A SECOND-ORDER TWO-LIQUID PHASE, NON-ISOTHERMAL REACTION IN AN IMPERFECTLY MIXED CONTINUOUS FLOW STIRRED TANK REACTOR

By

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Affectionately dedicated to my wife,

Amrit

and to my parents

ABSTRACT

The purpose of this research was to study the transient behaviour of an imperfectly mixed two-phase continuous flow stirred tank reactor. The mononitration of toluene, using a mixture of nitric and sulfuric acids as a nitrating agent, was chosen as the reaction to be studied. The flow rate of cooling water was varied from one steady state to another, and reactor temperature and concentration were determined. It was assumed that the reaction takes place only in the acid phase. The mass and energy balances in the system were described by four nonlinear differential equations which were solved on a computer by using the Runge-Kutta method. The transient solution required various parameters, such as heat of reaction, reaction rate constant, and mass transfer coefficient, which were obtained from the solution of the steady-

state equations. The only parameter which was used from the perfectly mixed system in the imperfectly mixed one was the reaction rate constant. The mathematical model adequately predicted the reactor temperature in the transient period for both perfectly and imperfectly mixed runs. The model was also satisfactory in predicting concentrations in the perfectly mixed runs but was somewhat inaccurate in prediction of the concentrations in the imperfectly mixed runs.

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INTRODUCTION

The nitration of aromatic compounds has gained great technical importance since the start of a synthetic organic chemical industry because of several factors. For example nitration usually proceeds easily; its products can readily be separated from the spent acid; and there is a wide range of possibilities in the practical use of nitro compounds both as intermediates and end products. The presence of a nitro group in the starting product made it possible to obtain a number of basic organic intermediates such as aniline and benzidine. Dyes with more than one nitrogroup, such as picric acid, were obtained. It has been found that higher nitrated nitro compounds and nitric acid esters have explosive properties and are of practical importance. Some nitro compounds are used in perfumes. Medicinal properties have lately been discovered in certain nitro compounds, e.g. chloramphenicol.

Despite this prominence, the amount of data available on such systems under conditions used on a technical scale is surprisingly sparse. The commercial nitration of aromatic compounds has been carried out in batch reactors for nearly a century. But in the past 40 years, an increasing number of plants have been designed for continuous production of nitro aromatics. The design of batch reactors has been based mainly on empirical rules but the efficient design of a continuous plant requires data on reaction velocities which are dependent on chemical kinetics and mass-transfer rates.

The purpose of this work was to study a two-phase, exothermic reaction under transient conditions in an imperfectly mixed continuous-flow, stirred-tank reactor. The objective was to set up a mathematical model which would predict the path to the steady state after the system was upset from the existing steady state. The reaction chosen for the study was mononitration of toluene using a mixture of sulfuric and nitrating acids as the nitrating agent. This study also aimed to carry out any improvements in the model for the perfectly mixed conditions.

No previous study has been made of an imperfectly mixed system. Most of the previous workers studied the behaviour of perfectly mixed systems under isothermal and steady state conditions. Okimoto(1969) studied transient behaviour of a perfectly mixed continuous flow stirred-tank reactor by using nitration of toluene as the reaction. Information about the mechanism of the nitration reaction was available in the literature.

Before taking any data under the imperfectly mixed conditions, some runs were made under the perfectly mixed conditions. Information concerning such parameters as the reaction rate constant k could be obtained from the perfectly mixed runs and used in the imperfectly mixed ones.

Experimental data were obtained by allowing the system to come to a first steady state. The flow rate of cooling-water was changed, and the system was allowed to come to a new steady state. For the imperfectly mixed runs, temperature in each phase was also measured.

The mathematical model consisted of four nonlinear coupled differential equations. These were solved by the Runge-Kutta method of numerical integration on an Equipment Data Corporation Computer at the Colorado School of Mines. The predicted results were compared with the experimental data.

LITERATURE SURVEY

Investigations on the nitration of aromatic hydrocarbons can be approached in two ways:

1. Study of the mechanism of the nitration reactions
2. Study of the kinetics, heat, and mass transfer effects and other factors which need to be considered in the design of the nitration equipment.

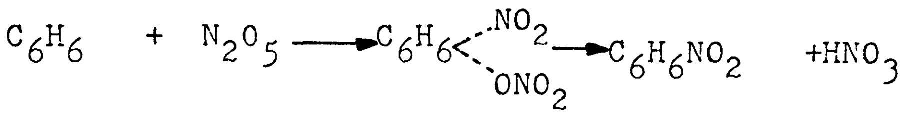
A brief review of work in both areas is given below.

Several mechanisms have been proposed by different authors to explain the mechanism of the nitration reactions. Urbanski (1964) has given an excellent review of these in his book on explosives. Most important of these are

1. Nitration through the formation of an addition product
2. Nitration through the formation of a nitronium ion(NO_2^+)

The first mechanism was supported by Schaarschmidt(1926, p.1457), who postulated the formation of nitric anhydride which is unstable and hence decomposes to give a nitro compound and nitric acid. This mechanism may be written as:

$$2HNO_3 + H_2SO_4 \rightleftarrows N_2O_5 + H_2SO_4.H_2O$$



$$C_6H_6 + N_2O_5 \longrightarrow C_6H_6<{}^{NO_2}_{ONO_2} \longrightarrow C_6H_6NO_2 + HNO_3$$

Lauer and Oda(1936, p.176) assumed the existence of nitracidium sulphate which decomposes to give nitro compound and sulfuric acid. Usanovich(1940, p.219) also assumed the existence of a different addition product which finally gave nitro compound and water. Based on the observations of these and other workers, Urbanski has concluded that the possibility of the formation of an addition product does exist. He further remarks that the mechanism of nitration reactions is rather a complicated one and under various conditions may proceed differently.

The nitronium ion theory has been more widely accepted than the addition product theory. The existence of this ion was proposed by as early as 1903 by Euler(1903, p.280). Additional evidence for the nitrnium ion came from the Raman spectra acids(Chedin, 1935, p.1937). The existence of this ion was further supported by Ingold and others(1950, p.2559) by the preparation of a number of its salts such as NO_2ClO_4, NO_2SO_3F and $(NO_2)_2S_2O_7$. Other investigators who did work on this theory were Bennet and others(1946, p.869) and Brand(1946, p.585, 880). Bunton and Halevi(1952, p.4917) have expressed the view that the nitronium ion mechanism is responsible for C-nitration even in highlyaqueous conditions. It has been concluded by Frost and Pearson (1953, p.301) that this ion is the active nitrating agent in those solutions where it is known to exist.

Based upon the nitronium ion theory, Albright(1966, p.169) has suggested that the mechanism of nitration process may be represented by

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^- \qquad (1)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \qquad (2)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad (3)$$

The actual nitration reaction is

$$ArH + NO_2^+ \longrightarrow ArH^+NO_2 \qquad (4)$$

$$ArH^+NO_2 \longrightarrow ArNO_2 + H^+ \qquad (5)$$

$$H^+ + HSO_4^- \rightleftharpoons H_2SO_4 \qquad (6)$$

where ArH represents an aromatic hydrocarbon Reaction(5) is probably the rate-controlling chemical step.

Besides sulfuric acid, several other strong acids can also be used for producing NO_2^+. These include perchloric acid,hydrogen flouride, selenic acid, acidic ion-exchange resins and boron trifluoride. However, sulfuric acid is the most economical nitronium producing reagent and hence most commonly used.

Ingold and his co-workers(1946, p.480; 1950a, p.2400; 1950b, p.2576; 1950c, p.2612) concluded from the results of of their studies that the nitration rate V_s, in the presence of sulfuric acid might be expressed by the equation:

$$V_s = k(ArH)(HNO_3)$$

Frost and Pearson (1953, p.307) also suggested that if the solvent is of fixed composition, then the concentration of NO_2^+ is directly proportional to the concentration of molecular nitric acid at any time which would lead to the above rate expression. From these observations, it can be concluded that the reaction is of second order and irreversible.

Hougen and Watson(1947, p.1053) have suggested a rate expression for the nitration of reactions which makes use of activities instead of concentrations and also incorporates the distribution equilibrium constants. However, after certain simplifying assumptions, one can get the same rate expression as given above. More discussion about these points is given in the development of the mathematical model.

There have been very few investigations on the nitration of aromatic hydrocarbons from an engineering point of view. An excellent review of work in this area up to 1965 is given by Hanson and others(1966, p.675).

Lewis and Suen(1940, p.1095) studied the influence of various parameters on the continuous nitration of benzene by mixed acids. They concluded that nitration takes place in both phases and the reaction becomes diffusion controlled if mixing speed is reduced below the point where emulsification occurs. Another important conclusion drawn by them was that a temperature rise of 10°C doubles the rate of reaction i.e. the temperature coefficient is doubled. They cite this as an evidence for the rate being controlled by chemical reaction rather than by diffusion.

McKinley and White(1944, p.143) published a paper on the continuous nitration of toluene with mixed acids. They correlated their results in terms of R_A/X_T where R_A is the rate of reaction based upon the acid phase and X_T is the mole fraction of toluene in the organic phase on an acid free basis. From this, it may appear that only reaction in the acid phase is important. But R_A based upon this definition also includes any reaction which does take place in the organic phase. Another assumption of McKinley and White was that mass transfer resistance can be eliminated by adequate agitation. They further quoted a value of 2.2 for the temperature coefficient to support their assumption that the process is kinetic rather than diffusion controlled. Hanson and others have indicated that this claim does not hold for all the runs and some of the data give much lower value of temperature coefficient. Hence, they cast considerable doubts on the value of McKinley and White's correlation and upon their fundamental concepts, particularly their implicit assumption of reaction being limited to the aqueous phase and their rejection of any mass transfer resistance.

Biggs and White(1956, p.26) studied the rate of mono-nitration of benzene in a continuous flow stirred tank reactor. They correlated their results by an empirical equation which gave the best fit to their experimental rate data. The equation had no kinetic significance and hence was not very useful for application in practice.

Brennecke and Kobe(1956, p.1298) carried out the study of nitration of toluene in a miniature continuous flow stirred tank reactor 0.5 in. in diameter and 0.5 in. in height, which was agitated by a turbine impeller at 20,000 rpm. They used higher nitric acid concentrations than those used by Mckinley and White and made some runs with a "spiked" feed containing 25 molar percent o-nitrotoluene. Brennecke and Kobe could not correlate their data by a single equation and reported that McKinley-White correlation could not be extrapolated to higher nitric acid concentrations. However, they supported the value of 2 for the temperature coefficient as given by McKinley and White. Hanson and others refuted this claim by showing the value of the temperature coefficient lower than 2 for a number of their experimental runs. Hanson also pointed out the effect of o-nitrotoluene in the feed in increasing the rate of reaction. This could be due to a catalytic effect on the formation of nitronium ions which requires further research.

Barduhn and Kobe(1956, p.1305) reported a study on the kinetics of toluene nitration in a continuous flow stirred-tank reactor under isothermal conditions with various acid concentrations. Their results were correlated by the following equation:

$$R_A = E\ k\ a_N\ x_T$$

The subscripts N and T refer to Nitric acid and Toluene respectively R_A is the rate of reaction based on the acid phase. This equation was derived from the kinetic equation of Hougen and Watson by assuming that activity coefficient of toluene in the organic phase to be unity and neglecting any reaction in the organic phase. E was defined as contactor effeciency and related to the mass transfer coefficient m by the equation:

$$E = \frac{1}{1 + \frac{aN}{m}}$$

They did not indicate the development of this equation and gave a plot of E vs. speed of agitation for two nitric acid concentrations. But they did point out that their data were not of sufficient precision to give useful predictions of transfer rates in other systems. Barduhn and Kobe also concluded that agitation in M ley and White's experiments was not sufficient to elimin he mass transfer resistance. They reported a value of heat nitration of toluene to be equal to 35.2 kcal per gram-mole.

One of the recent publications in this area is the work of Miller and others(1964, p.43), who carried out a study on the nitration of hexafluoro-m-xylene in a batch reactor fitted with a paddle agitator operating at 250 rpm. They concluded that mass transfer resistance played no significant role in the reactions. This conclusion was drawn from the fact that some runs in which the speeds varied from 150 to 350 rpm, the conversion differed only by 18% (other variables were not changed). They also mentioned the magnitude of the measured activation energy(18.1 kcal/mole) as evidence for the elimination of mass transfer resistance. However Albright(1965, p.53) crticised all of their claims. About the value of activation energy, he pointed out that this relatively high value could be caused by the effect of several factors: resistances to chemical reaction, mass transfer resistances, and changes in mutual solubilities of the two pahses.

As already mentioned, Hanson and others reviewed the work of various workers in this field. They concluded that the major uncertainity was whether the rates of nitration reactions were kinetic or mass trasnfer controlled. Though the majority of previous workers assumed the former, the justification could not be fully supported. On the basis of the effects of space velocity and phase ratio on the rates, they further stated that there was sufficient evidence to suggest that mass transfer resistance may be of equal importance to kinetics in determining the overall rate of reaction.

A series of papers was published by Schmitz and Amundson in 1962 and 1963 on the reactor stability and control for the two-phase chemical reacting systems. They discussed various theoretical models and various assumptions on which the models were based. They were developed only for perfectly mixed systems. These papers are very useful from theoretical view point and may be of some help in proposing any model for these type of reactors.

For the imperfectly mixed systems, Luss and Amundson (1967, p.267) published a paper concerning chemical reactor stability. They investigated the effect of stirring on the possible steady states and suggested that under certain conditions, heat transfer between the phases may be the controlling factor in the design of such reactors.

The most recent experimental investigation on nitration is the work of Okimoto and Dickson (1969). They studied the mono-nitration of toluene in a continuous-flow stirred-tank reactor with mixed acid as the nitrating agent under perfectly mixed conditions. They proposed a model which could satisfactorily predict a second steady state after upsetting the first steady state.

There has been no study on the imperfectly mixed systems. Urbanski has quoted the work of Orlova, who studied the effect of speed on the yield of nitrotoluene in mono-nitration of toluene. But this was done in an isothermal batch reactor. Hence, it does not give any useful information to engineers. However, his investigation indicates one important result: The yield of nitrotoluene tends to be constant at about 1000 r.p.m.

EXPERIMENTAL WORK

The experimental work will be described here in four sections:

1) Equipment,
2) Reagents,
3) Procedure,
4) Analytical procedure

Equipment

A flow diagram of the experimental equipment is shown in Figure 1.

Mixed acid and toluene were supplied by two polyethylene bottles into constant-head tanks. By gravity, they flowed through two rotameters to a constant temperature bath and then into the reactor. The flow meter for toluene gave a maximum flow of 100 cc per min and for feed acid a flow of 30 cc per min. Flow rates were calibrated for each run.

A constant temperature bath of 20 liter capacity was used to heat the feed streams. Mineral oil was used as the

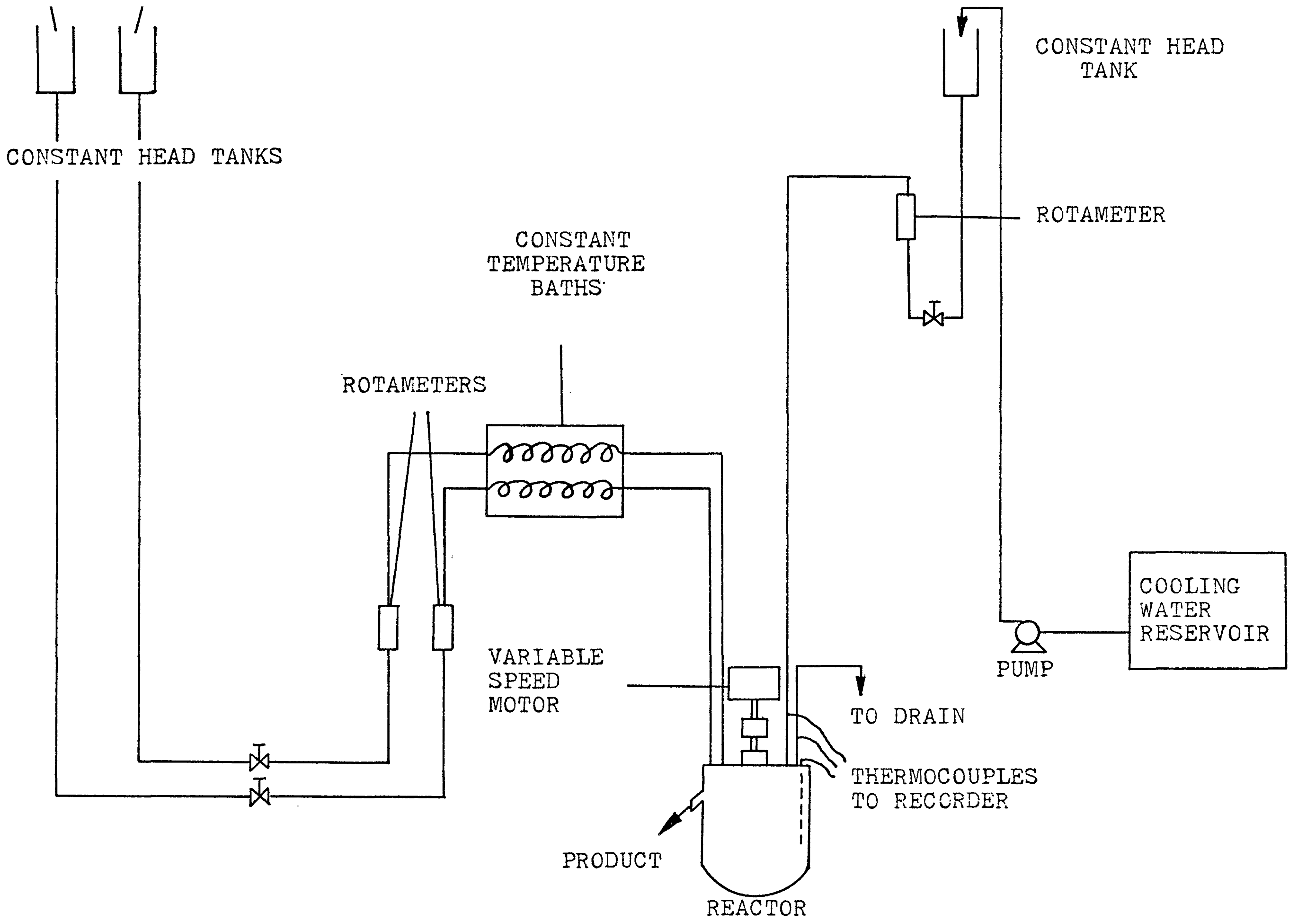


FIGURE 1 EQUIPMENT DIAGRAM

heating medium. The bath was provided with a heater and an automatic regulator which could control the temperature to 0.1°C. The bath was insulated with an asbestos layer to reduce the heat losses to the surroundings. A stirrer was used to keep the oil at uniform temperature in the bath. A stainless steel coil 20 ft long and 1/4 in. OD was used for heating the acid. For heating toluene, copper tubing 15 ft long and 3/8 in. OD was used. Inlet temperatures of toluene and feed acid were measured by two thermometers, which were calibrated with a precision thermometer graduated to 0.1°C.

Figure 2 shows the construction of the reactor system. The reactor was made from a pyrex glass-bowl 4 in. in diameter and 7 in. high. The outlet tube for the products was 2 in. from the top. With cooling coil in place, the reactor held 456 ml with no stirring. The reactor was insulated with a 1-in. layer of asbestos cement. The cover for the reactor consisted of a 7½-in.-diam piece of plexiglass 3/8 in. thick. A 1/16-in. teflon strip was used between the glass bowl and the plexiglass cover. A 1/4-in. stirrer-shaft coupling and bearings were mounted in a plexiglass support in the center of the cover. Holes were drilled to accommodate the stirrer shaft, acid and organic phase thermocouples, reactant inlet tubes, and cooling coil inlet and outlet connections.

A flexible rubber and stainless-steel coupling was used to connect the motor to the stirrer shaft, and a variable-speed motor was used for the imperfectly mixed runs. Perfectly

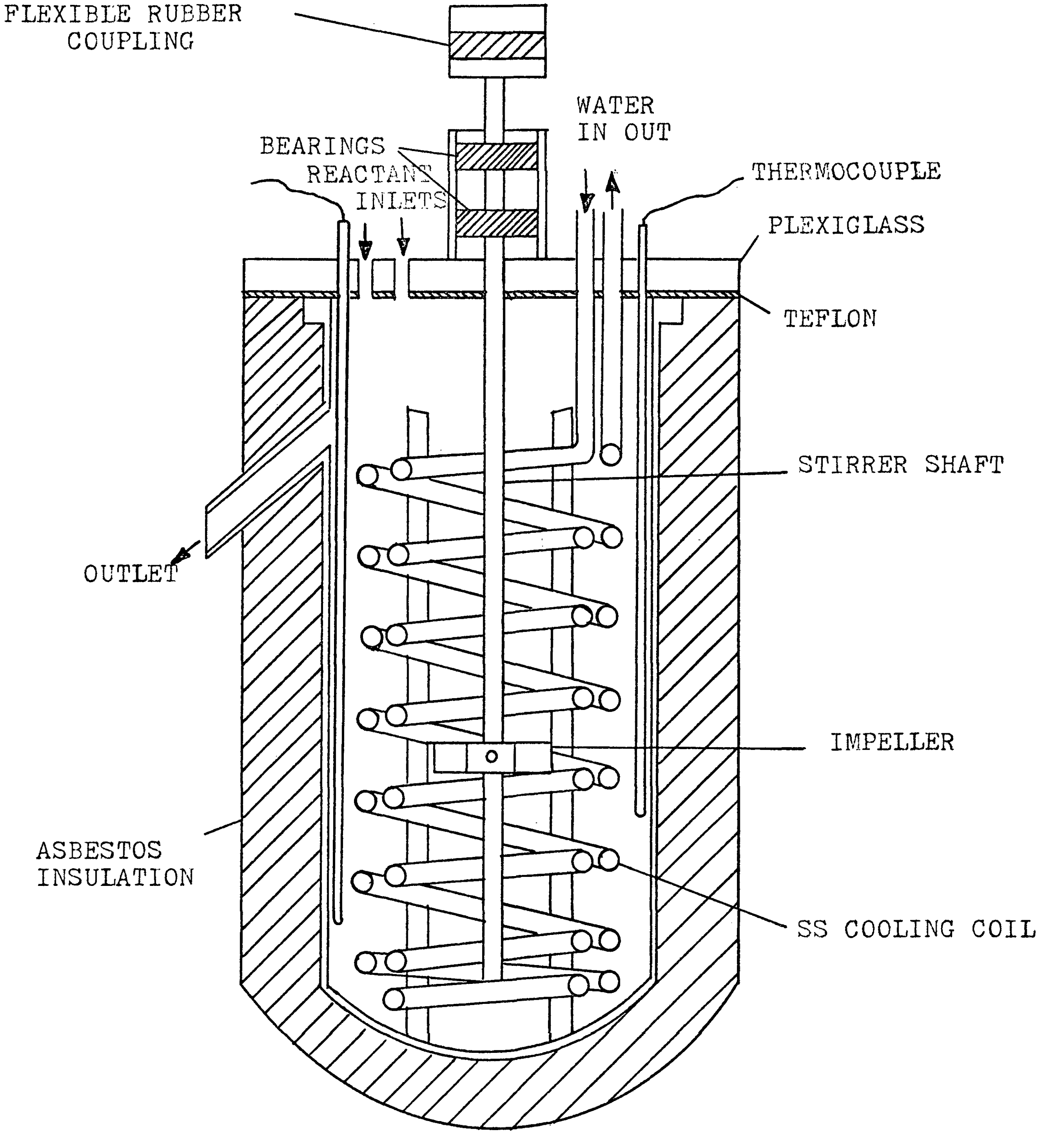


FIGURE 2 REACTOR

mixed runs were made with a second motor which could give 1050 rpm. The impeller consisted of two stainless-steel, type-304 blades.

The reactor was provided with a cooling coil constructed from stainless-steel tubing 1/4 in. O.D. It provided a surface area of 0.3087 sq ft. The outlet temperature of the cooling water was measured by imbedding a copper-constantan thermocouple in a tee fitted in the outlet section of the cooling coil.

Copper-constantan, stainless-steel sheathed thermocouples were used to measure the temperature of each phase in the reactor. All thermocouples were connected to two-channel Hewlett-Packard strip-chart recorders, model 7100 B. These thermocouples were calibrated by using a well insulated and stirred temperature bath and by comparing them with a precission. thermometer of E.H. Sargent Co. This thermometer gave readings to 0.1°C. The temperature of the reactor could be measured to ± 0.4°F.

The cooling water for the reactor was pumped from a constant-temperature reservoir into a constant-head tank. It flowed to the cooling coil of the reactor through a rotameter which was calibrated for each run. The inlet temperature of cooling water was read from a calibrated thermometer.

Reagents

DuPont's reagent grade 95 to 97 % sulfuric acid and 70 to 71 % nitric acid were used to make the feed-acid solution.

Nitration-grade toluene was purchased from the Denver Packaging Company. Its purity of toluene was greater than 99.5%. The mononitrotoluene solution(58% ortho, 38% para, and 4% meta) was made from Eastman Organic Chemicals.

Mallinckrodt Chemical Company's reagent-grade ferrous sulfate was used in the nitric acid analysis.

Baker's reagent-grade sodium hydroxide pellets were used for standardization of the acid solution. Sodium hydroxide solution was standardised by reagent-grade potassium acid phthalate.

Procedure

The temperature bath was turned on 3 to 4 hours before the run was to be made. The product quenching bath was set at 20°F and turned on a few hours before the run was to be made. The following steps were followed in making a run:

1. The reference junctions for the thermocouples were kept at 0°C by using a 50% mixture of distilled water and crushed ice. The recorders were turned on and calibrated,

2. Cooling-water flow rate was adjusted to the desired value,

3. The reactor was filled with toluene and mixed acid in the same proportion as in the feed,

4. The stirring motor was set at the desired speed,

5. The flow rates of toluene and feed acids were adjusted to the desired value by control of the valves,

6. The system was allowed to reach the first steady state in temperature, (this was achieved in 1 to 3 hours)

7. A 200-ml product sample from first steady state was placed in the quenching bath, and the phases were separated,

8. Flow rate of the cooling water was changed to a new value,

9. A stop watch was started, and the product samples were obtained at various time intervals, (each sample was collected for 2 minutes and placed in the quenching bath. Sampling was continued until the recorder indicated constant temperature of the second steady state) normally about 50 to 60 minutes,

10. A 200-ml sample from the second steady state was collected and placed in the quenching bath.

Analytical Procedure

Details of the analytical procedure are given in the appendix. A brief summary is given below.

The analytical procedure was used to determine

1. The concentrations of nitric acid in the acid-phase product and the organic-phase product,

2. The total acidity of the acid-phase product,

3. Densities of the acid-phase product and the organic-phase product.

In order to determine the above quantities, the following steps were carried out:

1. The density of the acid-phase product was determined,

2. A 10-ml sample (2-ml sample of the acid-phase product diluted to 25 ml with the distilled water was titrated with standardized ferrous sulfate to determine the concentration of nitric acid in the acid phase,

3. The density of the organic-phase product was determined,

4. The organic-phase product was diluted with an equal volume of water and the phases were separated. Aqueous phase was titrated with sodium hydroxide to determine the nitric acid concentration in the organic phase,

5. A sample of the washed organic extract was saved for refractive index analysis in order to determine the mononitro toluene concentration in the organic phase,

6. A 2-ml acid-phase product was titrated with sodium hydroxide to determine the total acidity of the acid phase product.

MATHEMATICAL MODEL FOR THE PERFECTLY MIXED SYSTEM

Before developing any mathematical model for the imperfectly mixed systems, it is essential to formulate one for the perfectly mixed system, the discussion for which is given in five sections:

1. Assumptions for the mathematical model
2. Reaction-rate expression
3. Transient mass and energy balances
4. Solution of the steady-state equations for unknown parameters
5. Solution of the transient equations

Assumptions for the Mathematical Model

The assumptions that were made in order to develop the mathematical model were that a lumped-parameter system is considered, uniform temperature within the reactor is assumed, reaction takes place only in the acid phase, and that the total reactor volume is constant.

Lumped parameter system: The mathematical models may be broadly classified into two groups

1. Lumped-parameter models.
2. Distributed-parameter models.

In stirred reactors, the first model, which is simply the perfectly mixed system, involves a single independent variable, time. But the second model takes into account the variations in the dependent variables with position as well as time, resulting in partial differential equations. This model would be quite complicated in theoretical development and would require much experimental information to be of any use in actual design. For the purpose of this study, a lumped-parameter model is assumed. The temperature and concentrations in each phase are assumed to be uniform.

Uniform temperature within the reactor: Since the temperature in each phase is assumed to be uniform, the temperature in the reactor will depend upon the degree of mixing and on the heat transfer rate between the phases. It was shown by Okimoto(1969) that the heat transfer between the two phases occurs much faster than the mass transfer. If the agitation speed is sufficient to cause the two phases to mix well, it can be safely assumed that the temperature in each phase is equal. In fact, this assumption was tested by measuring temperature in each phase by two separate thermocouples.

Reaction only in the acid phase: It is assumed that the reaction in the organic phase is negligible. This assumption was supported by McKinley and White(1944, p.143) and Barduhn and Kobe(1956, p.1305). Urbanski(1964) has also mentioned that the nitration takes place mainly in the acid phase. In case of benzene, nitration does take place in both the phases; but for mono-nitration of toluene, most investigators agree that no or a negligible amount of reaction occurs in the organic phase.

Constant Total Reactor Volume: Feed acid and toluene were fed to the reactor through constant-head tanks. The level of liquid in each of these tanks was kept constant, and flowmeters supplied a constant amount of each solution per unit of time. In the reactor, the liquid level was constant since the products flow out through an overflow tube. Speed of mixing was also constant for all the runs. Hence, this assumption was justified.

Reaction-Rate Expression

The simplest model which may be used to describe the rate processes of heat and mass transfer between phases is that in which reaction rate alone is controlling the rate of conversion. The heat and mass transfer rates to and from the interface are extremely rapid, and the system is in physical equilibrium. In such systems, the chemical resistance is dominant, and dynamic model considerations can be neglected. This model would be justified in case of very slow chemical reactions which are well agitated.

At the other extreme is a model based on the assumption that mass transfer is controlling. The diffusional resistance may be the rate-controlling step. This model would be right for very rapid chemical reactions. Then the system may be said to be subject to a fluid dynamic regime.

Between these two extremes are situations in which all rate processes must be considered. In these cases, the system may be said to be subject to a mixed regime.

The physical equilibrium model cannot be expected to hold in the present study because the nitration reaction occurs fairly rapidly. Similarly, the chemical equilibrium model is also ruled out because mass transfer cannot be controlling the rate if adequate mixing is provided, as is in the case of perfectly mixed system. Hence, for the perfectly mixed system, the third model is assumed.

For the general reaction $A + B \rightleftharpoons R + S$, the rate in each phase may be expressed (Hougen , 1947,p.1053) by the following equations:

$$\text{Phase a :} \quad r_a = k_a(a_{Aa}a_{Ba} - \frac{a_{Ra}a_{SA}}{K_a}) \qquad (1)$$

$$\text{Phase b :} \quad r_b = k_b(a_{Ab}a_{Bb} - \frac{a_{Rb}a_{SB}}{K_b}) \qquad (2)$$

Since it has been assumed that the reaction is irreversible and takes place only in the acid phase, say phase = a, the rate expression may be written as

$$r_a = r = k_a a_{Aa} a_{Ba} \qquad (3)$$

The activities may be replaced by the product of mole fractions and corresponding activity coefficient. Hence, we get

$$r = k_a x_{Aa} \cdot \gamma_{Aa} \cdot x_{Ba} \cdot \gamma_{Ba} \qquad (4)$$

To use the above rate equation, one needs information about the activity coefficients of toluene in the acid phase and of nitric acid in the acid phase. The activity coefficients vary both with temperature as well as concentrations. No information about the activity coefficients is available in the literature. Hougen and Watson(1947,p.1056) have given a plot for the activity coefficient of mixed acids. But this plot is based on a constant temperature assumption, and the values of activity coefficients are not given for all concentrations. The authors have stated that the extrapolation is highly unreliable. Hence it is not possible to use the above rate equation, and its modifications are necessary. Because of these limitations, the usual rate equation is used in this study i.e. $r = kC_{Aa}C_{Ba}$ which in the nomenclature of this work may be written as

$$r = k\,Cac\ Cbc \qquad (5)$$

Strictly speaking, the rate constant k in equation (5) also incorporates the two activity coefficients and is different from the rate constant normally used.

Transient mass and energy balance

The mass and energy balance equations for the perfectly mixed system are derived below.

(Mass balance for nitric acid in the acid phase)

Rate of accumulation of nitric acid in acid phase = Input rate from the feed (Qc Cbo)

- output rate in the acid phase (Qc Cbc)

- rate of disappearance by reaction (k Cac Cbc Vc)

- rate of mass transfer to the organic phase (MA)

$$\frac{d(Cbc\ Vc)}{dt}$$

Since the volume of each phase remains nearly constant from one steady state to another, the mass balance equation simplifies to

$$Vc\ \frac{d(Cbc)}{dt} = Qc\ Cbo - Qc\ Cbc - k\ Cac\ Cbc\ Vc - MA \qquad (6)$$

(Mass balance for toluene in the acid phase)

Rate of accumulation of toluene in the acid phase = Input rate by mass transfer from organic to acid phase(MT)

- output rate in the acid phase (Qc Cac)

- rate of disappearance by reaction (k Cac Cbc Vc)

$$Vc\ \frac{d(Cac)}{dt}$$

$$Vc\ \frac{d(Cac)}{dt} = MT - Qc\ Cac - k\ Cac\ Cbc\ Vc \qquad (7)$$

(Mass balance for toluene in the organic phase)

Rate of accumulation of toluene in organic phase = Input rate from the feed (Qd Cao)

- output rate in the organic phase (Qd Cad)

- rate of mass transfer to the acid phase(MT)

$$Vd\ \frac{d(Cad)}{dt}$$

$$Vd\,\frac{d(Cad)}{dt} = Qd\ Cao - Qd\ Cad - MT \qquad (8)$$

(Mass balance for nitric acid in the organic phase)

Rate of accumulation of nitric acid in the organic phase = Input rate by mass transfer from the acid phase(MA)

$Vd\,\frac{d(Cbd)}{dt}$ - output rate in the organic phase(Qd Cbd).

$$Vd\,\frac{d(Cbd)}{dt} = MA - Qd\ Cbd \qquad (9)$$

It was found in this study that the concentration of nitric acid in the organic phase remained nearly constant from one steady state to another steady state. Hence, equation (9) can be simplified to

$$MA = Qd\ Cbd \qquad (10)$$

It is evident from this equation that the mass transfer of nitric acid from the acid to the organic phase can be assumed constant from one steady state to another steady state.

(Energy balance)

Rate of accumulation of energy in the reactor = rate of energy in by flow of feed acid (Qc ρco Cpco Tbo

$(\rho cCpcVc + \rho dCpdVd)\frac{dT}{dt}$

\+ rate of energy in by flow of toluene(Qd ρdo Cpdo Tao

\- rate of energy out by flow from reactor (Qc ρc CpcT + QdρdCpdT)

\+ rate of energy generated by reaction (k Cac Cbc Vc (-ΔH)

- rate of energy removed by cooling fluid (Q)

$$(\rho c\ Cpc\ Vc + \rho d\ Cpd\ Vd)\frac{dT}{dt} = Qc\rho co\ Cpco\ Tbo + Qd\rho do\ Cpdo\ Tao$$
$$- T(Qc\ \rho c\ Cpc + Qd\ \rho d\ Cpd)$$
$$+ (-\Delta H)\ k\ Cac\ Cbc\ Vc - Q \qquad (11)$$

Equations 6,7, 8 and 11 are the four nonlinear, coupled differential equations for the perfectly mixed system.

Solution of the Steady-State Equations for unkonwn parameters

It is necessary to determine certain unkown parameters to solve the transient equations. These parameters are MA, MT, Cac, k and ($-\Delta H$). They can be obtained by algebraic manipulation of the steady-state equations as shown below.

Under steady-state conditions, equations 6,7,8 and 11 become,

$$0 = Qc\ Cbo - Qc\ Cbc - k\ Cac\ Cbc\ Vc - M_A$$

$$0 = MT - Qc\ Cac - k\ Cac\ Cbc\ Vc$$

$$0 = Qd\ Cao - Qd\ Cad - MT$$

$$0 = Qc\ \rho co\ Cpco\ Tbo + Qd\ \rho do\ Cpdo\ Tao - T(Qc\ \rho c\ Cpc + Qd\ \rho d\ Cpd) + (-\Delta H)\ k\ Cac\ Cbc\ Vc - Q$$

From these equations, the following parameters are easily obtained:

$$MT = Qd(Cao - Cad) \qquad (12)$$

$$Cac = \frac{Qc(Cbc - Cbo) + Qd(Cao + Cbd - Cad)}{Qc} \qquad (13)$$

$$k = \frac{Qc(Cbo - Cbc) - Qd\ Cbd}{Vc\ Cac\ Cbc} \qquad (14)$$

$$(-\Delta H) = \frac{(Qc\ \rho c\ Cpc + Qd\ \rho d\ Cpd)T + Q}{k\ Cac\ Cbc\ Vc} - \frac{(Qc\ \rho co\ Cpco\ Tco + Qd\ \rho do\ Cpdo\ Tdo)}{k\ Cac\ Cbc\ Vc} \qquad (15)$$

From equations 12, 13, 14 and 15, all the unknown parameters are determined.

Solution of the Transient Equations

In order to solve the transient equations, one must take into account the variation of various parameters viz k, MT, $(-\Delta H)$ and Q with temperature. The effect of temperature on various properties, like density and specific heat, also need to be considered. Procedure for considering the temperature effect on these parameters is discussed below.

1. Rate constant k: We know from the Arrhenius equation that the relationship between the rate constant k and the temperature is given by

$$k = p \exp(-E_a/RT)$$
$$= p \exp(E/T) \qquad (16)$$

In this equation, p and E are two unknowns. These can be obtained from data at two steady states. These constants should not vary appreciably in the data of different runs. Hence one can use some mathematical technique like the least square fit method to get the best average value of the constants.

2. Mass transfer rate of toluene MT: The rate of mass transfer of toluene can be written as

$$MT = Kma\ (Cad - Cad^{*})V$$

Difficulty is encountered in using the above equation because of two unknowns, Kma and Cad^{*}. Both of them vary with temperature as well as concentration. Hence, some approximation is necessary to consider the variation of mass transfer rate from one steady state to another. For this purpose, it was assumed that the mass transfer rate may be expressed by the following equation:

$$MT = k_m . Cad \qquad (17)$$

The mass transfer coefficient km also includes the interfacial area.

The variation of mass transfer coefficient with temperature is considered by a method suggested by Schmitz and Amundson(1963, p.447). On the basis of mass transfer correlations, the mass transfer coefficient may be written as

$$k_m \propto D^{\frac{1}{2}}/\mu^{\frac{1}{4}}$$

Diffusivities of liquids are proportional to T/μ. Hence

$$k_m \propto T^{\frac{1}{2}}/\mu^{3/4}$$

Viscosities of liquids usually vary as the exponential of the inverse temperature, $\mu = \mu_0 \exp(b/T)$. If the comparatively slowly varying $T^{\frac{1}{2}}$ is assumed constant at an average value, the temperature dependence may be approximately given by

$$k_m = k_o \exp(-0.75b/T)$$

$$= k_0 \exp(k_1/T) \qquad (18)$$

The two constants k_0 and k_1 may be obtained by data of mass transfer rate at two steady states. Hence, the mass transfer term becomes

$$MT = k_0 \exp(k_1/T)\ Cad \qquad (19)$$

3. Heat of reaction $(-\Delta H)$: Heat of reaction data were obtained at various steady state temperatures. It was found that a plot of logT vs. $(-\Delta H)$ yielded a very good straight line. Hence, the relationship between temperature and $(-\Delta H)$ may be written as

$$\log T = a + b(-\Delta H) \qquad (20)$$

The two constants a and b can be obtained from data at two steady states.

4. Heat removed by the cooling coil Q: Heat removed by the cooling coil may be written as

$$Q = UA(\Delta T)_m$$

Using log mean (ΔT),

$$Q = \frac{UA(Tco - Tci)}{\ln\dfrac{(T-Tci)}{(T-Tco)}}$$

It is convenient to eliminate the outlet temperature of cooling water from the above equation by the following procedure.

$$Q = m.Cpw(\ Tco - Tci\ )$$

$$\frac{UA}{mCpw} = M$$

$$\frac{T - Tci}{T - Tco} = e^{M}$$

$$(Tco - Tci) = (e^{M} - 1/e^{M})(T - Tci)$$

$$Q = UA(\Delta T)_{m} = mCpw(e^{M} - 1/e^{M})\ (T - Tci) \qquad (21)$$

To use this equation, we need an average value of overall heat transfer coefficient U, which is calculated from the transient reactor and coolant temperatures.

5. Density and specific heat variations: Variation of density and specific heat of various streams with temperature can be taken into account by polynomial approximations. These are discussed in the appendix.

MATHEMATICAL MODEL FOR THE IMPERFECTLY MIXED SYSTEM

The following assumptions were also made in the imperfectly mixed system:

1. Lumped parameter model,
2. Uniform temperature within the reactor,
3. Reaction only in the acid phase,
4. Constant total reactor volume

All these assumptions have already been discussed for the perfectly mixed system. However, the second assumption concerning reactor temperature needs clarification. Because of the lower speeds of mixing for the imperfectly mixed runs, it may be expected that the temperatures in the two phases are not equal. But it was found experimentally that they were equal. This was done by placing two thermocouples at different heights in the reactor. One thermocouple was placed approximately in the middle of the organic layer and other in the middle of the acid layer. The measured temperatures in an actual run did not indicate any difference. Hence, this assumption is also justified for the imperfectly mixed systems.

Again, the physical equilibrium model can not hold in this case because of fairly rapid reaction in the acid phase. The chemical equilibrium model may be expected to hold, and it is discussed below.

It has already been mentioned that, in the chemical equilibrium model, the reaction rates are assumed to be infinitely fast, and chemical equilibrium is attained instantaneously. In this model, the rate of reaction is controlled by the transfer of material across the interface. Some theoretical discussion about this type of model was given by Schmitz and Amundson(1963, p.447). There are two basic assumptions:

1. The reaction rate is controlled by the rate at which organic material can enter the acid phase. Thus at all times the mole fraction of organic in the acid phase is zero.
2. Due to the rapid irreversible reaction of organic in the acid phase, it is assumed that the resistance to mass transfer in this phase vanishes, and driving force is simply the mole fraction of organic component in the organic phase.

With these assumptions, the mass balance equations may be written as follows.

Nitric acid in the acid phase

$$\begin{aligned} Vc \frac{d(Cbc)}{dt} &= Qc\ Cbo - Qc\ Cbc - k\ Cac\ Cbc\ Vc - MA \\ &= Qc\ Cbo - Qc\ Cbc - MT - MA \end{aligned} \qquad (6')$$

Toluene in the acid phase

$$\begin{aligned} Vc \frac{d(Cac)}{dt} &= MT - Qc\ Cac - k\ Cac\ Cbc\ Vc \\ &= 0 \text{ (By assumption)} \end{aligned} \qquad (7')$$

Toluene in the organic phase

$$Vd \frac{d(Cad)}{dt} = Qd\ Cao - Qd\ Cad - MT \qquad (8')$$

Nitric acid in the organic phase

$$Vd \frac{d(Cbd)}{dt} = MA - Qd\ Cbd \qquad (9')$$

At steady state, equations 6', 8' and 9' become

$$0 = Qc\ Cbo - Qc\ Cbc - MT - MA$$

$$0 = Qd\ Cao - Qd\ Cad - MT$$

$$0 = MA - Qd\ Cbd$$

The rate of mass transfer of nitric acid from the acid phase to the organic is given by the last equation as $MA = Qd\ Cbd$. This is calculated from the experimental data. If this rate is substituted in the first equation, it is found that the value of MT as given by this equation is different from the one given by the second equation. Hence, the two equations cannot be satisfied. It may thus be concluded that the chemical equilibrium model cannot generally be applied in case of an imperfectly mixed system.

Hence, the only alternative is to test the same model as used for the perfectly mixed system.

Again for solving the transient equations, one needs the parameters MT, Cac, and ($-\Delta H$), which were obtained by solving equation 11, 12 and 14. The rate constant k should not be a function of the speed of mixing. Hence, the relationship between k vs. T as determined by the least squares fit method for the perfectly mixed runs was used in the transient solution of the imperfectly mixed runs. The temperature dependency of other parameters like MT, ($-\Delta H$) and Q was used as mentioned for the perfectly mixed system.

RESULTS AND INTERPRETATION

The objective of this study was to determine a mathematical model which would predict the path to steady state of an exothermic, two-phase reaction in an imperfectly mixed continuous-flow stirred-tank reactor. Nitration of toluene with mixed acids was chosen as the reaction to be studied. This reaction was investigated by Okimoto (1969) under perfectly mixed conditions. Before taking any data under the imperfectly mixed conditions, three runs were made under the perfectly mixed conditions. It was essential to test the equipment under the latter conditions to justify the data obtained under the former. Moreover, this data could be used to make any improvements, if possible, in the model proposed by Okimoto. Four runs were made under the imperfectly mixed conditions. Attempts were also made to see if any conversion could be obtained under conditions of zero speed of mixing.

The feed acid concentration was 30.746 wt percent nitric acid, 41.7 wt percent sulfuric acid, and the remainder, water. The volume ratio of the organic feed rate to the acid feed rate was kept nearly equal to 2. This ratio was constant for all the runs. Experimental data were obtained by varying the cooling-water flow rate. Reactant temperatures were not varied, as the data of Okimoto indicated that steady states were not affected much by the variation in either the temperature of the feed acid or the temperature of toluene. Reactant flow rates were also not varied so as to keep the volume of each phase in the reactor constant.

The mathematical model consisted of four simultaneous nonlinear differential equations. A FORTRAN IV program was written with the fourth-order Runge-Kutta method of solution. Computer runs were limited to 60 min of actual reactor time, which was greater than the time required to reach steady state in the experimental runs.

Before the transient equations could be solved, values for the mass-transfer rate of nitric acid(MA), mass-transfer rate for toluene(MT), concentration of toluene in the acid phase(Cac), heat of reaction ($-\Delta H$), and reaction rate constant(k) were required. These parameters were obtained by the solution of the steady-state equations. The results of the calculation are given in the appendix.

In the transient program, variation of MA, MT, ($-\Delta H$), Q and k with temperature was also taken into account by the methods already given in the mathematical model.

The effect of temperature on the density and specific heat of various streams was considered by polynomial approximations as shown in the appendix.

The mathematical model for the transient solution of the four differential equations differed from that of Okimoto in the following respects.

1. Rate constant (k). In Okimoto's study, the reaction rate constant k was calculated from the steady-state data of each run, those two values were used in the transient program of that particular run with the temperature dependence of k as given by Arrhenius equation. But actually, k should be a function of temperature only, and it should be possible to use a general equation for k in all the runs. Theoretically, it would be much easier to calculate k as a function of T, provided the value of energy of activation E is available. Unfortunately, no accurate value of E is available in the literature.

In this study, the values of k were obtained from the steady state data of all the runs, and then the least-squares method was used to get the best equation relating k and T. This equation was

$$\ln k = 14.41799 - 5923.04/T + 460.0$$

The energy of activation as given by the above equation is roughly 12 k-cal per gm-mole. Hougen and Watson gave a value of 14 k-cal in the temperature range from 15 to 50C.

2. Mass transfer rate of toluene(MT). Okimoto assumed that

the rate of mass transfer of toluene from the organic to the acid phase could be correlated by the following equation for going from one steady state to another

$$\text{Sacd} = \text{SACDA} + \text{SACDB} \times (T^{o}R)^{\frac{1}{2}}$$

where Sacd is the rate of mass transfer and SACDA and SACDB are two constants which can be evaluated from the steady-state data of a run under study.

It was felt by the author that the equation for mass transfer should contain one term for the mass transfer coefficient and another for the concentration of toluene in the organic phase. Hence, the equation for the mass transfer rate may be written as

$$MT = k_m \, Cad$$

As already mentioned, it was not possible to use a term for the driving force in the above equation. The temperature dependency of the mass transfer coefficient k_m was considered by the following equation

$$k_m = k_o \exp(k_1/T)$$

The reasons for choosing this form have been given in the discussion of the mathematical model.

3. Heat removed by the cooling coil(Q). In Okimoto's study, the heat removed by the cooling coil was calculated from the equation

$$\begin{aligned} Q &= UA(\Delta T)_m \\ &= UA(T - Tc) \end{aligned}$$

$$= hA(T - Tc)$$

where h is the heat transfer coefficient for the cooling fluid, and Tc is the average temperature of the cooling fluid.

Use of the above equation requires two approximations. Firstly, it makes use of the average temperature of the cooling fluid (Tc) in the entire transient program, which may not be fully justified, especially when the difference in the reactor temperature T and the cooling fluid temperature is large. Secondly, the above equation uses arithmetic average driving force whereas the calculation of heat transfer coefficient h is done from the heat balance equation of the cooling fluid by use of log-mean temperature difference. This difficulty was mentioned by Okimoto in his report, and he used some correction factor for each run.

In this study, both of the above-mentioned approximations were omitted, which was possible by elimination of the outlet coolant temperature from the heat balance equation. The method has already been discussed in the development of the mathematical model.

The concentration of sulfuric acid in the data of the three perfectly mixed runs is tabulated below.

Table 1

	Sulfuric acid Wt percent	
Run No	Steady State 1	Steady State 2
1	48.3	47.7
2	47.6	48.8
3	47.3	48.0

As already mentioned, wt percent sulfuric acid in the feed acid was 41.7. The sulfuric acid balance agreed within 5 percent. Hence, it was concluded that there was no significant loss of sulfuric acid by any side reaction such as sulfonation of toluene in the system. Conditions for this side reaction as suggested by Englund and others (1953, p.189) did not exist in this study, and it is safe to assume that no sulfonation of toluene took place.

Predicted values of the reactor temperature, concentration of toluene in the organic phase were compared with the experimental data.

Figures 3, 4 and 5 show reactor temperatures vs time and concentration of nitric acid vs.time for runs 1, 2 and 3. Figures 6 and 7 show concentration of toluene in the organic phase vs time. In all the plots, S1 indicates the first steady state and S2 indicates the second steady state reached after upset of the coolant flow rate. Steady state values are also tabulated in table 2.

Comparison of the temperature plots indicates that there is reasonably good agreement between the predicted and the experimental values. Examination of table 2 shows that the predicted value of the temperature at steady state two falls within 1 degree of the experimental value for runs 1 and 3 and within 2 degrees for run no 2. The transient values, of course, show more deviation. Most of the temperature change takes place in the first ten minutes

TABLE 2

Run No	Temperature			Concentration of nitric acid in acid phase			Concentration of toluene in organic phase		
	Steady State 1	Steady State 2	Predicted Steady State 2	Steady State 1	Steady State 2	Predicted Steady State 2	Steady State 1	Steady State 2	Predicted Steady State 2
1.	84.1	96.7	96.4	4.71	4.39	4.49	8.01	7.76	7.76
2.	89.1	109.5	111.2	4.67	4.09	4.02	7.79	7.47	7.47
3.	88.0	99.3	100.2	4.70	4.31	4.25	7.81	7.6	7.58

Figure 3
(Results of run 1)

_____ Computer results

0 Experimental results

RUN 1

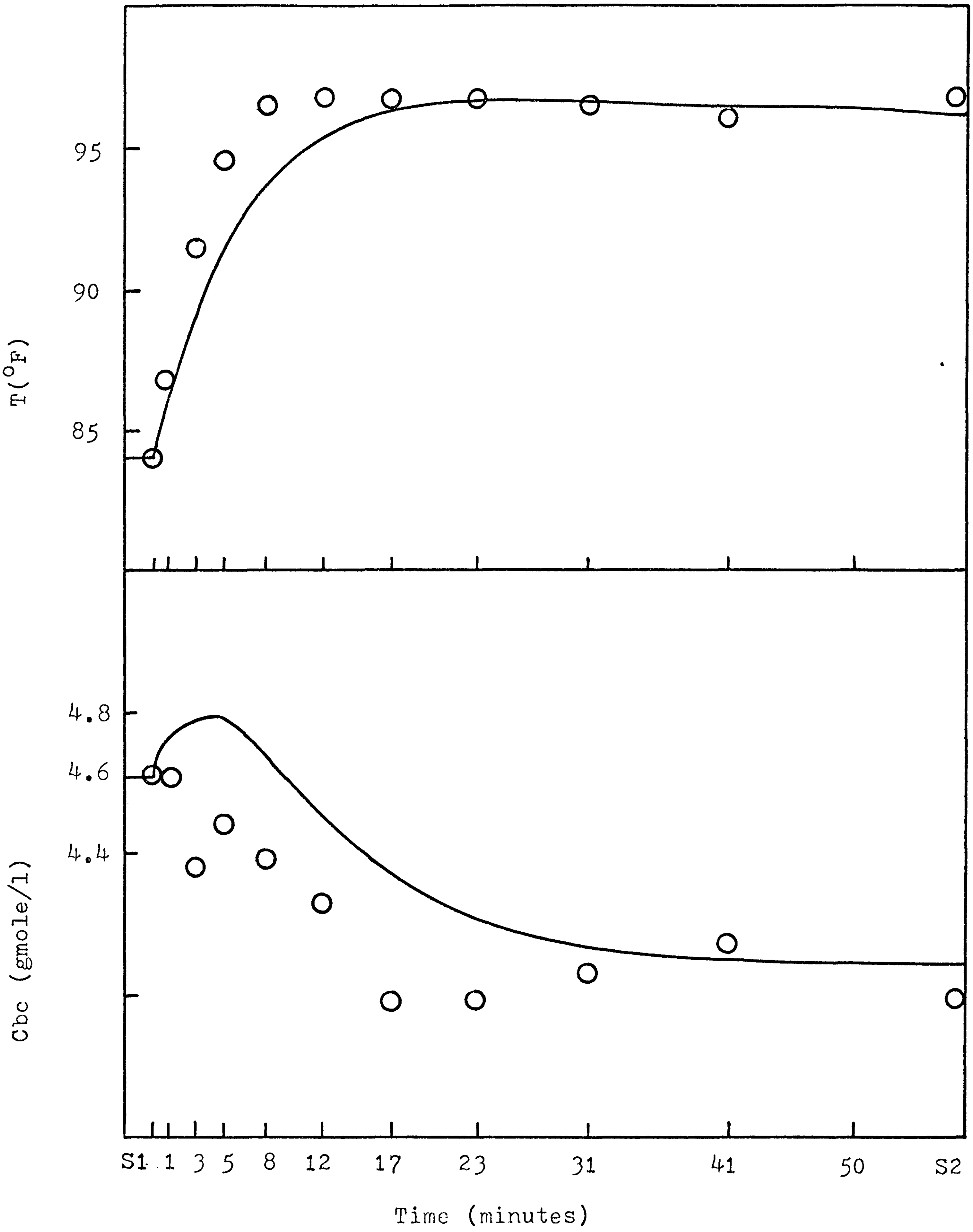

95
90
85
T(°F)
4.8
4.6
4.4
Cbc (gmole/l)
S1
1
3
5
8
12
17
23
31
41
50
S2
Time (minutes)

Figure 4

(Results of run 2)

______ Computer results

O Experimental results

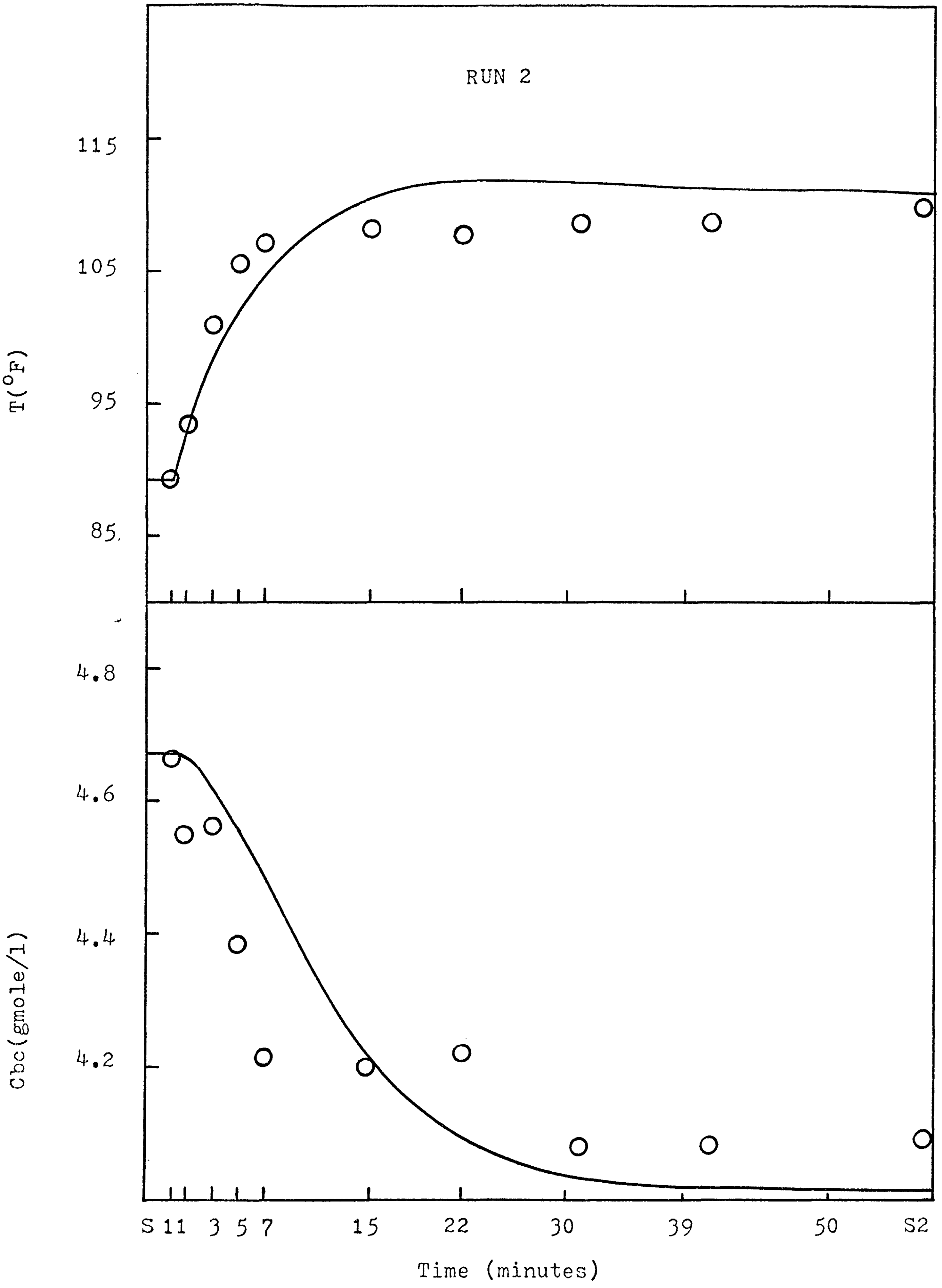
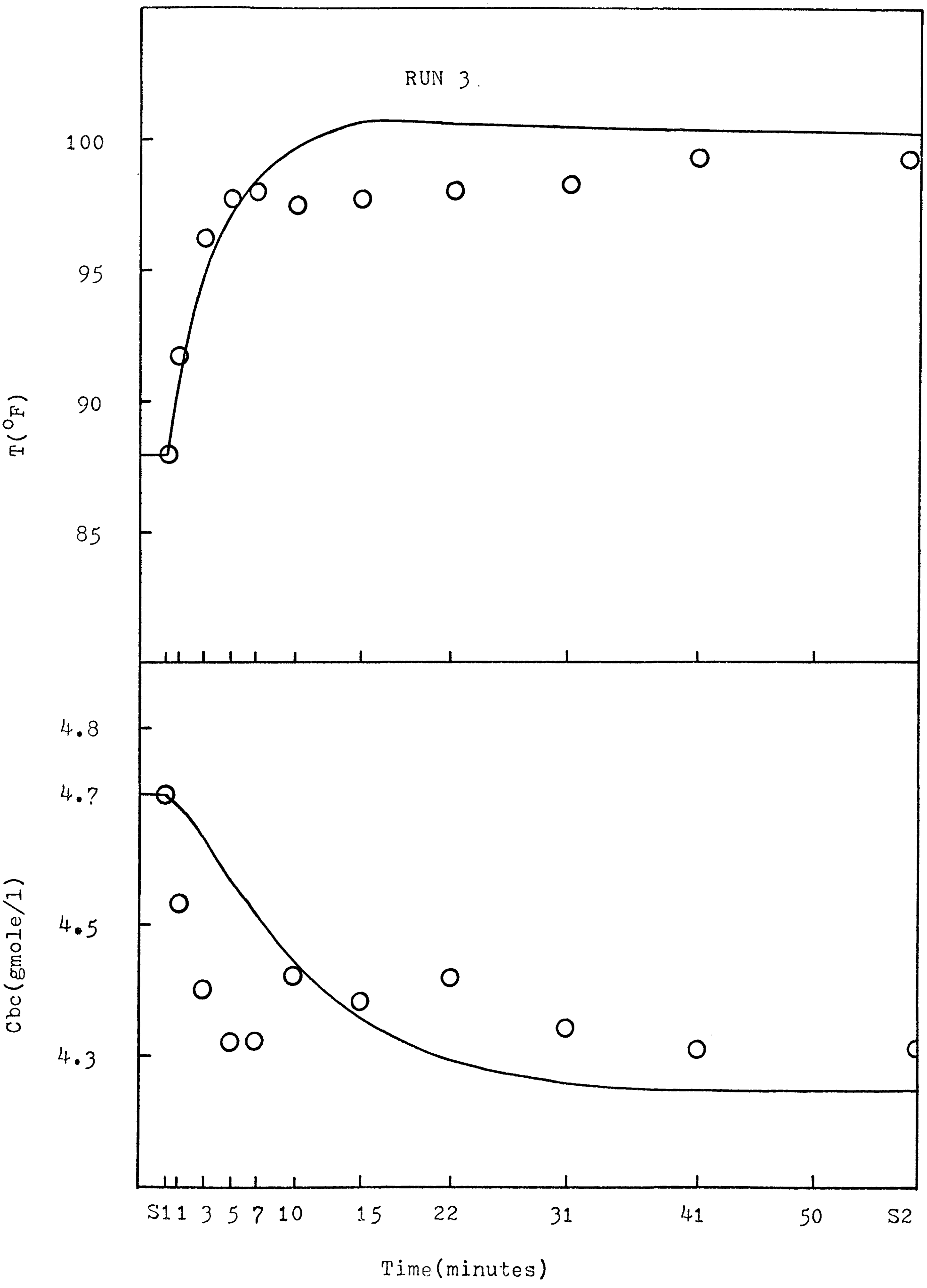

RUN 2
T(°F)
115
105
95
85
Cbc(gmole/l)
4.8
4.6
4.4
4.2
S 1 1 3 5 7 15 22 30 39 50 S2
Time (minutes)

Figure 5

(Results of run 3)

_______ Computer results

O Experimental results


RUN 3
T(°F)
100
95
90
85
Cbc(gmole/1)
4.8
4.7
4.5
4.3
S1
1
3
5
7
10
15
22
31
41
50
S2
Time(minutes)

after upsetting of the coolant flow rate. In this time period, the predicted reactor temperature is lower than the actual temperature in almost all the transient points, with the exception of two points of run no 3. In Okimoto's study, the predicted temperature was lower than the experimental value for all the transient time periods and in nearly all the runs. A possible explanation for this could be in the value of heat transfer coefficient. It was assumed that the value of heat transfer coefficient was constant in the transient program. But it is possible that both inside and outside film coefficients change with temperature. To consider this variation, one needs correlations for both inside and outside film coefficient. Unfortunately, no correlation was available for the outside film coefficient under laminar flow conditions. Accuracy in prediction of U may help in better prediction of the reactor temperature.

Plots of nitric acid concentration in the acid phase vs. time indicate that the model does predict the final concentration of nitric acid within reasonable accuracy. In the transient part, some of the points show very good agreement whereas others indicate large deviations between the predicted and the experimental values. The deviations are more pronounced in the earlier part of the transient period, which is logically expected. The deviation in the predicted temperatures also followed a similar pattern. Since the differential equations for the concentrations are coupled with the differential equation for the temperature, the inaccuracy in one is bound to show up in the other. The term for the rate equation will have significant effect on both the equations.

The rate equation which has been used in this study as well as previous investigation is of the form:

$$r = k\ Cac\ Cbc\ Vc$$

As already mentioned, this equation does not take into account the effect of activity coefficients which are really important in a nonideal liquid mixture of acids and the hydrocarbon. In fact, the value of rate constant k calculated from the above equation will not represent the true rate constant because the activity coefficients would also be lumped into the rate constant. These activity coefficients are functions of temperature as well as concentration. And their temperature dependency will be different from the temperature dependency of k, as given by the Arrhenious equation. No information about the activity coefficients is available in the literature. In fact, one needs large amounts of data to predict these for various temperatures and for different concentrations of sulfuric and nitric acids in the feed mixture.

Another important factor which will definitely affect the rate term is the reaction mechanism. Though a large number of investigators have supported the nitronium ion mechansim for the nitration of aromatics, the evidence in favor of this mechanism is not entirely conclusive. It needs more investigation to establish that the nitronium ion is the nitrating agent for all concentrations of nitric or sulfuric acids. And if not, what are the limiting values for the concentration of the two acids for which this mechanism may be safely assumed.

There is also a slight change in the sulfuric acid concentration. It may have some effect on the rate equation.

Figures 6 and 7 show that the predicted concentrations of toluene at the second steady state are very close to the experimental values. Predicted concentrations for the transient period of run no 2 are within experimental error, but for runs 1 and 3, the first few points do not show good agreement with the experimental data. Again, part of the explanation lies in the problem of predicting the accurate temperatures in the early part of the transient period. Concentration of toluene depends upon the rate of mass transfer of toluene from the organic to the acid phase, which in turn depends upon the mass transfer coefficient as well as the concentration driving force. Temperature will affect the mass transfer coefficient and the equilibrium concentration of toluene in the acid phase. The equation used for the mass transfer is

$$MT = k_0 \exp(k_1/T) Cad$$

This equation does not include the effect of equilibrium concentration for which no information was available in the literature. Hence, the predicted rates

Figure 6

(Results of run 1 and 2)

______ Computer results

O Experimental results

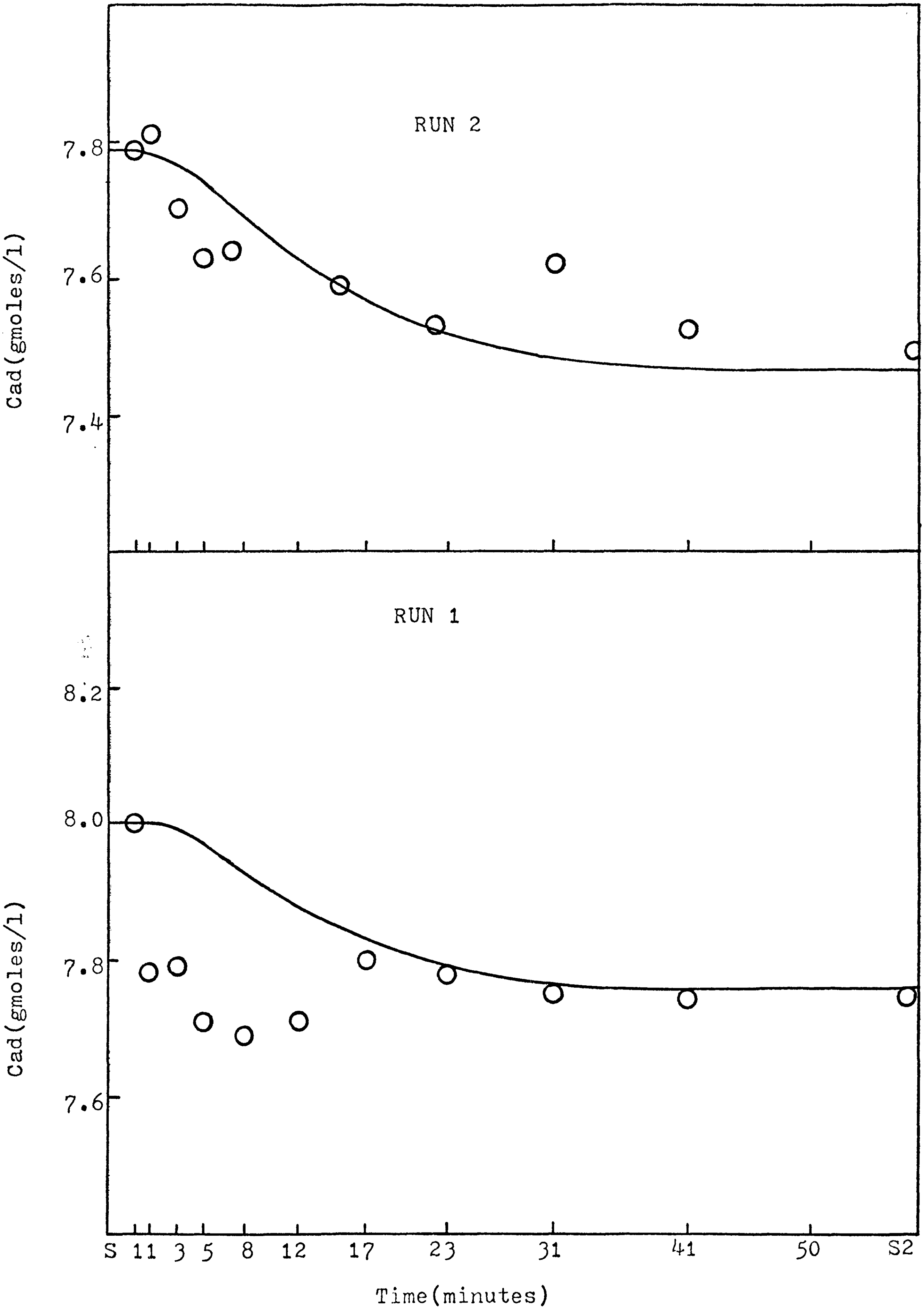

RUN 2
7.8
7.6
7.4
Cad(gmoles/l)
RUN 1
8.2
8.0
7.8
7.6
Cad(gmoles/l)
S
11
1
3
5
8
12
17
23
31
41
50
S2
Time(minutes)

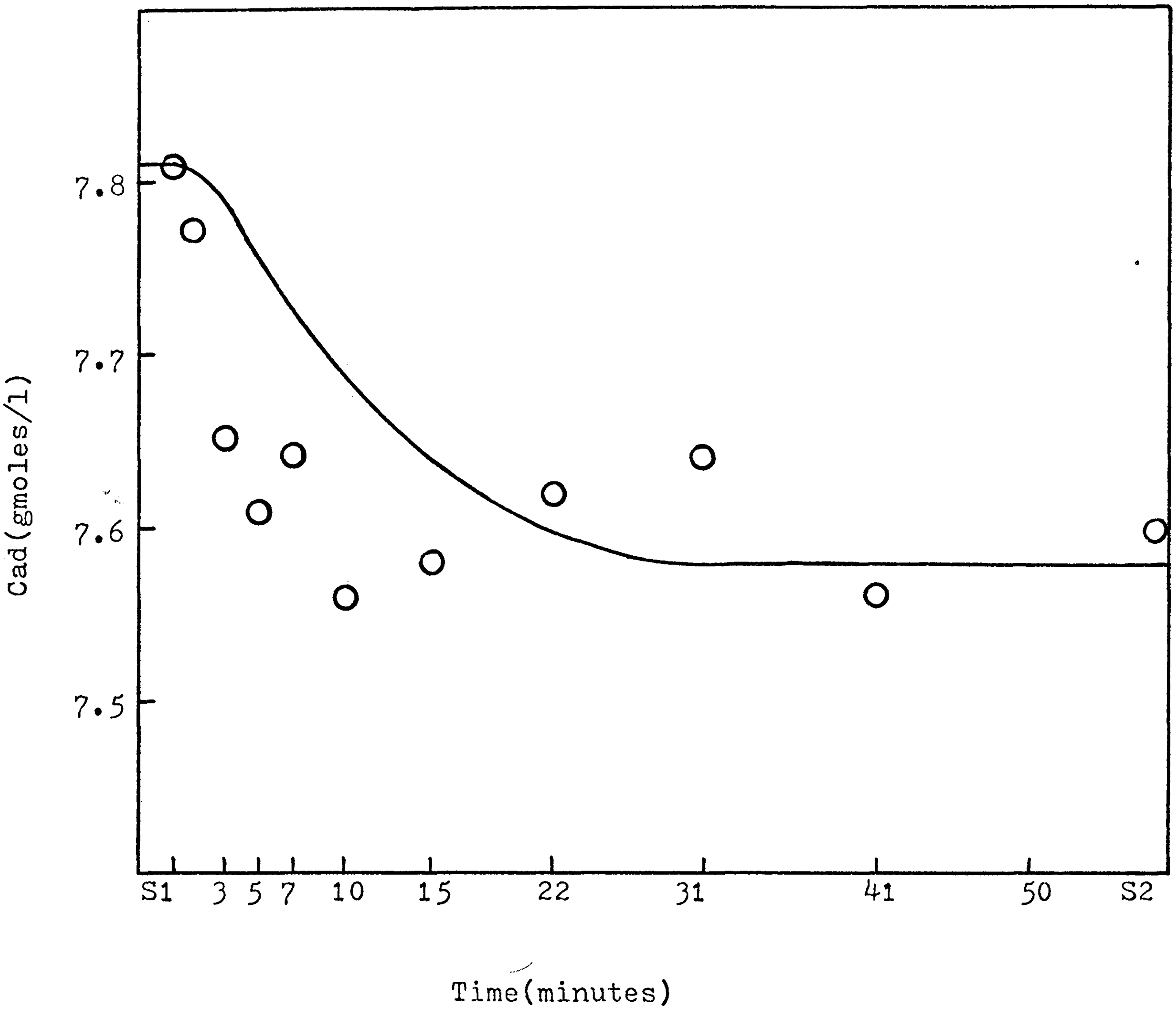
Figure 7

(Results of Run 3)

______ Computer results

O Experimental results

RUN 3



of mass transfer are bound to be in error, which would affect the predicted concentrations of toluene.

Run 4 through 7 were made at a mixing speed of 400 rpm compared to 1050 rpm used in runs 1 through 3. This lower speed of mixing results in imperfect mixing of the two phases. It may be expected that the temperature in each phase would be different. But experimentally, it was found that the temperatures in the two phases were equal. This fact was observed by placing a thermocouple approximately in the center of each phase and recording the temperatures. Thus, it may be concluded that the heat transfer between the two phases is very rapid.

Attempts were made to take some data at zero speed of mixing. It was found that there was no temperature rise in the reactor, a fact which implies that the conversion in the system was zero or negligibly small.

Figures 8,9,10 and 11 show the plots of predicted reactor temperatures and nitric acid concentrations vs. time for the imperfectly mixed runs 4 through 7 compared with the experimental values. The predicted values of the steady-state temperatures for runs 4 and 6 are close to the experimental values. For run no.5, the predicted temperature differs by about two degrees from the experimental value; but for run no. 7, the predicted value of temperature is much lower than that observed in the experiment.

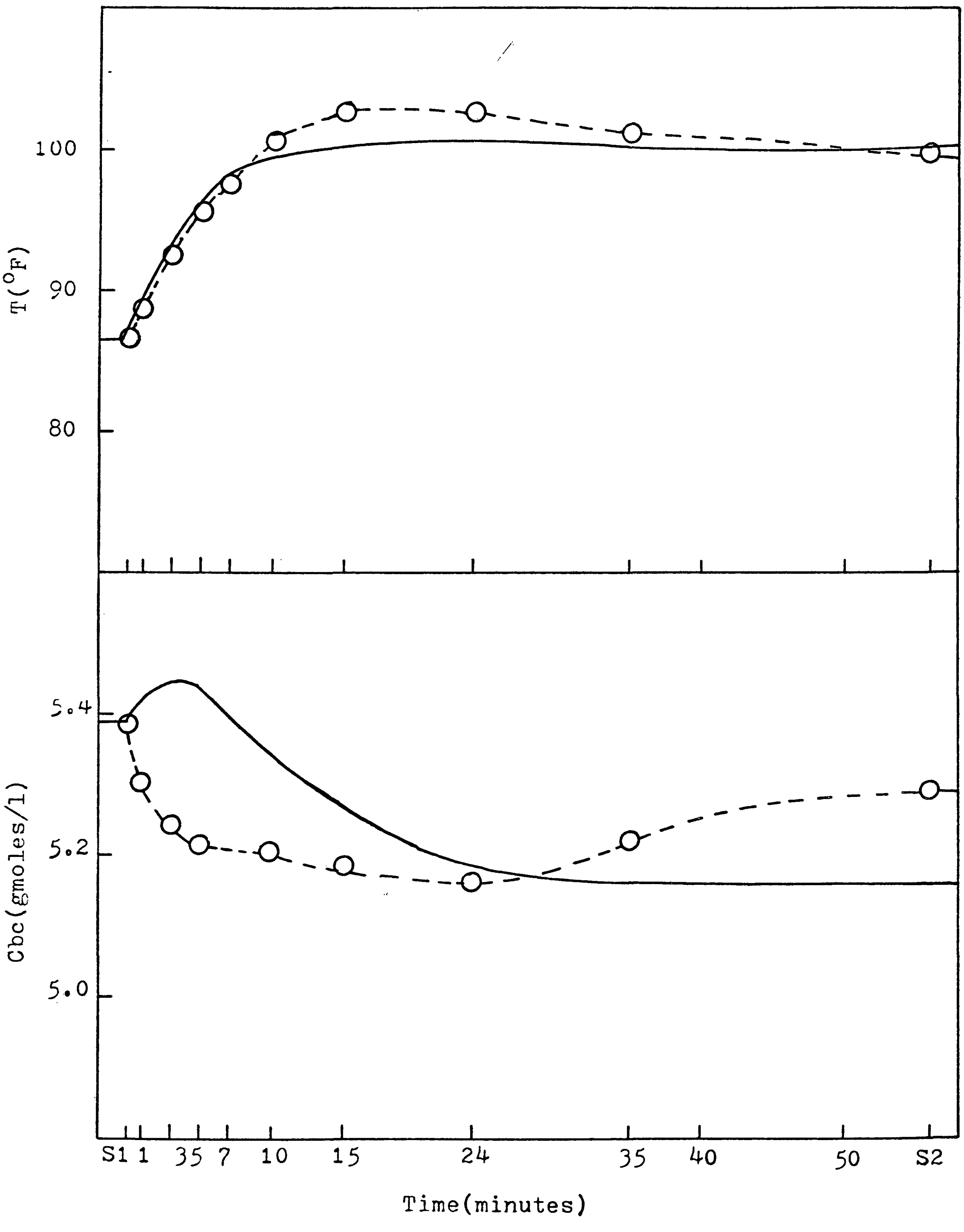
For the transient period, the predicted values of temperatures for runs 4 and 6 are in good agreement with the

Figure 8

(Results of run 4)

_____ Computer results

0 Experimental results


RUN 4

T(°F)
100
90
80
Cbc(gmoles/l)
5.4
5.2
5.0
S1
1
3
5
7
10
15
24
35
40
50
S2
Time(minutes)

Figure 9

(Results of run 5)

______ Computer results

0 Experimental results

RUN 5

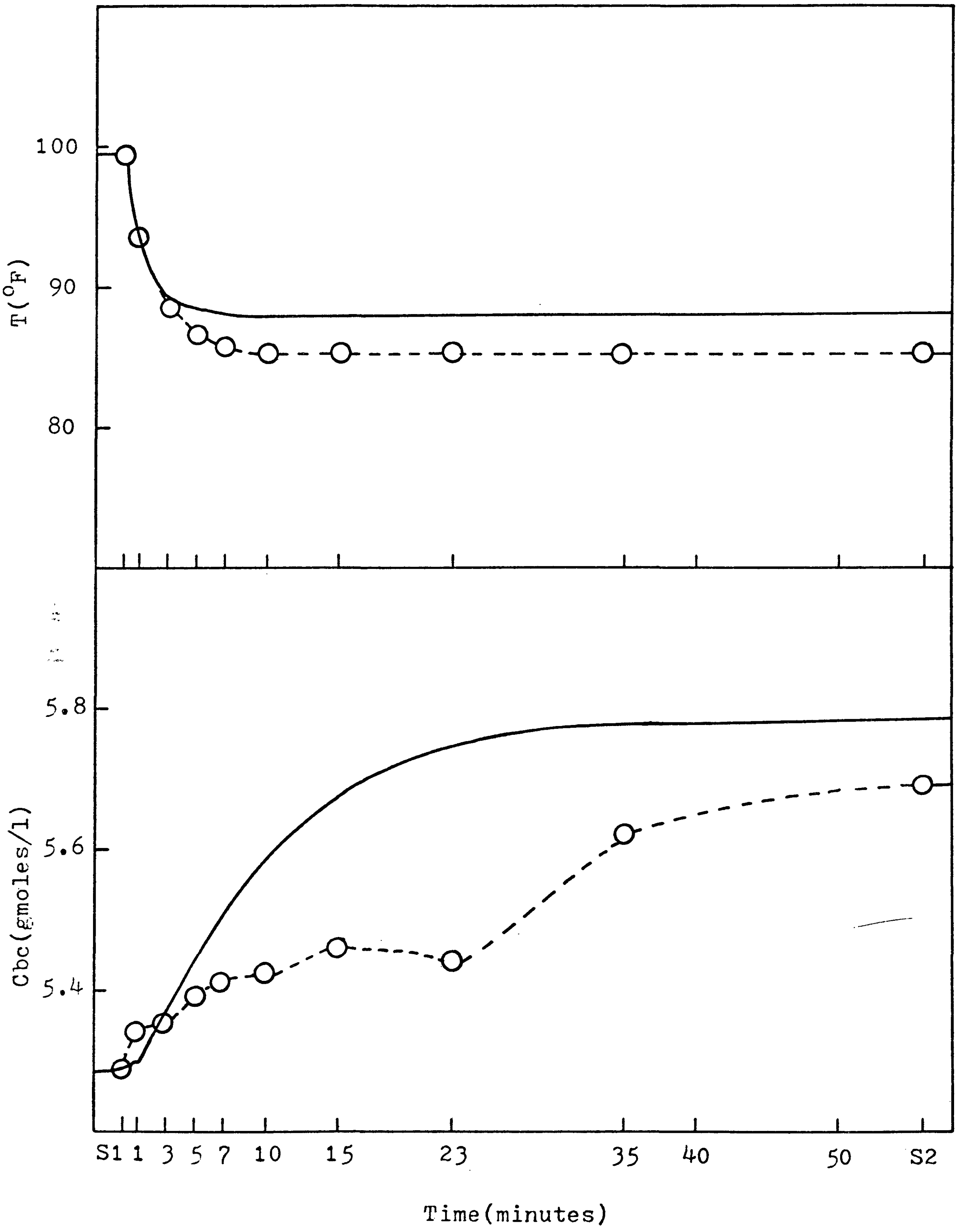

100
90
80
T(°F)
5.8
5.6
5.4
Cbc(gmoles/1)
S1
1
3
5
7
10
15
23
35
40
50
S2
Time(minutes)

Figure 10

(Results of run 6)

_______ Computer results

O Experimental results

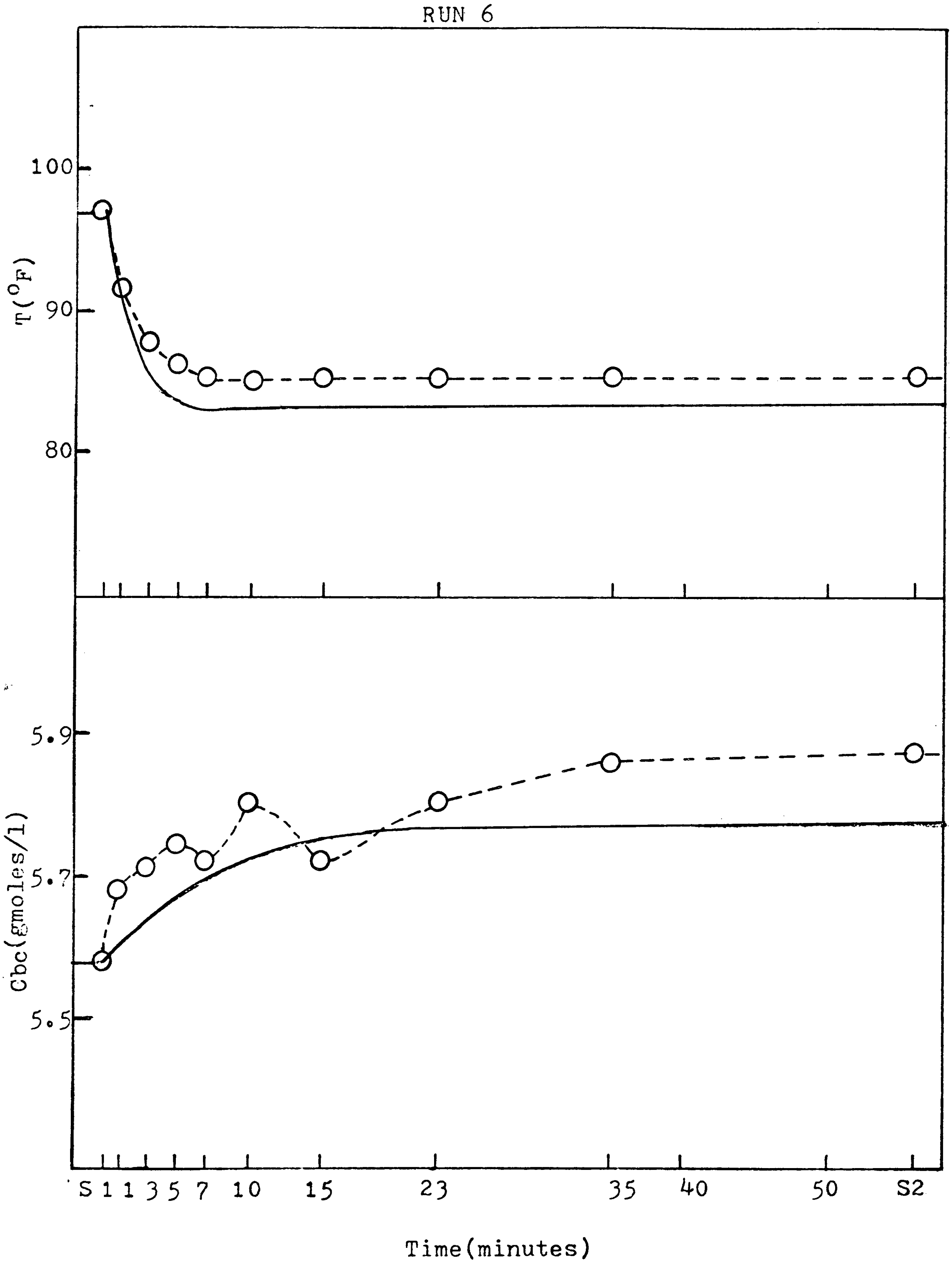
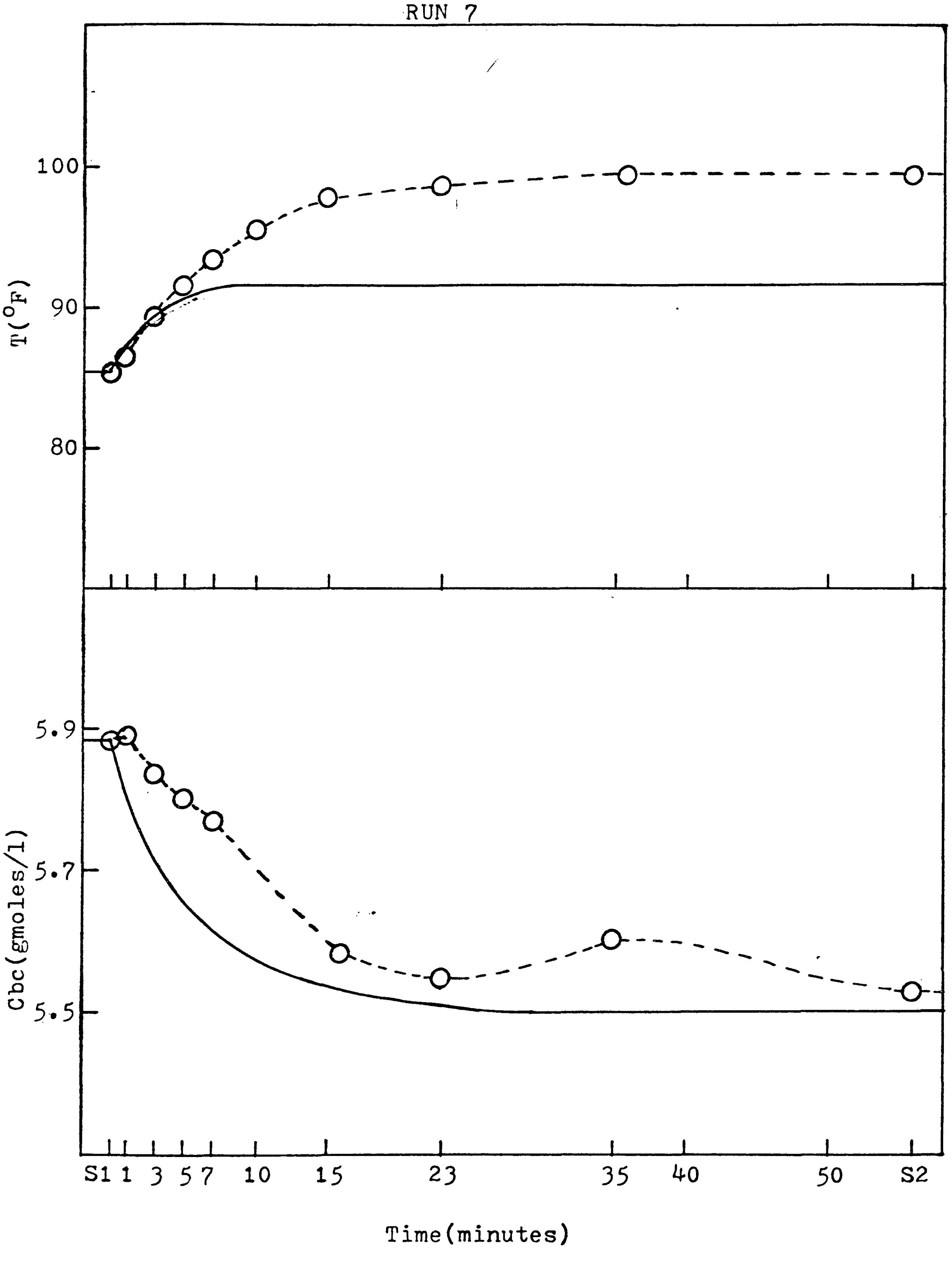

RUN 6
T(°F)
100
90
80
Cbc(gmoles/l)
5.9
5.7
5.5
S 1 1 3 5 7
10
15
23
35
40
50
S2
Time(minutes)

Figure 11

(Results of run 7)

______ Computer results

0 Experimental results


RUN 7
100
90
80
T(°F)
5.9
5.7
5.5
Cbc(gmoles/l)
S1
1
3
5
7
10
15
23
35
40
50
S2
Time(minutes)

data; but for runs 5 and 7 the agreement is good only for first few minutes of the upset period. For run 5, the predicted values are higher than the experimental data whereas for runs 6 and 7, the predicted values are lower than the experimental values. It is not possible to give any suitable explanation for this behaviour. The problem could be either in the experimental data or in accurately predicting the overall heat-transfer coefficient. The reasons for poor agreement for some of the transient points are the same as mentioned for runs 1 through 3. The outside film coefficients for the imperfectly mixed runs are bound to be different from those of perfectly mixed runs because of the difference in speeds of mixing. In the absence of any information on the outside film coefficient, it is not possible to say how it is going to vary for the two speeds.

The predicted steady-state nitric acid concentration for run 7 is close to the experimental value but for runs 4, 5 and 6 the agreement is poor. The transient data for some of the points are in close agreement with the experimental values. Runs 5 and 6 were different from the others in the sense that the flow rate of cooling water was upset from lower to the higher value, whereas in all other runs, the flow upset was from the higher to the lower value. All the plots show some oscillations in the experimental data but the mathematical model fails to predict these oscillations. The temperature plots did not show any significant oscillations. It is not possible to give any suitable explanation for the oscillations. They could be due to the interaction of various parameters in the system.

Figures 12 and 13 show the comparison of predicted toluene concentrations with the experimental data. The predicted steady-state values for run no. 4 and 6 are in close agreement with the experimental data. For run no. 5, the agreement is within experimental error; but for run no. 7, the predicted value of toluene concentration is much higher than that observed in the experiment. For the transient period, the pattern is somewhat similar to that of the nitric acid concentrations. The experimental data again show oscillations whereas the predicted data do not exhibit any such behaviour.

In general, the predicted results for the imperfectly mixed runs show poorer agreement with the experimental data than the perfectly mixed runs. This observation is especially true in prediction of the concentrations both that of the nitric acid and that of toluene. Insufficient mixing can result in low nitration rates due to the small interfacial area. It can also lead to a nonuniform nitration process. There is also the possibility of formation of dead spaces in which non-nitrated or not fully nitrated substances accumulate.

Figures 14 to 17 show the phase plane plots of concentration vs. temperature for runs 4 to 7. Experimental data for run 4 shows that the concentrations of both nitric acid and toluene increase beyond the final steady state value although the temperature is constant. This trend is also evident in the predicted values of concentration although the change is only in one direction at a constant temperature. In plot for run 7 the

Figure 12

(Results of run 4 and 5)

_______ Computer results

0 Experimental results

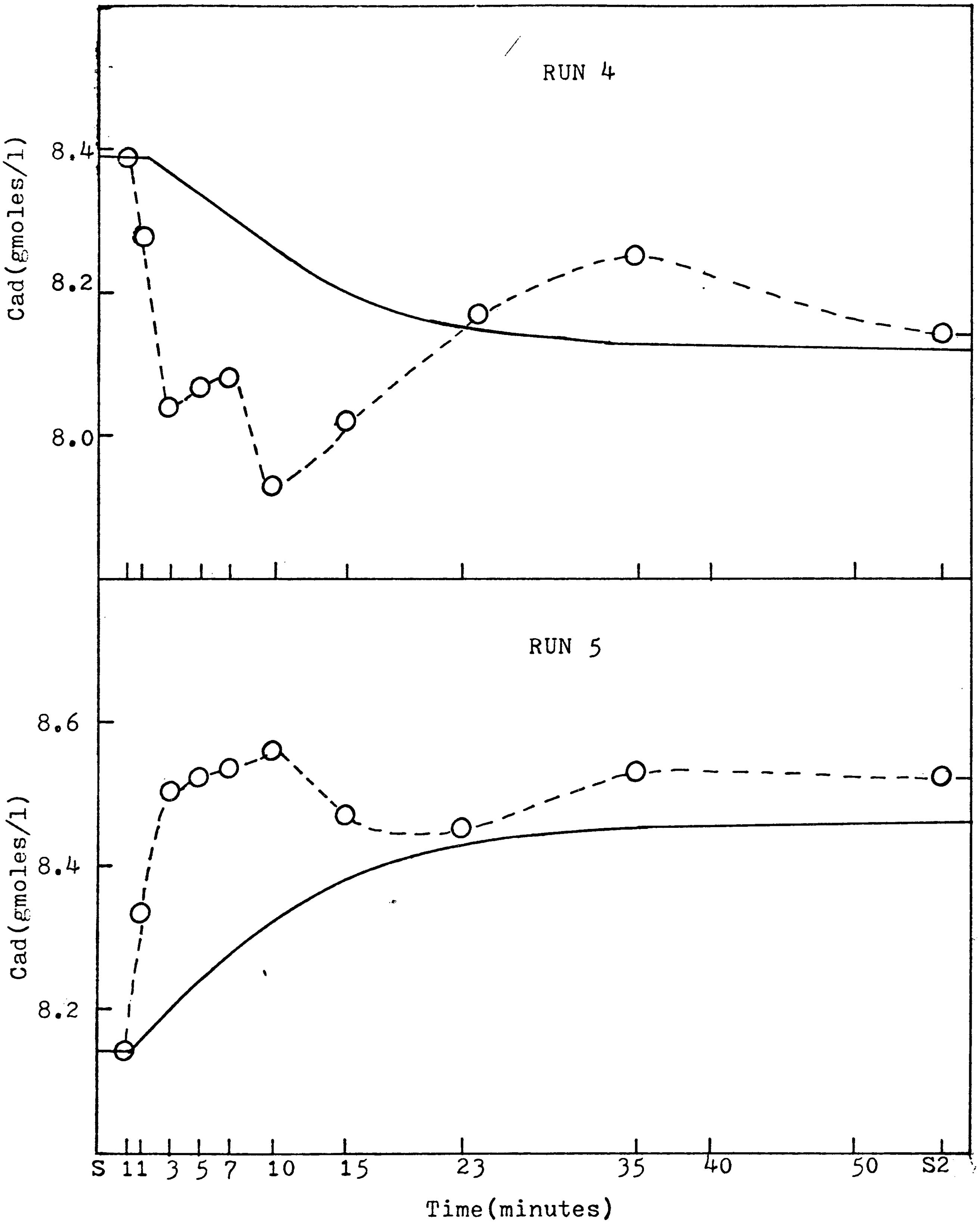
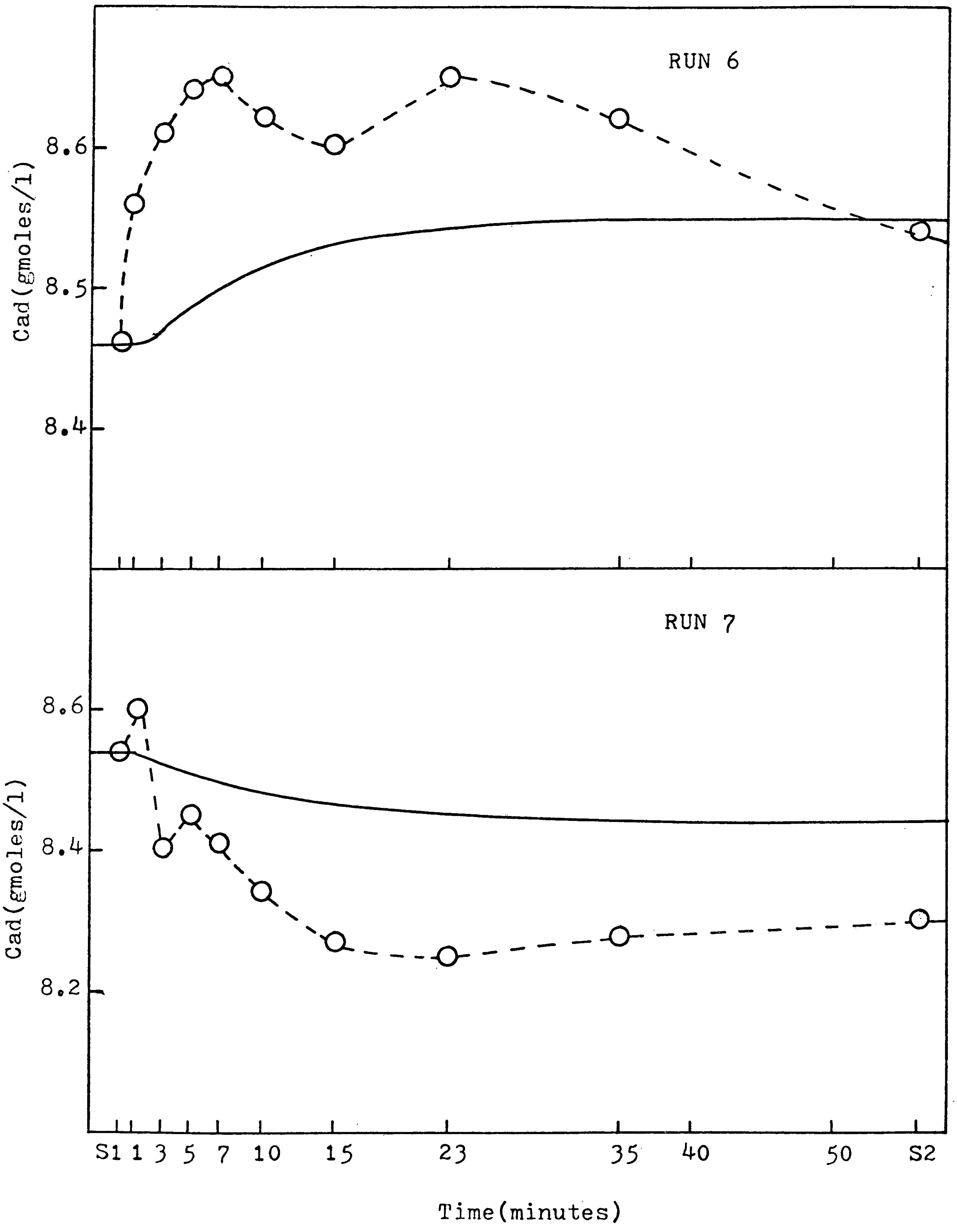

RUN 4
Cad(gmoles/l)
8.4
8.2
8.0
RUN 5
Cad(gmoles/l)
8.6
8.4
8.2
S
1
1
3
5
7
10
15
23
35
40
50
S2
Time(minutes)

Figure 13

(Results of run 6 and 7)

_____ Computer results

O Experimental results


RUN 6
RUN 7
8.6
8.5
8.4
8.6
8.4
8.2
Cad(gmoles/l)
Cad(gmoles/l)
S1
1
3
5
7
10
15
23
35
40
50
S2
Time(minutes)

RUN 4

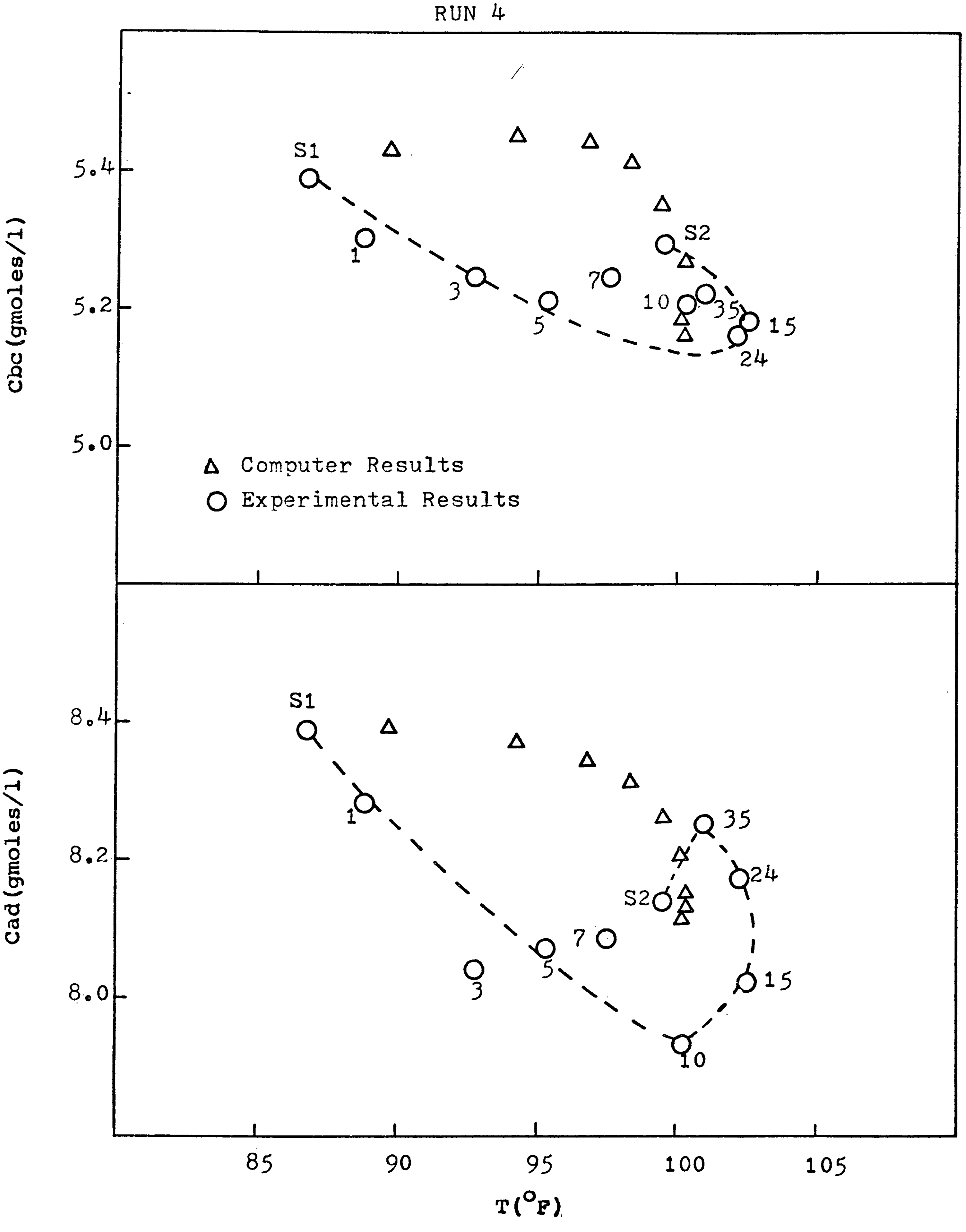


Figure 14

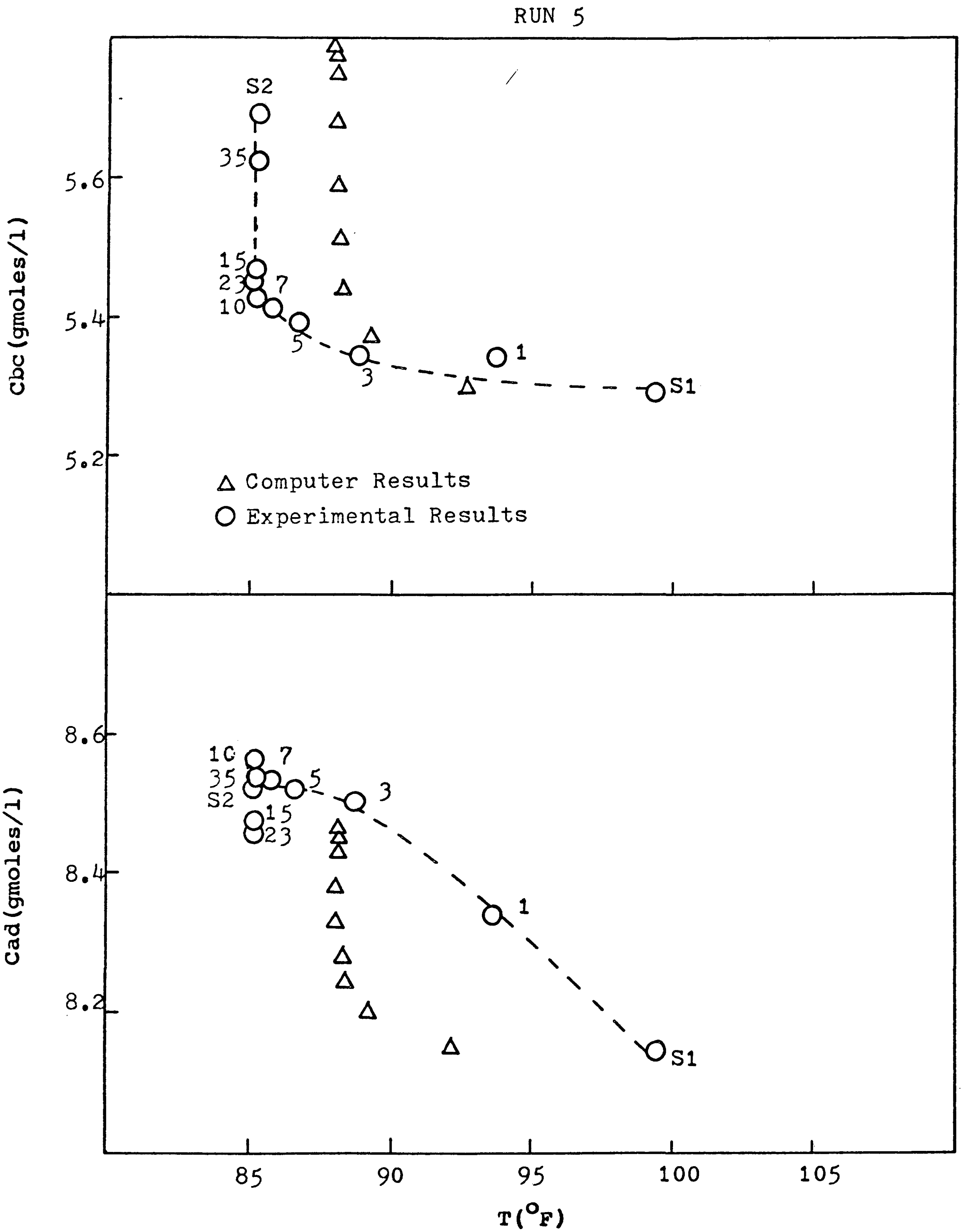

RUN 5
Cbc (gmoles/l)
5.6
5.4
5.2
S2
35
15
23
7
10
5
3
1
S1
△ Computer Results
○ Experimental Results
Cad (gmoles/l)
8.6
8.4
8.2
10
7
35
5
S2
3
15
23
1
S1
85
90
95
100
105
T(°F)

Figure 15.

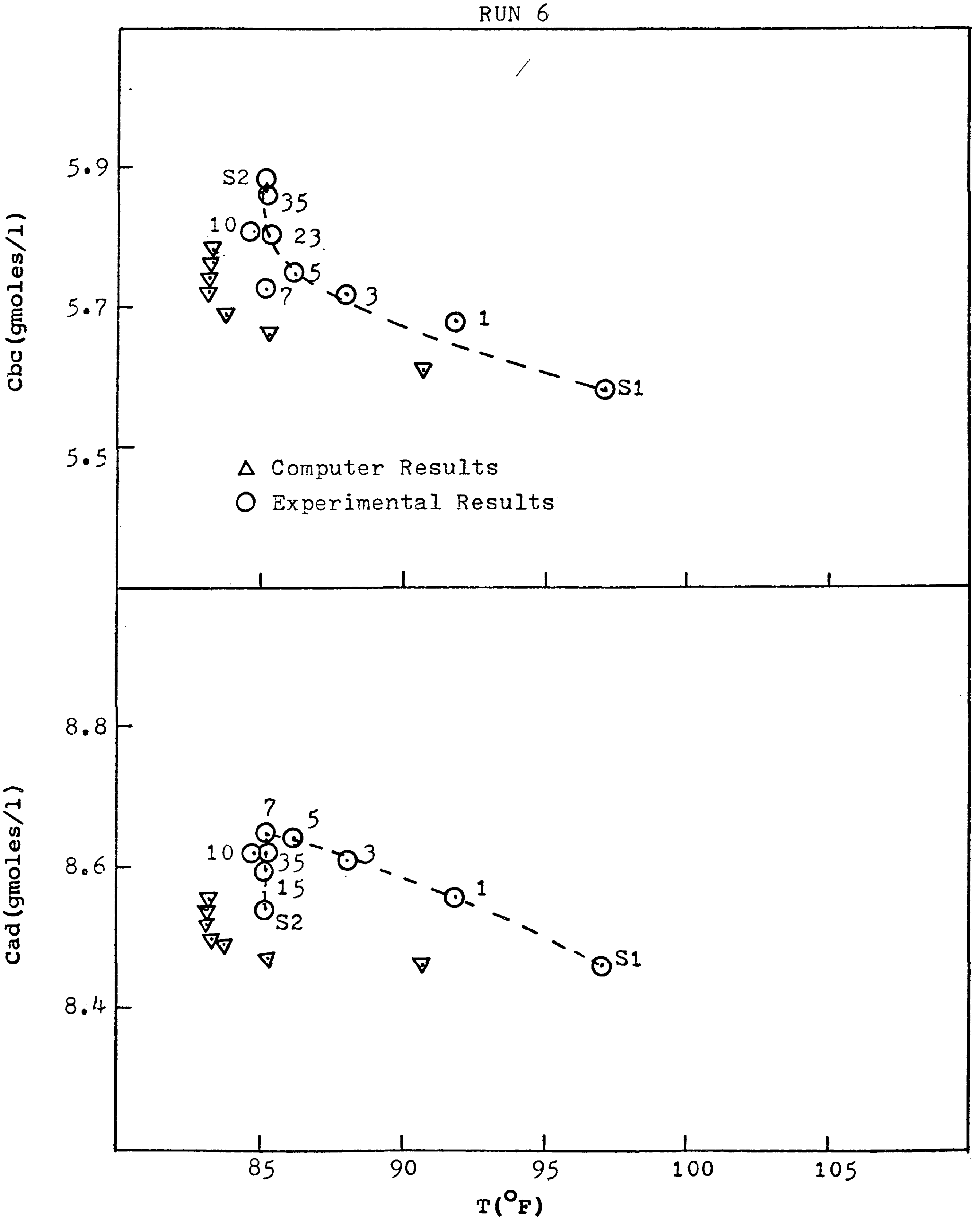

RUN 6
Cbc (gmoles/1)
5.9
5.7
5.5
S2
35
10
23
5
7
3
1
S1
△ Computer Results
○ Experimental Results
Cad (gmoles/1)
8.8
8.6
8.4
7
5
10
35
3
15
1
S2
S1
85
90
95
100
105
T(°F)

Figure 16

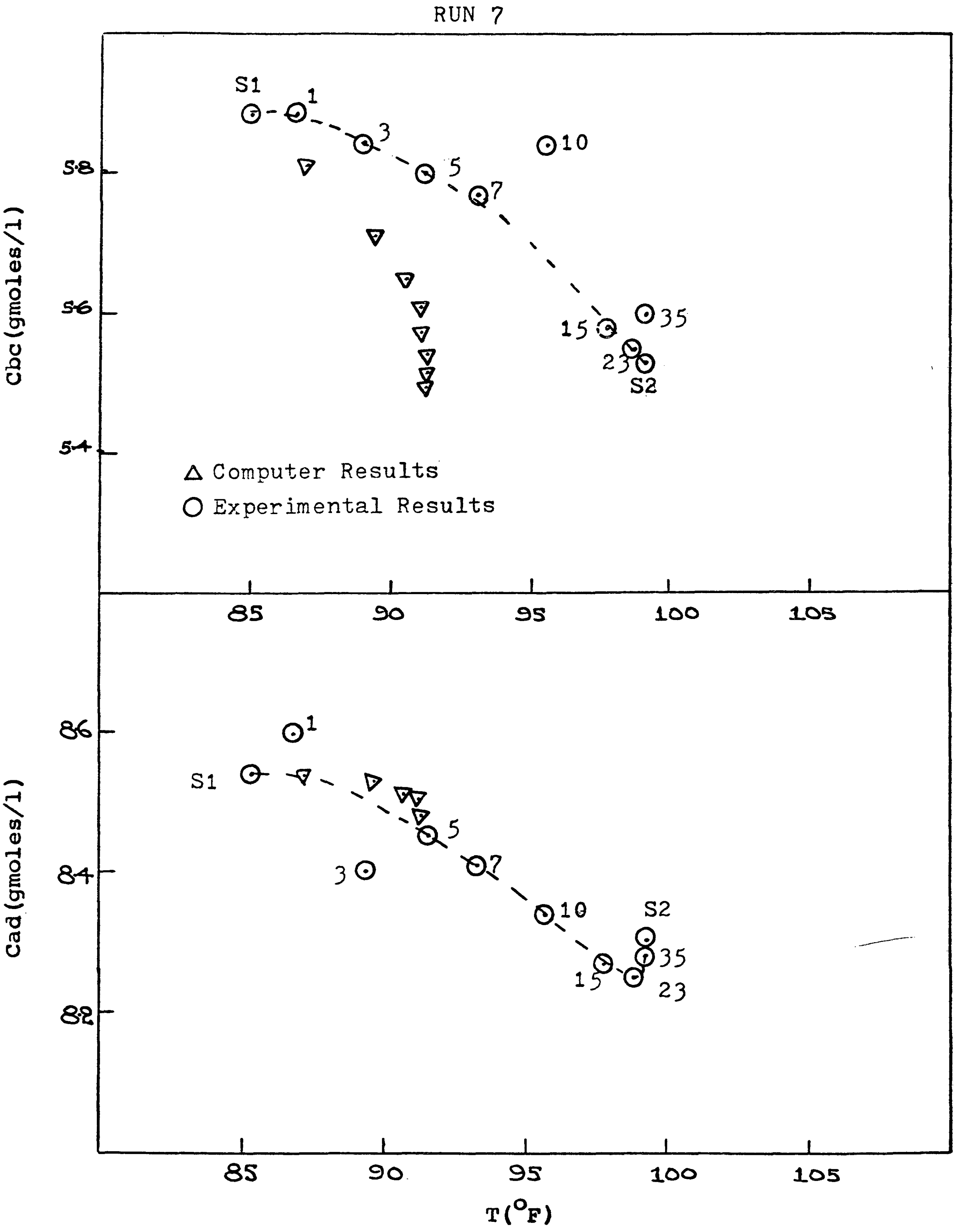

RUN 7
S1
1
3
5
7
10
15
23
35
S2
5.8
5.6
5.4
Cbc (gmoles/l)
△ Computer Results
○ Experimental Results
85
90
95
100
105
S1
1
3
5
7
10
S2
15
35
23
86
84
82
Cad (gmoles/l)
85
90
95
100
105
T(°F)

Figure 17.

predicted nitric acid concentrations are lower than the experimental data. The predicted toluene concentration lies close to the experimental points except for the final steady-state value.

The problems with the mathematical model for the imperfectly mixed runs are same as those for the perfectly mixed system. These are summarized below:

1. Rate constant (k): It cannot be predicted accurately unless more information is available about the activity coefficients and their dependence on the concentrations and temperatures.

2. Heat-transfer coefficient: In order to have better prediction of the temperatures, it is necessary to include temperature dependency of the overall heat-transfer coefficient, which would require information on the outside film coefficient. The effect of stirring on the overall heat-transfer coefficient may also be taken into account if the outside film coefficient can be calculated at various speeds of mixing.

3. Mass-transfer rate: In order to predict the mass-transfer rate of toluene from the organic to the acid phase, it is essential to have information about the equilibrium concentration of toluene in the acid phase.

4. Rate mechanism: Conclusive evidence is required to establish the mechanism of the nitration reaction by nitronium ion for various concentrations of the mixed acids.

In summary, it may be concluded that the mathematical model based on heat and mass-transfer resistances as used in this study is quite suitable for prediction of the temperature of the reactor under transient conditions for both perfectly and imperfectly mixed systems. The model can also reasonably predict the concentrations of nitric acid and toluene for the perfectly mixed system but is some what unsatisfactory for the imperfectly mixed systems. Further refinements are possible if more information is available about the activity coefficients, outside film coefficient, equilibrium concentration of aromatics in the acid phase, and the rate mechanism.

NOMENCLATURE

The following is a list of variables used in this study.

Variable	Units
Area	ft^2
Concentration	g mole/ml
Density	g/ml
Flow rate	ml/min
Heat of reaction	cal/ g mole
Mass transfer rate	g mole/min
Overall heat transfer coefficient	Btu/hr ft^2 ^oF
Specific heat	cal/g^oC
Temperature	^oF
Time	min
Volume	ml

a	Surface area for mass transfer
A	Surface area of cooling coil
Cac	Concentration of toluene in acid phase
Cad	Concentration of toluene in organic phase
Cao	Concentration of toluene in organic feed stream
Cbc	Concentration of nitric acid in acid phase
Cbd	Concentration of nitric acid in organic phase
Cbo	Concentration of nitric acid in mixed acid
Cpc	Specific heat of acid phase
Cpco	Specific heat of mixed acid
Cpd	Specific heat of organic phase
Cpdo	Specific heat of organic feed stream
Cpw	Specific heat of cooling water
D	Diffusivity
E	Energy of activation/universal gas constant
Fa	Acid fraction in sample
$(-\Delta H)$	Heat of reaction, mixing, and impeller
k	Reaction rate constant
k_o k_1	Constants in equation for mass transfer coefficient of toluene
k_m	Toluene mass transfer coeff* interfacial area
K_m	Toluene mass transfer coefficient
m	Mass flow rate of cooling water
M	A parameter defined as equal to UA/mcpw
MA	Rate of mass transfer of nitric acid
MNT	Mono nitro toluene

MT	Rate of mass transfer of toluene
n_D	Refractive index of toluene- MNT mixture
p	Pre-exponential constant in Arrhenius equation
Q	Heat removed by cooling water
Qc	Volumetric flow rate of acid phase
Qd	Volumetric flow rate of organic phase
QS1 QS2	Value of Q at two steady states
R	Universal gas constant
S1 S2	Steady state one and two
rpm	Revolutions per min
t	Time
T	Reactor temperature
$(\Delta T)_m$	Mean temperature difference between reactor and cooling fluid
Tao	Toluene feed temperature
Tbo	Nitric acid feed temperature
Tci	Inlet temperature of cooling water
Tco	Outlet temperature of cooling water
TS1 TS2	Reactor temperature at two steady states
U	Overall heat transfer coefficient
V	Total volume of reactor
Vc	Volume of acid phase in reactor
Vd	Volume of organic phase in reactor
ρc	Density of acid phase
ρco	Density of mixed acid
ρd	Density of organic phase

ρ_{do}	Density of organic feed stream
μ	Viscosity

APPENDIX I

(Data)

Data for seven experimental runs are presented in this section.

Run no. 1, 2, and 3 are the data obtained under perfectly mixed conditions.

Run no. 4,5, 6, and 7 are the data under imperfectly mixed conditions.

RUN 1(Perfectly mixed)

Toluene flow rate = 30.40 ml/min
Mixed acid flow rate = 14.67 ml/min
Toluene feed temperature = 95°F
Mixed acid feed temperature = 91.94°F
Cooling water flow rate = 294 ml/min
Upset water flow rate = 101.4 ml/min
Temperature of inlet cooling water = 76.46°F
Outlet temperature of cooling water at S1 = 82.74°F
Outlet temperature of cooling water at S2 = 96.25°F
Wt % H_2SO_4, S1 = 48.3
Wt % H_2SO_4, S2 = 47.7
Wt % HNO_3 in organic phase product, S1 = 3.44
Wt % HNO_3 in organic phase product, S2 = 3.48

Time (min)	Fa	n_D	T(°F)	Tco(°F)	ρ_c	Cbc	ρ_d	Cad gmole/l
S1	0.30	1.5008	84.09	82.74	1.5816	4.71	0.9045	8.01
S2	0.29	1.5020	96.66	96.25	1.5082	4.39	0.9026	7.75
0-2	0.33	1.5019	86.70	86.26	1.5126	4.71	0.9052	7.78
2-4	0.36	1.5020	91.48	90.61	1.5189	4.58	0.9074	7.79
4-6	0.34	1.5025	94.52	93.65	1.5150	4.64	0.9073	7.71
7-9	0.29	1.5024	96.50	95.83	1.4992	4.59	0.9036	7.69
11-13	0.27	1.5025	96.80	96.48	1.5190	4.53	0.9062	7.71
16-18	0.27	1.5018	96.70	96.26	1.4896	4.39	0.9012	7.80
22-24	0.33	1.5022	96.70	96.26	1.506	4.39	0.9038	7.78
30-32	0.29	1.5020	96.50	95.83	1.5106	4.43	0.8965	7,75
40-42	0.31	1.5021	96.20	95,39	1.5107	4.47	0.9012	7.75

RUN 2 (Perfectly mixed)

Toluene flow rate = 30,4 ml/min
Mixed acid flow rate = 14.67 ml/min
Toluene feed temperature = 96.8°F
Mixed acid feed temperature = 95.0°F
Cooling water flow rate = 252.0 ml/min
Upset water flow rate = 78.0 ml/min
Temperature of inlet cooling water at S1 = 80.06°F
Outlet temperature of cooling water at S1 = 86.96°F
Outlet temperature of cooling water at S2 = 107.83°F
Wt % H_2SO_4, S1 = 47.59
Wt % H_2SO_4, S2 = 48.80
Wt % HNO_3 in organic phase product, S1 = 3.21
Wt % HNO_3 is organic phase product, S2 = 3.19

Time (min)	Fa	n_D	T(°F)	Tco(°F)	ρ_c	Cbc gmole/l	ρ_d	Cad gmole/l
S1	0.33	1.5020	89.09	86.69	1.5177	4.67	0.9038	7.79
S2	0.31	1.5035	109.54	107.83	1.497	4.09	0.9034	7.49
0-2	0.30	1.5020	93.65	91.71	1.5115	4.55	0.9036	7.81
2-4	0.29	1.5029	101.04	98.60	1.5066	4.56	0.9033	7.70
4-6	0.28	1.5030	105.74	102.87	1.4979	4.38	0.9038	7.63
6-8	0.28	1.5026	107.04	105.22	1.4723	4.21	0.9005	7.64
14-16	0.29	1.5030	108.26	106.04	1.4831	4.20	0.9032	7.59
21-23	0.30	1.5034	107.87	105.74	1.4918	4.22	0.9045	7.53
30-32	0.31	1.5031	108.70	106.56	1.4951	4.08	0.9054	7.62
40-42	0.31	1.5035	108.91	107.22	1.4931	4.08	0.9056	7.52

RUN 3 (Perfectly mixed)

Toluene flow rate = 30.4 ml/min
Mixed acid flow rate = 14.67 ml/min
Toluene feed temperature = 98.6°F
Mixed acid feed temperature = 96.44°F
Cooling water flow rate = 286.2 ml/min
Upset water flow rate = 132.0 ml/min
Temperature of inlet cooling water at S1 = 79.16°F
Outlet temperature of cooling water at S1 = 85.83°F
Outlet temperature of cooling water at S2 = 97.96°F
Wt % H_2SO_4, S1 = 47.3
Wt % H_2SO_4, S2 = 48.0
Wt % HNO_3 in organic phase product, S1 = 3.29
Wt % HNO_3 in organic phase product, S2 = 3.10

Time (min)	Fa	n_D	T(°F)	Tco(°F)	ρ_c	Cbc gmole/l	ρ_d	Cad gmole/l
S1	0.31	1.5020	88.0	85.83	1.5211	4.7	0.9072	7.81
S2	0.31	1.5032	99.26	97.96	1.5029	4.31	0.9081	7.60
0-2	0.31	1.5021	91.71	91.71	1.5036	4.53	0.9004	7.77
2-4	0.32	1.5026	96.26	95.39	1.5061	4.40	0.9038	7.65
4-6	0.32	1.5030	97.74	96.26	1.5041	4.32	0.9033	7.61
6-8	0.31	1.5028	97.96	96.48	1.4969	4.32	0.9052	7.64
9-11	0.32	1.5027	97.46	96.26	1.5012	4.42	0.8937	7.56
14-16	0.31	1.5028	97.70	96.50	1.4986	4.38	0.8981	7.58
21-23	0.32	1.5030	98.0	96.63	1.5011	4.42	0.9066	7.62
30-32	0.32	1.5029	98.40	96.70	1.5035	4.34	0.9058	7.64
40-42	0.32	1.5032	99.26	97.74	1.5025	4.31	0.9055	7.56

Run 4(Imperfectly mixed)

Toluene flow rate = 31.1 ml/min
Mixed acid flow rate = 14.8 ml/min
Toluene feed temperature = 96.35°F
Mixed acid feed temperature = 94.82°F
Cooling water flow rate = 222.3 ml/min
Upset water flow rate = 51.4 ml/min
Temperature of inlet cooling water = 80.06°F
Outlet temperature of cooling water at S1 = 85.87 °F
Outlet temperature of cooling water at S2 = 97.74 °F
Wt % H_2SO_4, S1 = 47.15
Wt % H_2SO_4, S2 = 46.50
Wt % HNO_3 in organic phase product, S1 = 3.36 °F
Wt % HNO_3 in organic phase product, S2 = 2.51 °F

Time (min)	Fa	n_D	T(°F)	Tco(°F)	ρ_c	Cbc gmole/l	ρ_d	Cad gmole/l
S1	0.30	1.4985	86.70	85.87	1.5341	5.39	0.8951	8.39
S2	0.30	1.4986	99.48	97.74	1.5154	5.29	0.8616	8.14
0-2	0.30	1.4994	88.87	86.70	1.5173	5.30	0.8943	8.28
2-4	0.30	1.5000	92.57	89.26	1.5167	5.24	0.8940	8.04
4-6	0.31	1.5000	95.39	92.35	1.5204	5.21	0.8941	8.07
6-8	0.28	1.5001	97.46	94.96	1.4965	5.25	0.8918	8.08
9-11	0.31	1.5008	100.22	97.46	1.4989	5.20	0.8942	7.93
14-16	0.27	1.5001	102.52	100.13	1.5138	5.18	0.8926	8.02
23-25	0.30	1.4995	102.30	100.56	1.5025	5.16	0.8893	8.17
34-36	0.31	1.4990	101.00	99.26	1.5175	5.22	0.8852	8.25

RUN 5 (Imperfectly mixed)

Toluene flow rate = 31.1 ml/min
Mixed acid flow rate = 14.8 ml/min
Toluene feed temperature = 95.90°F
Mixed acid feed temperature = 94.82°F
Cooling water flow rate = 51.4 ml/min
Upset water flow rate = 222.3 ml/min
Temperature ofinlet cooling water = 80.33°F
Outlet temperature of cooling water at S1 = 97.74°F
Outlet temperature of cooling water at S2 = 85.39°F
Wt % H_2SO_4, S1 = 46.50
Wt % H2SO4, S2 = 46.41
Wt % HNO_3 in organic phase product, S1 = 2.51°F
Wt % HNO_3 in organic phase product, S2 = 2.69°F

Time (min)	Fa	n_D	T(°F)	T_{co}(°F)	ρ_c	Cbc	ρ_d	Cad
S1	0.30	1.4986	99.48	97.74	1.5154	5.29	0.8616	8.14
S2	0.29	1.4976	85.39	85.39	1.5229	5.69	0.8836	8.52
0-2	0.28	1.4985	93.65	93.65	1.5071	5.34	0.8838	8.33
2-4	0.26	1.4979	88.87	88.87	1.4973	5.35	0.8805	8.50
4-6	0.28	1.4976	86.70	86.70	1.5147	5.39	0.8808	8.52
6-8	0.30	1.4975	85.87	85.87	1.5154	5.41	0.8806	8.53
9-11	0.29	1.4974	85.39	85.39	1.5240	5.42	0.8802	8.56
14-16	0.32	1.4979	85.39	84.96	1.5151	5.46	0.8835	8.47
22-24	0.30	1.4980	85.39	85.39	1.5221	5.44	0.8874	8.45
34-36	0.29	1.4976	85.39	85.39	1.5165	5.62	0.8857	8.53

Run 6(Imperfectly mixed)

Toluene flow rate = 31.1 ml/min
Mixed acid flow rate = 14.8 ml/min
Toluene feed temperature = 96.8°F
Mixed acid feed temperature = 95.9°F
Cooling water flow rate = 51.3 ml/min.
Upset water flow rate = 222.3 ml/min.
Temperature of inlet cooling water = 80.96°F
Outlet temperature of cooling water at S1 = 95.39°F
Outlet temperature of cooling water at S2 = 84.74°F
Wt % H_2SO_4, S1 = 45.24
Wt % H_2SO_4, S2 = 45.79
Wt % HNO_3 in organic phase product, S1 = 2.72
Wt % HNO_3 in organic phase product, S2 = 3.55

Time (min)	Fa	n_D	T(°F)	Tco(°F)	ρ_c	Cbc gmole/l	ρ_d	Cad gmole/l
S1	0.32	1.4975	97.09	95.39	1.5053	5.59	0.8751	8.46
S2	0.31	1.4970	85.39	84.74	1.5324	5.88	0.8816	8.54
0-2	0.28	1.4972	91.91	91.48	1.5251	5.69	0.8788	8.56
2-4	0.28	1.4970	88.00	87.57	1.5066	5.72	0.8768	8.61
4-6	0.29	1.4968	86.26	85.87	1.5454	5.75	0.8780	8.64
6-8	0.29	1.4968	85.39	84.96	1.5268	5.73	0.8775	8.65
9-11	0.34	1.4969	84.96	84.52	1.5320	5.81	0.8758	8.62
14-16	0.31	1.4970	85.17	84.52	1.5136	5.73	0.8793	8.60
22-24	0.29	1.4970	85.39	84.52	1.5128	5.81	0.8830	8.65
34-36	0.32	1.4970	85.39	84.52	1.5499	5.87	0.8808	8.62

Run 7(Imperfectly mixed)

Toluene flow rate = 31.1 ml/min
Mixed acid flow rate = 14.8 ml/min.
Toluene feed temperature = 96.80^{o}F
Mixed acid feed temperature = 95.90^{o}F
Cooling water flow rate = 222.30
Upset water flow rate = 51.30
Temperature of inlet cooling water = 80.96
Outlet temperature of cooling water at S1 = 84.74 ^{o}F
Outlet temperature of cooling water at S2 = 97.46 ^{o}F
Wt % H_2SO_4, S1 = 45.79
Wt % H_2SO_4, S2 = 44.37
Wt % HNO_3 in organic phase product, S1 = 3.55 ^{o}F
Wt % HNO_3 in organic phase product, S2 = 3.20 ^{o}F

Time (min)	Fa	n_D	T(^{o}F)	Tco(^{o}F)	ρ_c	Cbc gmole/l	ρ_d	Cad gmole/l
S1	0.31	1.4970	85.39	84.74	1.5324	5.88	0.8816	8.54
S2	0.31	1.4985	99.26	97.46	1.5396	5.53	0.8840	8.30
0-2	0.35	1.4972	86.83	84.74	1.5202	5.89	0.8814	8.60
2-4	0.34	1.4979	89.30	87.22	1.5323	5.84	0.8801	8.40
4-6	0.29	1.4978	91.48	89.30	1.5267	5.80	0.8818	8.45
6-8	0.32	1.4980	93.22	91.48	1.5266	5.77	0.8841	8.41
9-11	0.33	1.4986	95.61	93.43	1.5472	5.84	0.8866	8.34
14-16	0.31	1.4990	97.74	95.83	1.5257	5.58	0.8874	8.27
22-24	0.32	1.4990	98.83	97.46	1.5259	5.55	0.8862	8.25
34-36	0.29	1.4986	99.26	97.46	1.5400	5.60	0.8797	8.28

APPENDIX II

Solution of the Steady State Equations

The steady state equations were solved to obtain the values of Cac, k, MA, MT and ($-\Delta H$) for both steady states. These parameters were then used to solve the transient program. From runs 1, 2 and 3, a relation between ln k and 1/T was obtained by fitting a least squares straight line to the following data points.

Temperature($^{\circ}$F)	rate constant k
96.67	48.2
89.09	38.19
109.54	54.60
88.00	35.20
99.26	44.02

The equation relating k and 1/T was

$\ln k = 14.41799 - 5923.04/460 + T$

This equation for the rate constant was used in the the transient solution of all the runs. Other parameters like Cac, MA, MT and ($-\Delta H$) were obtained by the solution of the steady state equations and used in the transient program by the methods which have already been mentioned. Tables 1 and 2 show the data used for the solution of steady state equations and table 3 shows the results.

Table 1

Run No	Cao	Cbo	Cbc_1^*	Cbc_2^*	Cad_1	Cad_2	Cbd	Qc	Qd	Vc	Vd
1.	.0092564	.0075191	.004715	.004391	.008011	.007751	.000495	14.67	30.40	143.64	312.36
2.	.009246	.0075097	.0046697	.0040916	.0077879	.0074853	.0004611	14.67	30.40	136.34	319.66
3.	.009236	.0075053	.0046958	.0043146	.0078095	.0075974	.0004741	14.67	30.40	143.64	312.36
4.	.0092491	.0076456	.00539	.005286	.008391	.008137	.0004771	14.8	31.1	135.89	320.11
5.	.0092516	.0076456	.005286	.005692	.008137	.008523	.0003431	14.8	31.1	132.70	323.30
6.	.0092467	.0076421	.005591	.005879	.008458	.008538	.0003775	14.8	31.1	138.17	317.83
7.	.0092467	.0076421	.005879	.005529	.008538	.008302	.0004966	14.8	31.1	144.55	311.45

* Subscripts 1 and 2 indicate the values for steady state one and two

Table 2

Run No	Tao	Tbo	TS_1	TS_2	QS_1	QS_2	Cpco	Cpc	Cpd
1	95.0	91.94	84.09	96.66	1027.1	1116.3	0.54	0.56	0.558
2	96.80	95.0	89.09	109.54	928.2	1203.4	0.54	0.56	0.558
3	98.60	96.44	88.00	99.26	1060.5	1378.6	0.54	0.56	0.558
4	96.35	94.82	86.7	99.48	717.50	504.90	0.54	0.58	0.558
5	95.90	94.82	99.48	85.39	496.20	624.90	0.54	0.58	0.558
6	96.80	95.90	97.09	85.39	411.30	466.80	0.54	0.58	0.558
7	96.80	95.90	85.39	99.26	466.80	470.20	0.54	0.58	0.558

For densities of the acid and organic phases, the equation determined by least squares program(as shown in appendix) was used.

Table 3

Run No	Cac SS_1^*	Cac SS_2^*	k SS_1	k SS_2	MA	MT SS_1	MT SS_2	H SS_1	H SS_2
1.	.0008016	.0010151	48.08	48.20	.015036	.037863	.0457489	40386.6	43184.0
2	.0011371	.001186	38.19	54.60	.014017	.044326	.0535253	36158.8	43724.5
3	.001129	.0011874	35.19	44.02	.014412	.0433656	.0498134	40842.9	48811.0
4	.0005502	.0006984	36.01	46.12	.012754	.0266869	.0345863	52389.80	32130.5
5	.0007035	.0003688	46.12	35.09	.0111913	.034664	.0226594	32218.9	65856.6
6	.0003995	.0007776	44.07	35.09	.0136501	.0245286	.0220406	43899.8	21514.8
7	.0007696	.0008153	35.09	45.93	.014702	.0220406	.0293801	20924.8	23558.8

SS_1^* indicates first steady state

SS_2^* indicates second steady state

APPENDIX III

Calculation of heat removed by cooling water in the transient period

The heat removed by cooling water was calculated from the equation

$$Q = m\ Cpw(e^{m}-1/e^{M})(T - Tci)$$

where $M = UA/m\ Cpw$

The value of the overall heat transfer coefficient was calculated for a number of points in the transient period and an average value of the heat transfer coefficient was computed. This calculation is shown for run no. 1. The values of U for various points in the transient period are shown in table 1.

Average value of $U = 135.37\ \mathrm{Btu/hr\ ft^2\ {}^oF}$

$$M = UA/\ m\ Cpw$$

$$= \frac{135.37*453.6*0.30867}{101.4 * 1.0 * 60.0}$$

$$= 3.1153$$

Knowing the value of M, Q can be easily computed.

The values of overall heat transfer coefficient U and parameter M are tabulated below for all the runs.

Run No.	Upset flow rate of cooling water cc/min.	Overall heat transfer coeff. U Btu/hr ft^2 ^{o}F.	Parameter M
1	101.4	135.37	3.1153
2	78.0	84.3	2.5220
3	132.0	147.5	2.6075
4.	51.4	46.40	2.1067
5	222.3	252.3	2.6486
6	222.3	193.13	2.0273
7	51.3	49.80	2.2653

Table 1

Time Min	Reactor temperature T(°F)	Outlet Water temperature Tco(°F)	Inlet water temperature Tci(°F)	$(\Delta T)_m$	Overall heat transfer coeff U Btu/hrft^2°F
1	86.70	86.26	76.46	3.1138	136.70
2	89.30	88.87	76.46	3.5692	151.00
3	91.48	90.61	76.46	4.9673	122.40
4	93.65	92.35	76.46	5.3258	129.64
5	94.52	93.65	76.46	5.6677	131.80
10	96.66	95.83	76.46	6.10757	137.80
S2	96.66	96.25	76.46	6.1600	139.60

APPENDIX IV

Physical Properties

The following physical properties and their temperature dependency was required for solution of the steady state and transient equations.

1. Specific heat of toluene vs. temperature
2. Specific heat of organic phase product
3. Wt % MNT vs. refractive index
4. Density of toluene vs. temperature
5. Specific heat of mixed acid
6. Specific heat of acid phase product
7. Density of mixed acid vs. temperature
8. Density of acid phase product vs. temperature
9. Density of organic phase product vs. temperature

The information about the first four properties was obtained from the study of Okimoto (1969).

Specific Heat of Toluene versus Temperature

The specific heat of toluene was related to temperature (deg C) by the equation

$$Cp = 0.38566 + 0.00076372T - 0.00000323T^2 + 0.00000004T^3$$

Specific Heat of Organic Phase Product

The specific heat of organic phase product was determined experimentally and found to be 0.558 cal/g°C

Wt % MNT versus Refractive Index

The wt % MNT in the toluene-MNT mixture was related to the refractive index n_D by the equation

$$\text{Wt \% MNT} = -3037.97819 + 2034.19999\ n_D$$

Density of Toluene Versus Temperature

The density of toluene was related to temperature(°F) by the equation

$$\text{Density} = 0.90058 - 0.00050198\ T$$

Specific Heat of Mixed Acid

The value of the specific heat of ternary H_2SO_4, HNO_3, and H_20 mixture was obtained from figure 4.5 of Groginns (1958 , p.86)

Cp mixed acid = 0.54 cal/g°C

Specific Heat of Acid Phase Product

The value of the acid phase specific heat was also obtained from Groginns.

Cp acid phase(Runs 1, 2 and 3) = 0.56 cal/g°C

Cp acid phase(Runs 4 through 7)= 0.58 cal/g°C

Density of Mixed Acid Versus Temperature

Figure 18 shows the plot of density of the mixed acid solution. The equation for the straight line fitting the experimental data was obtained by a least squares program. The equation was

Mixed Acid Density = 1.598447 - 0.0006253 T

Density of Acid Phase Product Versus Temperature

Figure 18 also shows the plot of density of the acid phase product versus temperature for run 3 at the first steady state. The density of the acid phase samples in the transient period was obtained from the density at the analysis temperature and the slope of figure 18. A least squares program was used to relate the temperature and the density in the transient program. The fitted equation was of the form

Density Acid Phase = a + bT

The values of a and b for different runs are tabulated below

Run Number	a	b
1.	1.6004595	0.0009659
2.	1.6509747	-0.0015002
3.	1.6448173	-0.00146659
4.	1.6355538	-0.0012648
5.	1.5679589	-0.00060
6.	1.6885317	-0.0018661
7.	1.4752756	0.0006018

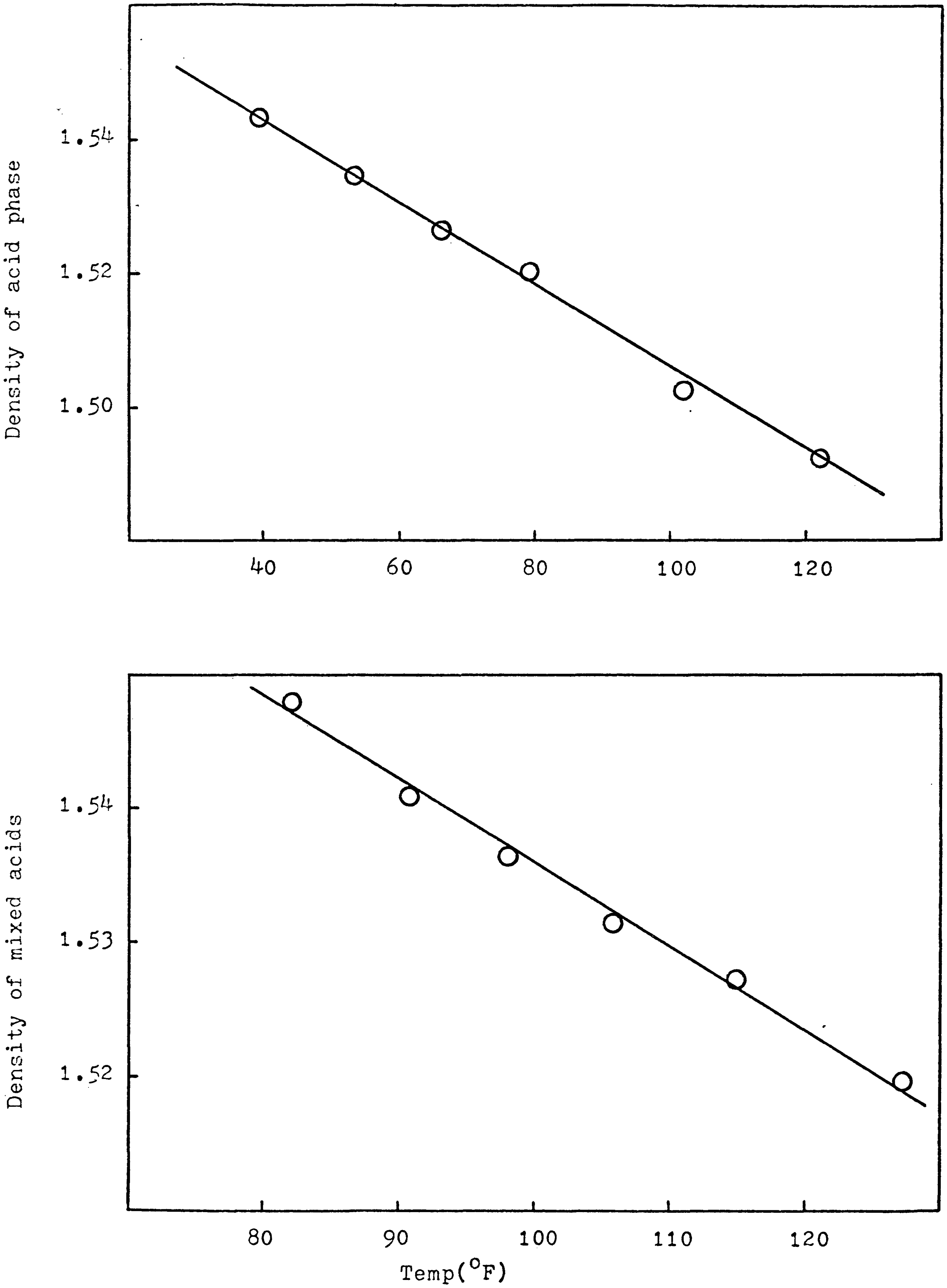

1.54
1.52
1.50
Density of acid phase
40
60
80
100
120
1.54
1.53
1.52
Density of mixed acids
80
90
100
110
120
Temp(°F)

Figure 18

Density of Organic Phase Product Versus Temperature

Figure 19 shows the organic phase product density versus temperature. The method for calculation of the density in the transient program was same as used for the acid phase product. The values of constants a and b are tabulated below.

Run Number	a	b
1.	0.925489	0.0002334
2.	0.9033154	0.0000027
3.	0.9071657	0.0000389
4.	0.9501008	-0.000629899
5.	0.9868246	-0.0012031
6.	0.9064005	-0.0003169
7.	0.8585127	0.0002644

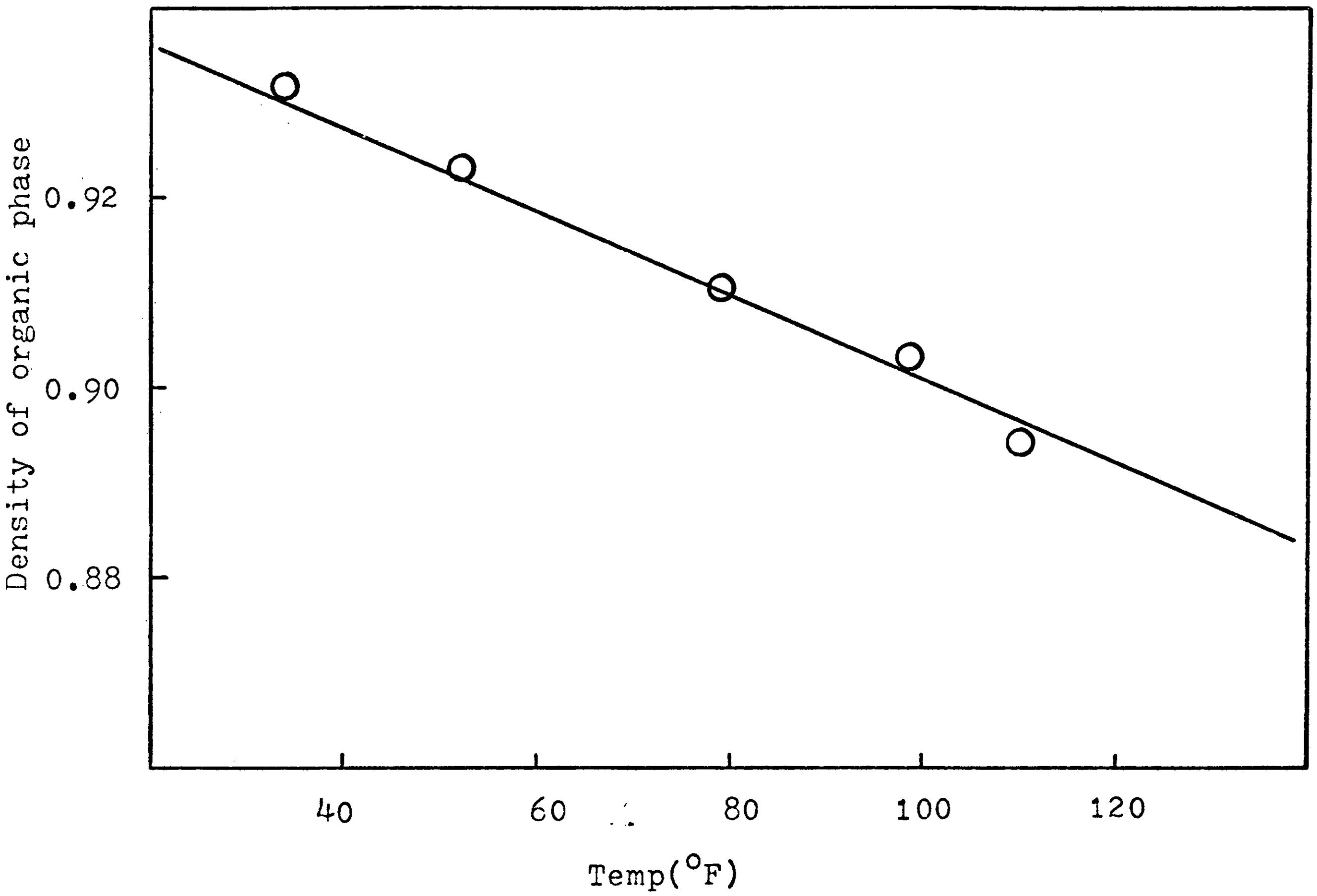


Figure 19

APPENDIX V

Analytical Procedure

The analytical procedure was used to determine

1. The concentration of nitric and sulfuric acids in the acid-phase product

2. The concentration of toluene, mono-nitrotoluene and nitric acid in the organic phase product.

In order to determine the above quantities, the following steps were carried out:

The total volume and the acid fraction of the sample were recorded. The acid phase was separated and its analysis was carried out in the following steps:

1. The density of the acid phase was determined with a specific gravtiy bottle of known volume. The temperature of the acid phase was recorded.

2. Nitric acid concentration was determined by titrating a 10-ml diluted acid phase solution (2-ml of the acid-phase

product diluted to 25 ml with the distilled water) with standardized ferrous sulfate solution. The details of this titration are given separately.

3. Total acidity was determined by titrating a 2-ml acid phase sample with standardized sodium hydroxide.

4. Knowing total acidity and the nitric acid concentration, sulfuric acid concentration was calculated.

Total Acidity as Sulfuric Acid

1. A 2-ml sample of the acid phase was mixed with about 50-ml distilled water in a conical flask. The contents were agitated and allowed to cool.

2. A few drops of phenolphthalein indicator was added and titrated with standardized sodium hydroxide(approximately 1 Normal solution). The end point was reached when a permanent pink color appeared.

3. The total % acidity was determined from the equation

$$\begin{array}{l}\text{Wt \% total acidity} \\ \text{as sulfuric acid}\end{array} = \frac{\text{ml NaOH x Normality NaOH x 4.9039}}{\text{sample weight in gm}}$$

The relationship among total acidity, sulfuric acid, and nitric acid was

$$\begin{array}{l}\text{Wt \% total acidity} \\ \text{as sulfuric acid}\end{array} = \begin{array}{l}\text{wt \% sulfuric acid + Wt \%} \\ \text{nitric acid x 0.7782.}\end{array}$$

The total acidity of the mixed acid was also determined by the above method.

Organic phase

1. The density of the organic phase was determined with a

specific gravity bottle of known volume.

2. A 50-ml sample of organic extract was combined with the same volume of distilled water and the mixture was thoroughly shaked. The phases were separated.

3. A 25-ml sample of aqueous phase was titrated with standardized sodium hydroxide to determine the nitric acid concentration. Since the amount of sulfuric acid in the organic phase was less than 0.5 wt%, it was assumed that all acid in the organic phase was nitric acid.

4. The organic phase was mixed with a large amount of water and the phases were separated.

5. The resulting organic phase was placed in a desiccator to remove any water.

6. The refractive index of the toluene-MNT was determined to calculate the wt % of mono-nitrotoluene in the organic phase.

7. The concentration of toluene was determined by substracting the masses of nitric acid and MNT from the mass of 1 ml of the original organic phase.

8. A small portion of the acid free organic phase(0.1 g of nitro-compound) was measured and dissolved in 10 ml of acetone. A 5-ml solution of 5% aqueous sodium hydroxide was added and allowed to stand for 3 to 5 min. The presence of di-nitrotoluene was judged as follows:

if no color change - only MNT present
if deep purplish blue-di-nitrotoluene
if blood red - tri-nitrotoluene

Nitric Acid Concentration in Mixed Acid using Ferrous Sulfate

1. A 250-ml conical flask containing 100 ml of 93% sulfuric acid was placed in a beaker filled with a mixture of ice and water.

2. The mixed acid was diluted to contain 0.1 g to 0.8 g nitric acid. 10 ml of the diluted sample was added to the conical flask. The flask was given a constant circular motion in order to avoid local heating.

3. The mixed acid sample was titrated by adding Ferrous sulfate from a burette until the yellow color that first formed changed to a faint brownish tinge. The titration was completed when the yellow-brown color reappeared.

4. The wt % nitric acid was determined by using the equation

$$\text{wt \% nitric acid} = \frac{\text{ml FeSO}_4 - 0.2) \times F \times 100}{\begin{array}{l}\text{fraction of}\\ \text{total sample}\\ \text{used in titration}\end{array} \times \begin{array}{l}\text{sample}\\ \text{weight in}\\ \text{grams}\end{array}}$$

$$\text{where} \quad F = \frac{\text{g nitric acid}}{\text{ml FeSO}_4 - 0.2}$$

Preparation and Standardisation of Sodium Hydroxide solution

1. Approximately 41 g of sodium hydroxide pellets were dissolved in about 500 ml of water and the solution was diluted to 1-l in a volumetric flask.

2. Three portions of approximately 8 g of KHP were accurately weighed and dissolved in about 300 ml of water.

3. The solution of KHP was titrated with sodium hydroxide using phenolphthalein as the indicator.

4. Normality of sodium hydroxide was determined from the equation

$$\text{N NaOH} = \frac{\text{g KHP}}{204.2 \times \text{l of NaOH used}}$$

Preparation and Standardisation of Ferrous Sulfate Solution

1. Approximately 176 g of reagent-grade $FeSO_4.7H_2O$ was dissolved in 400 ml of water. Approximately 500 ml of 60 % sulfuric acid was cooled by tap water and added to the ferrous sulphate solution.

2. The solution was cooled and diluted to exactly 1-1 in a volumetric flask.

3. 10 ml of a standardized nitric acid solution(approximately 40 g nitric acid/1) was added to 100 ml of 93 % sulfuric acid and the mixture was cooled with ice water.

4. The mixed acid solution was titrated by running ferrous sulphate from a burette as described in Nitric Acid concentration in Mixed Acid, to determine the g of nitric acid equivalent to 1 ml of ferrous sulfate,

$$F = \frac{\text{g nitric acid}}{\text{total ml } FeSO_4 - 0.2}$$

Analytical procedures were taken from the reference text, Scott's Standard Methods of Chemical Analysis: New York, D. Van Nostrand Co., 5th edition, v.1 and 2, (1939).

APPENDIX VI

Computer program and results

NOMENCLATURE FOR THE COMPUTER PROGRAM

The following is a list of symbols used in the transient program

A1 A2	Constants in the equation for density of the acid phase
AA	Density of mixed acid
AB	Density of toluene
AD	Density of acid phase
AE	Specific heat of mixed acid
AG	Specific heat of toluene
AH	Heat of reaction, mixing and impeller (- H)
AK	Reaction rate constant
AS	Specific heat of acid phase
AHA AHB	Value of (- H) for two steady states
AMA AMB	Constants in the equation for rate of mass transfer of toluene
AMT	Rate of mass transfer of toluene

AMAC	Rate of mass transfer of nitric acid
AMTA AMTB	Rate of mass transfer of toluene at two steady states
BD	Density of organic phase
BS	Specific heat of organic phase
C1 C2	Constants in the equation for density of organic phase
CAC	Concentration of toluene in acid phase
CAD	Concentration of toluene in organic phase
CAO	Concentration of toluene in organic feed stream
CBC	Concentration of nitric acid in acid phase
CBD	Concentration of nitric acid in mixed acid feed stream
CBO	Concentric of nitric acid in mixed acid feed stream
CACO	Value of CAC at steady state one
CADO CADS	Value of CAD at steady states one and two
CBCO CBCS	Value of CBC at steady states one and two
HA HB	Constant in heat of reaction equation
QC	Flow rate of mixed acid stream
QD	Flow rate of organic stream
QW	Flow rate of cooling water
RW	Value of ((exp M) - 1)/exp M in equation for Q
T	Reactor Temperature
TA	Temperature of mixed acid feed stream
TM	Time step in Runge-Kutta method for numerical integration

TO	Reactor temperature at steady state one
TT	Temperature of organic feed stream
TCI	Inlet temperature of cooling water
TSA TSB	Reactor temperature at two steady states
TIME	Time in the transient period
VC	Volume of acid phase in reactor
VD	Volume of organic phase in reactor

```
F40      V23      3-FEB-71          15:08   PAGE 1


      READ(1,100)CAO,CBO,CBCO,CBCS,CACO,CADS,CBD,AE
      READ(1,100)QC,QD,VC,VD,TA,TT,TSA,TSB
      READ(1,100)AS,BS,TO,QW,RW,TCI,CACO,AMAC
      READ(1,100)A1,A2,C1,C2,AHA,AHB,AMTA,AMTB
 100  FORMAT(8F10.7)
 101  FORMAT(10X,37H TRANSIENT PROGRAM RESULTS FOR RUN    )
      WRITE(2,101)
     WRITE(2,111)CAO,CBO,CBCO,CBCS,CADO,CADS,CBD,AE
     WRITE(2,111)QC,QD,VC,VD,TA,TT,TSA,TSB
     WRITE(2,111)AS,BS,TO,QW,RW,TCI,CACO,AMAC
     WRITE(2,111)A1,A2,C1,C2,AHA,AHB,AMTA,AMTB
 111  FORMAT(7X,1PE14.7,3X,1PE14.7,3X,1PE14.7,3X,1PE14.7)
      WRITE(2,102)
 102 FORMAT(10X,4HTIME,8X,4HTEMP,10X,3HCAC,10X,3HCAD,10X,3HCBC)
      WRITE(2,103)
 103  FORMAT(10X,6H(MIN.),4X,7H(DEG.F),5X,10H(GMOLE/ML),3X,10H(GMOLE/ML
    1),3X,10H(GMOLE/ML))
      AA=1.598447-(0.0006253*TA)
      T=TO
      CAC=CACO
      CAD=CADO
      CBC=CBCO
      AB=0.90258-(0.00250198*TT)
      AG=0.38566+(0.00076372*(TT-32.0)/1.8)-(0.00000323*(((TT-32.0)/
    1 1.8)**2.0))+(0.00000004*(((TT-32.0)/1.8)**3.0))
      B1=(QD*AB*AG*(TT-32.0)/1.8)+(QC*AA*AE*(TA-32.0)/1.8)
       AN=QC/VC
      P=QD/VD
      AM=QC*CBO/VC
      TM=0.05
      M=1
      TIME=0.0
      HB=(ALOG(TSB)-ALOG(TSA))/(2.3020508*(AHB-AHA))
      HA=TSA/(10.0**(HB*AHA))
      TSA=TSA+460.0
      TSB=TSB+460.0
       TP=TSA*TSB/(TSB-TSA)
      AMB=TP*ALOG(AMTA*CADS/(AMTB*CADO))
      AMA=AMTA/(CADO*EXP(AMB/TSA))
  60  TO=T
      CACO=CAC
      CADO=CAD
      CBCO=CBC
      AD=A1+(A2*T)
      BD=C1+(C2*T)
      B2=(QC*AD*AS)+(QD*BD*BS)
      B3=(AD*AS*VC)+(BD*BS*VD)
      AMT=AMA*CAD*EXP(AMB/(T+460.0))
      AK=EXP(14.418-(5923.0/(460.0+T)))
      AH=(ALOG(T)-ALOG(HA))/(2.302585*HB)
  55  WA=TM*((AMT/VC)-(AK*CAC*CBC)-(AN*CAC))
      WB=TM*((P*CAO)-(P*CAD)-(AMT/VD))
      WC=TM*((AM)-(AN*CBC)-(AK*CAC*CBC)-(AMAC/VC))
```

```
F40      V23      3-FEB-71          16:19    PAGE 2


         WD=(TM*1,0/B3)*(B1-(B2*(T-32,0)/1,8)+(AK*CAC*CBC*AH*VC)-(0,55555
       1 *QW*RW*(T-TCI)))
         CAC=CACO+(WA/2,0)
         CAD=CADO+(WB/2,0)
         CBC=CBCO+(WC/2,0)
         T=TO+(WD*1,8/2,0)
         AK=EXP(14,418-(5923,0/(460,0+T)))
         XA=TM*((AMT/VC)-(AK*CAC*CBC)-(AN*CAC))
         XB=TM*((P*CAO)-(P*CAD)-(AMT/VD))
         XC=TM*((AM)-(AN*CBC)-(AK*CAC*CBC)-(AMAC/VC))
         XD=(TM*1,0/B3)*(B1-(B2*(T-32,0)/1,8)+(AK*CAC*CBC*AH*VC)-(0,55555
       1 *QW*RW*(T-TCI)))
         CAC=CACO+(XA/2,0)
         CAD=CADO+(XB/2,0)
         CBC=CBCO+(XC/2,0)
         T=TO+(XD*1,8/2,0)
         AK=EXP(14,418-(5923,0/(460,0+T)))
         YA=TM*((AMT/VC)-(AK*CAC*CBC)-(AN*CAC))
         YB=TM*((P*CAO)-(P*CAD)-(AMT/VD))
         YC=TM*((AM)-(AN*CBC)-(AK*CAC*CBC)-(AMAC/VC))
         YD=(TM*1,0/B3)*(B1-(B2*(T-32,0)/1,8)+(AK*CAC*CBC*AH*VC)-(0,55555
       1 *QW*RW*(T-TCI)))
         CAC=CACO+YA
         CAD=CADO+YB
         CBC=CBCO+YC
         T=TO+(YD*1,8)
         AK=EXP(14,418-(5923,0/(460,0+T)))
         ZA=TM*((AMT/VC)-(AK*CAC*CBC)-(AN*CAC))
         ZB=TM*((P*CAC)-(P*CAD)-(AMT/VD))
         ZC=TM*((AM)-(AN*CBC)-(AK*CAC*CBC)-(AMAC/VC))
         ZD=(TM*1,0/B3)*(B1-(32*(T-32,0)/1,8)+(AK*CAC*CBC*AH*VC)-(0,55555
       1 *QW*RW*(T-TCI)))
         CACN=(WA+(2,0*XA)+(2,0*YA)+ZA)/6,0
         CADN=(WB+(2,0*XB)+(2,0*YB)+ZB)/6,0
         CBCN=(WC+(2,0*XC)+(2,0*YC)+ZC)/6,0
         TN=(WD+(2,0*XD)+(2,0*YD)+ZD)/6,0
         CAC=CACO+CACN
         CAD=CADO+CADN
         CBC=CBCO+CBCN
         T=TO+(TN*1,8)
         M=M+1
         IF(M-20,0)60,60,62
   62    TIME=TIME+1,0
   61    WRITE(2,39)TIME,T,CAC,CAD,CBC
   39    FORMAT(10X,F6,2,4X,F7,2,1PE16,4,1PE13,4,1PE13,4)
         M=M-20,0
         IF(TIME-60,0)60,60,66
   66    STOP
         END


4541     1          201631147512       2        166407135165       3          20071506151
```

```
 TRANSIENT PROGRAM RESULTS FOR RUN 1
9,2564000E-03    7,5110000E-03    4.7148000E-03    4,3907000E-03
8,0109000E-03    7,7515001E-03    4.9462000E-04    5,4000000E-01
1,4670000E+01    3,0400000E+01    1.4364000E+02    3.1236000E+02
9,1940000E+01    9,5000000E+01    8,4786999E+01    9,6659999E+01
5,6000000E-01    5,5800000E-01    8,4086999E+01    1,0140000E+02
9,5563500E-01    7,6459999E+01    8.0162000E-04    1.5035800E-02
1,6004595E+00   -9,6600000E-04    9.2548879E-01   -2,3300000E-04
4,0386600E+04    4,3184000E+04    3,7863200E-02    4,5749000E-02
  TIME        TEMP          CAC          CAD          CBC
 (MIN,)      (DEG,F)     (GMOLE/ML)   (GMOLE/ML)   (GMOLE/ML)
   1,00       85,96      8,4879E-04   8,0097E-03   4,7570E-03
   2,00       87,61      8,8696E-04   8,0035E-03   4,7826E-03
   3,00       89,06      9,1778E-04   7,9952E-03   4,7949E-03
   4,00       90,32      9,4270E-04   7,9848E-03   4,7968E-03
   5,00       91,42      9,6294E-04   7,9729E-03   4,7909E-03
   6,00       92,37      9,7948E-04   7,9599E-03   4,7791E-03
   7,00       93,17      9,9312E-04   7,9463E-03   4,7633E-03
   8,00       93,86      1,0045E-03   7,9325E-03   4,7447E-03
   9,00       94,43      1,0140E-03   7,9187E-03   4,7244E-03
  10,00       94,90      1,0221E-03   7,9051E-03   4,7034E-03
  11,00       95,30      1,0290E-03   7,8920E-03   4,6823E-03
  12,00       95,61      1,0349E-03   7,8795E-03   4,6616E-03
  13,00       95,87      1,0400E-03   7,8676E-03   4,6417E-03
  14,00       96,07      1,0445E-03   7,8566E-03   4,6227E-03
  15,00       96,23      1,0483E-03   7,8463E-03   4,6049E-03
  16,00       96,35      1,0517E-03   7,8367E-03   4,5883E-03
  17,00       96,44      1,0547E-03   7,8280E-03   4,5731E-03
  18,00       96,51      1,0572E-03   7,8201E-03   4,5591E-03
  19,00       96,56      1,0595E-03   7,8128E-03   4,5464E-03
  20,00       96,59      1,0614E-03   7,8063E-03   4,5349E-03
  21,00       96,61      1,0631E-03   7,8004E-03   4,5246E-03
  22,00       96,62      1,0646E-03   7,7951E-03   4,5154E-03
  23,00       96,63      1,0658E-03   7,7904E-03   4,5071E-03
  24,00       96,63      1,0669E-03   7,7862E-03   4,4998E-03
  25,00       96,62      1,0679E-03   7,7825E-03   4,4933E-03
  26,00       96,61      1,0687E-03   7,7792E-03   4,4876E-03
  27,00       96,60      1,0694E-03   7,7763E-03   4,4825E-03
  28,00       96,59      1,0700E-03   7,7737E-03   4,4781E-03
  29,00       96,58      1,0705E-03   7,7714E-03   4,4742E-03
  30,00       96,57      1,0710E-03   7,7695E-03   4,4709E-03
  31,00       96,56      1,0713E-03   7,7677E-03   4,4679E-03
  32,00       96,55      1,0716E-03   7,7662E-03   4,4654E-03
  33,00       96,53      1,0719E-03   7,7649E-03   4,4632E-03
  34,00       96,52      1,0721E-03   7,7637E-03   4,4613E-03
  35,00       96,51      1,0723E-03   7,7627E-03   4,4596E-03
  36,00       96,51      1,0724E-03   7,7618E-03   4,4582E-03
  37,00       96,50      1,0726E-03   7,7611E-03   4,4570E-03
  38,00       96,49      1,0727E-03   7,7604E-03   4,4560E-03
  39,00       96,48      1,0728E-03   7,7599E-03   4,4551E-03
  40,00       96,48      1,0728E-03   7,7594E-03   4,4544E-03
  41,00       96,47      1,0729E-03   7,7590E-03   4,4537E-03
  42,00       96,47      1,0729E-03   7,7586E-03   4,4532E-03
  43,00       96,46      1,0730E-03   7,7583E-03   4,4527E-03
  44,00       96,46      1,0730E-03   7,7580E-03   4,4524E-03
  45,00       96,45      1,0730E-03   7,7578E-03   4,4520E-03
  46,00       96,45      1,0730E-03   7,7576E-03   4,4518E-03
  47,00       96,45      1,0730E-03   7,7574E-03   4,4516E-03
  48,00       96,45      1,0730E-03   7,7573E-03   4,4514E-03
  49,00       96,44      1,0730E-03   7,7572E-03   4,4512E-03
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50,00          96,44          1,0730E-03    7,7571E-03    4,4511E-03
51,00          96,44          1,0730E-03    7,7570E-03    4,4510E-03
52,00          96,44          1,0730E-03    7,7569E-03    4,4509E-03
53,00          96,44          1,0730E-03    7,7568E-03    4,4509E-03
54,00          96,44          1,0730E-03    7,7568E-03    4,4508E-03
55,00          96,44          1,0730E-03    7,7567E-03    4,4508E-03
56,00          96,43          1,0730E-03    7,7567E-03    4,4508E-03
57,00          96,43          1,0730E-03    7,7567E-03    4,4507E-03
58,00          96,43          1,0730E-03    7,7566E-03    4,4507E-03
59,00          96,43          1,0730E-03    7,7566E-03    4,4507E-03
60,00          96,43          1,0730E-03    7,7566E-03    4,4507E-03
61,00          96,43          1,0730E-03    7,7566E-03    4,4507E-03
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  TRANSIENT PROGRAM RESULTS FOR RUN 2
9,2640001E-03    7,5096999E-03    4,6697000E-03    4,0916000E-03
7,7879000E-03    7,4853000E-03    4,6110000E-04    5,4000000E-01
1,4670000E+01    3,0400000E+01    1.3634000E+02    3,1966000E+02
9,5000000E+01    9,6799999E+01    8,9290000E+01    1.0954000E+02
5,6000000E-01    5,5800000E-01    8,9290000E+01    7,7999999E+01
9,1970301E-01    8,0060000E+01    1.1371000E-03    1,4017000E-02
1,6509747E+00   -1,5200000E-03    9.0331541E-01    2,7000000E-06
3,6158800E+04    4,3724500E+04    4,4324001E-02    5,3525300E-02
  TIME          TEMP            CAC            CAD            CBC
 (MIN.)        (DEG,F)      (GMOLE/ML)     (GMOLE/ML)     (GMOLE/ML)
    1,00          92,44       1,1395E-03     7,7870E-03     4,6652E-03
    2,00          95,34       1,1391E-03     7,7813E-03     4,6491E-03
    3,00          97,86       1,1393E-03     7,7719E-03     4,6245E-03
    4,00         100,04       1,1393E-03     7,7597E-03     4,5938E-03
    5,00         101,93       1,1394E-03     7,7455E-03     4,5590E-03
    6,00         103,57       1,1397E-03     7,7299E-03     4,5218E-03
    7,00         104,99       1,1403E-03     7,7135E-03     4,4833E-03
    8,00         106,20       1,1413E-03     7,6966E-03     4,4448E-03
    9,00         107,23       1,1426E-03     7,6797E-03     4,4069E-03
   10,00         108,11       1,1441E-03     7,6630E-03     4,3702E-03
   11,00         108,86       1,1460E-03     7,6467E-03     4,3352E-03
   12,00         109,48       1,1480E-03     7,6311E-03     4,3021E-03
   13,00         109,99       1,1501E-03     7,6162E-03     4,2712E-03
   14,00         110,41       1,1523E-03     7,6021E-03     4,2426E-03
   15,00         110,76       1,1545E-03     7,5890E-03     4,2162E-03
   16,00         111,03       1,1568E-03     7,5768E-03     4,1921E-03
   17,00         111,25       1,1590E-03     7,5655E-03     4,1703E-03
   18,00         111,42       1,1611E-03     7,5551E-03     4,1505E-03
   19,00         111,55       1,1631E-03     7,5456E-03     4,1328E-03
   20,00         111,64       1,1650E-03     7,5370E-03     4,1170E-03
   21,00         111,71       1,1667E-03     7,5292E-03     4,1030E-03
   22,00         111,75       1,1684E-03     7,5221E-03     4,0906E-03
   23,00         111,77       1,1699E-03     7,5158E-03     4,0797E-03
   24,00         111,78       1,1713E-03     7,5102E-03     4,0702E-03
   25,00         111,78       1,1725E-03     7,5052E-03     4,0620E-03
   26,00         111,76       1,1736E-03     7,5008E-03     4,0548E-03
   27,00         111,74       1,1746E-03     7,4969E-03     4,0487E-03
   28,00         111,72       1,1755E-03     7,4935E-03     4,0434E-03
   29,00         111,69       1,1763E-03     7,4905E-03     4,0390E-03
   30,00         111,66       1,1769E-03     7,4878E-03     4,0352E-03
   31,00         111,63       1,1775E-03     7,4856E-03     4,0321E-03
   32,00         111,60       1,1780E-03     7,4836E-03     4,0294E-03
   33,00         111,56       1,1785E-03     7,4819E-03     4,0273E-03
   34,00         111,53       1,1788E-03     7,4805E-03     4,0255E-03
   35,00         111,51       1,1791E-03     7,4792E-03     4,0241E-03
   36,00         111,48       1,1794E-03     7,4782E-03     4,0230E-03
   37,00         111,45       1,1796E-03     7,4773E-03     4,0222E-03
   38,00         111,43       1,1797E-03     7,4765E-03     4,0215E-03
   39,00         111,41       1,1799E-03     7,4759E-03     4,0211E-03
   40,00         111,38       1,1800E-03     7,4754E-03     4,0207E-03
   41,00         111,37       1,1801E-03     7,4750E-03     4,0205E-03
   42,00         111,35       1,1801E-03     7,4746E-03     4,0204E-03
   43,00         111,33       1,1802E-03     7,4743E-03     4,0204E-03
   44,00         111,32       1,1802E-03     7,4741E-03     4,0205E-03
   45,00         111,31       1,1802E-03     7,4739E-03     4,0206E-03
   46,00         111,30       1,1802E-03     7,4738E-03     4,0207E-03
   47,00         111,29       1,1802E-03     7,4737E-03     4,0209E-03
   48,00         111,28       1,1802E-03     7,4736E-03     4,0210E-03
   49,00         111,27       1,1802E-03     7,4736E-03     4,0212E-03
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50.00      111.26      1.1801E-03    7.4736E-03    4.0214E-03
51.00      111.26      1.1801E-03    7.4735E-03    4.0216E-03
52.00      111.25      1.1801E-03    7.4735E-03    4.0218E-03
53.00      111.25      1.1801E-03    7.4735E-03    4.0220E-03
54.00      111.24      1.1800E-03    7.4735E-03    4.0222E-03
55.00      111.24      1.1800E-03    7.4736E-03    4.0224E-03
56.00      111.24      1.1800E-03    7.4736E-03    4.0226E-03
57.00      111.23      1.1799E-03    7.4736E-03    4.0227E-03
58.00      111.23      1.1799E-03    7.4736E-03    4.0229E-03
59.00      111.23      1.1799E-03    7.4736E-03    4.0230E-03
60.00      111.23      1.1799E-03    7.4737E-03    4.0232E-03
61.00      111.23      1.1798E-03    7.4737E-03    4.0233E-03
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  TRANSIENT PROGRAM RESULTS FOR RUN 3
9,2360000E-03     7,5053200E-03     4,6957999E-03      4,3146000E-03
7,8095000E-03     7,5974000E-03     4,7410000E-04      5,4200000E-01
1,4670000E+01     3,0400000E+01     1,4364000E+02      3,1236000E+02
9,6440000E+01     9,8600000E+01     8.8000000E+01      9,9259999E+01
5,6000000E-01     5,5800000E-01     8.8000000E+01      1,3220000E+02
9,2628500E-01     7,9159999E+01     1.1290000E-03      1,4412600E-02
1,6448173E+00    -1,4670000E-03     9.0716570E-01     -3,9200000E-05
4,0843000E+04     4,0811000E+04     4.3365600E-02      4,9813400E-02
   TIME          TEMP             CAC             CAD            CBC
  (MIN,)       (DEG,F)       (GMOLE/ML)     (GMOLE/ML)     (GMOLE/ML)
    1.00         90,90        1,1217E-03     7.8066E-03     4,6822E-03
    2,00         93,12        1,1183E-03     7,7988E-03     4,6618E-03
    3,00         94,86        1,1175E-03     7,7877E-03     4,6371E-03
    4,00         96,21        1,1185E-03     7,7746E-03     4,6098E-03
    5,00         97,27        1,1206E-03     7,7603E-03     4,5813E-03
    6,00         98,10        1,1234E-03     7,7456E-03     4,5526E-03
    7,00         98,75        1,1266E-03     7,7309E-03     4,5243E-03
    8,00         99,25        1,1299E-03     7,7165E-03     4,4972E-03
    9,00         99,64        1,1333E-03     7,7028E-03     4,4714E-03
   10,00         99,94        1,1366E-03     7,6899E-03     4,4473E-03
   11,00        100,16        1,1397E-03     7,6778E-03     4,4250E-03
   12,00        100,33        1,1426E-03     7,6666E-03     4,4046E-03
   13,00        100,44        1,1453E-03     7,6564E-03     4,3859E-03
   14,00        100,52        1,1477E-03     7,6471E-03     4,3691E-03
   15,00        100,57        1,1500E-03     7,6387E-03     4,3540E-03
   16,00        100,60        1,1520E-03     7,6312E-03     4,3405E-03
   17,00        100,61        1,1538E-03     7,6245E-03     4,3286E-03
   18,00        100,61        1,1554E-03     7,6185E-03     4,3180E-03
   19,00        100,59        1,1568E-03     7,6132E-03     4,3087E-03
   20,00        100,58        1,1581E-03     7,6085E-03     4,3006E-03
   21,00        100,55        1,1591E-03     7,6044E-03     4,2936E-03
   22,00        100,53        1,1601E-03     7,6008E-03     4,2874E-03
   23,00        100,50        1,1609E-03     7,5977E-03     4,2821E-03
   24,00        100,47        1,1616E-03     7,5950E-03     4,2776E-03
   25,00        100,45        1,1622E-03     7,5926E-03     4,2736E-03
   26,00        100,42        1,1627E-03     7,5906E-03     4,2703E-03
   27,00        100,40        1,1631E-03     7,5888E-03     4,2675E-03
   28,00        100,37        1,1635E-03     7,5873E-03     4,2651E-03
   29,00        100,35        1,1638E-03     7,5860E-03     4,2630E-03
   30,00        100,33        1,1640E-03     7,5849E-03     4,2613E-03
   31,00        100,32        1,1642E-03     7,5840E-03     4,2599E-03
   32,00        100,30        1,1644E-03     7,5832E-03     4,2587E-03
   33,00        100,29        1,1646E-03     7,5825E-03     4,2577E-03
   34,00        100,27        1,1647E-03     7,5820E-03     4,2569E-03
   35,00        100,26        1,1648E-03     7,5815E-03     4,2563E-03
   36,00        100,25        1,1648E-03     7,5811E-03     4,2558E-03
   37,00        100,24        1,1649E-03     7,5808E-03     4,2553E-03
   38,00        100,23        1,1649E-03     7,5805E-03     4,2550E-03
   39,00        100,23        1,1649E-03     7,5802E-03     4,2547E-03
   40,00        100,22        1,1650E-03     7,5801E-03     4,2545E-03
   41,00        100,22        1,1650E-03     7,5799E-03     4,2544E-03
   42,00        100,21        1,1650E-03     7,5798E-03     4,2542E-03
   43,00        100,21        1,1650E-03     7,5797E-03     4,2542E-03
   44,00        100,20        1,1650E-03     7,5796E-03     4,2541E-03
   45,00        100,20        1,1650E-03     7,5795E-03     4,2541E-03
   46,00        100,20        1,1650E-03     7,5795E-03     4,2541E-03
   47,00        100,20        1,1650E-03     7,5794E-03     4,2540E-03
   48,00        100,20        1,1650E-03     7,5794E-03     4,2541E-03
   49,00        100,19        1,1650E-03     7,5794E-03     4,2541E-03
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50,00      100,19      1,1649E-03   7,5793E-03   4,2541E-03
51,00      100,19      1,1649E-03   7,5793E-03   4,2541E-03
52,00      100,19      1,1649E-03   7,5793E-03   4,2541E-03
53,00      100,19      1,1649E-03   7,5793E-03   4,2542E-03
54,00      100,19      1,1649E-03   7,5793E-03   4,2542E-03
55,00      100,19      1,1649E-03   7,5793E-03   4,2542E-03
56,00      100,19      1,1649E-03   7,5793E-03   4,2542E-03
57,00      100,19      1,1649E-03   7,5793E-03   4,2543E-03
58,00      100,19      1,1649E-03   7,5793E-03   4,2543E-03
59,00      100,19      1,1649E-03   7,5793E-03   4,2543E-03
60,00      100,19      1,1649E-03   7,5793E-03   4,2543E-03
61,00      100,19      1,1649E-03   7,5793E-03   4,2544E-03
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   TRANSIENT PROGRAM RESULTS FOR RUN 4
9.2491000E-03    7.6455999E-03    5.3900000E-03    5.2860000E-03
8.3910000E-03    8.1370001E-03    4.7710000E-04    5.4000000E-01
1.4800000E+01    3.1100000E+01    1.3589000E+02    3.2011000E+02
9.4819999E+01    9.6349999E+01    8.6699999E+01    9.9479999E+01
5.8000000E-01    5.5800000E-01    8.6699999E+01    5.1400000E+01
8.7836000E-01    8.0060000E+01    5.5020000E-04    1.2754100E-02
1.6355538E+00   -1.2648000E-03    9.5010082E-01   -6.2989999E-04
5.2389300E+04    3.2130600E+04    2.6686900E-02    3.4586300E-02
  TIME         TEMP           CAC          CAD          CBC
 (MIN.)      (DEG.F)      (GMOLE/ML)   (GMOLE/ML)   (GMOLE/ML)
   1.00        89.83      5.7864E-04   8.3880E-03   5.4261E-03
   2.00        92.29      6.0467E-04   8.3800E-03   5.4463E-03
   3.00        94.21      6.2761E-04   8.3683E-03   5.4537E-03
   4.00        95.70      6.4727E-04   8.3542E-03   5.4514E-03
   5.00        96.84      6.6380E-04   8.3387E-03   5.4419E-03
   6.00        97.71      6.7749E-04   8.3226E-03   5.4274E-03
   7.00        98.37      6.8872E-04   8.3065E-03   5.4098E-03
   8.00        98.87      6.9788E-04   8.2907E-03   5.3905E-03
   9.00        99.23      7.0531E-04   8.2756E-03   5.3706E-03
  10.00        99.50      7.1133E-04   8.2614E-03   5.3508E-03
  11.00        99.70      7.1620E-04   8.2481E-03   5.3316E-03
  12.00        99.85      7.2014E-04   8.2358E-03   5.3134E-03
  13.00        99.95      7.2333E-04   8.2245E-03   5.2965E-03
  14.00       100.02      7.2592E-04   8.2142E-03   5.2809E-03
  15.00       100.07      7.2802E-04   8.2048E-03   5.2666E-03
  16.00       100.11      7.2973E-04   8.1963E-03   5.2536E-03
  17.00       100.13      7.3112E-04   8.1886E-03   5.2420E-03
  18.00       100.14      7.3225E-04   8.1817E-03   5.2315E-03
  19.00       100.15      7.3317E-04   8.1755E-03   5.2222E-03
  20.00       100.15      7.3393E-04   8.1700E-03   5.2140E-03
  21.00       100.15      7.3454E-04   8.1650E-03   5.2066E-03
  22.00       100.15      7.3504E-04   8.1605E-03   5.2002E-03
  23.00       100.14      7.3545E-04   8.1565E-03   5.1945E-03
  24.00       100.14      7.3578E-04   8.1530E-03   5.1895E-03
  25.00       100.13      7.3605E-04   8.1498E-03   5.1851E-03
  26.00       100.13      7.3626E-04   8.1470E-03   5.1813E-03
  27.00       100.12      7.3644E-04   8.1445E-03   5.1779E-03
  28.00       100.12      7.3658E-04   8.1422E-03   5.1750E-03
  29.00       100.11      7.3669E-04   8.1402E-03   5.1724E-03
  30.00       100.11      7.3677E-04   8.1385E-03   5.1702E-03
  31.00       100.10      7.3684E-04   8.1369E-03   5.1683E-03
  32.00       100.10      7.3689E-04   8.1355E-03   5.1666E-03
  33.00       100.09      7.3693E-04   8.1342E-03   5.1652E-03
  34.00       100.09      7.3696E-04   8.1331E-03   5.1640E-03
  35.00       100.09      7.3697E-04   8.1321E-03   5.1629E-03
  36.00       100.09      7.3699E-04   8.1313E-03   5.1620E-03
  37.00       100.08      7.3699E-04   8.1305E-03   5.1612E-03
  38.00       100.08      7.3699E-04   8.1298E-03   5.1605E-03
  39.00       100.08      7.3699E-04   8.1292E-03   5.1599E-03
  40.00       100.08      7.3698E-04   8.1286E-03   5.1594E-03
  41.00       100.08      7.3698E-04   8.1282E-03   5.1590E-03
  42.00       100.07      7.3697E-04   8.1277E-03   5.1586E-03
  43.00       100.07      7.3696E-04   8.1273E-03   5.1583E-03
  44.00       100.07      7.3694E-04   8.1270E-03   5.1581E-03
  45.00       100.07      7.3693E-04   8.1267E-03   5.1578E-03
  46.00       100.07      7.3692E-04   8.1264E-03   5.1576E-03
  47.00       100.07      7.3691E-04   8.1262E-03   5.1575E-03
  48.00       100.07      7.3690E-04   8.1260E-03   5.1574E-03
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49.00        100,07        7,3689E-04     8,1258E-03     5,1573E-03
50.00        100,07        7,3687E-04     8,1256E-03     5,1572E-03
51.00        100,07        7,3686E-04     8,1255E-03     5,1571E-03
52.00        100,07        7,3685E-04     8,1254E-03     5,1570E-03
53.00        100,07        7,3684E-04     8,1252E-03     5,1570E-03
54.00        100,07        7,3683E-04     8,1251E-03     5,1569E-03
55.00        100,06        7,3683E-04     8,1250E-03     5,1569E-03
56.00        100,06        7,3682E-04     8,1250E-03     5,1569E-03
57.00        100,06        7,3681E-04     8,1249E-03     5,1569E-03
58.00        100,06        7,3680E-04     8,1248E-03     5,1569E-03
59.00        100,06        7,3679E-04     8,1248E-03     5,1569E-03
60.00        100,06        7,3679E-04     8,1247E-03     5,1569E-03
61.00        100,06        7,3678E-04     8,1247E-03     5,1568E-03
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   TRANSIENT PROGRAM RESULTS FOR RUN 5
9,2516000E-03     7,6455999E-03     5,2860000E-03     5,6920000E-03
8,1370001E-03     8,5230000E-03     3,4310000E-04     5,4000000E-01
1,4800000E+01     3,1100000E+01     1,3270000E+02     3,2330000E+02
9,4819999E+01     9,5920000E+01     9,9479999E+01     8,5390000E+01
5,8000000E-01     5,5800000E-01     9,9479999E+01     2,2230000E+02
9,2924760E-01     8,0329999E+01     7,0350001E-04     1,1191300E-02
1,5679589E+00    -6,0000000E-04     9,8682463E-01    -1,2031000E-03
3,2218900E+04     6,5856700E+04     3,4664060E-02     2,2659460E-02
  TIME            TEMP             CAC              CAD             CBC
  (MIN,)         (DEG,F)        (GMOLE/ML)       (GMOLE/ML)      (GMOLE/ML)
   1,00           92,60          6,9679E-04       8,1491E-03      5,3050E-03
   2,00           90,13          6,7594E-04       8,1723E-03      5,3364E-03
   3,00           89,15          6,5519E-04       8,1972E-03      5,3718E-03
   4,00           88,70          6,3758E-04       8,2214E-03      5,4081E-03
   5,00           88,46          6,2338E-04       8,2439E-03      5,4436E-03
   6,00           88,32          6,1213E-04       8,2647E-03      5,4774E-03
   7,00           88,22          6,0329E-04       8,2836E-03      5,5091E-03
   8,00           88,16          5,9635E-04       8,3008E-03      5,5385E-03
   9,00           88,12          5,9090E-04       8,3165E-03      5,5656E-03
  10,00           88,09          5,8661E-04       8,3307E-03      5,5902E-03
  11,00           88,07          5,8323E-04       8,3435E-03      5,6126E-03
  12,00           88,06          5,8055E-04       8,3551E-03      5,6328E-03
  13,00           88,05          5,7843E-04       8,3655E-03      5,6510E-03
  14,00           88,04          5,7675E-04       8,3749E-03      5,6673E-03
  15,00           88,04          5,7540E-04       8,3834E-03      5,6819E-03
  16,00           88,04          5,7433E-04       8,3910E-03      5,6949E-03
  17,00           88,05          5,7348E-04       8,3979E-03      5,7065E-03
  18,00           88,05          5,7279E-04       8,4040E-03      5,7167E-03
  19,00           88,05          5,7224E-04       8,4096E-03      5,7259E-03
  20,00           88,06          5,7180E-04       8,4146E-03      5,7339E-03
  21,00           88,06          5,7144E-04       8,4191E-03      5,7411E-03
  22,00           88,07          5,7116E-04       8,4231E-03      5,7474E-03
  23,00           88,07          5,7093E-04       8,4267E-03      5,7529E-03
  24,00           88,07          5,7075E-04       8,4299E-03      5,7578E-03
  25,00           88,08          5,7060E-04       8,4328E-03      5,7621E-03
  26,00           88,08          5,7048E-04       8,4354E-03      5,7660E-03
  27,00           88,08          5,7039E-04       8,4378E-03      5,7693E-03
  28,00           88,08          5,7032E-04       8,4399E-03      5,7722E-03
  29,00           88,09          5,7027E-04       8,4418E-03      5,7748E-03
  30,00           88,09          5,7022E-04       8,4435E-03      5,7771E-03
  31,00           88,09          5,7019E-04       8,4450E-03      5,7791E-03
  32,00           88,09          5,7017E-04       8,4463E-03      5,7808E-03
  33,00           88,09          5,7015E-04       8,4475E-03      5,7823E-03
  34,00           88,10          5,7014E-04       8,4486E-03      5,7837E-03
  35,00           88,10          5,7014E-04       8,4496E-03      5,7848E-03
  36,00           88,10          5,7014E-04       8,4505E-03      5,7858E-03
  37,00           88,10          5,7014E-04       8,4513E-03      5,7867E-03
  38,00           88,10          5,7014E-04       8,4520E-03      5,7875E-03
  39,00           88,10          5,7014E-04       8,4526E-03      5,7882E-03
  40,00           88,10          5,7015E-04       8,4532E-03      5,7888E-03
  41,00           88,10          5,7016E-04       8,4537E-03      5,7893E-03
  42,00           88,10          5,7017E-04       8,4542E-03      5,7897E-03
  43,00           88,10          5,7018E-04       8,4546E-03      5,7901E-03
  44,00           88,11          5,7018E-04       8,4550E-03      5,7905E-03
  45,00           88,11          5,7019E-04       8,4553E-03      5,7908E-03
  46,00           88,11          5,7020E-04       8,4556E-03      5,7910E-03
  47,00           88,11          5,7021E-04       8,4558E-03      5,7912E-03
  48,00           88,11          5,7022E-04       8,4561E-03      5,7914E-03
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49,00        88,11        5,7023E-04    8,4563E-03    5,7916E-03
50,00        88,11        5,7024E-04    8,4565E-03    5,7917E-03
51,00        88,11        5,7024E-04    8,4567E-03    5,7918E-03
52,00        88,11        5,7025E-04    8,4568E-03    5,7919E-03
53,00        88,11        5,7026E-04    8,4570E-03    5,7920E-03
54,00        88,11        5,7026E-04    8,4571E-03    5,7921E-03
55,00        88,11        5,7027E-04    8,4572E-03    5,7922E-03
56,00        88,11        5,7028E-04    8,4573E-03    5,7922E-03
57,00        88,11        5,7028E-04    8,4574E-03    5,7923E-03
58,00        88,11        5,7029E-04    8,4575E-03    5,7923E-03
59,00        88,11        5,7029E-04    8,4575E-03    5,7924E-03
60,00        88,11        5,7030E-04    8,4576E-03    5,7924E-03
61,00        88,11        5,7030E-04    8,4577E-03    5,7924E-03
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  TRANSIENT PROGRAM RESULTS FOR RUN 6
9,2467000E-03     7,6421000E-03     5,5910000E-03     5,8790000E-03
8,4580000E-03     8,5380001E-03     3,7750000E-04     5,4000000E-01
1,4800000E+01     3,1100000E+01     1,3817000E+02     3,1783000E+02
9,5900000E+01     9,6799999E+01     9,7090000E+01     8,5390000E+01
5,8000000E-01     5,5800000E-01     9,7090000E+01     2,2230000E+02
8,6831460E-01     8,0960000E+01     3,9950000E-04     1,3650100E-02
1,6885317E+00    -1,8661000E-03     9,0640050E-01    -3,1690000E-04
4,3899800E+04     2,1514800E+04     2,4528600E-02     2,2040600E-02
  TIME         TEMP           CAC          CAD          CBC
 (MIN,)      (DEG,F)      (GMOLE/ML)   (GMOLE/ML)   (GMOLE/ML)
    1,00       90,68       4,3077E-04   8,4604E-03   5,6147E-03
    2,00       87,23       4,5364E-04   8,4659E-03   5,6383E-03
    3,00       85,37       4,7054E-04   8,4726E-03   5,6598E-03
    4,00       84,39       4,8308E-04   8,4795E-03   5,6785E-03
    5,00       83,86       4,9236E-04   8,4863E-03   5,6943E-03
    6,00       83,60       4,9922E-04   8,4926E-03   5,7074E-03
    7,00       83,46       5,0427E-04   8,4984E-03   5,7183E-03
    8,00       83,40       5,0799E-04   8,5037E-03   5,7274E-03
    9,00       83,37       5,1071E-04   8,5084E-03   5,7349E-03
   10,00       83,36       5,1270E-04   8,5128E-03   5,7411E-03
   11,00       83,36       5,1415E-04   8,5166E-03   5,7463E-03
   12,00       83,36       5,1521E-04   8,5201E-03   5,7506E-03
   13,00       83,37       5,1599E-04   8,5233E-03   5,7543E-03
   14,00       83,37       5,1656E-04   8,5261E-03   5,7574E-03
   15,00       83,38       5,1698E-04   8,5286E-03   5,7600E-03
   16,00       83,38       5,1729E-04   8,5309E-03   5,7623E-03
   17,00       83,38       5,1753E-04   8,5330E-03   5,7642E-03
   18,00       83,39       5,1770E-04   8,5348E-03   5,7659E-03
   19,00       83,39       5,1783E-04   8,5364E-03   5,7673E-03
   20,00       83,39       5,1793E-04   8,5379E-03   5,7686E-03
   21,00       83,39       5,1801E-04   8,5393E-03   5,7696E-03
   22,00       83,39       5,1808E-04   8,5405E-03   5,7706E-03
   23,00       83,39       5,1813E-04   8,5415E-03   5,7714E-03
   24,00       83,40       5,1817E-04   8,5425E-03   5,7721E-03
   25,00       83,40       5,1820E-04   8,5434E-03   5,7727E-03
   26,00       83,40       5,1823E-04   8,5442E-03   5,7733E-03
   27,00       83,40       5,1826E-04   8,5449E-03   5,7737E-03
   28,00       83,40       5,1828E-04   8,5455E-03   5,7742E-03
   29,00       83,40       5,1831E-04   8,5461E-03   5,7745E-03
   30,00       83,40       5,1832E-04   8,5466E-03   5,7748E-03
   31,00       83,40       5,1834E-04   8,5470E-03   5,7751E-03
   32,00       83,40       5,1836E-04   8,5475E-03   5,7753E-03
   33,00       83,40       5,1837E-04   8,5478E-03   5,7755E-03
   34,00       83,40       5,1838E-04   8,5482E-03   5,7757E-03
   35,00       83,40       5,1840E-04   8,5485E-03   5,7759E-03
   36,00       83,40       5,1841E-04   8,5487E-03   5,7760E-03
   37,00       83,40       5,1842E-04   8,5490E-03   5,7761E-03
   38,00       83,40       5,1843E-04   8,5492E-03   5,7762E-03
   39,00       83,40       5,1844E-04   8,5494E-03   5,7763E-03
   40,00       83,40       5,1845E-04   8,5496E-03   5,7764E-03
   41,00       83,40       5,1845E-04   8,5497E-03   5,7764E-03
   42,00       83,40       5,1846E-04   8,5499E-03   5,7765E-03
   43,00       83,40       5,1847E-04   8,5500E-03   5,7765E-03
   44,00       83,40       5,1847E-04   8,5501E-03   5,7766E-03
   45,00       83,40       5,1848E-04   8,5502E-03   5,7766E-03
   46,00       83,40       5,1849E-04   8,5503E-03   5,7767E-03
   47,00       83,40       5,1849E-04   8,5504E-03   5,7767E-03
   48,00       83,40       5,1849E-04   8,5505E-03   5,7767E-03
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49,00          83,40          5,1850E-04     8,5506E-03     5,7767E-03
50,00          83,40          5,1850E-04     8,5506E-03     5,7767E-03
51,00          83,40          5,1851E-04     8,5507E-03     5,7767E-03
52,00          83,40          5,1851E-04     8,5507E-03     5,7768E-03
53,00          83,40          5,1851E-04     8,5508E-03     5,7768E-03
54,00          83,40          5,1852E-04     8,5508E-03     5,7768E-03
55,00          83,40          5,1852E-04     8,5508E-03     5,7768E-03
56,00          83,40          5,1852E-04     8,5509E-03     5,7768E-03
57,00          83,40          5,1852E-04     8,5509E-03     5,7768E-03
58,00          83,40          5,1852E-04     8,5509E-03     5,7768E-03
59,00          83,40          5,1853E-04     8,5509E-03     5,7768E-03
60,00          83,40          5,1853E-04     8,5510E-03     5,7768E-03
61,00          83,40          5,1853E-04     8,5510E-03     5,7768E-03
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  TRANSIENT PROGRAM RESULTS FOR RUN  7
9.2467000E-03     7,6421000E-03     5,8790000E-03     5,5290000E-03
8.5380001E-03     8,3020001E-03     4,9660000E-04     5,4000000E-01
1.4800000E+01     3,1100000E+01     1,4455000E+02     3,1145000E+02
9.5900000E+01     9,6799999E+01     8,5390000E+01     9,9259999E+01
5.8000000E-01     5,5800000E-01     8,5390000E+01     5,1300000E+01
8,9620241E-01     8,0960000E+01     7,6970000E-04     1,4702000E-02
1.4752756E+00     6,0180000E-04     8,5851271E-01     2,6440000E-04
2.0928800E+04     2,3558800E+04     2,2040600E-02     2,9380200E-02
  TIME           TEMP            CAC             CAD            CBC
 (MIN,)         (DEG,F)      (GMOLE/ML)      (GMOLE/ML)     (GMOLE/ML)
    1,00         87,31        6,9774E-04      8,5364E-03     5,8086E-03
    2,00         88,66        6,4754E-04      8,5324E-03     5,7541E-03
    3,00         89,59        6,1293E-04      8,5269E-03     5,7117E-03
    4,00         90,23        5,8928E-04      8,5206E-03     5,6782E-03
    5,00         90,67        5,7323E-04      8,5141E-03     5,6514E-03
    6,00         90,96        5,6241E-04      8,5076E-03     5,6297E-03
    7,00         91,16        5,5517E-04      8,5014E-03     5,6117E-03
    8,00         91,30        5,5034E-04      8,4955E-03     5,5968E-03
    9,00         91,39        5,4716E-04      8,4900E-03     5,5841E-03
   10,00         91,44        5,4507E-04      8,4850E-03     5,5733E-03
   11,00         91,48        5,4373E-04      8,4804E-03     5,5641E-03
   12,00         91,50        5,4288E-04      8,4762E-03     5,5560E-03
   13,00         91,52        5,4236E-04      8,4725E-03     5,5490E-03
   14,00         91,52        5,4205E-04      8,4691E-03     5,5429E-03
   15,00         91,52        5,4188E-04      8,4661E-03     5,5375E-03
   16,00         91,52        5,4180E-04      8,4633E-03     5,5328E-03
   17,00         91,52        5,4177E-04      8,4609E-03     5,5286E-03
   18,00         91,51        5,4178E-04      8,4587E-03     5,5250E-03
   19,00         91,51        5,4180E-04      8,4567E-03     5,5217E-03
   20,00         91,51        5,4184E-04      8,4550E-03     5,5189E-03
   21,00         91,50        5,4187E-04      8,4535E-03     5,5164E-03
   22,00         91,50        5,4191E-04      8,4521E-03     5,5142E-03
   23,00         91,49        5,4195E-04      8,4508E-03     5,5122E-03
   24,00         91,49        5,4198E-04      8,4498E-03     5,5105E-03
   25,00         91,48        5,4201E-04      8,4488E-03     5,5089E-03
   26,00         91,48        5,4204E-04      8,4479E-03     5,5076E-03
   27,00         91,48        5,4206E-04      8,4471E-03     5,5064E-03
   28,00         91,47        5,4208E-04      8,4465E-03     5,5054E-03
   29,00         91,47        5,4210E-04      8,4459E-03     5,5045E-03
   30,00         91,47        5,4211E-04      8,4453E-03     5,5036E-03
   31,00         91,46        5,4212E-04      8,4448E-03     5,5029E-03
   32,00         91,46        5,4213E-04      8,4444E-03     5,5023E-03
   33,00         91,46        5,4214E-04      8,4440E-03     5,5018E-03
   34,00         91,46        5,4214E-04      8,4437E-03     5,5013E-03
   35,00         91,46        5,4214E-04      8,4434E-03     5,5009E-03
   36,00         91,45        5,4215E-04      8,4431E-03     5,5005E-03
   37,00         91,45        5,4215E-04      8,4429E-03     5,5002E-03
   38,00         91,45        5,4215E-04      8,4427E-03     5,4999E-03
   39,00         91,45        5,4215E-04      8,4425E-03     5,4996E-03
   40,00         91,45        5,4215E-04      8,4423E-03     5,4994E-03
   41,00         91,45        5,4215E-04      8,4422E-03     5,4992E-03
   42,00         91,45        5,4215E-04      8,4421E-03     5,4990E-03
   43,00         91,45        5,4215E-04      8,4420E-03     5,4989E-03
   44,00         91,45        5,4215E-04      8,4419E-03     5,4988E-03
   45,00         91,45        5,4215E-04      8,4418E-03     5,4987E-03
   46,00         91,45        5,4215E-04      8,4417E-03     5,4986E-03
   47,00         91,45        5,4215E-04      8,4416E-03     5,4985E-03
   48,00         91,44        5,4215E-04      8,4416E-03     5,4984E-03
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49,00        91,44        5,4214E-04    8,4415E-03    5,4983E-03
50,00        91,44        5,4214E-04    8,4415E-03    5,4983E-03
51,00        91,44        5,4214E-04    8,4414E-03    5,4982E-03
52,00        91,44        5,4214E-04    8,4414E-03    5,4982E-03
53,00        91,44        5,4214E-04    8,4413E-03    5,4982E-03
54,00        91,44        5,4214E-04    8,4413E-03    5,4981E-03
55,00        91,44        5,4214E-04    8,4413E-03    5,4981E-03
56,00        91,44        5,4214E-04    8,4413E-03    5,4981E-03
57,00        91,44        5,4214E-04    8,4412E-03    5,4981E-03
58,00        91,44        5,4213E-04    8,4412E-03    5,4981E-03
59,00        91,44        5,4213E-04    8,4412E-03    5,4980E-03
60,00        91,44        5,4213E-04    8,4412E-03    5,4980E-03
61,00        91,44        5,4213E-04    8,4412E-03    5,4980E-03
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