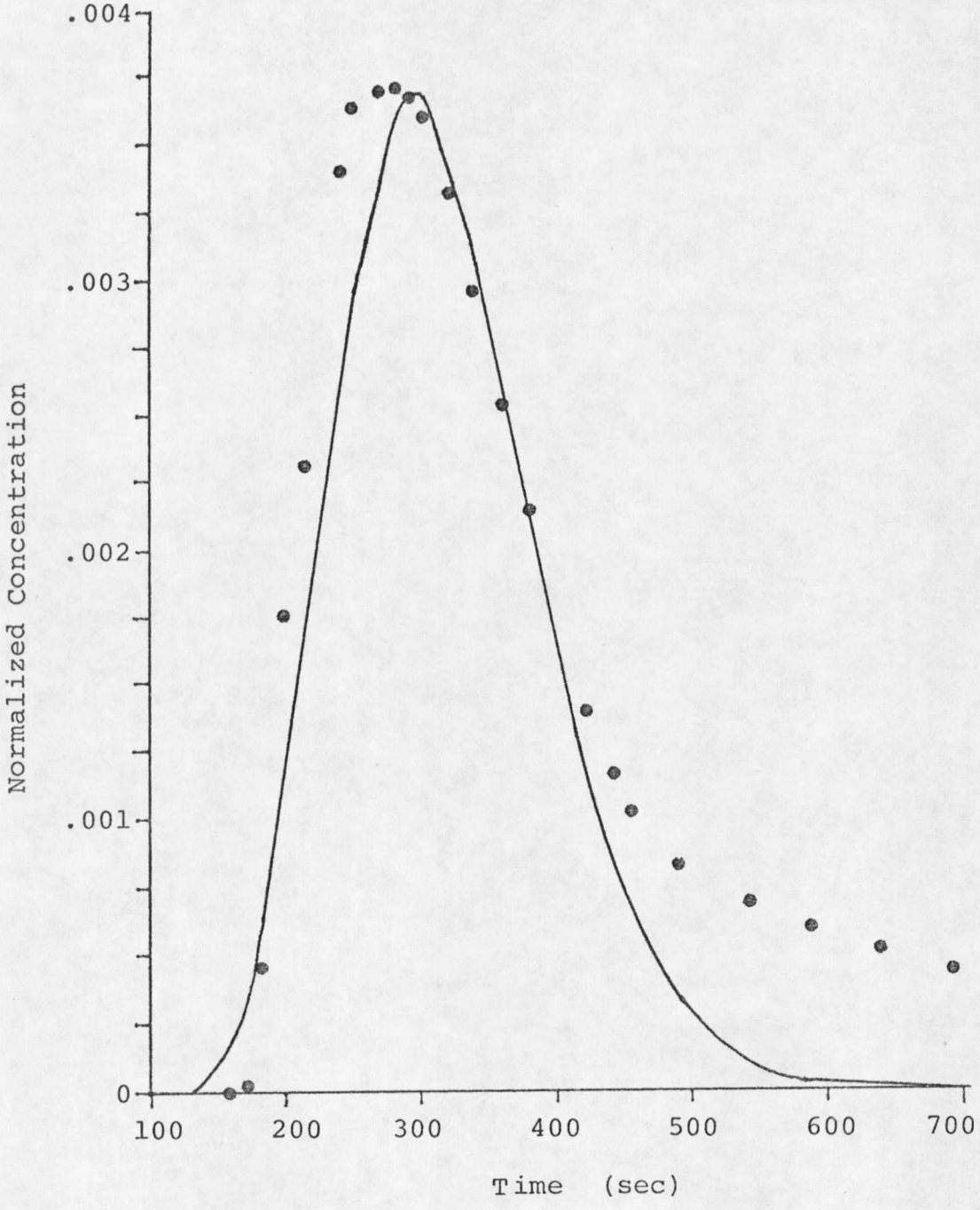


FIGURE 19: $Ca(NO_3)_2$ (20°C) RESPONSE CURVES (TRIAL 2)

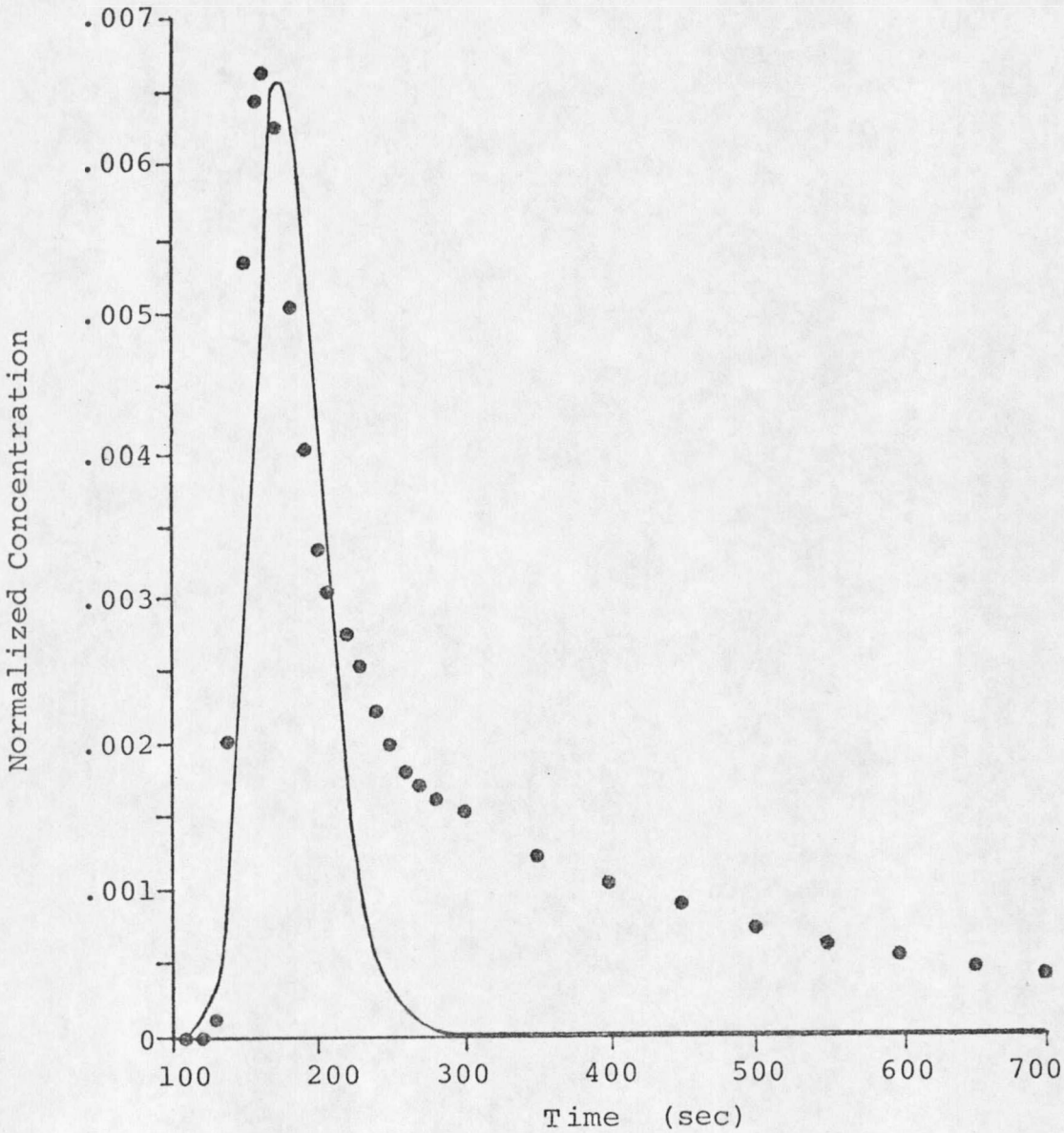


FIGURE 20: $Ca(NO_3)_2$ (50°C) RESPONSE CURVES (TRIAL 1)

TABLE IV: EXPERIMENTAL VALUES FOR Kx AND ξ FROM THE RESPONSE CURVES

CHEMICAL SPECIES	TEMPERATURE (°C)	Kx (sec)	ξ (sec)
$CaCl_2$	10	140	7.5
		169	11.4
	20	148	13.0
		159	24.0
	50	84	6.0
		91	7.0
$Ca(NO_3)_2$	10	114	7.3
		153	12.2
	20	174	13.0
		198	14.5
	50	71	4.5

TABLE V: EXPERIMENTAL VALUES OF Kx FOR $CaCl_2$ BASED ON THE EQUILIBRIUM CONSTANT

TEMPERATURE (^oC)	INTERSTITIAL VELOCITY (cm/sec)	x (sec)	Kx (sec)
10	.130	214.5	1030
	.118	236.3	1134
20	.111	251.2	879
	.130	214.5	750
50	.130	214.5	365
	.136	205.0	349

TABLE VI: EXPERIMENTAL VALUES OF Kx FOR $Ca(NO_3)_2$ BASED ON THE EQUILIBRIUM CONSTANT

TEMPERATURE (^oC)	INTERSTITIAL VELOCITY (cm/sec)	x (sec)	Kx (sec)
10	.136	205.0	1496
	.124	224.8	1596
20	.148	188.4	1714
	.130	214.5	1952
50	.142	196.3	2041

TABLE VII: COMPARISON OF Kx VALUES FROM THE EQUILIBRIUM ANALYSIS AND RESPONSE CURVES FOR $CaCl_2$

TEMPERATURE (^oC)	EQUILIBRIUM ANALYSIS	RESPONSE CURVE
10	1030 1134	140 169
20	879 750	148 159
50	365 349	84 91

TABLE VIII: COMPARISON OF Kx VALUES FROM THE EQUILIBRIUM ANALYSIS AND RESPONSE CURVES FOR $Ca(NO_3)_2$

TEMPERATURE (^oC)	EQUILIBRIUM ANALYSIS	RESPONSE CURVE
10	1496 1596	114 153
20	1714 1952	174 198
50	2041	71

Comparison of Kx Values From the Equilibrium Analysis And the Response Curves

As a check on Kx a second value can be calculated directly from the equilibrium constant. This simply involves multiplying K by x where:

$$x = \frac{z}{\eta^u} \qquad \text{(II-18)}$$

Tables V and VI summarize the values of Kx determined using the equilibrium analysis. Tables VII and VIII compare the values of Kx determined by the equilibrium approach and from the response curves.

There are two discrepancies that are evident in Tables VII and VIII. These are:

(1) There is a wide difference in magnitude of Kx between the two methods.

(2) The values of Kx from the equilibrium analysis either steadily increase or decrease while those from the response curves show a distinct peak at 20°C.

The difference in magnitude can be explained by examining the equilibrium curves, especially those of $CaCl_2$. The equilibrium studies performed in this re-

search used a fairly wide concentration range. The voltage readings at the more dilute concentrations were not very accurate so it was not possible to base the slope on these points alone. There, however does seem to be a trend that these points are lower.

In order to explain the peak at 20°C a second model will be discussed.

Application of the Dispersion Model

The justification in applying this model is the fact that the column residence times in this project were far less than those in similar research, such as Foo (14). This means that the particle diffusion which is dominant in the first model did not have the time necessary to fully develop. Axial dispersion is assumed to be the most dominant form of mass transfer in the dispersion model.

The derivation of the dispersion model is fairly simple, however, it will not be given at this time. For easy reference it has been included in Appendix D.

Wen and Fan (15) have listed response curves for pulse injections into packed columns assuming that the dispersion model is valid. The curves are generated

based upon a parameter M where:

$$M = \frac{uz}{2E_z} \qquad \text{(II-19)}$$

E_z is the axial dispersion coefficient. The response curves are reproduced in Figure 21.

These response curves were then treated exactly as if they were experimental response curves. Data points were again read off of each curve. These points were then input into the computer program to estimate values for Kx and $\mathcal{E}$ in which to compare in a purely qualitative manner to the experimental values.

Table IX shows the values of Kx and $\mathcal{E}$ estimated for these curves. Due to a lack of accuracy in this estimation no direct numerical comparisons are possible. Only trends such as the direction of increasing magnitude can be studied. Note, however, that the values of Kx do not steadily increase or decrease but rather show a relative minimum and maximum.

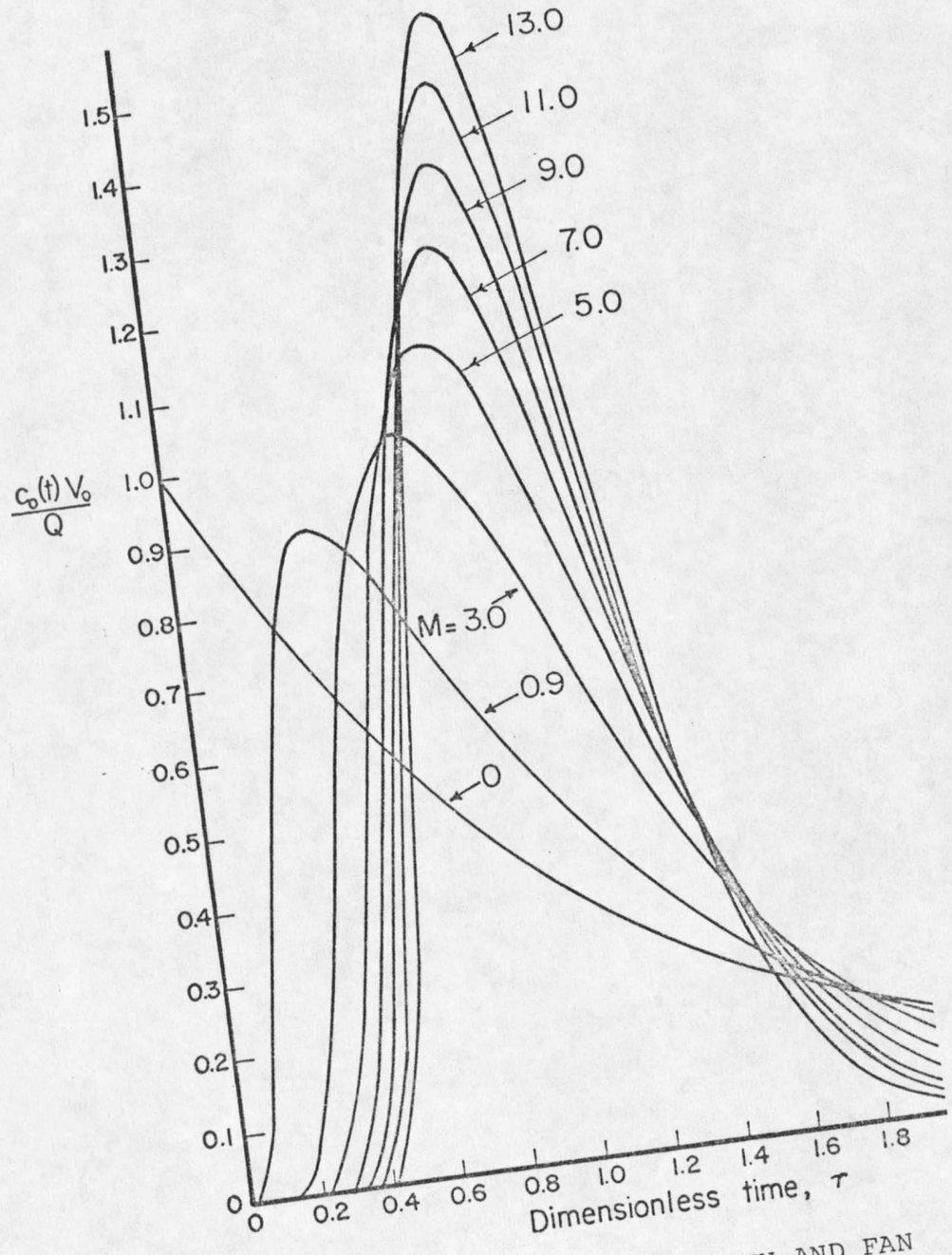


FIGURE 21: RESPONSE CURVES OF WEN AND FAN (15)

TABLE IX: VALUES OF Kx AND $\mathcal{E}$ FROM THE DISPERSION MODEL CURVES

M	Kx (sec)	$\mathcal{E}$ (sec)
0.9	0.84	0.15
3.0	0.93	0.10
5.0	0.98	0.08
7.0	0.92	0.06
9.0	0.98	0.05
11.0	1.00	0.04

CONCLUSIONS

The following conclusions can be drawn from this research project:

1. The equilibrium constants decrease with rising temperature for $CaCl_2$ but increase for $Ca(NO_3)_2$, $CdCl_2$, and $ZnCl_2$. The reason for this is not clear. Similar studies in the literature all found K to decrease as the temperature is increased.

2. Based upon the equilibrium graphs, especially of $CaCl_2$, it appears that an equilibrium analysis performed at lower concentrations would yield smaller equilibrium constants.

3. The model of the adsorption system fits the experimental results best at $50^{o}C$. Overall the curves based upon the model of the system and Anderssen and White's optimum weighting factor compare fairly well with the experimental results.

4. The values of Kx estimated by the equilibrium analysis show no correlation to the values found using the response curves. The main reason for this is inaccurate equilibrium constants. As mentioned earlier performing the equilibrium studies at more dilute con-

centrations would lower the equilibrium constants. This would also decrease the values for Kx, making them more comparable with those obtained from the response curves.

5. The values for Kx determined from the response curves show a maximum value at 20°C. The average values of Kx for $CaCl_2$ do drop slightly but this averaging cannot be justified. This maximum value disagrees totally with the results of the equilibrium analysis.

6. The use of the dispersion model to analyze similar response curves produced values of Kx which did not steadily increase or decrease. There is a range of curves for which a maximum value of Kx can be obtained. This indicates that the dispersion model may have some application in this particular system. No experimentation to calculate dispersion coefficients was performed so no exact parameter values can be found. The only thing that can be concluded is that it is possible in the dispersion model for the Kx values to have a maximum.

FUTURE EXPERIMENTATION

Much more research along the basic lines of this project is needed. There are three areas of this research which could be improved. The first two would require more sophisticated equipment. These are:

(1) The equilibrium analysis should be performed at more dilute concentrations. This would give a more accurate estimation of the equilibrium constants.

(2) The recording of the exiting concentrations should be taken for a longer period of time.

(3) A longer column with the same interstitial velocity should be used. This would give the particle diffusion more time to develop. The fit between the experimental and theoretical response curves would then be likely to improve.

Another area of work that could be investigated concerns the estimation of the solid diffusivity, D_s, and the film coefficient, h. This would enable a direct calculation of ξ from data in which to compare to the result obtained from the response curves.

More work is needed to compare the effects of varying the anion of the inorganic salt. Also the effects of the

ionic radius, molecular weight, and charges on the anion and cation need to be more directly correlated.

Only one run was made per batch of resin in this research. It could be very useful to see what the effects of making several runs per batch are. The washing or regeneration of the resin could also be investigated.

NOMENCLATURE

NOMENCLATURE

Symbol	Definition	Units
a	Variable for exponential decay curve	mmoles/ml
a_o	Variable for parabolic solid phase composition profiles	$mmoles/cm^3$
a_2	Variable for parabolic solid phase composition profiles	$mmoles/cm^5$
b	Variable for exponential decay curve	sec^{-1}
C	Concentration	mmoles/ml
C_o	Initial Concentration	mmoles/ml
D_s	Solid diffusivity	cm^2/sec
E	General dispersion coefficient	cm^2/sec
E_r	Radial dispersion coefficient	cm^2/sec
E_z	Axial dispersion coefficient	cm^2/sec
h	Film coefficient	cm^2/sec
K	Equilibrium constant	dimensionless
Kx	Equilibrium parameter	sec
K_1	Ratio of first to zeroth weighted moments	sec
K_2	Ratio of second to zeroth weighted moments	sec^2

Symbol	Definition	Units
M	Parameter from Wen and Fan response curves	dimensionless
M_k	k^{th} weighted moment about the origin	sec^{k+1}
M'_k	k^{th} weighted moment about the mean	sec^{k+1}
p	Weighting factor	sec^{-1}
Q	Solid phase composition	$mmoles/cm^3$
q	Solid phase composition	$mmoles/cm^3$
R	Particle radius	cm
r	Radial coordinate	cm
s	Kx/ξ	dimensionless
t	Time	sec
u	Interstitial fluid velocity	cm/sec
V	Volume of inorganic solution	cm^3
V_m	Volume of moisture in resin	cm^3
V_0	Volume of packed column	cm^3
w	Mass of dry resin	grams
x	$z/\eta u$	sec
z	Packed bed height	cm
ϵ	Bed void fraction	dimensionless

Symbol	Definition	Units
η	$\epsilon/1-\epsilon$	dimensionless
θ	$t - z/u$	sec
ξ	Rate parameter	sec
τ	θ/ξ	dimensionless
μ_k	k^{th} simple ordinary moment	sec^{k+1}
β	Dummy variable of integration	dimensionless
ρ_p	Particle density	grams/ml
ρ_s	Dry compressed particle density	grams/ml

APPENDICES

APPENDIX A

TABLE A-I: $CaCl_2$ EQUILIBRIUM DATA

TEMP. (°C)	CALIBRATION SOLUTION CONCENTRATION (mmoles/ml)	EQUILIBRIUM LIQUID CONCENTRATION (mmoles/ml)	Q (mmoles/cm^3)
10	0	0	0
	.0040	.0029	.0108
	.0080	.0060	.0194
	.0200	.0152	.0464
	.0396	.0270	.1280
	.0591	.0400	.1950
	.0784	.0530	.2610
	.0976	.0660	.3270
	.1165	.0800	.3780
20	0	0	0
	.0040	.0028	.0115
	.0080	.0060	.0195
	.0120	.0100	.0176
	.0159	.0120	.0380
	.0198	.0162	.0329
	.0392	.0305	.0842
	.0583	.0430	.1540
	.0769	.0570	.2030
	.0952	.0700	.2600
	.1043	.0770	.2830
50	0	0	0
	.0040	.0030	.0095
	.0080	.0070	.0080
	.0120	.0110	.0062
	.0159	.0145	.0092
	.0198	.0175	.0178
	.0392	.0330	.0550
	.0583	.0490	.0838
	.0769	.0640	.1190

TABLE A-II: $Ca(NO_3)_2$ EQUILIBRIUM DATA

TEMP. (°C)	CALIBRATION SOLUTION CONCENTRATION (mmoles/ml)	EQUILIBRIUM LIQUID CONCENTRATION (mmoles/ml)	Q (mmoles/cm^3)
10	0	0	0
	.0040	.0030	.0097
	.0080	.0045	.0367
	.0198	.0120	.0812
	.0392	.0240	.1600
	.0583	.0350	.2490
	.0769	.0500	.2860
	.0952	.0620	.3560
	.1132	.0770	.3880
20	0	0	0
	.0040	.0020	.0211
	.0080	.0040	.0424
	.0198	.0110	.0931
	.0392	.0210	.1947
	.0583	.0320	.2840
	.0769	.0450	.3450
	.0952	.0590	.3920
	.1132	.0720	.4490
50	0	0	0
	.0040	.0025	.0154
	.0080	.0040	.0424
	.0198	.0100	.1040
	.0392	.0200	.2070
	.0583	.0300	.3080
	.0769	.0440	.3570
	.0952	.0570	.4160
	.1132	.0690	.4850

TABLE A-III: $CdCl_2$ EQUILIBRIUM DATA

TEMP. (°C)	CALIBRATION SOLUTION CONCENTRATION (mmoles/ml)	EQUILIBRIUM LIQUID CONCENTRATION (mmoles/ml)	Q (mmoles/cm^3)
10	0	0	0
	.0040	.0025	.0153
	.0080	.0050	.0310
	.0198	.0130	.0698
	.0392	.0250	.1498
	.0583	.0400	.1890
	.0769	.0550	.2260
	.0952	.0690	.2730
	.1132	.0860	.2790
20	0	0	0
	.0040	.0015	.0270
	.0080	.0045	.0370
	.0198	.0100	.1040
	.0392	.0210	.1947
	.0583	.0320	.2840
	.0769	.0460	.3330
	.1132	.0730	.4370
50	0	0	0
	.0040	.0010	.0326
	.0080	.0040	.0424
	.0198	.0090	.1160
	.0392	.0200	.2070
	.0583	.0310	.2960
	.0769	.0440	.3570
	.0952	.0560	.4280
	.1132	.0700	.4730

TABLE A-IV: $ZnCl_2$ EQUILIBRIUM DATA

TEMP. (°C)	CALIBRATION SOLUTION CONCENTRATION (mmoles/ml)	EQUILIBRIUM LIQUID CONCENTRATION (mmoles/ml)	Q (mmoles/cm^3)
10	0	0	0
	.0040	.0030	.0097
	.0080	.0060	.0195
	.0198	.0160	.0352
	.0392	.0320	.0667
	.0583	.0490	.0838
	.0769	.0650	.1076
	.0952	.0800	.1406
	.1132	.0960	.1584
20	0	0	0
	.0040	.0030	.0110
	.0080	.0060	.0194
	.0198	.0140	.0583
	.0392	.0270	.1250
	.0583	.0420	.1660
	.0769	.0560	.2150
	.0952	.0690	.2730
	.1132	.0820	.3280
50	0	0	0
	.0040	.0025	.0154
	.0080	.0050	.0310
	.0198	.0130	.0698
	.0392	.0250	.1490
	.0583	.0395	.1950
	.0769	.0520	.2620
	.0952	.0660	.3080
	.1132	.0770	.3880

APPENDIX B

TABLE B-I: $CaCl_2$ (10°C) RESPONSE DATA (TRIAL 1)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
120	19	0
150	19	0
160	20	.000006
170	39	.000117
180	84	.000380
200	189	.000994
210	224	.001200
220	254	.001370
230	273	.001490
240	275	.001500
250	264	.001430
270	225	.001200
290	179	.000936
310	142	.000719
330	109	.000526
350	83	.000374
370	64	.000263
390	54	.000205
410	45	.000152
440	39	.000117
470	35	.000094
570	29	.000058

TABLE B-II: $CaCl_2$ (10°C) RESPONSE DATA (TRIAL 2)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
130	15	0
170	15	0
180	29	.000069
190	49	.000167
210	114	.000485
220	135	.000588
230	154	.000681
240	164	.000730
260	177	.000793
270	179	.000803
280	177	.000793
290	174	.000779
300	165	.000735
320	144	.000632
350	116	.000495
370	95	.000392
390	78	.000309
420	59	.000215
440	45	.000147
460	40	.000122
480	37	.000108
580	28	.000064

TABLE B-III: $CaCl_2$ (20°C) RESPONSE DATA (TRIAL 1)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
140	15	0
160	16	.000006
170	32	.000094
180	55	.000222
190	102	.000483
220	207	.001091
230	217	.001156
240	223	.001195
260	222	.001188
280	212	.001123
300	187	.000956
320	162	.000817
340	132	.000650
360	112	.000539
380	94	.000439
400	83	.000378
420	76	.000339
440	69	.000300
460	66	.000283
480	62	.000261
500	61	.000256
580	52	.000206

TABLE B-IV: $CaCl_2$ (20°C) RESPONSE DATA (TRIAL 2)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
120	17	0
140	17	0
150	20	.000016
160	33	.000086
190	150	.000715
210	218	.001098
220	238	.001225
230	249	.001295
240	251	.001308
250	252	.001314
260	251	.001308
270	248	.001289
310	175	.000849
330	156	.000747
350	120	.000554
370	100	.000446
400	85	.000366
430	73	.000301
460	66	.000263
490	61	.000237
520	59	.000226
620	50	.000177

TABLE B-V: $CaCl_2$ (50°C) RESPONSE DATA (TRIAL 1)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
120	6	0
140	6	0
150	51	.000426
160	125	.001130
170	167	.001520
180	182	.001670
190	181	.001660
200	156	.001420
210	134	.001210
220	117	.001050
230	100	.000890
240	90	.000790
250	81	.000710
260	74	.000640
270	68	.000590
280	62	.000530
290	57	.000483
300	53	.000445
310	51	.000426
320	46	.000378
340	41	.000330
440	30	.000227

TABLE B-VI: $CaCl_2$ (50°C) RESPONSE DATA (TRIAL 2)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
120	8	0
130	8	0
140	22	.000076
150	91	.000449
160	167	.000859
170	210	.001092
180	212	.001103
190	187	.000968
200	162	.000832
210	147	.000751
220	133	.000676
230	122	.000606
240	113	.000568
250	106	.000530
260	97	.000481
270	89	.000438
290	82	.000400
310	76	.000368
330	71	.000341
350	67	.000319
370	62	.000292
470	46	.000205

TABLE B- VII: $Ca(NO_3)_2$ ($10^{o}C$) RESPONSE DATA (TRIAL 1)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
130	22	0
140	24	.000010
150	36	.000068
160	97	.000362
180	259	.001145
190	306	.001372
200	325	.001464
210	325	.001464
220	306	.001372
230	281	.001251
240	256	.001130
260	191	.000816
270	161	.000671
280	138	.000560
290	119	.000469
310	91	.000333
330	71	.000237
350	60	.000184
370	54	.000155
400	46	.000116
420	43	.000101
520	36	.000068

TABLE B-VIII: $Ca(NO_3)_2$ (10°C) RESPONSE DATA (TRIAL 2)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
150	23	0
160	28	.000026
170	56	.000174
180	93	.000368
190	132	.000574
200	160	.000721
210	179	.000821
220	192	.000889
230	202	.000942
240	203	.000947
250	204	.000953
260	204	.000953
270	203	.000947
280	195	.000905
300	173	.000789
320	144	.000636
350	111	.000463
370	92	.000363
390	77	.000284
420	62	.000205
440	55	.000168
540	41	.000095

TABLE B-IX: $Ca(NO_3)_2$ ($20^{o}C$) RESPONSE DATA (TRIAL 1)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
110	14	0
130	14	0
140	16	.000012
150	26	.000073
160	45	.000188
180	107	.000564
200	158	.000873
210	173	.000964
220	179	.001000
230	184	.001030
240	185	.001040
250	184	.001030
260	179	.001000
280	158	.000873
300	134	.000727
320	112	.000594
240	97	.000503
360	84	.000424
380	74	.000364
400	67	.000321
420	63	.000297
520	51	.000224

TABLE B-X: $Ca(NO_3)_2$ (20°C) RESPONSE DATA (TRIAL 2)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
160	23	0
170	28	.000019
180	63	.000151
200	179	.000589
210	228	.000774
240	325	.001140
250	346	.001220
260	348	.001230
270	349	.001240
280	349	.001240
290	348	.001230
300	343	.00121
320	316	.001110
340	285	.000989
360	248	.000849
380	213	.000717
420	148	.000472
440	126	.000389
460	113	.000340
490	98	.000283
510	91	.000257
610	73	.000189

TABLE B-XI: $Ca(NO_3)_2$ (50°C) RESPONSE DATA (TRIAL 1)

TIME (seconds)	VOLTAGE (mv)	CONCENTRATION (moles/liter)
110	11	0
120	11	0
130	15	.000019
140	73	.000290
150	171	.000748
155	203	.000898
160	209	.000926
170	198	.000875
180	162	.000706
190	132	.000566
200	111	.000468
210	101	.000421
220	93	.000384
230	86	.000351
240	77	.000309
250	71	.000281
260	66	.000267
270	63	.000243
280	61	.000234
300	57	.000215
320	52	.000192
420	41	.000140

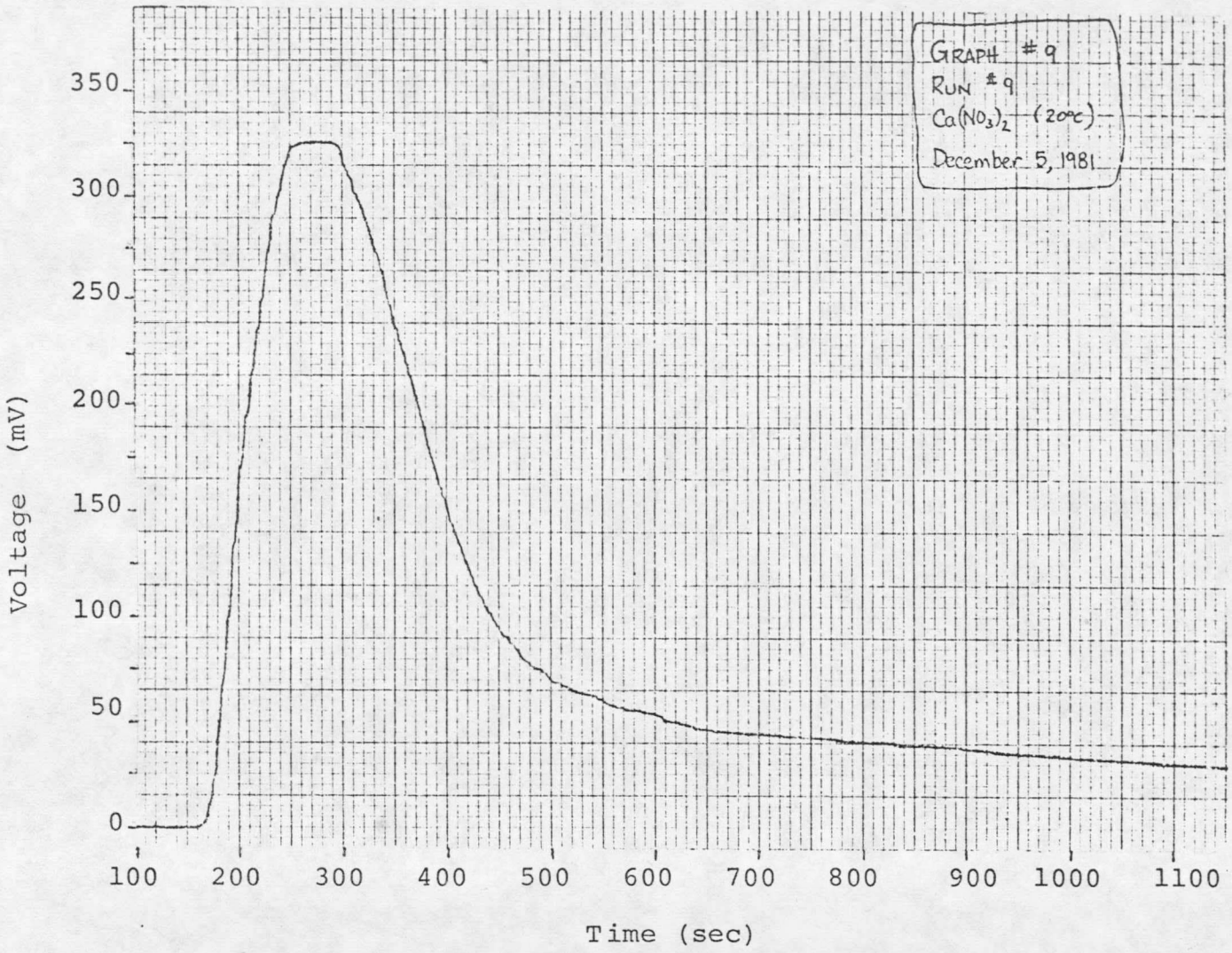


FIGURE C-1: TYPICAL RAW RESPONSE CURVE

APPENDIX D

DISPERSION MODEL

The dispersion model (15) is based on diffusion combined with plug flow. For a non-reacting system the general expression of this model is:

$$\frac{\partial C}{\partial t} = \nabla\cdot(E\,\nabla C) - u\nabla C \qquad \text{(A-1)}$$

Assuming an isothermal operation with incompressible flow under a constant flow rate in a cylindrical vessel, equation (A-1) can be rewritten as:

$$\frac{\partial C}{\partial t} = E_z\frac{\partial^2 C}{\partial z^2} + E_r\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) - u\frac{\partial C}{\partial z} \qquad \text{(A-2)}$$

E_z is the axial dispersion coefficient and E_r is the radial dispersion coefficient. Both of these are assumed to be independent of concentration and position. For application to packed beds radial dispersion can be neglected when compared to axial dispersion. This simplifies equation (A-2) to:

$$\frac{\partial C}{\partial t} = E_z\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} \qquad \text{(A-3)}$$

Three boundary conditions are necessary to solve this par-

tial differential equation. These are:

$$C_{z\to 0^-} = C_{z\to 0^+} - \frac{E_z}{u}\left(\frac{\partial C}{\partial z}\right)_{z\to 0^+} \qquad \text{(A-4)}$$

$$\left(\frac{\partial C}{\partial z}\right)_{z=L} = 0 \quad \text{for all } t \qquad \text{(A-5)}$$

$$C = 0 \text{ at } t=0 \text{ and all } z \qquad \text{(A-6)}$$

The derivation of these boundary conditions involves analyzing the packed column as a series of completely mixed compartments. This process is fairly lengthy and tedious and will not be presented. A detailed description is given by Wen and Fan (15).

Response equations for different types of inputs have been solved by many authors. Detailed explanations can be found in the following references: (16), (17), (18), and (19).

Wen and Fan list the solution to the model described by equations (A-3) through (A-6) for a pulse input. This solution is extremely lengthy and complicated so it will not be listed. Using a computer is a fairly simple task to generate response curves from this equation for various values of the parameter, M. These response curves have previously been shown in Figure 21.

APPENDIX E

PROGRAM LISTINGS

```
 0.500    50 REM **PROGRAM TO ESTIMATE EXPERIMENTAL PARAMETERS**
 1.000   100 DIM T(100),X(100),C(100),C1(100)
 2.000   110 INPUT N,M,L,P
 4.000   130 FOR I=1 TO N
 5.000   140 READ T(I)
 6.000   145 X(I)=T(I)-L
 7.000   150 NEXT I
 8.000   160 FOR I=1 TO N
 9.000   170 READ C1(I)
10.000   190 NEXT  I
15.000   200 REM  ***INTEGRATION AND NORMALIZATION***
19.000   241 S=0
20.000   242 FOR I=1 TO 19
21.000   243 D= T(I+1)-T(I)
22.000   244 A=.5*D*(C1(I+1)+C1(I))
23.000   245 S=S+A
24.000   246 NEXT I
25.000   247 FOR I=1 TO 20
26.000   248 C(I)=C1(I)/S
27.000   249 NEXT I
```

```
30.000   252 REM  ***CALCULATION OF THE MOMENTS***
32.000   254 PRINT
33.000   255 PRINT S
34.000   256 PRINT
34.500   258 M0=0
35.000   260 M1=0
36.000   270 M2=0
37.000   280 M3=0
38.000   290 FOR I=1 TO 19
39.000   295 D=X(I+1)-X(I)
40.000   300 W1=EXP(-P*X(I))
41.000   305 W2=EXP(-P*X(I+1))
42.000   309 A0=D*(C(I)*W1+C(I+1)*W2)/2
43.000   310 A1=D*(C(I)*X(I)*W1+C(I+1)*X(I+1)*W2)/2
44.000   320 A2=D*(C(I)*W1*X(I)^2+C(I+1)*W2*X(I+1)^2)/2
45.000   330 M0=M0+A0
46.000   340 M1=M1+A1
47.000   350 M2=M2+A2
48.000   370 NEXT I
49.000   371 K1=M1/M0
50.000   373 FOR I=1 TO 19
51.000   374 D=X(I+1)-X(I)
52.000   375 W1=EXP(-P*X(I))
53.000   377 W2=EXP(-P*X(I+1))
54.000   380 K1=M1/M0
55.000   381 A3=D*C(I)*W1*(X(I)-K1)^2
56.000   382 A4=D*C(I+1)*W2*(X(I+1)-K1)^2
57.000   383 A5=(A3+A4)/2
58.000   385 M3=M3+A5
59.000   386 NEXT I
60.000   387 K2=M3/M0
61.000   388 X1=(K2/K1)/(2-P*K2/K1)
62.000   389 PRINT M0,M1,M2,M3
63.000   390 K0=K1*(1+P*X1)^2
64.000   400 PRINT K1,K2,X1,K0,P
69.000   420 END
```

```
  5.000 5     REM   PROGRAM TO GENERATE A THEORETICAL RESPONSE CURVE
 10.000 10    DIM C(1000),T(1000),C1(1000)
 20.000 20    INPUT K1,X1,D,C0,L
 30.000 30    S=K1/X1
 40.000 40    FOR I=2 TO 100
 50.000 50    T(I)=L+(I-1)*D
 60.000 60    T1=T(I)-L
 70.000 70    X=SQR(4*S*T1/X1)
 80.000 80    Q=X/3.75
 90.000 90    IF(X<3.75) THEN 150
100.000 100   Z=.39894228-.03988024/Q-.00362018/Q**2
110.000 110   Z1=.00163801/Q**3-.01031555/Q**4+.02282967/Q**5
120.000 120   Z2=-.02895312/Q**6+.01787654/Q**7-.00420059/Q**8
130.000 130   I1=EXP(X)/SQR(X)*(Z+Z1+Z2)
140.000 140   GOTO 180
150.000 150   Z=.5+.87890594*Q**2+.51498869*Q**4+.15084934*Q**6
160.000 160   Z1=.02658733*Q**8+.00301532*Q**10+.00032411*Q**12
170.000 170   I1=X*(Z+Z1)
180.000 180   C1(I)=SQR(S/T1/X1)*EXP(-S-T1/X1)*I1*C0
190.000 190   NEXT I
200.000 200   S1=0
210.000 210   FOR I=1 TO 99
220.000 220   T=20*.5*(C1(I+1)+C1(I))
230.000 230   S1=S1+T
240.000 240   NEXT I
245.000 245   C(1)=0
250.000 250   FOR I=1 TO 100
260.000 260   C(I)=C1(I)/S1
270.000 270   NEXT I
280.000 280   FOR I=1 TO 60 STEP 2
290.000 290   PRINT T(I),C(I)
300.000 300   NEXT I
310.000 310   END
```

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