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EFFECT OF THE DISTRIBUTION OF RESIDENCE TIMES UPON THE PERFORMANCE OF AGITATED REACTORS

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STATEMENT OF THE PROBLEM

To evaluate the applicability of distributions of residence times for calculating the first-order conversion occurring in continuous, homogeneous, liquid-phase, flow-systems.

CHAPTER I

INTRODUCTION

Greater and greater use is being made of continuous processes in the chemical industry. A continuous process consists of a number of individual units of equipment through which materials are moving in a more or less continuous manner. The different units vary greatly in design from the point of view of flow behavior. Some units, which have a great deal of mixing in the direction of overall flow, behave like perfectly-mixed systems. Others, which have very little or no mixing in the direction of overall flow, behave like ideal slug-flow systems. Then there are others whose behavior is neither perfectly-mixed nor slug-flow. These are the pieces of equipment for which there is a great need for having general methods for predicting their performance.

Danckwerts(10) has suggested how the distribution of residence times for many of these systems could be used as a model for predicting their performance. There is yet very little data which has been taken to evaluate the distribution of residence times model as applied to many processes. Among these is chemical reaction. Very little experimental work has been published in the literature to determine whether or not the distribution of residence times model proposed for predicting the amount of conversion in homogeneous, first-order systems is valid. This research was undertaken in order to evaluate the distribution of residence times model for homogeneous, first-order, reacting systems.

Related Data in the Literature

In determining flow patterns and the amount of chemical reaction occurring in continuous systems some investigators have made measurements inside the systems; others have made measurements only on the outlet stream. In the former group are Aiba(1), who has measured flow patterns in stirred reactors and Prausnitz(25,26), who has measured concentration fluctuations in a packed column. In the latter group are Gilliland(16), who has measured the distribution of residence times and conversion occurring in fluidized systems; Cleland(6), who has predicted the distribution of residence times and has measured the amount of first-order conversion occurring in viscous-tubular reactors; Kawamura(20), who has measured the distribution of residence times and the amount of second-order conversion occurring in a horizontal cylindrical reactor, and Nagata(23) who has measured the distribution of residence times and the amount of first-order conversion occurring in columns with various numbers of compartments and stirrers. Danckwerts(9,11,12) has suggested methods for measuring concentration fluctuations both inside a system and on the exit stream.

Measurements made inside a flow system have the advantage that in general, they describe the flow system more completely than measurements made only on the outlet stream, but measurements made inside a system are in general more difficult experimentally and tedious than measurements made on the outlet stream. In the experimental work which was performed for this thesis all measurements were made on the outlet stream.

CHAPTER II

THEORY

Suppose that to a continuous reactor of constant volume V the inlet and outlet flow rates are constant and equal to v. The bulk residence time for the system is $\frac{V}{v}$. Some elements of liquid will spend a time less than $\frac{V}{v}$ in the system and others will spend a time greater than $\frac{V}{v}$ in the system, that is, the elements will have a distribution of residence times in the system.

Pulse Experiment

In order to visualize the distribution of residence times suppose that at time t = 0 a pulse of tracer of quantity Q is injected into the inlet stream to the reactor. Let C(t) be the concentration of tracer in the outlet stream for such an experiment. A graph of C(t) against t might appear as shown in Figure 1. The rate at which tracer leaves the reactor is

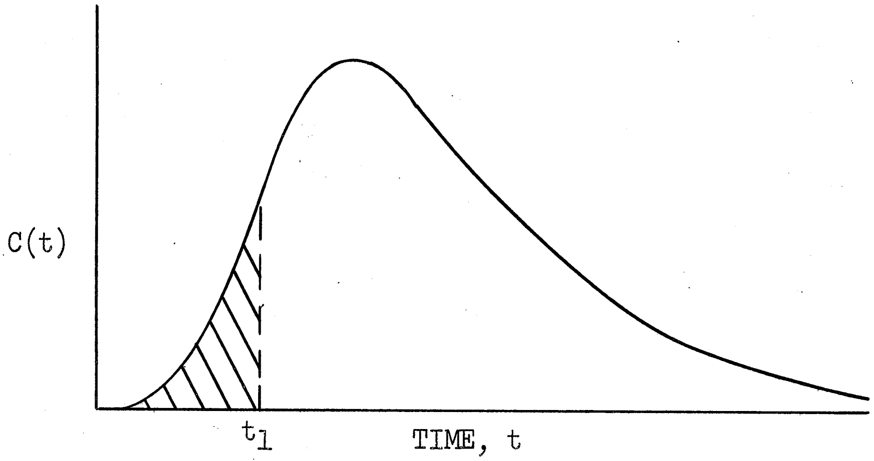


Figure 1. Concentration as a Function of Time.

$vC(t)$ and the amount of tracer leaving during the interval 0 to t is $\int_0^t vC(t)dt$. Then the fraction of tracer leaving during time 0 to t is $\int_0^t \frac{vC(t)}{Q}dt$. Since $\frac{V}{v}$ is the length of 1 residence time, then $\Theta = \frac{tv}{V}$ = the number of residence times. Then

$$\int_0^t \frac{vC(t)dt}{Q} = \int_0^\Theta \frac{VC(\Theta)}{Q}\,d\Theta$$

Let $\frac{VC(\Theta)}{Q} = E(\Theta)$ be the distribution of residence times for a pulse input. Then the fraction of tracer leaving during 0 to Θ residence times is $\int_0^\Theta E(\Theta)d\Theta$. Let

$$F(\Theta) = \int_0^\Theta E(\Theta)d\Theta \qquad (1)$$

so that $F(\Theta)$ is the fraction of tracer leaving during 0 to Θ residence times. If the reactor is under steady-state flow conditions then $F(\Theta)$ is also the fraction of liquid throughput which has been in the reactor residence times ranging from 0 to Θ.

When time becomes very great all the dye has left the reactor. Therefore

$$\lim_{\Theta \to \infty} \int_0^\Theta E(\Theta)d\Theta = 1.0 \qquad (2)$$

Step-Function Experiment

Suppose tracer is fed to a continuous flow system as a step-function. For $\Theta < 0$ no tracer has entered the system. For $\Theta > 0$ all the liquid entering is tracer. Let $F'(\Theta)$ be the fraction of liquid in the outlet stream at residence time Θ which is tracer. But tracer is liquid which has been in the system residence times ranging from 0 to Θ. Therefore $F'(\Theta)$ is the fraction of liquid in the outlet stream which has been in the system residence times ranging from 0 to Θ. But in the previous section the fraction of liquid in the outlet stream which had been in the system residence times ranging from 0 to Θ was $F(\Theta)$. Therefore $F'(\Theta) = F(\Theta)$ and from now on the prime will be omitted. Note that by Equation (1)

$$F(\Theta) = \int_0^{\Theta} E(\Theta)d(\Theta)$$

In the step-function experiment the rate at which tracer leaves the reactor is $vF(\Theta)$ and the amount of tracer which has left during 0 to Θ residence times is

$$\int_0^{t} vF(\Theta)dt = V\int_0^{\Theta} F(\Theta)d\Theta$$

Let $\int_0^{\Theta} I(\Theta)d\Theta$ be the fraction of liquid in the system at residence time Θ which is tracer. The quantity of tracer in the system at residence time Θ is $V\int_0^{\Theta} I(\Theta)d\Theta$.

Upon Summarizing:

Moles of tracer in during time 0 to $\Theta = vt = V\Theta = V\int_0^{\Theta} d\Theta$

Moles of tracer out during time 0 to $\Theta = V\int_0^{\Theta} F(\Theta)d\Theta$

Moles of tracer in the system at time $\Theta = V\int_0^{\Theta} I(\Theta)d\Theta$

Moles of tracer in the system at time $0^- = 0$

A material balance for the system for the interval 0 to θ is:

Tracer in - Tracer out = Tracer present at time θ

$$V \int_0^\theta d\theta - V \int_0^\theta F(\theta) d\theta = V \int_0^\theta I(\theta) d\theta$$

$$\int_0^\theta [1 - F(\theta)]\, d\theta = \int_0^\theta I(\theta)\, d\theta$$

but

$$\lim_{\theta \to \infty} \int_0^\theta I(\theta) d\theta = 1.0 \qquad (3)$$

that is, when time becomes great, only tracer is present in the reactor.

Therefore,

$$\lim_{\theta \to \infty} \int_0^\theta [1 - F(\theta)]\, d\theta = 1.0 \qquad (4)$$

$F(\theta)$ might appear as shown in Figure 2.

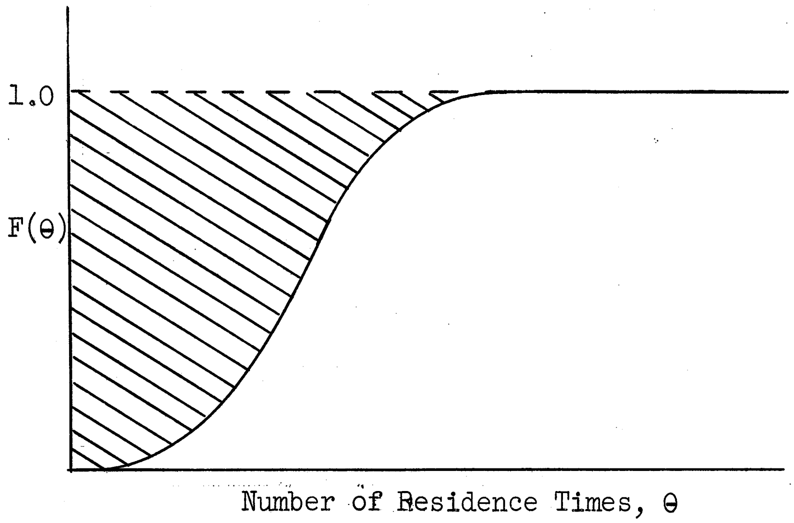


Figure 2. $F(\theta)$ as a Function of θ.

First Moment

The first moment of the distribution of residence times $E(\theta)$ is $\lim_{\theta \to \infty} \int_0^\theta \theta E(\theta) d\theta$. But from Equation (1) it follows that $E(\theta)d\theta = dF(\theta)$. Therefore

$$\lim_{\theta \to \infty} \int_0^\theta \theta E(\theta) d\theta = \lim_{\theta \to \infty} \int_0^\theta \theta dF(\theta)$$

From Figure 2 it can be seen that the $\lim_{\theta \to \infty} \int_0^\theta \theta dF(\theta)$ is the cross-hatched area which was proven by Equation (4) to be 1.0. Therefore,

$$\lim_{\theta \to \infty} \int_0^\theta \theta E(\theta) d\theta = \lim_{\theta \to \infty} \int_0^\theta [1 - F(\theta)]\, d\theta = 1.0 \qquad (5)$$

that is, the first moment about an abscissa of zero of the $E(\theta)$ function is 1.0.

For any continuous flow system there are two material balances. The first is that the total fraction of material of all ages leaving the system in the outlet stream is 1.0. This is Equation (2). The second is that the total fraction of material of all ages inside the system is 1.0. This is Equation (3). Equation (5) shows that the first moment of $E(\theta)$ is identical to the internal material balance. Thus either the two material balances or the outlet material balance and the first moment can be used to check to determine whether tracer is actually behaving as a tracer. Capen(5) and Truesdale(29) have discussed the value of these equations as checks.

Distribution of Residence Times Model

Danckwerts(10) has proposed the distribution of residence times model for predicting the amount of first-order conversion occurring in homogeneous, liquid-phase, flow systems. Suppose that for any system the distribution function $E(\theta)$ and the reaction rate constant k are known. By the distribution of residence times model any flow system is equivalent to a series of slug flow reactors in parallel in which liquid spends time θ, where θ may be anywhere from 0 to ∞. The fraction of the total reactors in which liquid spends times ranging from 0 to θ is the fraction of the liquid which has residence times ranging from 0 to θ in the system and by Equation (1) equals $\int_0^\theta E(\theta)\,d\theta$. The conversion in each reactor is $1 - e^{-k\tau\theta}$ where τ is the length of one residence time. The conversion for the system is then the average conversion for all the reactors

$$f_D = \lim_{\theta \to \infty} \int_0^\theta (1 - e^{-k\tau\theta})E(\theta)\,d\theta \qquad (6)$$

It is the object of this research to evaluate this model, that is, Equation (6), for calculating the amount of conversion occurring in first-order, homogeneous, liquid-phase flow systems.

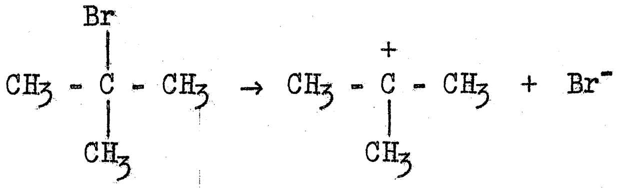
CHAPTER III

BATCH REACTION RATE CONSTANTS

In order to predict conversion using the distribution of residence times model it is necessary to know the reaction rate constant as well as the distribution function. Reaction rate constants were measured by a series of batch experiments and correlated over the range of variables used for continuous runs.

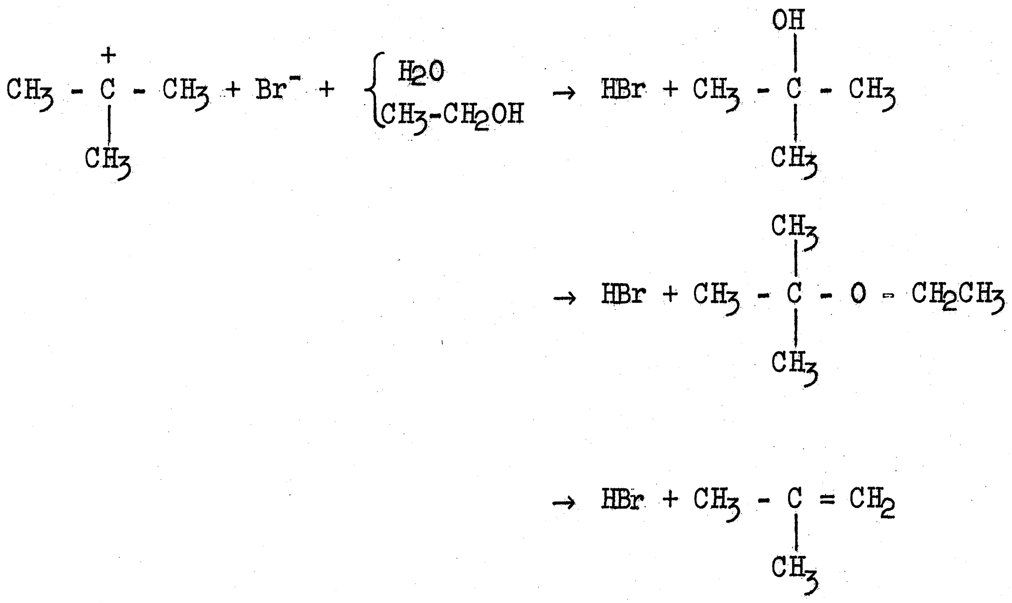
Description of the Reaction

The reactfon used for all experimental work was the hydrolysis of tertiary-butyl-bromide in aqueous ethyl alcohol. The mechanism of this reaction is simultaneous, nucleophilic, substitution and elimination.(18,19,27) The first step, the ionization of tertiary-butyl-bromide, is the rate-controlling step and is common to both substitution and elimination.(19)



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}}-CH_3 \rightarrow CH_3-\underset{\displaystyle CH_3}{\overset{+}{\underset{|}{C}}}-CH_3 + Br^-$$

The bromide ions then react by any one of three fast reactions to form HBr quantitatively.



$$CH_3-\overset{+}{\underset{CH_3}{C}}-CH_3 + Br^- + \left\{\begin{array}{l} H_2O \\ CH_3-CH_2OH \end{array}\right. \rightarrow HBr + CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

$$\rightarrow HBr + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_2CH_3$$

$$\rightarrow HBr + CH_3-\underset{CH_3}{C}=CH_2$$

According to Bateman(3) the amount of second order reaction is not measurable and so the reaction consists essentially of the unimolecular ionization of tertiary-butyl-bromide followed by rapid formation of HBr. From the mixing viewpoint the reaction is first-order and is the same as a radioactive decay reaction.

Materials

The aqueous ethyl alcohol was C.P., 95 percent alcohol which was diluted to the desired concentration with distilled water.

Tertiary-butyl-bromide was prepared by a modification of the method of Sudborough.(28) Silica gel was used in place of calcium chloride as the drying agent. Final purification of tertiary-butyl-bromide was by distillation, the fraction boiling between 73.1 and 73.6°C/760 mm. being used for all kinetic work.

Other materials which were used were C.P. acetone to quench the reaction, carbonate-free sodium hydroxide as the alkali for titrating the solutions and phenolphthalein as indicator.

Analytical Methods

Analysis of Tertiary-Butyl-Bromide Solutions

Samples of the tertiary-butyl-bromide in aqueous ethyl alcohol solution were removed from the reacting system by a 25 ml. pipette. The contents of the pipette were drained into approximately 250 ml. of cold acetone in order to quench the reaction. While the tertiary-butyl-bromide solution drained into the acetone the flask containing the acetone was shaken vigorously in order to dissolve the tertiary-butyl-bromide solution in the acetone as quickly as possible in order to obtain a rapid quench. The time at which the solution began and finished leaving the pipette was recorded and the arithmetic average time was used to compute kinetic constants.

The quenched tertiary-butyl-bromide solution was then immediately titrated with carbonate-free sodium hydroxide using phenolphthalein as the indicator. A blank correction was made for the acidity of acetone and ethyl alcohol.

Using estimates of the maximum values of temperature of quenched solution, time required for titration and water content of acetone, the maximum error in fractional conversion by assuming zero conversion to be occurring while the solution was quenched was 0.0012. The actual error in general was probably considerably less because maximum estimates of each of the variables were used.

In order to determine the initial quantity of tertiary-butyl-bromide in the solution samples were allowed to react to completion during a period of from ten to twenty hours at 20 to 25°C. The samples were then titrated, as described previously for the partially-reacted samples, with carbonate-free sodium hydroxide.

Determination of the Concentration of Ethyl Alcohol in the Solvent

The concentration of ethyl alcohol in the aqueous ethyl alcohol used in the reaction was determined by a Westphal balance. The balance was calibrated by solutions whose concentrations were determined by a pycnometer.

Equipment

The reaction vessel was a five hundred ml., three-necked, glass flask with two vertical creases each 1/2 in. deep. The flask was creased in order to increase the rate of mixing. Weissberger(30) has described the creasing of glass vessels. The stirrer was a bent glass rod and was 7/8 in. in diameter. The diameter of the vessel between creases was 2-3/8 in. The speed of stirring was approximately 1000 r.p.m. MacDonald(21) has summarized what several investigators have found to be high enough stirrer speeds to ensure sufficient mixing for kinetic purposes. Using this discussion as a basis it was considered that 1000 r.p.m. was high enough for the creased reactor which has just been described. The stirrer was sealed by the glass tubing seal described by Morton.(22) Temperature was maintained constant by immersing the reaction vessel in a constant-temperature, water bath. The reactor temperature was measured by a thermometer which could be read to 0.01°C and was calibrated against a National Bureau of Standards thermometer.

Procedure

Four hundred ml. of aqueous ethyl alcohol were placed in the creased flask, described in the previous section, and brought to temperature in the constant temperature bath. After the temperature of the alcohol had remained constant for at least fifteen minutes 4 ml. of tertiary-butyl-bromide were injected into the aqueous ethyl alcohol by a 5 ml. hypodermic. The mean time of injection was considered to be the time of start of reaction. Periodically samples were withdrawn by a 25 ml. pipette, quenched and titrated as described on page 11. The creased flask was stirred except when samples were being withdrawn. Stirring was stopped during sampling in order to prevent the pipette from being broken by the stirrer. The temperature of the reacting solution was recorded at least once between samples.

Calculations and Data

Batch reaction rate constants were calculated for the time intervals between successive samples using the integrated form of the first-order rate equation.

$$k = \frac{2.3026}{t} \log \frac{1}{1 - f} \qquad (7)$$

Since temperature changes up to ± 0.1°C during the course of the reaction the temperature for each interval was determined by plotting temperature as a function of time and using the average temperature for each interval. The average temperature for each interval was the integrated average temperature for the interval.

For the tertiary-butyl-bromide reaction, rate of reaction varies greatly with both temperature and concentration of ethyl alcohol. A series of batch runs at temperatures varying from 23 to 28°C and aqueous alcohol concentrations varying from .64 to .68 mass fraction ethyl alcohol were made. These data are presented in Table I. The columns are as follows:

Column	Description
1	Run number
2	Temperature, °C
3	Mass fraction alcohol in the aqueous ethyl alcohol
4	Initial concentration of tertiary-butyl-bromide, moles / l.
5	Time between samples, sec.
6	Fractional conversion for the interval, based upon there being zero conversion at the beginning of the interval
7	Reaction rate constant, sec.^{-1}

TABLE I. BATCH KINETIC DATA

1 Run Number	2 Temp. T°C.	3 C_{EtOH}	4 C_o	5 Time t, Sec.	6 Conversion	7 10^3k Sec^{-1}
J-7	25.02	.6589	.088	250	.2600	1.204
J-7	25.14	.6589	.088	440	.4065	1.186
J-7	25.11	.6589	.088	450	.4324	1.259
J-8	24.90	.6589	.088	250	.2429	1.113
J-8	25.03	.6589	.088	380	.3568	1.161
J-8	25.06	.6589	.088	390	.3771	1.214
J-8	25.06	.6589	.088	400	.4011	1.282
J-9	25.03	.6434	.088	260	.3027	1.387
J-9	25.16	.6434	.088	340	.3842	1.426
J-9	25.19	.6434	.088	390	.4457	1.513
J-10	24.98	.6434	.088	250	.2834	1.333
J-10	25.08	.6434	.088	410	.4387	1.409
J-10	25.07	.6434	.088	360	.4129	1.479
J-11	23.03	.6434	.088	250	.2380	1.087
J-11	23.14	.6434	.088	380	.3463	1.119
J-11	23.13	.6434	.088	510	.4498	1.172
J-12	22.99	.6589	.088	240	.1912	.884
J-12	23.12	.6589	.088	360	.2789	.908
J-12	23.13	.6589	.088	450	.3475	.949
J-12	23.08	.6589	.088	470	.3754	1.001
J-13	24.98	.6612	.088	262	.2541	1.119
J-13	25.13	.6612	.088	390	.3614	1.150
J-13	25.18	.6612	.088	340	.3436	1.238
J-14	24.90	.6612	.088	242	.2310	1.085
J-14	25.07	.6612	.088	288	.2824	1.152
J-14	25.13	.6612	.088	350	.3435	1.202
J-14	25.13	.6612	.088	360	.3463	1.181
J-15	22.91	.6612	.088	240	.1875	.865
J-15	23.05	.6612	.088	320	.2491	.895
J-15	23.14	.6612	.088	420	.3245	.934
J-16	23.00	.6788	.088	260	.1702	.718
J-16	23.11	.6788	.088	340	.2224	.740
J-16	23.12	.6788	.088	330	.2263	.778
J-16	23.14	.6788	.088	340	.2270	.757

TABLE I. BATCH KINETIC DATA (CONT'D)

1	2	3	4	5	6	7
Run Number	Temp. T°C.	C_{EtOH}	C_o	Time t, Sec.	Conversion	10^3k Sec^{-1}
J-17	24.88	.6788	.088	250	.1982	.884
J-17	25.01	.6788	.088	290	.2376	.935
J-17	25.03	.6788	.088	310	.2537	.944
J-17	25.03	.6788	.088	370	.2981	.957
J-18	24.96	.6788	.088	240	.1938	.898
J-18	25.06	.6788	.088	310	.2475	.917
J-18	25.06	.6788	.088	350	.2877	.969
J-18	25.06	.6788	.088	360	.2957	.974
J-19	28.05	.6788	.088	230	.2588	1.302
J-19	28.16	.6788	.088	250	.2926	1.385
J-19	28.07	.6788	.088	350	.3870	1.398
J-20	27.78	.6612	.088	220	.2845	1.522
J-20	27.95	.6612	.088	320	.4094	1.646
J-20	28.02	.6612	.088	320	.4167	1.685
J-21	27.85	.6612	.088	220	.2832	1.513
J-21	27.93	.6612	.088	260	.3473	1.635
J-21	27.97	.6612	.088	290	.3881	1.694
J-26	24.97	.6568	.088	290	.2841	1.152
J-26	25.10	.6568	.088	280	.2872	1.209
J-26	25.09	.6568	.088	310	.3200	1.244
J-26	25.05	.6568	.088	390	.3763	1.210

Correlation of Batch Constants

Grunwald$^{(17)}$ has suggested that the best way to correlate reaction rate constants for tertiary-butyl-chloride over a wide range of alcohol concentrations is

$$\log k = A' - B'\,C'_{ETOH} \qquad (8)$$

where A' and B' are constants and C'_{ETOH} is the mole fraction of ethyl alcohol. Over the narrow range of alcohol concentrations used in this research mass fraction and mole fraction are nearly exactly proportional to one another. Therefore Equation (8) can be rewritten as

$$\log k = A'' - BC_{ETOH}$$

where A" and B are constants and C_{ETOH} is the mass fraction of ethyl alcohol.

The variation of k with temperature is normally correlated by

$$\log k = A''' - \frac{E}{R(T + 273.1)}$$

where A" ' and E/R are constants and T is the temperature in °C.

The expression used to correlate data in terms of both alcohol concentration and temperature was

$$\log k = A - BC_{ETOH} - \frac{E}{R(T + 273.1)} \qquad (9)$$

This equation is the sum of the two previous equations. Since the ranges of variables were small it was not considered necessary to add the term $\frac{DC_{ETOH}}{T + 273.1}$. The constants in Equation (9) were determined by a least square fit of the data in Table I, and the equation became

$$\log k_{.088} = 15.9501 - 5.0223\, C_{ETOH} - \frac{4{,}641.22}{T + 273.10} \qquad (10)$$

$$.64 < C_{ETOH} < .68$$

$$23 < T°C < 28$$

$$C_o = .088$$

where T is the temperature in °C.

C_{ETOH} is the mass fraction of ethyl alcohol on the tertiary-butyl-bromide free basis.

C_o is the initial concentration of tertiary-butyl-bromide.

The 95 percent confidence limits for the general type of correlation of which Equation (10) is an example are given on page 530 of Duncan(14).

Hence the 95 percent confidence limits for $\log k_{.088}$ are:

$$15.9501 - 5.0223\, C_{ETOH} - \frac{4{,}641.22}{T + 273.10} \pm .02957 \Big(.0182 + 134.7\,(C_{ETOH} - .6623)^2 + 614.6 \times 10^5 \left(\frac{1}{T + 273.10} - .00335436\right)^2 + 1.243 \times 10^4\,(C - .6623)\left(\frac{1}{T + 273.10} - .00335436\right)\Big)^{1/2}$$

TABLE II

PERCENTAGE DIFFERENCE BETWEEN CONFIDENCE LIMITS AND VALUE PREDICTED BY EQUATION (10)

C_{ETOH}	T°C	Percentage of k
.6623	25.02	0.93
.6400	25.02	2.01
.6800	25.02	1.69
.6623	23.00	1.55
.6623	28.00	2.01

At C_{ETOH} and T equal to .6623 and 25.02 respectively, the mid-point of the correlation, the confidence limit is narrowest. Most of the continuous runs were made very close to this point. Therefore the 95% confidence limits for the continuous runs would, in general, be the value predicted by Equation (10) ± 1%. The multiple correlation coefficient $r_{1.23} = 0.988$.

A series of runs were made at various initial concentrations of tertiary-butyl-bromide. These data are presented in Table III. Columns 1 through 7 are the same as described on page 14 for Table I. Column 8 is the rate constant at 25.10°C and was computed from the data in column 7 by using the activation energy given by Equation (10). All the data were taken in the same aqueous ethyl alcohol solution. By performing a least square fit of the data in Table III, the change in k is

$$k_{C_o} - k_{.088} = k_{.088}(0.580)(.0880 - C_o) \qquad (11)$$

where 0.580 is the constant determined by the least square fit and C_o is the initial concentration of tertiary-butyl-bromide in moles/l. The slope of Equation (11) is significantly different from zero at a significance level of 5 percent.

The 95% confidence interval for $k_{C_o} - k_{.088}$ is

$$k_{.088}(0.580)(.0880 - C_o) \pm .0425 \sqrt{.0714 + 63.72\,(C_o - .0668)^2}$$

This is equal to $k_{C_o} - k_{.088} \pm 0.13\%$ at the ends of the interval specified by Equation (11).

TABLE III

BATCH KINETIC CONSTANTS AT VARIOUS INITIAL CONCENTRATIONS OF TERTIARY-BUTYL-BROMIDE

1	2	3	4	5	6	7	8
Run Number	Temp. T°C	C_{EtOH}	C_0	Time t, Sec.	Conversion	$10^3 k$ Sec^{-1}	10^3 $k_{25.10°C}$
J-26	24.97	.6568	.0880	290	.2841	1.152	1.172
J-26	25.10	.6568	.0880	280	.2872	1.209	1.209
J-26	25.09	.6568	.0880	310	.3200	1.244	1.246
J-26	25.05	.6568	.0880	390	.3763	1.210	1.218
J-27	24.98	.6568	.0453	260	.2678	1.199	1.217
J-27	25.06	.6568	.0453	320	.3229	1.219	1.225
J-27	25.05	.6568	.0453	310	.3230	1.258	1.266
J-27	25.01	.6568	.0453	370	.3640	1.223	1.237
J-28	24.92	.6568	.0754	270	.2700	1.166	1.193
J-28	25.05	.6568	.0754	280	.2895	1.221	1.229
J-28	25.03	.6568	.0754	340	.3367	1.207	1.217
J-28	24.98	.6568	.0754	440	.4124	1.208	1.226
J-29	24.92	.6568	.0584	288	.2864	1.172	1.199
J-29	24.98	.6568	.0584	290	.2998	1.229	1.247
J-29	25.01	.6568	.0584	370	.3694	1.246	1.260
J-29	24.96	.6568	.0584	460	.4338	1.237	1.258

Discussion

For the hydrolysis of tertiary-butyl-bromide in aqueous ethyl alcohol a survey of the literature revealed that no measurements of reaction rate constants have been reported in 70 volume percent ethyl alcohol.

Bateman(3) has measured constants at 60, 80 and 90 volume percent ethyl alcohol. These data were later checked by Cropper(8). If Equation (9) is used to interpolate between the values at 60 and 80 volume percent alcohol then the following comparison can be made by using Equations (10) and (11) at 25.00°C and $C_o = .05$.

Mol Fraction ETOH	k Bateman	k Equations 10 & 11	% Difference
.4102	.001479	.001499	+ 1.33
.4316	.001179	.001190	- 0.60
.4539	.000959	.000946	- 1.41

When the approximate nature of the correlation is considered and also that Bateman(3) did not indicate that he made more than one measurement at each concentration, the agreement is within the generally accepted limit of 1 to 2% for reaction rate constants.

Equation (10) gives an energy of activation of 21,240 compared to the value of 21,700 reported by Bateman(3).

CHAPTER IV

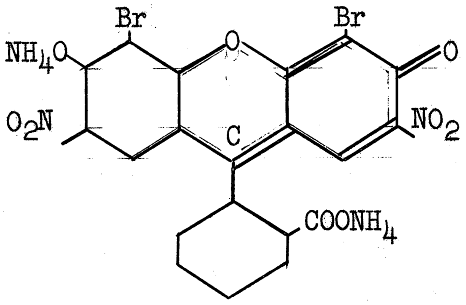
CONTINUOUS FLOW SYSTEMS

The pulse response technique, which was used by Yagi(32), Ebach(15) and De Maria(13), was used for measuring all distribution functions. The mathematics of the pulse technique is discussed in Chapter II. From this point on in this thesis a distribution function or the distribution of residence times will always refer to $E(\theta)$ rather than $F(\theta)$ or $I(\theta)$. Also t will be time and θ the number of residence times. τ will be the length of 1 residence time, so that, $t = \tau\theta$.

Description of Dyes

Pontamine Fast Turquoise 8GLD Conc. 150%, which was manufactured by E.I. du Pont de Nemours and Company, was used to measure some of the distribution functions in distilled water.

For the remainder of the runs in water and all the runs in aqueous ethyl alcohol, eosin bluish, manufactured by the National Aniline Division of Allied Chemical and Dye Corp. of Pharmaceutical Laboratories was used as dye. The formula for eosin bluish is



Eosin Bluish (4,5 - dibromo - 2, 7 - dinitrofluorescein)

For all runs in the presence of tertiary-butyl-bromide Pontachrome Blue Black R.M. Conc. was used. This is a vegetable black and was manufactured by E.I. du Pont de Nemours and Company.

Flow System

The flow diagram for the continuous reactor system is shown in Figure 3. The system can be broken up into the following sections:

1. Inlet flow system which includes equipment to measure and control the rates of flow and the temperatures of the inlet streams to the reactor.
2. The reactors
   - (a) One-compartment reactor
   - (b) Glass-bead reactor
   - (c) Two-compartment reactor.
3. Colorimeter, recorder and dye injection system.
4. The reactor outlet system which included level control, flow measurement and sampling.

Equipment

Reactor Inlet Flow System

The feed to the reactor consisted of a solution of unreacted tertiary-butyl-bromide dissolved in aqueous ethyl alcohol. The tertiary-butyl-bromide and aqueous ethyl alcohol streams were combined just before entering the reactor. Before coming together each of the two streams was controlled with regard to flowrate and temperature.

Prior to each run ethyl alcohol was diluted to the desired concentration, thoroughly mixed and pumped to either a 12 or 5 gallon glass bottle which was used as a storage and constant-head tank. Constant head was maintained by the method described by Page(24). The storage bottle was calibrated with respect to volume, and the flow rate was determined by the displacement from storage during an interval of time. An inclined

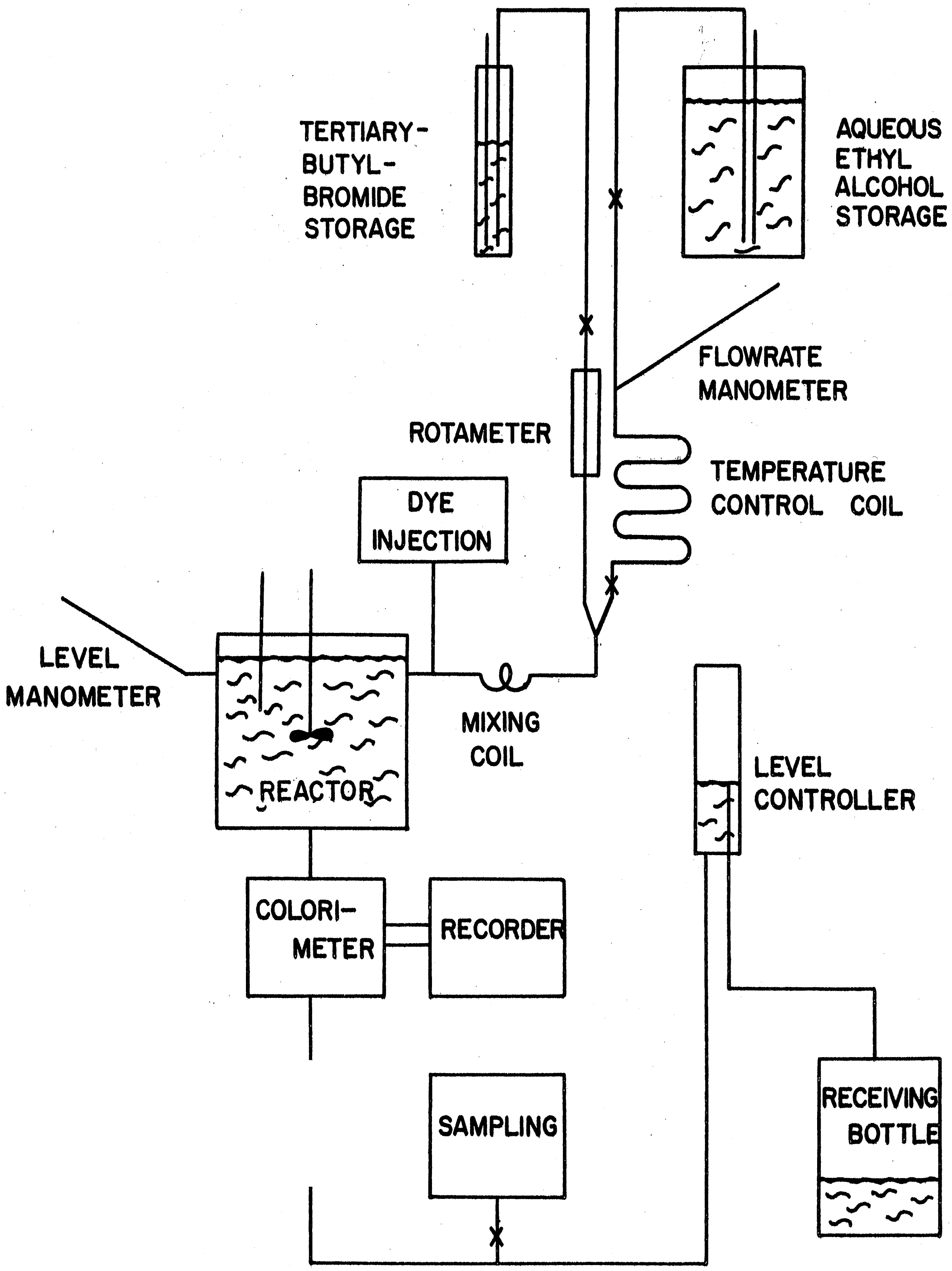


Figure 3. Flow Diagram

manometer was used to indicate whether the flow-rate was constant. The flow-rate was adjusted by means of the stop-cock nearest the reactor. The aqueous ethyl alcohol was brought to the temperature of the constant-temperature bath by passing the aqueous ethyl alcohol through 16 feet of 7 mm. glass coils immersed in the constant-temperature bath. Either 1/4 in. inside diameter Tygon tubing or 7 mm. glass tubing was used for the ethyl alcohol lines from storage to the junction between the aqueous ethyl alcohol and tertiary-butyl-bromide streams.

The tertiary-butyl-bromide storage vessel was a 1-3/4 in. I.D. glass vessel which was 18 in. long. It was maintained as a constant head tank in the same manner as the aqueous ethyl alcohol storage tank. Flow was adjusted by the stop-cock shown in Figure 3 and the constancy of flow rate was indicated by a small rotameter which had a sapphire bead. Flow-rate was measured by displacement from storage. The lines between the storage tank and the junction with the aqueous ethyl alcohol line were either 1/8 in. I.D. polyethylene tubing or 6 mm. glass tubing.

Before entering the reactor the aqueous ethyl alcohol and tertiary-butyl-bromide streams were brought together by a 7 mm. glass Y joint. Following the Y was a short, irregularly bent glass coil, the diameter of which increased and decreased irregularly. This coil served to dissolve the tertiary-butyl-bromide in the aqueous ethyl alcohol. The volume of the mixing coil was included in the reactor volume.

Reactors

The reactor temperatures were controlled by placing the reactors in a constant-temperature bath. The temperature of the bath was controlled by a heater operated by a mercury-switch and Trimount Electronic Relay System. Cooling water was passed through coils in the bath in order to help equalize the times of heating and cooling.

An Eastern, model 8, heavy-duty laboratory stirrer was used for all reactors. The number of revolutions of the stirrer in a measured time interval was measured by a mechanical counter which was connected directly to the upper end of the stirrer shaft. This eliminated any possibility of the stirrer shaft rotating a different number of times than the shaft of the counter. The voltage to the stirrer was maintained constant by a constant-voltage transformer. The shaft and propeller stirrers were 316 stainless steel.

The space between the shaft of the stirrer and the reactor Plexiglas cover was sealed by the glass tube seal recommended by Morton(22). Some of the details of the seal are indicated in Figure 4. The seal consisted of a 1 1/4 in. length of 12 mm. glass tubing whose I.D. was 10 mm. The glass tubing was held in place by a rubber stopper which served as a shoulder to rest on the Plexiglas cover. The stopper was sealed to the reactor cover by Sauereisen cement and Pyseal. Vapor was prevented from passing up the narrow annulus between the glass tube and stirrer shaft by a piece of rubber tubing which on one end fitted over the end of the glass tube and on the other end pressed against the stirrer shaft. Also some Dow Corning stopcock grease was placed inside the annulus.

One-Compartment Reactor

The reactor which was used for all runs in which a one-compartment reactor was run under reacting conditions is shown in Figure 4. The reactor

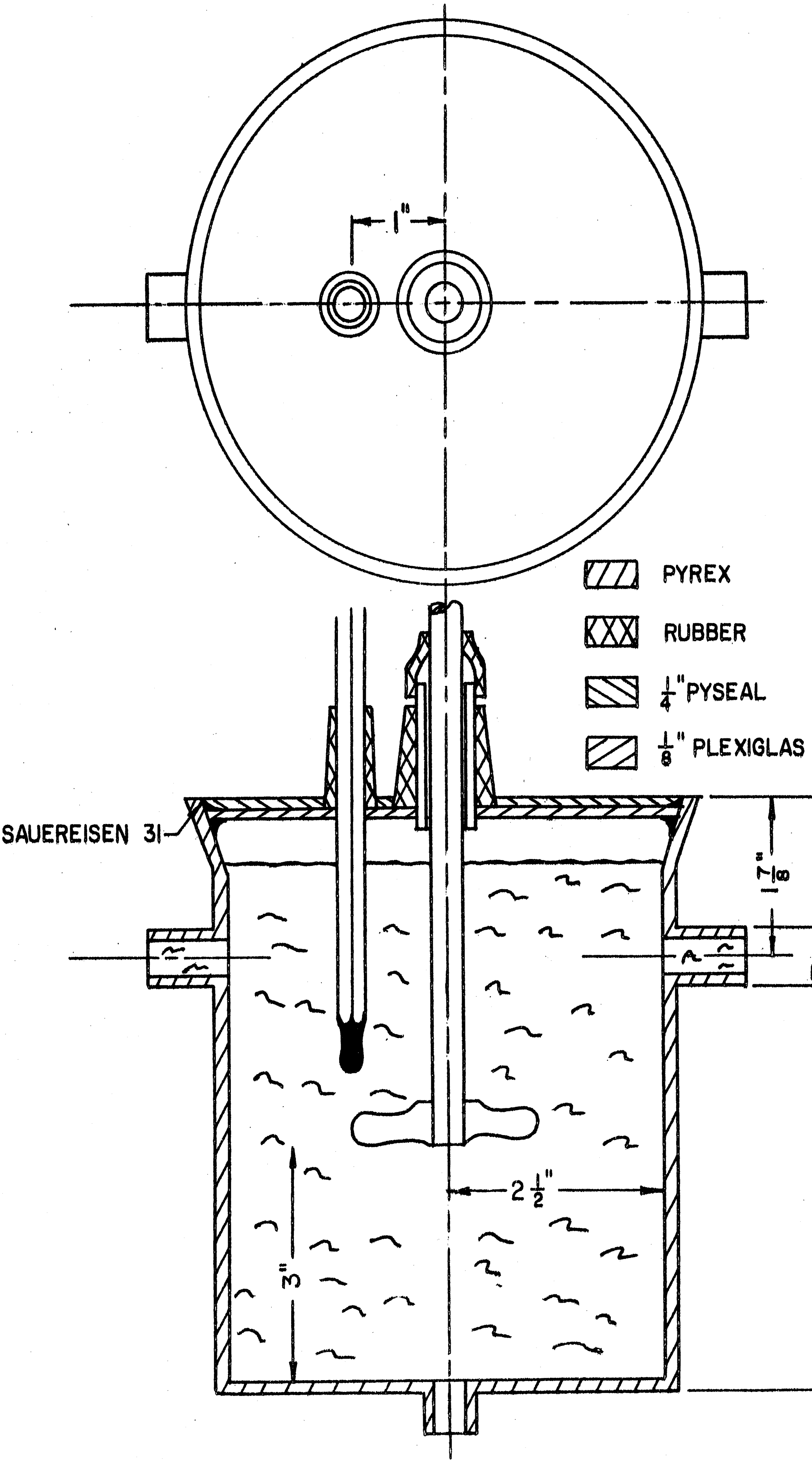


Figure 4. One-Compartment Reactor

was a 2000 ml. glass beaker with 7 mm. glass tubes for inlet and outlet lines and a line to the reactor level-measuring monometer.

The reactor cover consisted of 1/8 in. Plexiglas which was sealed to the reactor wall by number 31 Sauereisen cement. The Plexiglas cover and Sauereisen cement were coated with a 1/4 in. layer of Pyseal in order to insure the tightness of the reactor. The cover contained two holes. One was for the stirrer shaft. This seal was described in the previous section. The other hole was for the reactor thermometer. The thermometer seal is shown in Figure 4. It consisted of a rubber stopper through which extended the thermometer. The stopper was sealed to the Plexiglas cover with Sauereisen cement and Pyseal.

Stirring was accomplished by a 1 1/2 in. diameter three-bladed propeller, which the Mixing Equipment Co. claimed was a model of commercial propellers. The stirrer shaft was mounted vertically in the center of the reactor and the stirrer was 3 in. from the bottom of the reactor.

Liquid volume in the reactor was measured by a calibrated inclined manometer. A calibration curve is shown in Figure 28.

Glass-Bead Reactor

The two glass-bead reactors, which are shown in Figures 5 and 6, were slightly different from each other in that the depth of the glass beads, the height of the side tubes and the height of the reactors were different. Each reactor consisted of two concentric compartments. Each inner compartment was a 2 5/16 in. I.D., 2 17/32 in. O.D., glass tube in a 2000 ml. beaker. A space of 1/4 in. existed between the end of the tube and the bottom of the reactor. The inner compartment in each reactor contained

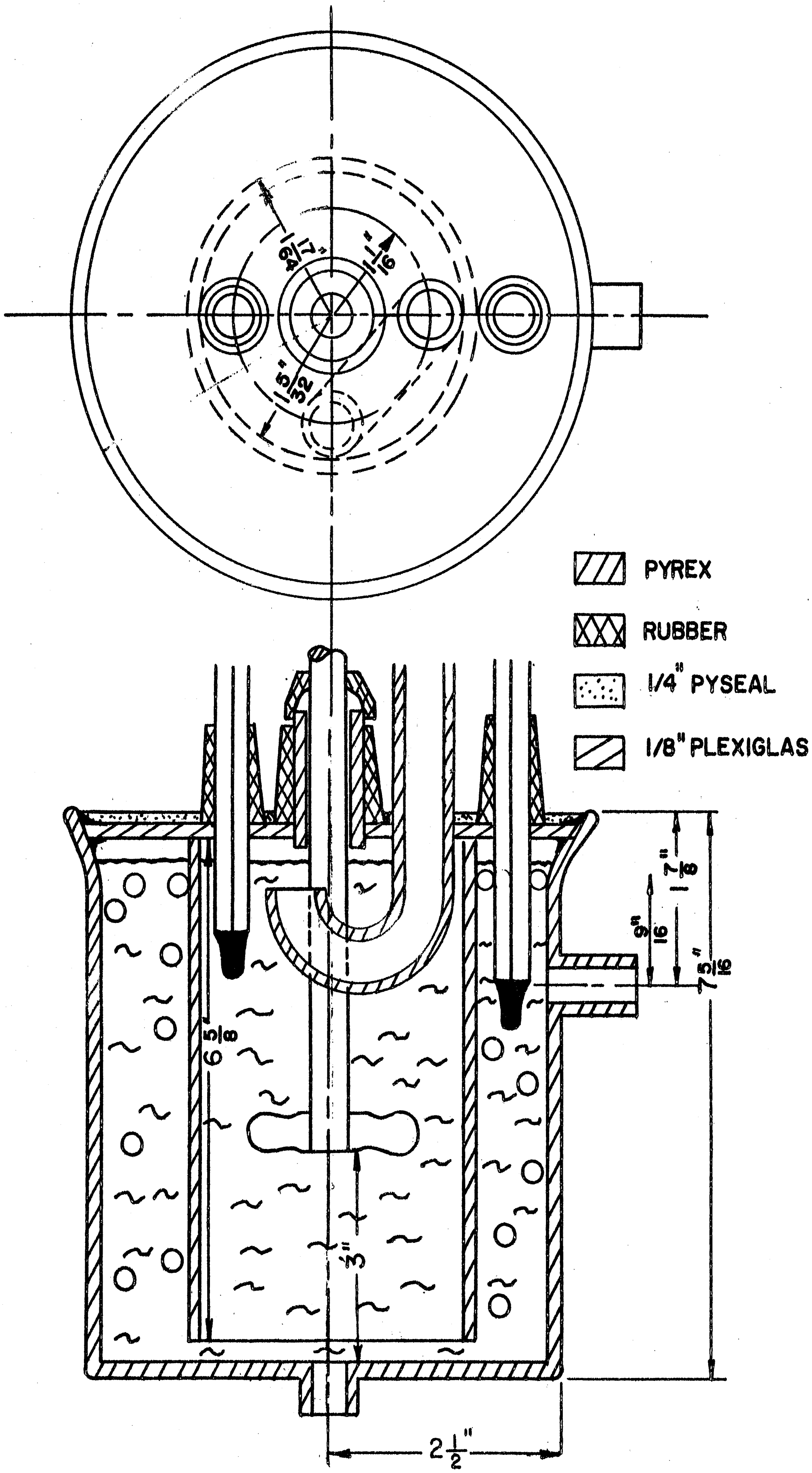


Figure 5. Glass-Bead Reactor for Runs 27 to 30.

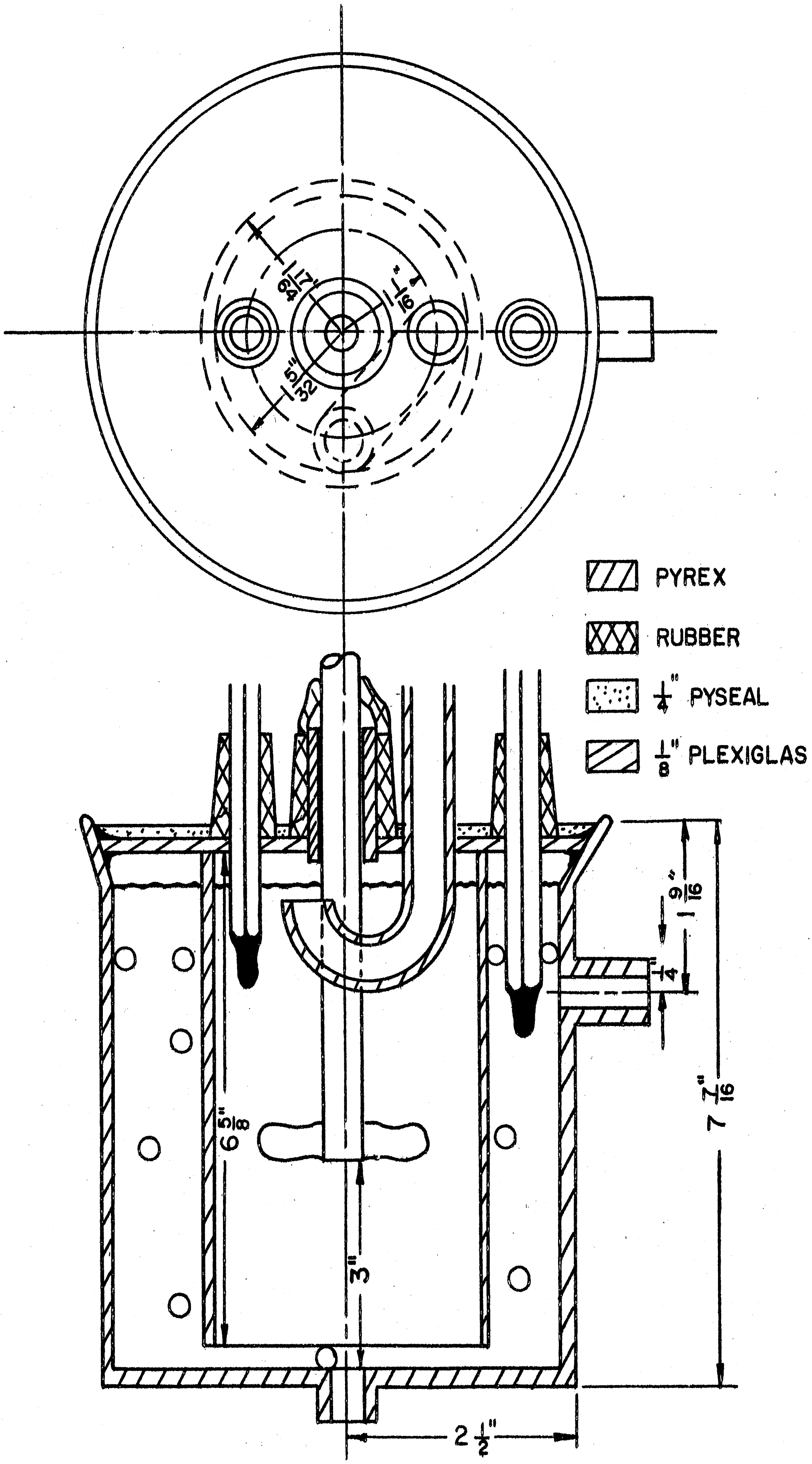


Figure 6. Glass-Bead Reactor for Runs 37 to 41.

a 1 in. diameter propeller stirrer while the outer compartment, which was the space between the tube and the reactor wall, was filled with 6 mm. glass beads. Overall flow in the reactor was down through the inner compartment and up through the glass beads.

The reactor cover and method of sealing were the same as for the one-compartment reactor described in the previous section. Each cover contained four holes. One was for the stirrer shaft. Two more were for reactor thermometers in both compartments. The fourth was for the inlet feed line. The seals on all four of these holes were the same as for the one-compartment reactor. The reactor level manometer was connected to the bottom of the reactor.

Two-Compartment Reactor

The two-compartment reactor, which is shown in Figure 7, was a 2000 ml. beaker in which a horizontal circular baffle divided the reactor into two compartments, one above the other. Flow was into the upper compartment and down through the four holes in the baffle, down through the lower compartment and out through the reactor outlet at the bottom of the reactor. The upper compartment contained a 1 1/2 in. diameter propeller stirrer which was mounted concentric to the reactor and 1 3/8 in. above the baffle. The reactor cover and seal were the same as for the one-compartment reactor. The cover contained three holes. One was for the stirrer and the other two were for the thermometers for the two compartments. The seals for these holes were again the same as for the one-compartment reactor.

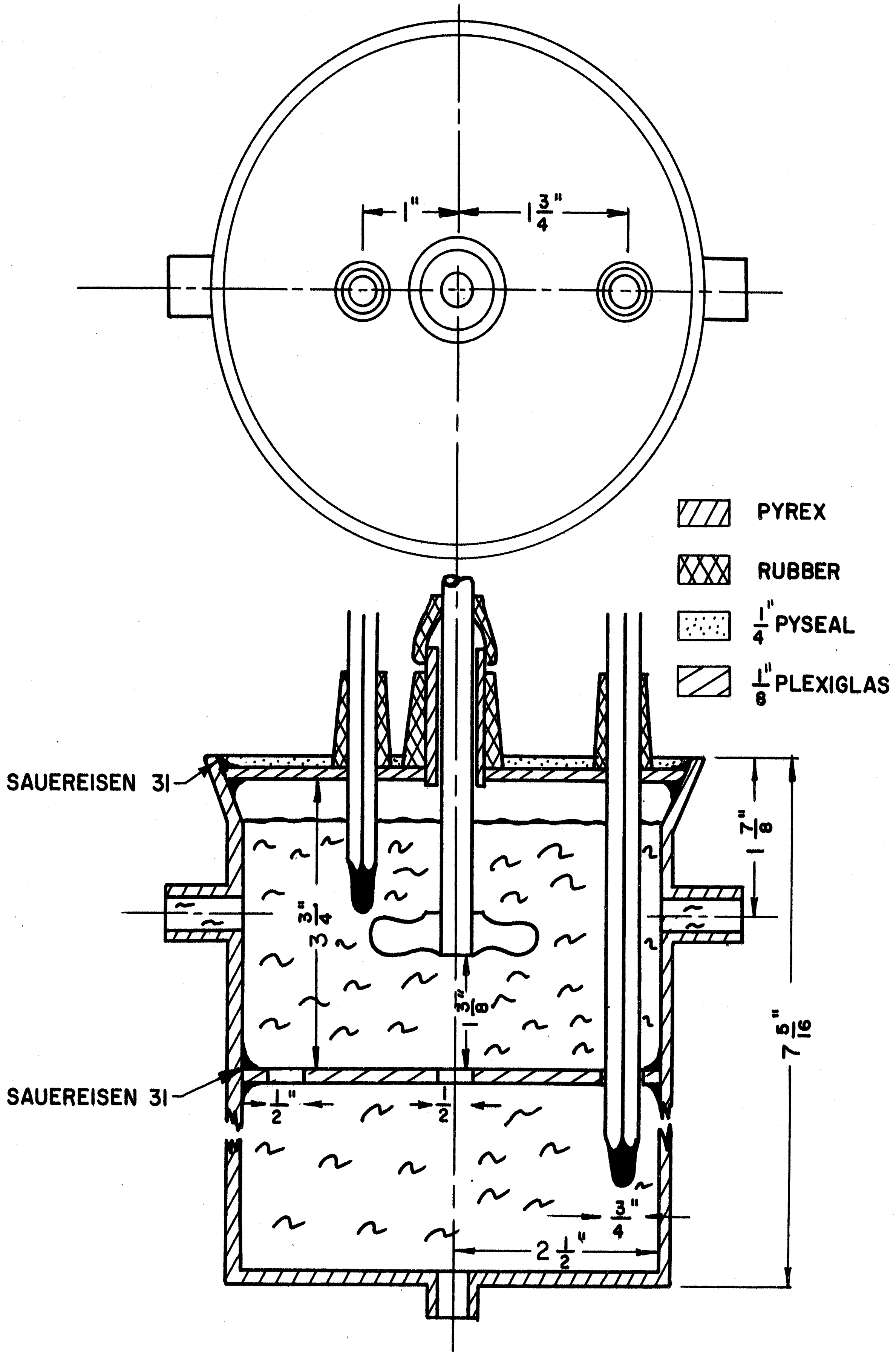


Figure 7. Two-Compartment Reactor

Colorimeter Recorder and Dye Injection

The dye concentration in the exit stream leaving the reactor during the tracer part of each run was measured continuously by a Beckman Model C colorimeter. This type of colorimeter is designed for measuring concentrations of solutions in test-tubes. The colorimeter was converted to a continuous colorimeter by running the 7 mm. glass tube from the reactor through the space in the colorimeter where a test-tube normally is placed. The response of the colorimeter was fed to a Speedomax, Type G, one-second-response recorder so that a continuous record of the distribution function could be obtained. The wiring of the colorimeter was modified as shown in Figure 8 so that the output of the colorimeter could be fed to the recorder. The voltage to the colorimeter and recorder was controlled by a constant-voltage transformer. The calibration of the colorimeter in terms of dye concentration is described in Appendix III.

Dye, the concentration of which was 60 g./l., was injected through a piece of Tygon tubing into the inlet stream by a hypodermic at a point between the mixing coil and the inlet to the reactor. The volume of dye varied from 2 to 6 ml., depending upon whether the reactor volume was 1100 or 2200 ml. and on how high the peak in the distribution of residence times was. MacDonald(21) used 3 ml. for a 1950 ml. reactor. The time of injection was from five to ten seconds. The dye was injected into the inlet stream nearly perpendicular to the direction of flow. The dye hit the tube wall and was dissolved in the inlet stream. If the dye had been injected in the direction of flow then the dye would have entered the reactor at a velocity much higher than that of the inlet stream. The hypodermic needle was stainless steel.

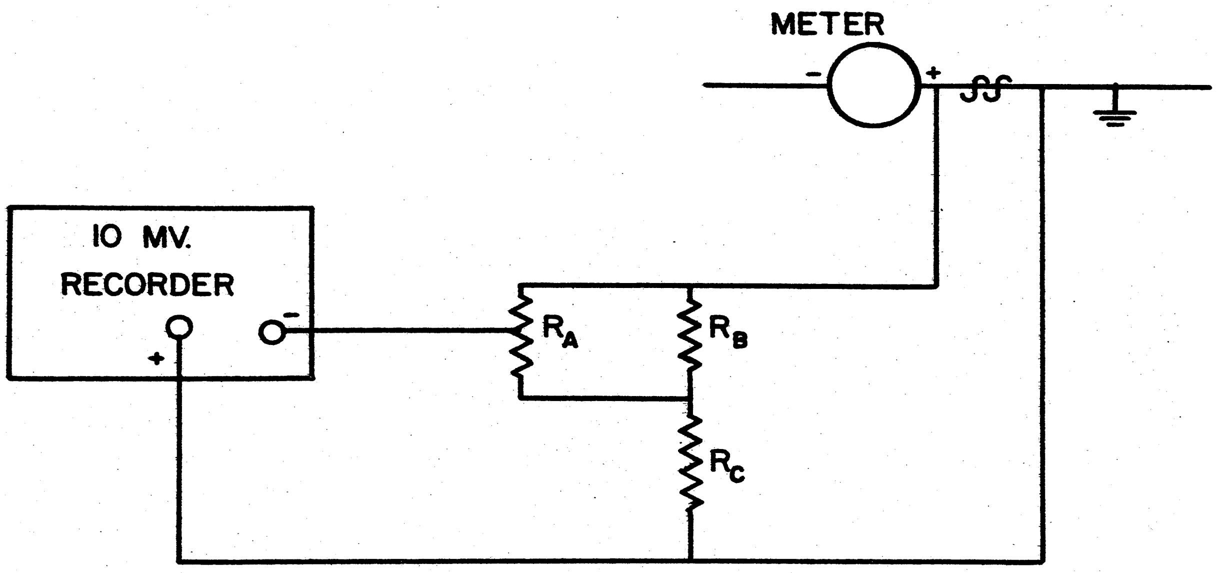


Figure 8. Modification of the Colorimeter Circuit.

R_A	IRC WPK 2000 ohm potentiometer
R_B	IRC BW 1/2 ohm resistor
R_C	IRC BW 1/2 ohm resistor

Reactor Outlet Flow System

All lines in which there was tertiary-butyl-bromide, that is, all lines from the Y to the end of the outlet line, were either 7 mm. glass tubing or 1/4 in. inside diameter polyethylene tubing. The only exception was the short length of Tygon tubing through the wall of which dye was injected.

Samples of the outlet stream were removed through the T which is shown in Figure 3. The T was located vertically below the reactor and at a low enough point so that the liquid would flow into a 25 ml. pipette at the same rate that liquid was flowing in the outlet stream. During sampling the outlet line was shut off just beyond the sampling point and the sample was withdrawn at, as close as possible, the outlet stream flow-rate from the reactor. Before sampling the sampling tee was thoroughly purged in order to obtain a good sample. The conversion as measured in the samples was corrected for time of withdrawal and for the time required for flow of liquid from the reactor outlet to the sample point. This correction is described more fully in sample calculations on page 75 in Appendix II.

The reactor level controller is shown in Figure 9. The bottom of the level controller was a rubber stopper. Since the level controller was at least three feet beyond the sample point there was no possibility of the rubber influencing the sample compositions.

The liquid from the level controller was collected and measured in order to measure the reactor outlet stream rate. Measurements were made during periods when no sampling or purging were occurring.

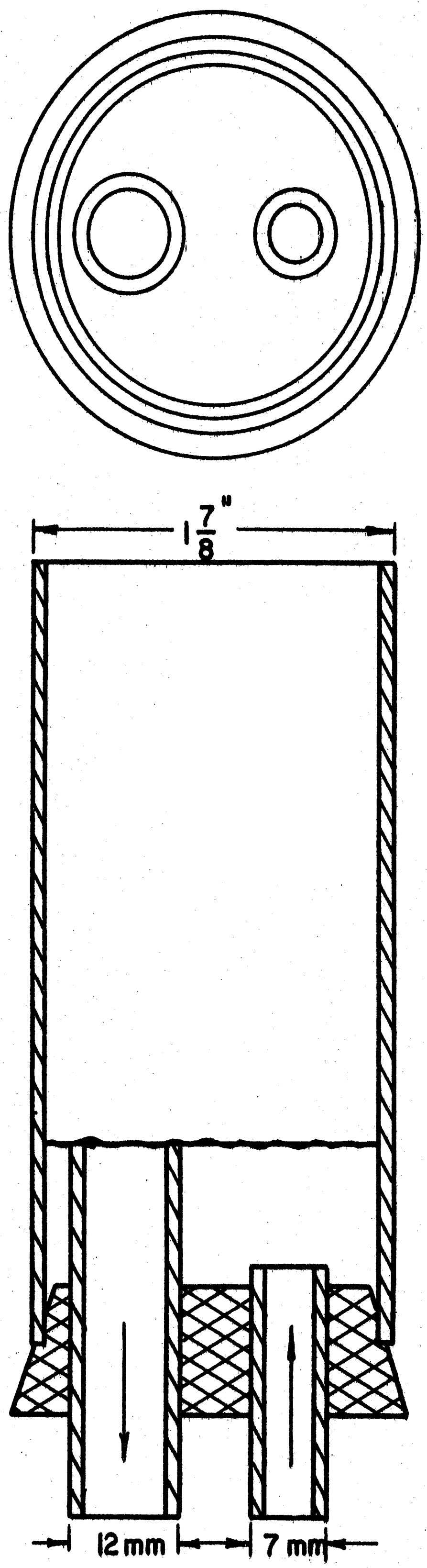


Figure 9. Reactor Level Controller

Procedure

In most runs both the distribution of residence times and conversion were measured.

Before the run was begun the aqueous ethyl alcohol and tertiary-butyl-bromide feed tanks were filled. A sample of aqueous ethyl alcohol was taken in order to measure its ethyl alcohol content. The method for measuring the concentration of ethyl alcohol is described on page 12. The constant temperature bath, in which the reactor and coils preceding the reactor were immersed, was brought up to the desired temperature which in general was between 24.5 and 25.5°C. The stirrer, colorimeter and record amplifier were turned on so that they could warm up and reach steady-state conditions. After the bath had reached temperature the aqueous ethyl alcohol and tertiary-butyl-bromide streams to the reactor were begun. While the reactor was filling, flow-rates were checked and adjusted until they were approximately the desired values. Then the level controller was adjusted until the desired volume of liquid in the reactor was maintained. From time to time, while the system was approaching steady-state, flow-rates, reactor liquid level, reactor temperatures and concentration of reacted tertiary-butyl-bromide in the exit stream were checked.

After the system had reached steady-state the following measurements were made. A sample set of data is shown in Table X in Appendix II.

Time of reading

Level of aqueous ethyl alcohol in the feed tank

Level of tertiary-butyl-bromide in the feed tank

Aqueous ethyl alcohol flow manometer

Tertiary-butyl-bromide rotameter

Reactor level

Reactor temperatures

Bath temperature

Propeller speed

Flowrate of the outlet stream from the reactor

Room temperature

Samples from the outlet stream were then taken. Sample data are presented in Table IX on page 76. The following readings were taken.

Time of start of sampling

Time of completion of sampling

Time of start of quenching

Time of completion of quenching

Total ml. of standard alkali to neutralize the partially reacted sample less blank correction

Total ml. of standard alkali to neutralize the completely reacted sample less blank correction.

The remaining columns in Table IX were quantities calculated from these measurements. All the measurements shown in Tables IX and X were then repeated.

The distribution of residence times for the system was then measured. The recorder trace for run 45 in the two-compartment reactor is shown in Figure 23. Before dye was injected recorder traces corresponding to 0 and 100% transmittance were made. Zero % transmittance occurred when the colorimeter light was turned off. One hundred % transmittance was the transmittance of clear solution. The time corresponding to a mark made on the recorder trace was recorded. At the end of the distribution function a second such measurement was made. These two readings not only served to relate the time of pulse injection to the recorder time but also served to check the recorder speed. The mean time of dye injection into the inlet stream to the reactor was recorded. Further details of dye injection appear on page 33. From time to time while the tracer experiment was being run checks were made on temperatures, flow-rates and liquid levels to see that the system was remaining at steady-state. The distribution function was run until the recorder did not change value for approximately one residence time. The traces corresponding to 100 and 0% transmittance were again made. The colorimeter and recorder were then shut off. Then two more sets of readings as shown in Tables IX and X were made of flow-rates, temperatures, etc. This completed one run. Each run consisted of one measurement of the distribution of residence times and four measurements of reactor composition and reactor variables. The calculations for obtaining the distribution of residence times and material balances are shown in Appendix II.

The procedure for runs in which the distribution of residence times was measured under non-reacting conditions was the same as described in the previous paragraph, except that no outlet compositions were measured. The procedure for runs in which the distribution of residence times was not measured, but reaction was taking place, was the same as described in the previous paragraph except that the tracer experiment was omitted.

Data

Preliminary

Twenty-one, preliminary, pulse runs were made to determine whether the distribution of residence times, $E(\theta)$, in a one-compartment reactor was changed appreciably by changing reactor variables such as length of residence time, propeller speed, etc. The data for these runs are presented in Table IV.

Column	Description
1	Run number
2	Volume of liquid in the reactor, ml.
3	Flowrate, ml/min.
4	Length of one residence time, min.
5	Reactor temperature, °C.
6	Propeller speed, r.p.m.
7	Dye used as tracer
8	Liquid
9 to 29	Distribution of residence times, $E(\theta)$, as a function of the number of residence times.
30	Internal material balance or first moment
31	Conversion predicted by the measured distribution of residence times using $k\tau = 1.0$.
32	Conversion predicted by the perfectly-mixed distribution using $k\tau = 1.0$.
33	Conversion in column 31 - conversion in column 32.

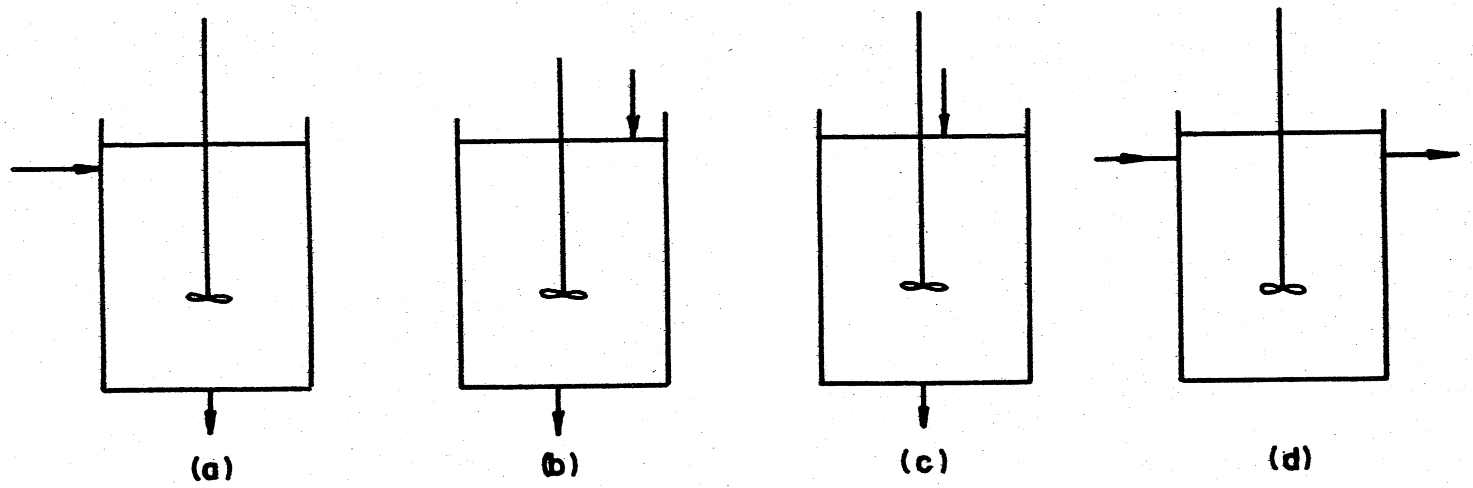


Figure 10. Sketch Showing the Inlet Stream Positions for the One-Compartment Reactor.

TABLE IV

PRELIMINARY DATA

DISTRIBUTION FUNCTIONS UNDER NON-REACTING CONDITIONS

ONE-COMPARTMENT REACTOR

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
								Distribution of Residence Times $E(\theta) = \frac{VC(\theta)}{Q}$																								
Run Number	Volume V Ml.	Flowrate v Ml/Min.	$\tau = \frac{V}{v}$ Min.	Temp. °C	R.P.M.	Dye	Liquid	θ = .1	.3	.5	.7	.9	1.1	1.3	1.5	1.7	1.9	2.2	2.6	3.0	3.4	3.8	4.2	4.6	5.0	5.4	5.8	6.2	First Moment	$f_{M.D.}$	$f_{P.M.D}$	$f_{M.D.} - f_{P.M.D.}$
T14	1980	91.1	21.7	24.7	287	Fast Turquoise	Water	.899	.727	.596	.485	.394	.323	.263	.212	.182	.152	.111	.081	.051	.040	.030	.020	.014	.010	.007	.004	.002	1.062	.5110	.5000	.0110
15	1963	83.8	23.2	--	163	"	Water	.871	.719	.585	.479	.393	.326	.268	.220	.192	.163	.125	.086	.058	.038	.029	.023	.015	.011	.007	.004	.002	1.062	.5170	.5000	.0170
16	1976	88.2	22.4	27.0	172	"	Water	.906	.732	.604	.497	.401	.319	.252	.202	.167	.140	.111	.081	.059	.040	.030	.021	.015	.013	.011	.007	.003	1.059	.5083	.5000	.0083
19	1906	139.0	13.70	24.9	97	"	Water	.921	.756	.612	.499	.410	.331	.271	.226	.188	.153	.110	.061	.050	.033	.022	.014	.010	.007	.005	.003	.001	.986	.4969	.5000	.0031
20	2149	155.4	13.83	24.7	61	"	Water	.915	.714	.593	.491	.399	.326	.265	.215	.176	.149	.114	.075	.052	.035	.027	.017	.013	.009	.007	.004	.002	1.001	.4973	.5000	.0027
21	2074	160.7	12.92	25.2	76	"	Water	.900	.734	.599	.496	.405	.330	.274	.229	.192	.159	.118	.078	.058	.041	.024	.011	.004	.003	.002	.001	.001	1.023	.5047	.5000	.0047
22	2107	162.6	12.97	25.0	69	"	Water	.860	.692	.555	.463	.384	.324	.277	.238	.204	.172	.137	.099	.069	.044	.025	.014	.011	.008	.005	.003	.001	1.080	.5256	.5000	.0256
23	2126	162.4	13.11	25.3	69	"	Water	.864	.705	.592	.489	.408	.338	.274	.220	.179	.149	.112	.080	.057	.041	.032	.024	.015	.012	.008	.006	.003	1.074	.5169	.5000	.0169
24	2093	78.2	26.77	25.2	78	"	Water	.857	.714	.585	.480	.396	.328	.273	.224	.184	.150	.111	.075	.061	.043	.032	.023	.016	.012	.008	.006	.003	1.097	.5205	.5000	.0205
25	2123	159.2	13.35	24.7	209	"	Water	.882	.706	.587	.488	.403	.330	.266	.218	.182	.152	.118	.085	.058	.038	.026	.020	.015	.011	.006	.004	.002	1.074	.5155	.5000	.0155
26	2128	166.3	12.80	24.4	47	Eosin Bluish	Water	.906	.720	.594	.491	.410	.335	.276	.225	.182	.152	.113	.076	.052	.041	.030	.016	.011	.007	.004	.003	.002	1.021	.5073	.5000	.0073
27	2086	157.5	13.26	24.6	66	"	Water	.910	.762	.601	.482	.395	.327	.272	.223	.180	.146	.110	.078	.055	.039	.029	.019	.010	.006	.004	.002	.001	1.004	.5025	.5000	.0025
28	2112	166.6	12.68	24.1	72	"	Water	.909	.725	.590	.494	.414	.343	.281	.226	.183	.151	.115	.075	.054	.037	.026	.018	.010	.005	.003	.002	.001	.999	.5050	.5000	.0050
29	2077	161.7	12.83	24.3	89	"	Water	.855	.700	.585	.490	.403	.332	.273	.231	.193	.162	.120	.083	.060	.041	.030	.021	.012	.008	.005	.003	.002	1.067	.5199	.5000	.0199
30	2099	160.6	13.08	24.4	93	"	Water	.870	.706	.591	.495	.412	.348	.289	.234	.192	.159	.121	.083	.059	.040	.021	.013	.006	.004	.002	.001	.001	1.007	.5118	.5000	.0118
31	2058	158.2	13.00	24.6	113	"	Water	.881	.712	.586	.481	.400	.338	.282	.234	.192	.155	.109	.082	.060	.042	.031	.019	.012	.009	.006	.003	.002	1.046	.5142	.5000	.0142
U1	2055	176.7	11.63	24.6	71	"	ETOH	.656	.856	.676	.535	.429	.344	.279	.228	.189	.150	.109	.076	.050	.033	.022	.017	.010	.006	.004	.002	.001	1.009	.5157	.5000	.0157
2	2045	110.3	18.54	24.7	50	"	ETOH	.940	.765	.625	.495	.394	.321	.260	.213	.179	.151	.112	.072	.047	.031	.023	.016	.010	.007	.005	.004	.002	.982	.4947	.5000	- .0053
3	2085	175.5	11.89	24.7	217	"	ETOH	.902	.745	.609	.505	.411	.332	.272	.224	.187	.150	.110	.074	.050	.031	.020	.014	.009	.007	.005	.004	.003	.997	.5012	.5000	.0012
4	2068	178.2	11.61	24.8	59	"	ETOH	.906	.789	.631	.514	.410	.323	.273	.215	.176	.146	.106	.070	.045	.030	.020	.015	.010	.008	.006	.004	.003	.979	.4946	.5000	- .0054
5	2085	174.7	11.95	24.4	59	"	ETOH	.946	.767	.616	.505	.415	.334	.268	.218	.179	.149	.108	.069	.046	.030	.021	.013	.007	.004	.002	.001	.001	.942	.4902	.5000	- .0098

Reactor was as shown in Figure 10a except:

T27 - Two propellers
T28 - Vertical inlet near center, Figure 10c
T29 - Vertical inlet near wall, Figure 10b
T30 - Horizontal outlet at top, Figure 10d
T31 - Same as T30 except propeller was 1 in. from the bottom of the reactor.

One-Compartment Reactor

Following the one-compartment reactor preliminary runs under non-reacting conditions, a series of runs under reacting conditions were performed in the one-compartment reactor. The details of the reactor are described on page 26 and the procedure is discussed on page 37. The data for these runs are given in Tables V and VI. The headings for Table V are:

Column	
1	Run number
2 - 44	$E(\theta)$ as a function of the number of residence times
45	Internal material balance or first moment
46	Material balance for all the liquid entering and leaving the reactor
47	Material balance for tertiary-butyl-bromide

The distribution functions are shown in Figure 11.

In Table VI the headings are:

Column	
1	Run number
2	Volume of liquid in reactor, ml.
3	Mean overall flow-rate, ml./min.
4	Length of one residence time, min.
5	Reactor temperature, °C
6	Propeller speed, r.p.m.
7	Mass fraction of alcohol in the aqueous ethyl alcohol.

TABLE V

DISTRIBUTION FUNCTIONS UNDER REACTING CONDITIONS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47
	Distribution of Residence Times $E(\theta) = \frac{VC(\theta)}{Q}$																																												Material Balances	
Run Number	θ = .025	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.8	6.2	6.6	7.0	First Moment	Overall	t-BuBr
ONE-COMPARTMENT REACTOR																																														
12		.880		.731		.596		.486		.396		.328		.274		.228		.189		.158			.112		.071		.050		.038		.029		.023		.016		.011		.006	.004	.003	.002	.001	1.052	1.012	.988
13		.910		.736		.593		.484		.405		.336		.280		.231		.188		.148			.107		.073		.054		.036		.025		.017		.011		.007		.005	.004	.003	.002	.001	1.018	.990	1.009
33		.894		.760		.623		.502		.408		.334		.281		.229		.189		.152			.112		.076		.049		.031		.019		.011		.008		.004		.001					.959	1.008	1.005
GLASS-BEAD REACTOR																																														
30				.306	.587	.716	.810	.886	.940	.940	.874	.756	.634	.520	.424	.342	.272	.212	.170	.128	.101	.081	.065	.051	.022	.016	.011	.006	.004	.003	.002	.001												1.013	.984	.981
39				.045	.220	.511	.807	1.003	1.062	1.043	.961	.833	.699	.576	.470	.379	.301	.241	.188	.143	.112	.089	.070	.043	.027	.019	.014	.009	.006	.003	.002	.001												1.085	.980	.985
41				.123	.415	.756	.988	1.094	1.040	.935	.815	.696	.577	.474	.384	.314	.250	.198	.157	.122	.098	.078	.061	.039	.030	.020	.016	.012	.008	.006	.004	.001												1.024	.991	.977
27			.046	.278	.592	.731	.821	.879	.884	.842	.781	.700	.614	.527	.440	.363	.298	.241	.190	.145	.112	.086	.069	.044	.026	.013	.007	.003	.001															1.002	.985	.982
40				.124	.421	.769	1.002	1.111	1.055	.950	.829	.707	.586	.481	.390	.318	.254	.201	.160	.124	.100	.079	.062	.040	.030	.020	.016	.012	.008	.006	.004	.001												1.025	.993	.973
28			.072	.350	.581	.709	.787	.802	.796	.779	.739	.680	.609	.527	.449	.380	.318	.260	.212	.173	.142	.117	.097	.066	.044	.029	.019	.012	.009	.004	.002	.001												1.070	.994	.984
37				.192	.478	.830	1.032	1.099	1.085	.986	.827	.692	.579	.473	.382	.301	.231	.178	.137	.104	.081	.061	.050	.034	.020	.012	.008	.005	.003	.002	.001													.973	.991	.989
29			.088	.370	.557	.673	.752	.803	.832	.854	.810	.736	.622	.523	.438	.365	.306	.249	.200	.157	.121	.096	.079	.052	.036	.025	.020	.013	.011	.008	.005	.003	.001											1.058	.987	.995
TWO-COMPARTMENT REACTOR																																														
44	.230	.484	.570	.610	.632	.644	.650	.647	.626	.588	.533	.481	.432	.388	.348	.310	.278	.241	.211		.157		.111	.080	.057	.039	.030	.021	.014	.012	.009	.007	.005	.004	.003	.002	.001							1.005	.991	.994
48	.000	.431	.516	.572	.610	.634	.655	.670	.671	.642	.604	.551	.483	.421	.372	.324	.281	.243	.211		.151		.105	.072	.050	.037	.027	.021	.016	.009	.004	.003	.002	.001	.001									1.008	.992	.988
42	.221	.370	.469	.540	.600	.653	.695	.706	.696	.623	.560	.502	.452	.403	.359	.318	.278	.240	.211		.161		.121	.085	.056	.038	.026	.018	.015	.013	.009	.005	.003	.002	.001									1.022	1.006	.989
43	.153	.409	.549	.619	.644	.655	.654	.645	.620	.579	.529	.480	.436	.390	.348	.308	.273	.235	.206		.154		.117	.086	.063	.050	.039	.031	.022	.019	.012	.008	.007	.006	.004	.002	.001							1.044	.998	.986
45	.000	.332	.479	.572	.635	.676	.706	.695	.665	.621	.566	.511	.459	.410	.362	.322	.280	.243	.201		.160		.120	.082	.061	.041	.030	.021	.016	.011	.009	.007	.006	.005	.004	.003	.002	.001	.001					1.044	.988	.992

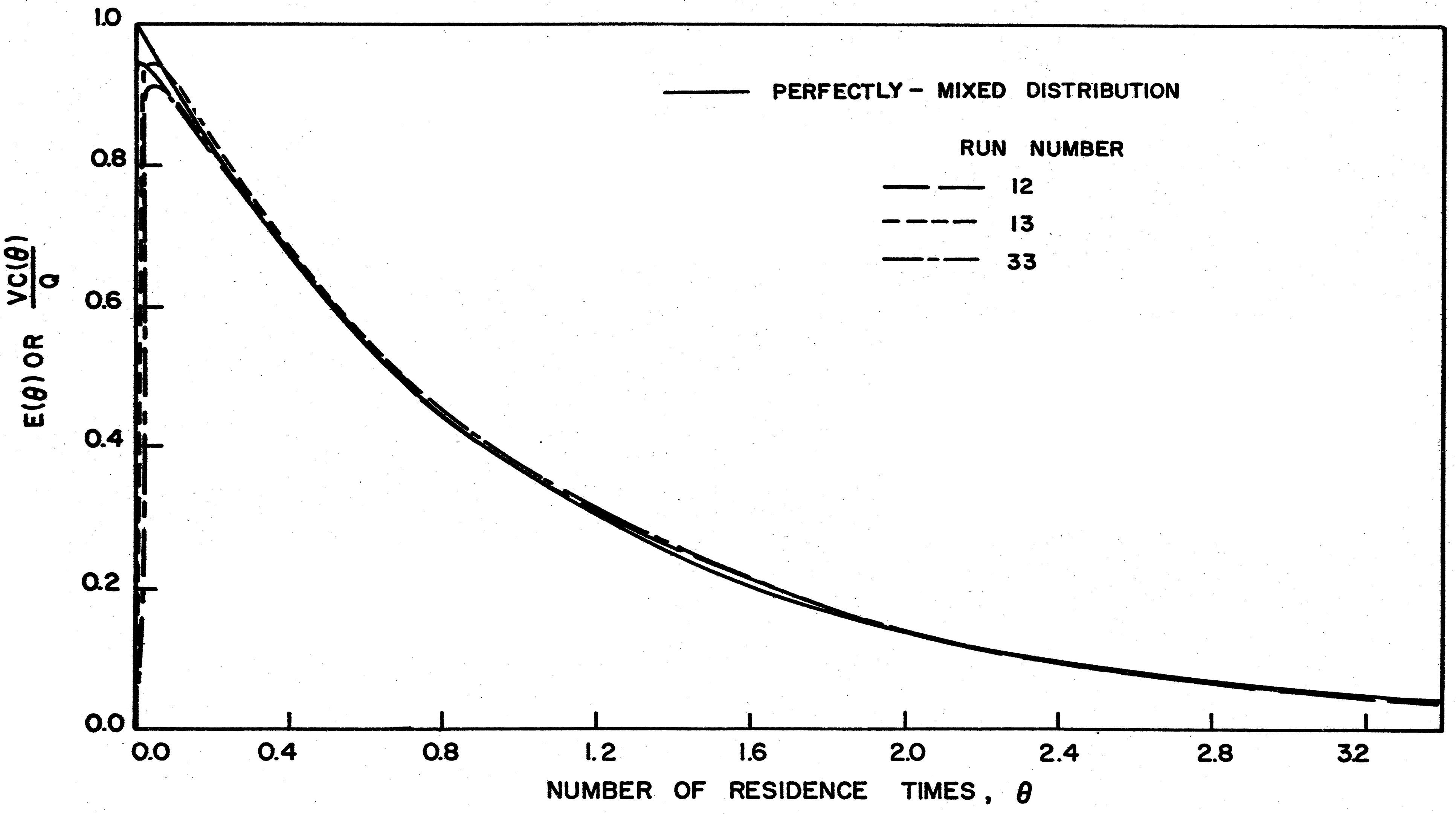


Figure 11. Distribution Functions for the One-Compartment Reactor.

TABLE VI

ONE-COMPARTMENT REACTOR DATA

1 Run Number	2 Volume V Ml.	3 Flowrate v Ml/Min.	4 $\tau = V/v$ Min.	5 Temp. T°C	6 R.P.M.	7 Mass Fraction ETOH	8 Was Dye Present?	9 f	10 $f_{P.M.D.}$	11 $f_{M.D.}$	12 $F_{P.M.D.}$	13 $F_{M.D.}$
11	2028	182.4	11.12	26.50	257	.6536	No	.5019	.5036		-.013	
	2068	170.8	12.11	26.52	240			.5161			.094	
	2007	184.0	10.91	26.45	245			.5079			.032	
	1991	179.4	11.10	26.43	256			.5022			-.011	
12	2023	168.5	12.01	26.35	268	.6565	Yes	.5168	.5085	.5201	.061	-.024
	1991	168.9	11.79	26.35	263			.5143			.043	-.043
	1995	168.1	11.88	26.37	264			.5202			.086	.001
	1994	167.3	11.92	26.40	268			.5119			.025	-.060
13	1950	181.7	10.73	26.77	274	.6556	Yes	.5004	.4990	.5059	.011	-.042
	1984	178.5	11.11	26.74	273			.5020			.023	-.032
	1975	180.3	10.95	26.84	284			.4917			-.055	-.108
	1974	179.1	11.02	26.66	269			.4973			-.013	-.065
14	1953	182.6	10.70	24.69	323	.6697	Yes	.4081	.4050		.035	
	--	--	--	--	--			.4185			.152	
	1955	170.3	11.48	24.69	322			.4139			.100	
	1988	172.1	11.55	24.70	302			.4165			.130	
15	2015	175.2	11.50	24.90	376	.6635	No	.4473	.4380		.090	
	1980	172.6	11.47	24.89	344			.4409			.028	
	1976	167.2	11.82	24.89	355			.4409			.028	
	1982	166.0	11.94	24.90	364			.4426			.044	
16	1978	163.3	12.11	26.36	329	.6566	Yes	.5140	.5061		.059	
	1932	161.7	11.95	26.37	311			.5101			.030	
	1917	161.7	11.86	26.36	271			.5120			.044	
	1902	162.3	11.72	26.37	269			.5100			.029	
17	2004	174.3	11.50	25.86	351	.6613	No	.4739	.4699		.034	
	1995	174.7	11.42	25.86	340			.4838			.118	
	1995	171.5	11.63	25.87	331			.4890			.162	
	2004	171.3	11.70	25.89	337			.4833			.114	
33	2127	139.8	15.22	24.74	492	.6552	Yes	.5311	.5198	.5191	.080	.085
	2113	142.0	14.88	24.74	496			.5313			.081	.086
	2112	143.4	14.80	24.74	463			.5216			.013	.018
	2121	143.4	14.79	24.74	487			--			--	--
MEAN											.053	-.017

Column	
8	Was a tracer experiment attempted?
9	Measured fractional conversion.
10	Fractional conversion calculated by using the perfectly-mixed distribution of residence times.
11	Fractional conversion calculated by using the measured distribution of residence times.
12	Relative conversion difference based upon the perfectly-mixed distribution of residence times.
13	Relative conversion difference based upon the measured distribution of residence times.

Glass-Bead Reactor

The glass-bead reactor is discussed in detail on page 28. Figures 5 and 6 show sketches of the reactors used in runs 27 through 30 and 37 through 41 respectively. The distribution functions are given in Table V and are shown in Figure 12. The remainder of the data for the glass-bead reactor is given in Table VII. The column headings are:

Column	
1	Run number
2	Volume of liquid in reactor, ml.
3	Mean overall flow-rate, ml./min.
4	Length of one residence time, min.
5	Inlet reactor temperature, °C
6	Outlet reactor temperature, °C

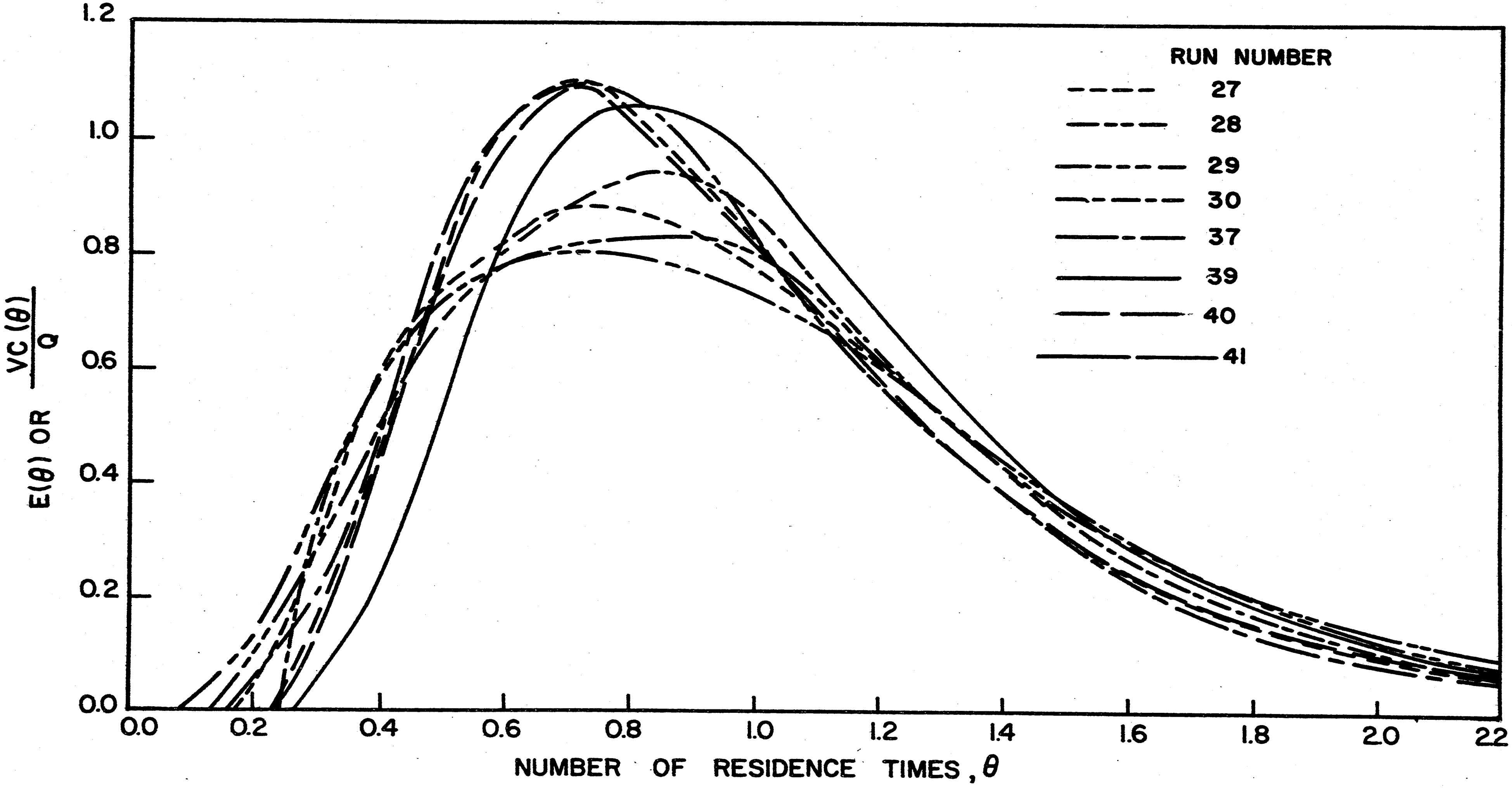


Figure 12. Distribution Functions for the Glass-Bead Reactor.

TABLE VII

GLASS-BEAD REACTOR DATA

1	2	3	4	5	6	7	8	9	10	11
Run Number	Volume V Ml.	Flowrate v Ml/Min.	$\tau = V/v$ Min.	Temperatures °C		R.P.M.	Mass Fraction ETOH	f	$f_{M.D.}$	$F_{M.D.}$
				Inlet	Outlet					
30	1107	142.1	7.79	24.89		400	.6536		.4127	
	1080	147.5	7.32	24.92		421		.4218		.131
	1107	149.1	7.42	24.76		423		.4194		.096
	1102	147.1	7.49	24.84		420		.4234		.154
39	1150	115.8	9.93	25.04	25.20	444	.6560	.5205	.5229	-.025
	1149	113.6	10.11	25.04	25.20	444		.5102		-.131
	1155	116.2	9.94	25.03	25.19	463		.5106		-.127
	1149	116.8	9.84	25.00	25.19	445		.5089		-.144
41	1144	97.6	11.72	24.92	25.07	396	.6543	.5561	.5660	-.084
	1144	95.8	11.94	24.91	25.07	383		.5622		-.032
	1143	96.4	11.86	24.89	25.06	393		.5562		-.083
	1143	96.8	11.81	24.91	25.07	409		.5589		-.060
27	1111	91.6	12.13	25.05		349	.6542	.5971	.5777	.158
	1082	89.4	12.10	25.12		342		.5885		.088
	1095	90.2	12.14	25.03		312		.5887		.090
	1081	88.4	12.23	24.97		288		.5820		.035
40	1139	58.8	19.37	25.22	25.29	409	.6584	.7248	.7199	.028
	1149	57.8	19.84	25.22	25.29	413		.7097		-.059
	1140	57.8	19.72	25.15	25.25	389		.7243		.026
	1147	56.2	20.41	25.13	25.24	402		.7423		.130
28	1111	55.9	19.87	25.25		303	.6563	.7108	.7294	-.106
	1078	53.7	20.07	25.27		306		.7261		-.019
	1100	58.7	18.74	25.23		314		.7367		.042
	1068	56.7	18.84	25.23		298		.7312		.010
37	1146	66.7	17.18	25.22	25.30	410	.6443	.7351	.7214	.077
	1148	66.3	17.32	25.29	25.36	417		.7396		.103
	1149	65.9	17.44	25.19	25.30	409		.7432		.123
	1142	62.5	18.27	25.17	25.28	402		.7401		.106
29	1098	61.0	18.00	25.24		292	.6556	.7364	.7214	.087
	1121	57.7	19.43	25.24		288		.7498		.164
	1110	59.0	18.81	25.25		304		.7508		.170
	1093	58.0	18.84	25.21		328		.7428		.124
MEAN										.034

7	Propeller speed, r.p.m.
8	Mass fraction of alcohol in the aqueous ethyl alcohol
9	Measured fractional conversion
10	Fractional conversion calculated by using the measured distribution of residence times.
11	Relative conversion difference based upon the measured distribution of residence times.

Two-Compartment Reactor

The two-compartment reactor is described on page 31 and shown in Figure 7. The distribution functions are given in Table V and are shown in Figure 13. The remainder of the data for the glass-bead reactor is given in Table VIII. The columns headings are the same as those for Table VII and are given on page 47.

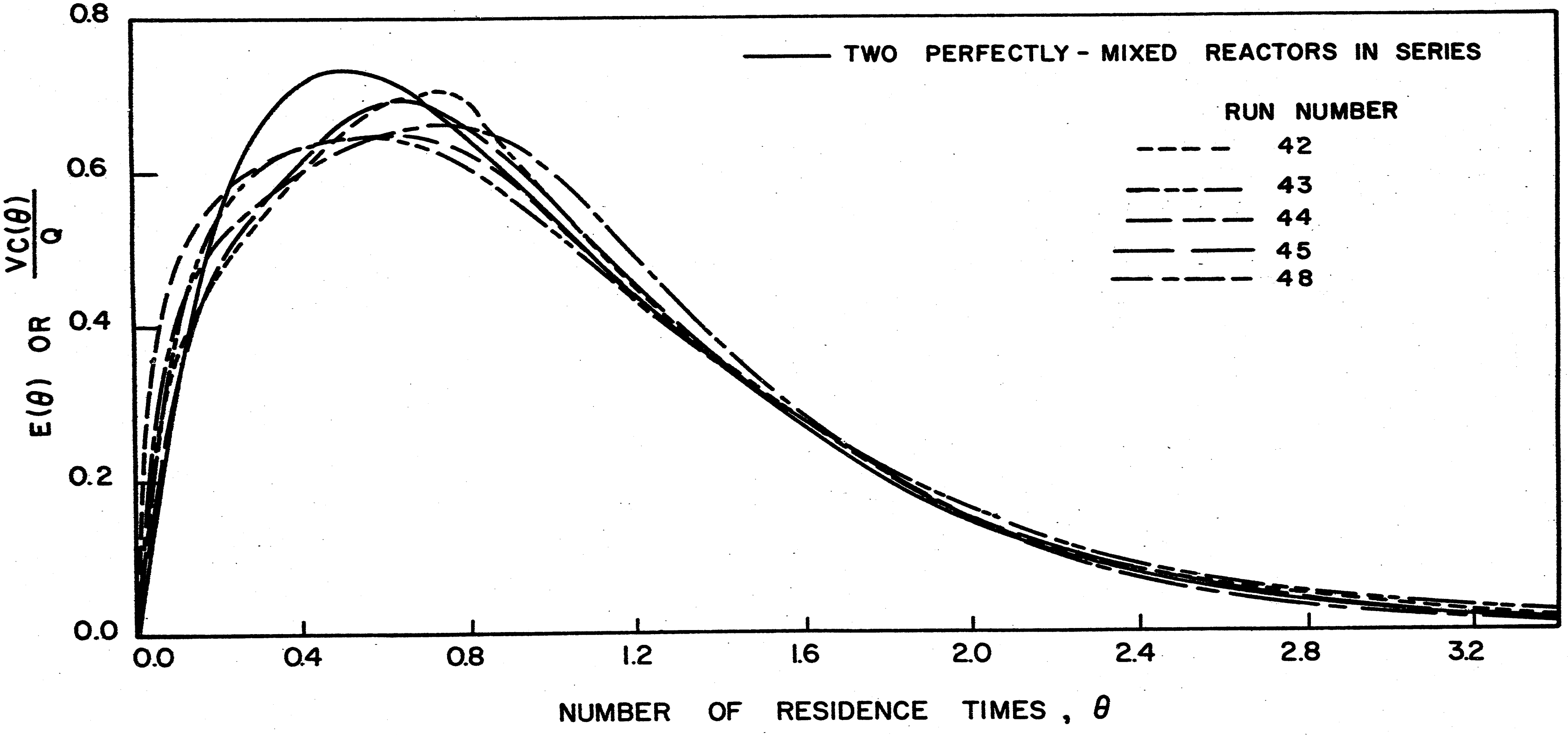


Figure 13. Distribution Functions for the Two-Compartment Reactor.

TABLE VIII

TWO-COMPARTMENT REACTOR DATA

1	2	3	4	5	6	7	8	9	10	11
Run Number	Volume V Ml.	Flowrate v Ml/Min.	$\tau = V/v$ Min.	Temperatures °C		R.P.M.	Mass Fraction ETOH	f	$f_{M.D.}$	$F_{M.D.}$
				Inlet	Outlet					
44	2074	176.8	11.73	24.79	25.01	116	.6570	.5354	.5043	.278
	2076	174.8	11.88	24.77	25.04	116		.5197		.138
	2077	176.4	11.77	24.76	25.00	112		.5172		.116
	2077	177.0	11.73	24.76	25.00	101		.5375		.297
48	2091	164.2	12.73	24.88	25.17	159	.6661	.5600	.5135	.420
	2091	162.0	12.91	24.88	25.17	150		.5378		.219
	2090	161.8	12.92	24.94	25.18	146		.5276		.127
	2095	164.2	12.76	24.95	25.17	150		.5461		.294
42	2097	161.3	13.00	24.88	25.09	167	.6606	.5885	.5365	.434
	2090	158.9	13.15	24.87	25.09	161		.5525		.134
	2098	158.4	13.24	24.87	25.07	163		.5495		.109
	2093	160.1	13.07	24.87	25.09	173		.5742		.315
43	2095	176.5	11.87	24.73	24.95	289	.6573	.5178	.5124	.049
	2099	176.1	11.92	24.74	24.97	303		.5166		.038
	2091	177.5	11.78	24.68	24.91	304		.5215		.082
	2080	175.9	11.82	24.68	24.91	307		.5127		.003
45	2084	173.1	12.04	25.03	25.19	378	.6539	.5676	.5452	.184
	2086	176.5	11.82	25.05	25.19	374		.5579		.105
	2080	175.7	11.84	25.06	25.19	372		.5573		.100
	2079	174.9	11.89	25.07	25.19	380		.5747		.244
MEAN								.5436	.5224	.184

CHAPTER V

DISCUSSION OF THE CONTINUOUS REACTOR DATA

The data are discussed from both an engineering approach and from a statistical approach. The engineering approach is to discuss whether the differences between measured conversions and conversions calculated from the measured distributions are of engineering importance while the statistical approach is to show whether the differences are real.

Engineering Approach

Preliminary Data

The distributions of residence times, $E(\theta)$, for twenty-one preliminary runs under non-reacting conditions in the one-compartment reactor are presented in Table IV and the column headings are described on page 40. Using an arbitrary value of $k\tau = 1.0$ the conversions, calculated by using these measured distributions of residence times in Equation (6), are shown in column 31. The conversion assuming a perfectly-mixed distribution and $k\tau = 1.0$ is 0.5000. Column 33 is the difference between conversion as calculated by the measured distributions and the conversion calculated by a perfectly-mixed distribution. From an engineering viewpoint these differences are small and their effect is generally not important compared to the uncertainty in kinetic constants and the ability to control reactors. These data indicate that in general for a small one-compartment reactor in which the diameter and height are approximately equal that the distribution of residence times from the engineering viewpoint is rather insensitive to: changes in propeller speed provided that the speed is greater than 30 r.p.m.; changes in residence time for residence times greater than eight minutes; differences in the position of the feed entrances to the reactor as shown in Figure 10; changes in baffling arrangements provided that the baffles do not essentially divide the reactor into two or more compartments; changes in the number of propellers on the same shaft; and changes in the distance of the propeller from the bottom of the reactor.

One-Compartment Reactor Data

Following the one-compartment reactor preliminary runs under non-reacting conditions a series of runs under reacting conditions were performed in the one-compartment reactor. The distributions of residence times, $E(\theta)$, are presented in Table V and are shown in Figure 11.

The conversion data are presented in Table VI and are shown in Figure 14. In addition to the measured conversions, included also are conversions calculated by Equation (6) from the perfectly-mixed distribution and from the measured distributions of residence times.

From Figure 14 it is seen that conversion level varies from run to run. These differences in level are not important because they are caused by differences in temperature, residence time and ethyl alcohol concentration between runs. The important part of the figure is the differences between measured and calculated conversions.

The measured conversions are, in 27 out of 31 samples, higher than conversions calculated by making the assumption of perfect mixing. Based on complete conversion being 100% this difference averages $(0.5 \pm 0.2)\%$. See page 90 for the calculation of 0.2, the 95% confidence interval. From an engineering viewpoint this difference is unimportant.

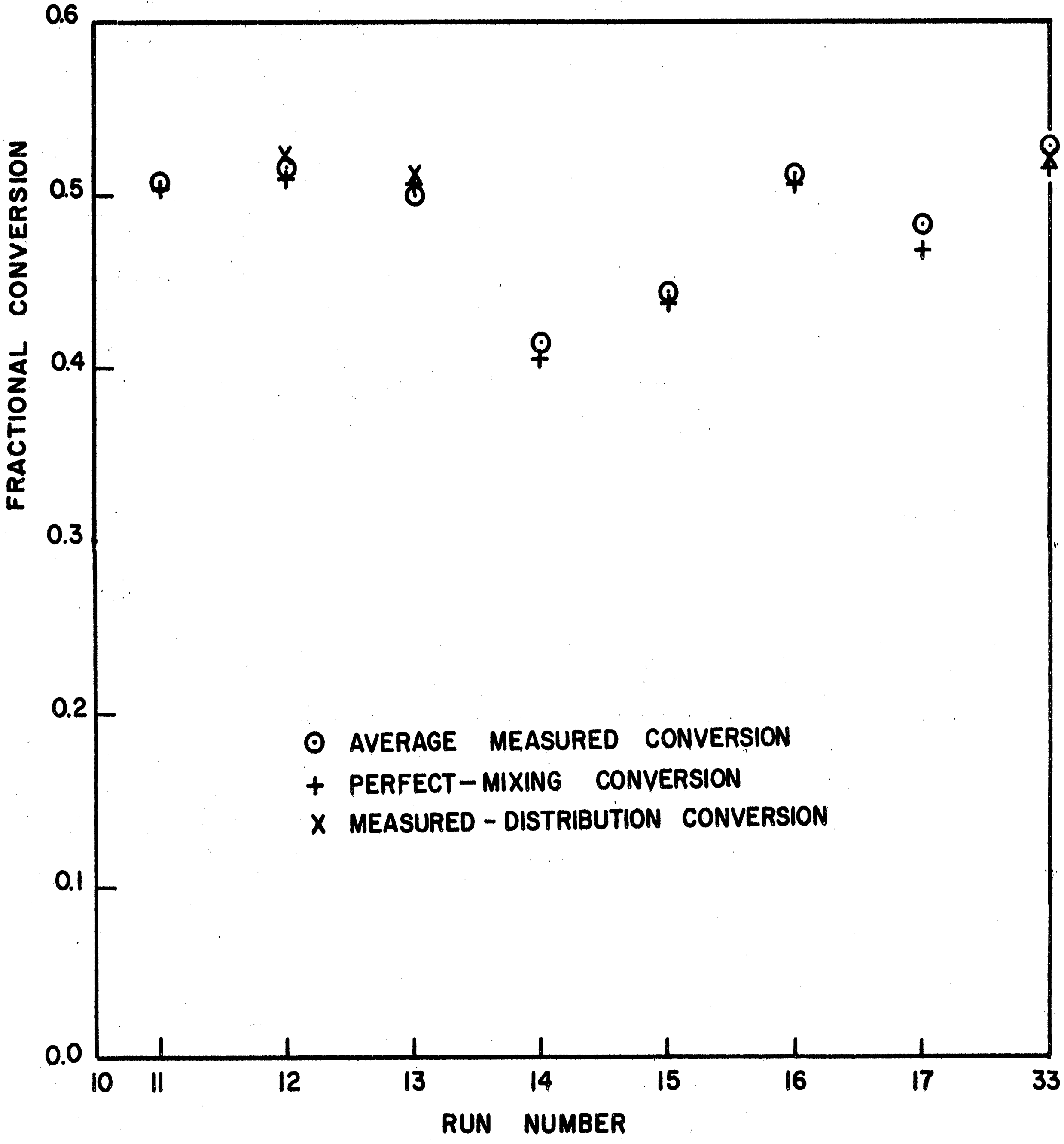


Figure 14. Fractional Conversions for the One-Compartment Reactor.

For the one-compartment reactor, measured conversions and those calculated from the measured distributions are presented in columns 9 and 11 of Table VI. In four out of eleven samples the measured conversions are higher than the calculated conversions. Based on complete conversion being 100% the average difference in conversion is (-0.2 ± 0.4)% and is of no engineering importance.

Glass-Bead Reactor Data

The details of the glass-bead reactors are described on page 28. The data for these reactors are presented in Tables V and VII and the column headings for these tables are described on pages 43 and 47. Figure 15 shows conversion as calculated by the measured distribution of residence times as a function of measured conversion where the measured conversion is the average of 4 samples for the run.

Upon comparing measured and calculated conversions in columns 9 and 10 of Table VII it is seen that for 20 out of 31 samples the measured conversions are higher than those calculated by the distribution of residence times. The difference between measured and calculated conversions is even smaller than that shown in Table VII, because the calculated conversions are based upon the temperature of the first compartment which was cooler than the second compartment. The difference in temperature, when measured, was not more than 0.25°C. In any case the difference between measured and calculated conversion is not of engineering importance.

Two-Compartment Reactor Data

The two-compartment reactor is described on page 31 and a sketch of the reactor is shown in Figure 7. The distribution functions for these

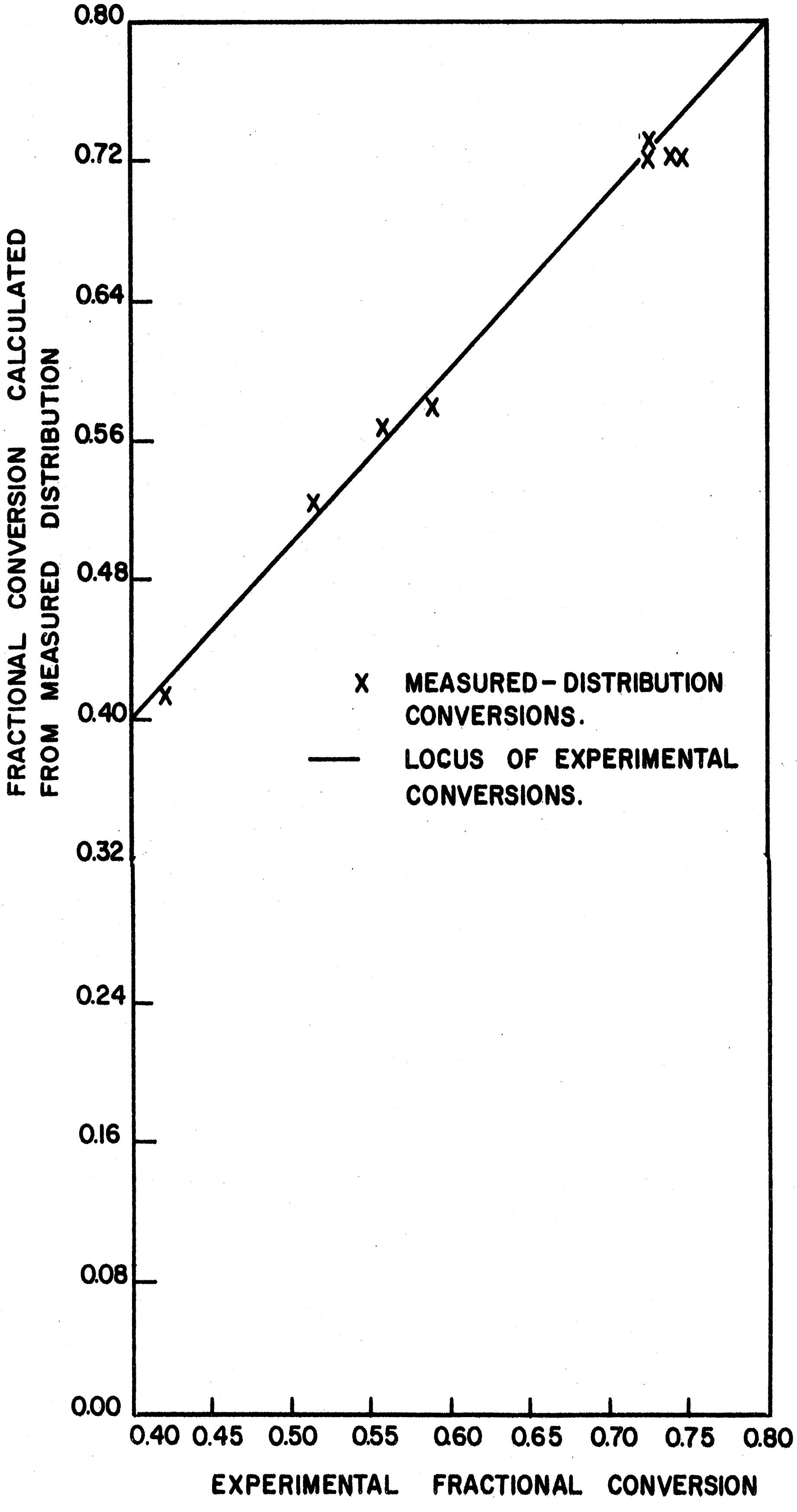


Figure 15. Fractional Conversions for the Glass-Bead Reactor.

runs are presented in Table V and are shown in Figure 13. The remainder of the data for these runs are presented in Table VIII. The column headings for these tables are described on pages 43 and 50.

The average of the 4 measured conversions for each run and the conversions calculated by the measured distributions of residence times are shown in Figure 16. Based upon complete conversion being 100% the measured conversions are on the average (2.1 ± 0.7)% higher than the conversions calculated by the measured distributions of residence times. In addition all 20 measured conversions are higher than the corresponding calculated conversions. The difference in conversion for the two-compartment reactor is much larger than for the other reactors and may be of engineering importance.

Statistical Approach

In the previous section differences between measured and calculated conversions were discussed from the viewpoint of engineering importance. In this section the statistical significance of the differences will be discussed.

In order to evaluate statistically the differences between measured and calculated conversions it is desirable to consider a difference which would be expected to be constant for all runs. If such a difference is used then there is the possibility of considering all the data at once in one statistical test.

The continuous reactor conversions being considered in this thesis vary in level from run to run. Differences between measured and predicted conversions would be expected to vary with conversion level. A quantity,

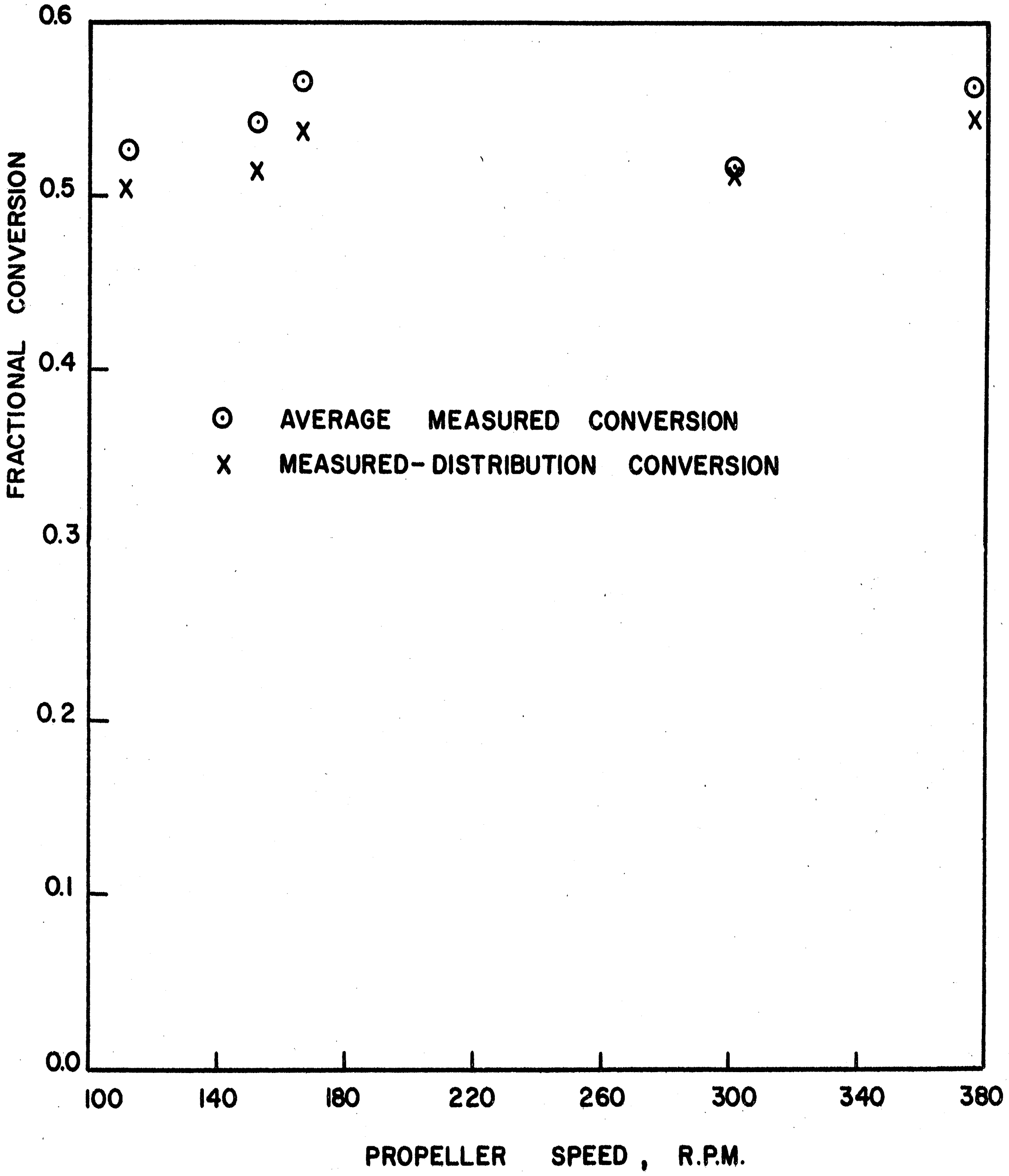


Figure 16. Fractional Conversions for the Two-Compartment Reactor.

F_i, which will be called the relative conversion difference based upon the distribution of residence times i is defined as

$$F_i = \frac{f - f_i}{f_{S.F.D.} - f_{P.M.D.}}$$

where f is the measured conversion

f_i is the conversion calculated by using the distribution of residence times i in Equation (6).

$f_{S.F.D.}$ is the conversion calculated by using the slug-flow distribution of residence times in Equation (6).

$f_{P.M.D.}$ is the conversion calculated by using the perfectly-mixed distribution of residence times in Equation (6).

Conversion level was varied much more widely for the glass-bead reactor than for the other reactors. Figure 19 shows relative conversion differences based upon measured distributions for the glass-bead reactor. The slope of the least square straight line is not significantly different from zero at a significance level of 5 percent. Since conversion level was varied much more widely for the glass-bead reactor than for any other reactor, then relative conversion difference is a satisfactory quantity to use for statistical tests when conversion level varies from run to run.

The statistical procedures for testing and evaluating relative conversion differences for each reactor were:

(1) An $\bar{X}$-chart, Duncan(14) page 285, was used to determine whether the mean value of F for any run was significantly different from the mean, $\bar{\bar{F}}$, for all the runs. In no case was the difference sufficiently great to reject the null hypothesis that the means came from the same

universe of values. The upper and lower limits were

$$\bar{\bar{F}} \pm \frac{3\hat{\sigma}_{\bar{F}}}{\sqrt{N}}$$

where $\bar{\bar{F}}$ is the mean value of F for all runs

N is the number of samples per run

$\hat{\sigma}_{\bar{F}}$ is an estimate of $\sigma'_{\bar{F}}$, the universe standard deviation of means of all runs.

The universe standard deviation of means is the standard error of $\bar{F}$.

(2) Bartlett's test, Duncan(14) page 470, of homogeneity of variances was used to determine whether the variances for each run came from the same normal universe. The null hypothesis was that the variances were a homogeneous set. Using a significance level of 5%, for no series of runs was the hypothesis rejected.

(3) After the two previous tests had shown that the hypotheses, that the means and variances for each run were from the same universe, did not need to be rejected, then a χ^2 test, Duncan(14) page 412, was performed to determine whether the data were approximately normally distributed. The null hypothesis, that the values of F were approximately normally distributed, was not rejected at a significance level of 5%.

(4) Tests (1) through (3) indicated that it was reasonable to assume that the data for each reactor were homogeneous and approximately normally distributed. The data were then used to estimate a universe variance and mean. This variance and mean were used in evaluating the null hypothesis that the relative conversion differences were zero. A 5% significance level was used. The results of these tests will be discussed in the sections which follow.

One-Compartment Reactor Data

The relative conversion differences based upon the perfectly-mixed and the measured distributions of residence times are shown in columns 12 and 13 respectively of Table VI.

In some of the runs dye was present and in others it was not present. The mean values of relative conversion difference based upon the perfectly-mixed distribution when dye was present and not present were .060 and .049 respectively. At a 5 percent significance level the difference between these means was not significantly different from zero. Thus it was not necessary to reject the hypothesis that dye does not have a significant effect upon fractional conversion. The data were then combined and treated together.

The relative conversion differences based upon the perfectly-mixed distribution are shown in Figure 17. Tests (1) through (4), as described in the previous section, were performed upon this data. The mean value of relative conversion difference was .053 and the estimated universe standard deviation was .052 and the number of samples was 31. For the test of the null hypothesis that the mean value of relative conversion difference was not significantly different from zero the value of Z was 5.7. (See page 102 for the definition of Z.) Upon using a 5% significance level the null hypothesis was rejected and it was concluded that measured conversions were significantly higher than those predicted by the perfectly-mixed distribution for the one-compartment reactor.

Relative conversion differences based upon the measured distributions of residence times are shown in Figure 18. Tests (1) through (4),

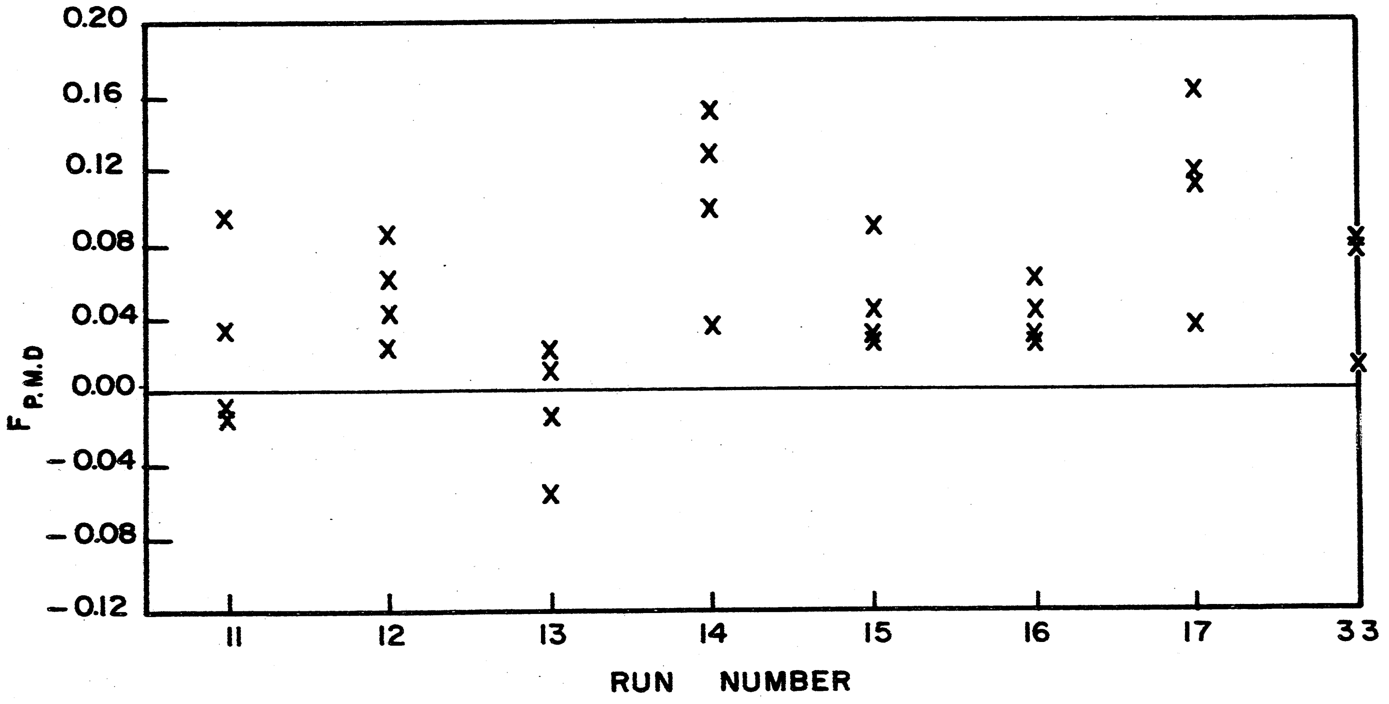


Figure 17. One-Compartment Reactor Relative Conversion Differences Based Upon the Perfectly-Mixed Distribution.

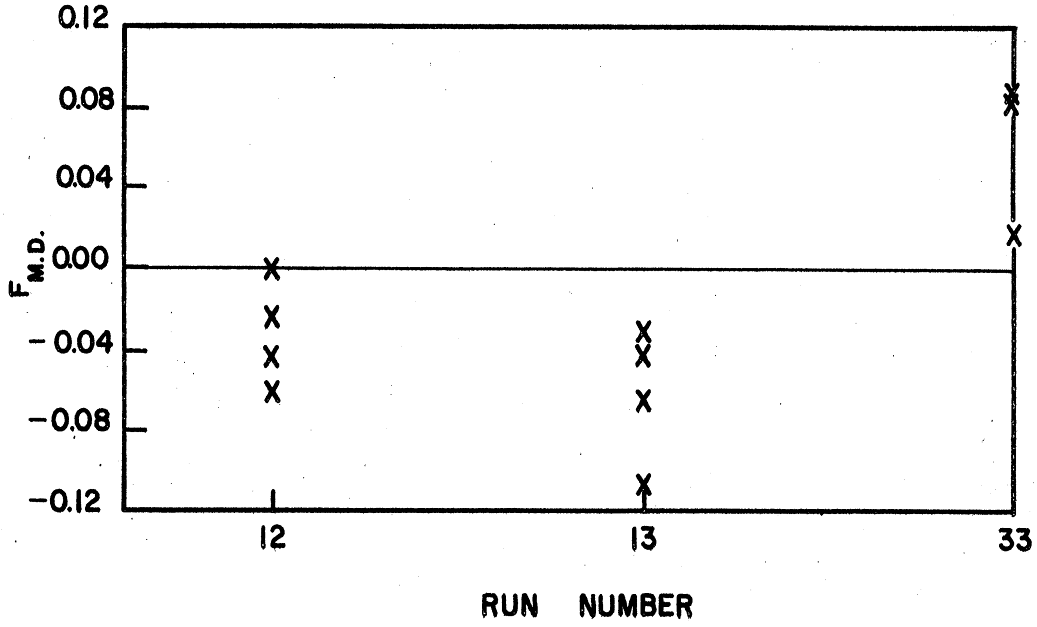


Figure 18. One-Compartment Reactor Relative Conversion Differences Based Upon Measured Distribution Functions.

which are described in the previous section, were performed on these data. For the test of the null hypothesis that the mean conversion difference was zero, the mean value of relative conversion difference was -.017 and the standard deviation was .060. For a sample size of 11 this difference was not significantly different from zero at a significance level of 5% when using a t-test. (See page 102 for the definition of t.) Therefore the differences between measured conversions and those calculated by the measured distributions of residence times were not significantly different from zero for the one-compartment reactor.

Glass-Bead Reactor Data

The relative conversion differences based upon the measured distributions of residence times for the glass-bead reactor are presented in column 11 of Table VII and these data are shown in Figure 19. Tests (1) through (4) described on page 60 were performed upon these data. The mean value of relative conversion difference was .034 and the estimated universe standard deviation was .099. The number of samples was 31. At a 5% significance level the mean difference was not large enough to make it necessary to reject the hypothesis that the difference was zero. On page 56 it was discussed why this mean difference is actually even smaller than .034. Therefore, for the glass-bead reactor, measured conversions were not significantly different from those calculated by the measured distributions of residence times.

Two-Compartment Reactor Data

The two-compartment reactor relative conversion differences based upon the measured distributions of residence times are presented in column

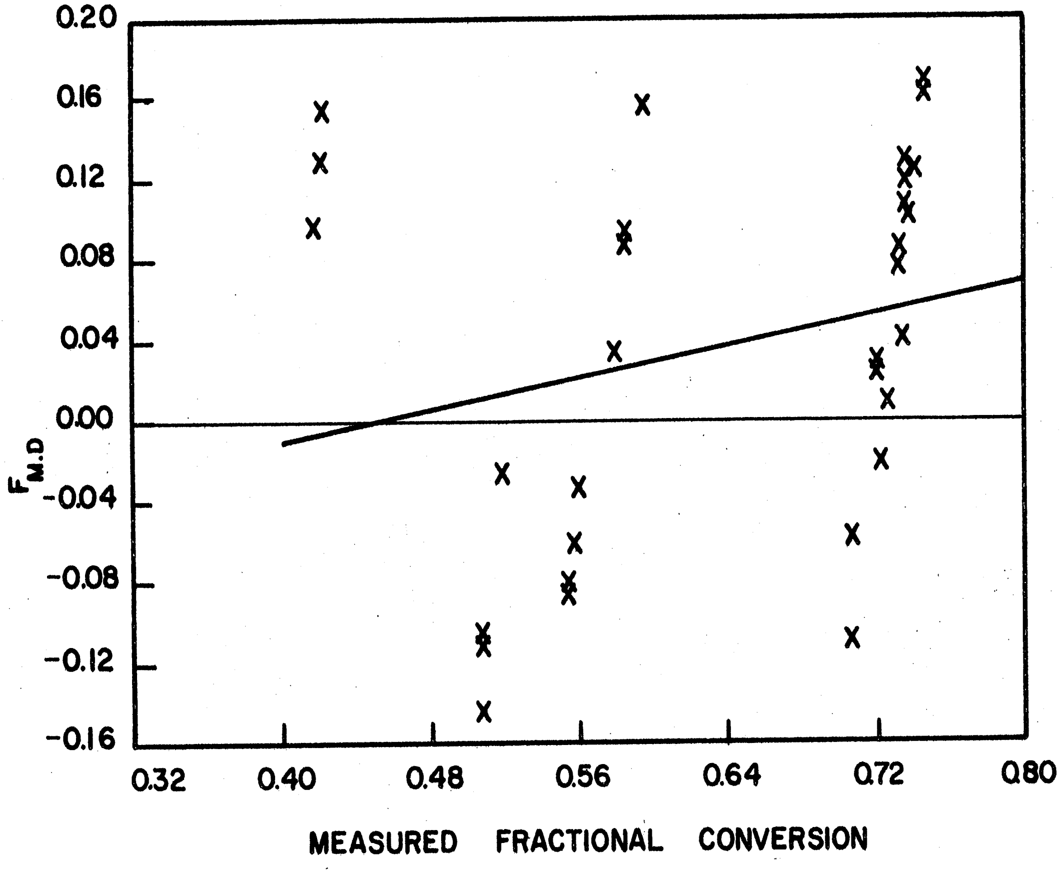


Figure 19. Glass-Bead Reactor Relative Conversion Differences Based Upon Measured Distribution Functions.

11 of Table VIII and are shown in Figure 20. All 20 relative conversion differences are greater than zero. The null hypothesis, that the mean value of relative conversion difference was zero, was rejected and it was concluded for the two-compartment reactor that the measured conversions were significantly higher than those calculated by the distribution of residence times.

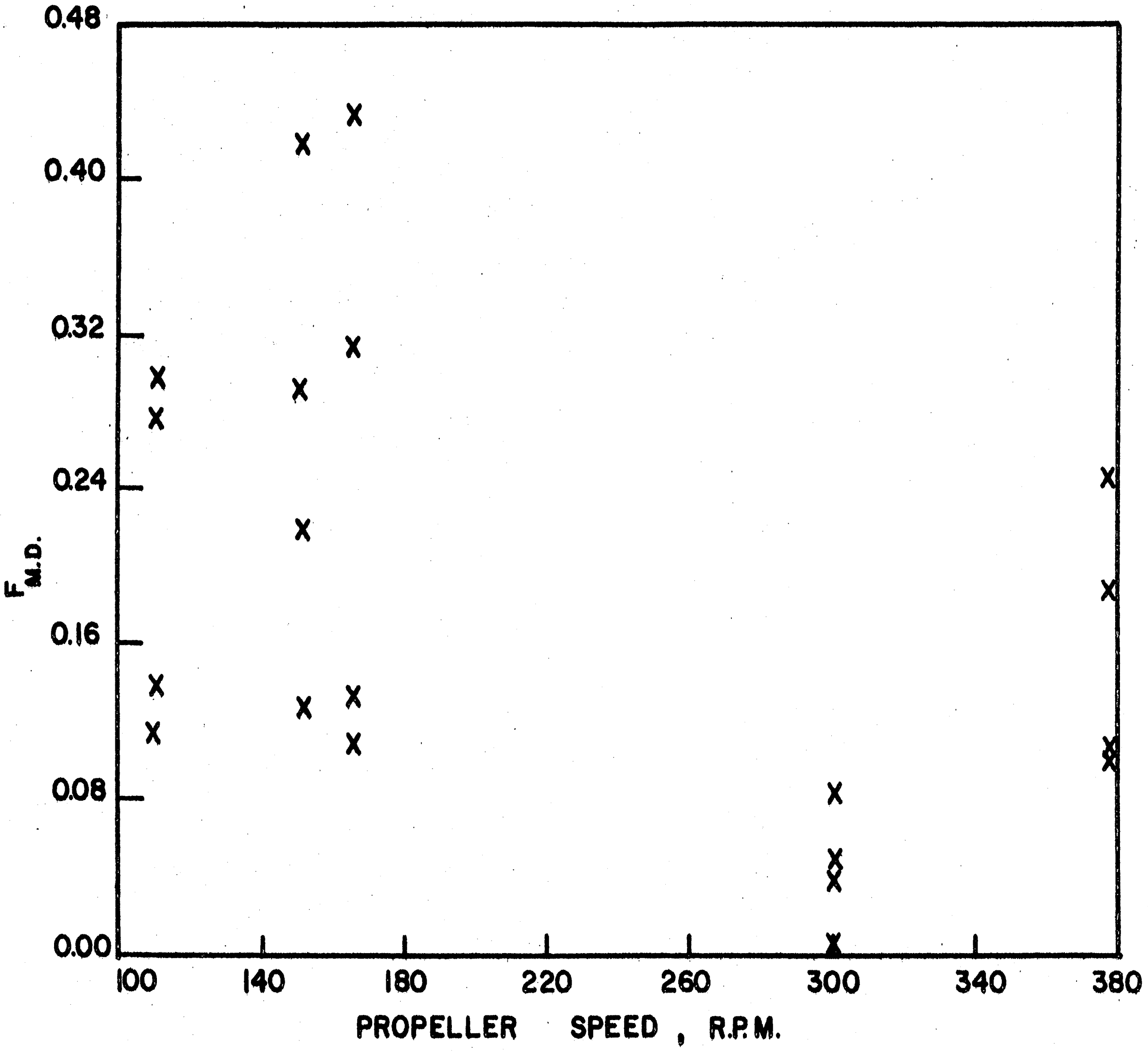


Figure 20. Two-Compartment Reactor Relative Conversion Differences Based Upon Measured Distribution Functions.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Summary

Conversions calculated from the measured distributions of residence times for the one-compartment reactor were about five percent of the distance between conversions calculated by the perfectly-mixed and slug-flow distributions. Similarly conversions calculated from the glass-bead and the two-compartment reactor distributions were 80 and 55% respectively, of the distance between the perfectly-mixed and slug-flow conversions. For the reactors with distribution functions relatively close to perfect-mixing or relatively close to slug-flow, measured conversions were not significantly different, at the 5% significance level, from conversions calculated by the measured distributions of residence times. For the reactor with a distribution function intermediate between perfect mixing and slug flow, measured conversions, at the 5% significance level, were significantly higher than those calculated by the measured distributions of residence times.

Representative distribution functions for the three reactors are shown in Figure 21.

Conclusions

(1) A preliminary survey of the distributions of residence times for a small, stirred, one-compartment reactor in which height and diameter were about equal indicated that differences between conversions calculated from the measured distributions and conversions calculated by assuming a

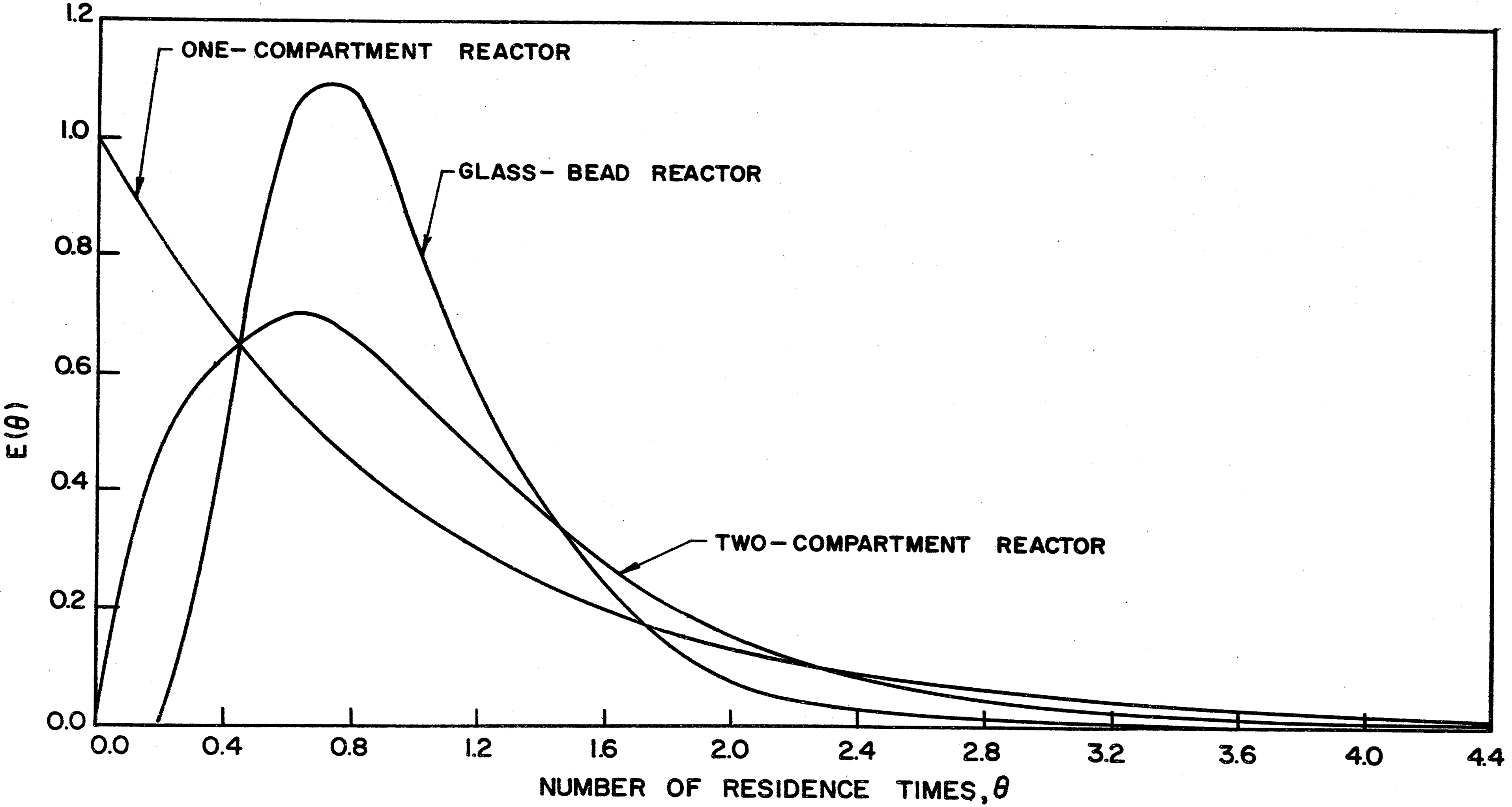


Figure 21. Representative Distribution Functions.

perfectly-mixed distribution were not important in most engineering applications. The ranges of conditions investigated were for propeller speeds greater than 30 r.p.m.; for residence times greater than 8 min.; for entrance positions of the feed as shown in Figure 10; for any baffling arrangements in which the reactor was not divided essentially into two or more compartments; and for either one or two propellers on the same shaft at various distances from the bottom of the reactor.

(2) For the one-compartment reactor, measured conversions, at a 5% significance level, were not significantly different from conversions calculated from the measured distributions of residence times. The conversions were about 5% of the distance between conversions calculated for a perfectly-mixed and a slug-flow distribution of residence times.

(3) For a reactor in which conversions were about 80% of the distance between conversions calculated for a perfectly-mixed and a slug-flow distribution of residence times, measured conversions, at a 5% significance level, were not significantly different from conversions calculated from the measured distributions of residence times.

(4) For a reactor in which calculated conversions were about 55% of the distance between conversions calculated from a perfectly-mixed and a slug-flow distribution of residence times, measured conversions, at a 5% significance level were significantly higher than conversions calculated by the measured distributions of residence times. Based upon complete conversion being 100% this difference between measured and predicted conversions, at a 50% conversion level, was (2.1 ± 0.7)% and may have been of engineering importance.

(5) The reaction rate constant for the hydrolysis of tertiary-butyl-bromide in aqueous ethyl alcohol was given by the following correlation

$$\log k_{.088} = 15.9501 - 5.0223C - \frac{4,641.22}{T + 273.10}$$

over the following ranges of conditions

$$.64 < C < .68$$

$$23 < T°C < 28$$

$$C_o = .088$$

For other initial concentrations of tertiary-butyl-bromide the following correction was applied to the reaction rate constant

$$k_{C_o} - k_{.088} = k_{.088} (.580)(.0880 - C_o)$$

$$.045 < C_o < .088$$

APPENDIX I

ADDITIONAL DERIVATIONS

Calculation of Conversion which has Occurred Before Sampling

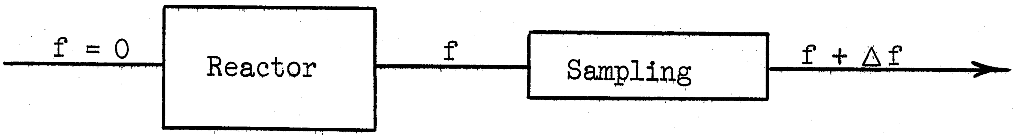


Figure 22. Sampling Model

Let f be the fractional conversion occurring in the reactor and Δf the additional conversion occurring during sampling time Δt. If the conversion occurring during sampling is assumed to be equal to the conversion occurring in a batch reactor in time Δt, then

$$\Delta f = (1 - f)(1 - e^{-k\Delta t}) \tag{13}$$

and therefore

$$f = \frac{(f + \Delta f) - (1 - e^{-k\Delta t})}{e^{-k\Delta t}} \tag{14}$$

Maximum Error Caused by Using a Mean k

The temperatures in the two-compartment reactor differed by a maximum of 0.25°C. The maximum error caused by using a mean k instead of k's for each compartment will now be estimated.

From Figure 13 it can be seen that the distributions of residence times for the two-compartment reactor are approximately that for two perfectly-mixed reactors in series. The error caused by using a mean k will be estimated by using the distribution for two perfectly-mixed reactors in series.

Using the data of run 44

$t_1 = 24.77°C \qquad k_1 = .001187 \text{ sec.}^{-1}$

$t_2 = 25.02°C \qquad k_2 = .001222 \text{ sec.}^{-1}$

$\tau_1 = \tau_2 = 5.89 \text{ min.}$

Conversion Using k's for Each Compartment

$$f_1 = \frac{k_1 \tau_1}{1 + k_1 \tau_1} = \frac{.001187 \times 60 \times 5.89}{1 + .001187 \times 60 \times 5.89} = .29552$$

$$f_2 = \frac{k_2 \tau_2}{1 + k_2 \tau_2} = \frac{.001222 \times 60 \times 5.89}{1 + .001222 \times 60 \times 5.89} = .30161$$

$$f = f_1 + f_2 (1 - f_1) = .50800$$

Conversion Using an Average k

$$f_1 = f_2 = \frac{k \tau_1}{1 + k \tau_1} = \frac{.0012045 \times 60 \times 5.89}{1 + .0012045 \times 60 \times 5.89} = .29858$$

$$f = f_1 + f_2 (1 - f_1) = .50801$$

$$\% \text{ error} = \frac{1}{50{,}800} = .002\%$$

Therefore the error caused by using a mean k for the two-compartment reactor is negligible.

APPENDIX II

DETAILED DATA AND SAMPLE CALCULATIONS

Calculations for Run 45

In this section detailed data and sample calculations for run 45 are presented. Also sample calculations for the statistical tests are given on page 86 . For Table IX the column headings are:

Column	Description
1	Sample number
2	Time of start of sample withdrawal from the system.
3	Time of completion of sample withdrawal from the system.
4	Time of start of quench of sample.
5	Time of completion of quench of sample.
6	Sampling time, sec.
7	Net ml. of NaOH required to titrate the sample.
8	Net ml. of NaOH required to titrate a sample which has completely reacted.
9	Product of reaction rate constant and sampling time.
10	Conversion occurring in the reactor and during sampling.
11	Calculated conversion occurring in the reactor.

The volume of the system between the colorimeter and the sampling point wás 14 ml. The total volume of liquid withdrawn during sampling was 28 ml. The sampling time equalled the average time for liquid to flow from the reactor outlet to the sampling point, plus the difference between the average quenching time and the average time for sample withdrawal.

TABLE IX

SAMPLE DATA OF TERTIARY-BUTYL-BROMIDE SAMPLES

1	2	3	4	5	6	7	8	9	10	11
Sample Number	Time: Hrs., Mins., Secs., 1	2	3	4	Sampling Time Δt Sec.	Net* cc NaOh	Infinite* Titer	$k\Delta t$	$f + \Delta f$	f
1	3.03:00	3.03:13	3.03:23	3.03:46	34.5	23.70	40.45	.0433	.5859	.5676
2	3.18:00	3.18:15	3.18:26	3.18:49	37.5	23.55	40.73	.0470	.5782	.5579
3	4.38:00	4.38:13	4.38:23	4.38:47	35.0	23.48	40.74	.0440	.5763	.5573
4	4.58:00	4.58:14	4.58:23	4.58:46	34.5	25.06	42.28	.0433	.5927	.5747
MEAN							41.05			

* Blank correction also made

$$\Delta t = \frac{14}{28} \times 13 + \frac{(46 + 23) - (13 + 0)}{2} = 34.5 \text{ sec.}$$

In column 9, k = .001281. See page 85 for the calculation of k from the batch correlation.

In column 10, $f + \Delta f = \frac{23.70}{40.45} = .5859$

From Equation (14)

$$f = \frac{(f + \Delta f) - (1 - e^{-k\Delta t})}{e^{-k\Delta t}}$$

$$= .5676$$

For Table X the column headings are:

Column	Description
1	Time corresponding to the measurement in column 2 or 3.
2	Level of aqueous ethyl alcohol in storage.
3	Level of tertiary-butyl-bromide in storage.
4	Reading of the inclined manometer indicating the aqueous ethyl alcohol flow-rate.
5	Reading of the tertiary-butyl-bromide rotameter.
6	Reading of the inclined manometer indicating liquid level in the reactor.
7	Temperature of compartment 1, °C.
8	Temperature of compartment 2, °C.
9	Temperature of bath, °C.
10	Propeller speed, r.p.m.
11	Flow rate of liquid leaving reactor, ml./min.
12	Room temperature, °F.

TABLE X

SAMPLE DATA OF REACTOR VARIABLES

1	2	3	4	5	6	7	8	9	10	11	12
Time, Hr. Min. Sec.	Level in Storage		EtOH Flowmeter	t-Bu-Br Rotameter	Reactor Level	Reactor Temp. °C		Bath Temp °C	R.P.M.	Outlet Flow-rate Ml./Min.	Room Temp °F
	Aqueous EtOH Cm.	t-BuBr Cm.				1	2				
2.55-3.00			9.0	35.0	53.9	24.96	25.21	25.00	377.8	172.0	79.1
2.55:30	32.0										
2.56:00		15.86									
3.10-3.15			9.0	34.0	54.1	24.98	25.21	25.01	374.0	175.4	79.3
3.10:30	29.9										
3.11:00		14.60									
3.45:00	Tracer	Injected									
4.30-4.35			9.0	33.4	53.6	24.99	25.21	25.03	371.8	174.6	78.7
4.30:30	18.65										
4.31:00		7.84									
4.50-4.55			9.0	32.1	53.5	25.00	25.21	25.00	380.1	173.8	78.9
4.50:30	15.8										
4.51:00		6.13									
MEAN					53.8	24.98	25.21	25.01	375.9	173.9	79.0
Thermometer Correction						.09	- .02	- .04			
CORRECTED MEAN					53.8	25.05	25.19	24.97	375.9	174.0	79.0

Aqueous Ethyl Alcohol Flowrate

The aqueous ethyl alcohol flowrate was measured by the displacement from the storage bottle.

Time	Level	Volume
2.55:30	32.0	31.40
4.50:30	15.8	11.30
1.55:00		20.10

The volume of liquid in the storage bottle was obtained from the level in storage by the calibration given on page 95.

$$\text{Aqueous ethyl alcohol flowrate} = \frac{20,100}{115.00} = 174.8 \text{ ml./min.}$$

Tertiary-Butyl-Bromide Flowrate

The tertiary-butyl-bromide flowrate was also measured by the amount of liquid leaving the storage bottle.

Time	Level
2.56:00	15.86
4.51:00	6.13
1.55:00	9.73

The volume of the storage bottle was calibrated in terms of liquid level. The calibration on page 97 showed that volume was directly proportional to level.

$$\text{Tertiary-butyl-bromide flowrate} = \frac{16.64 \times 9.73}{115.00} = 1.408 \text{ ml./min.}$$

Reactor Material Balance

Total flowrate to reactor = 174.8 + 1.4 = 176.2 ml./min.

Outlet flowrate from reactor = 174.0

$$\text{Overall material balance} = \frac{\text{Volume out}}{\text{Volume in}} = \frac{174.0}{176.0} = .988$$

Average overall flowrate = 175.1 ml./min.

Bulk Residence Time

The reactor volume was calibrated in terms of the height of liquid in the reactor inclined manometer. From the calibration on page 99 the reactor volume was 2085 ml.

$$\text{Bulk residence time} = \frac{V}{v} = \frac{2085}{175.1} = 11.91 \text{ min.}$$

Tertiary-Butyl-Bromide Material Balance

Concentration of tertiary-butyl-bromide in the combined inlet stream to the reactor $= \dfrac{1.408 \times 1.186}{137.0 \times 175.1} = .06961$ moles/l.

Concentration of tertiary-butyl-bromide in the outlet stream from the reactor $= \dfrac{41.05 \times .04204}{25.00} = .06903$ moles/l.

Tertiary-butyl-bromide material balance

$$= \frac{\text{Material out}}{\text{Material in}} = \frac{.06903}{.06961} = .992$$

Calculation of the Distribution Function from the Recorder Trace

The data and calculations of the distribution function from the recorder trace, shown in Figure 23, are presented in Table XI. Points read off the recorder trace are shown in columns 1 and 2.

Column	Description
1	Number of chart divisions and proportional to time.
2	Height of trace.
3	Relative height of trace or fractional transmittance.
4	Concentration of dye in outlet stream; obtained from column 3 by the calibration on page 92.
5	Number of residence times $\theta = \dfrac{1.664n}{11.91}$, where the chart speed was 1.664 divisions/min.
6	Distribution of residence times $E(\theta) = \dfrac{VC(\theta)}{Q}$

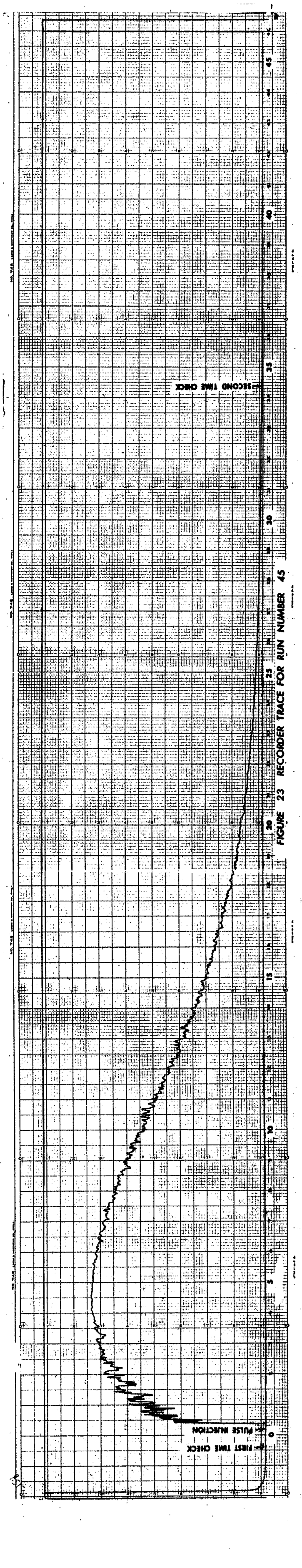


FIGURE 23 RECORDER TRACE FOR RUN NUMBER 45

TABLE XI

SAMPLE CALCULATION OF THE DISTRIBUTION FUNCTION FROM A RECORDER TRACE

1	2	3	4	5	6
n	I	I/I_o	$C(\theta)$	$\theta = \frac{1.664n}{11.91}$	$E(\theta)$
0.38	.830	1.000	.0000	.03	.000
1	.381	.460	.0680	.11	.354
2	.270	.326	.0988	.25	.513
3	.212	.256	.1207	.39	.626
4	.188	.227	.1311	.53	.682
5	.181	.218	.1348	.67	.700
6	.199	.240	.1261	.81	.656
7	.230	.277	.1138	.95	.590
8	.268	.323	.0996	1.09	.513
9	.318	.384	.0840	1.23	.437
10	.365	.440	.0720	1.37	.374
11	.419	.505	.0601	1.51	.312
12	.473	.570	.0494	1.65	.257
13	.524	.631	.0405	1.79	.210
14	.568	.684	.0337	1.93	.174
15	.611	.736	.0271	2.07	.141
16	.649	.781	.0218	2.21	.113
17	.682	.821	.0171	2.35	.089
18	.711	.856	.0139	2.49	.072
20	.750	.904	.0089	2.77	.046
22	.780	.940	.0053	3.05	.028
24	.799	.961	.0034	3.32	.018
26	.810	.976	.0022	3.60	.011
28	.816	.984	.0015	3.92	.008
30	.820	.987	.0012	4.16	.006
32	.822	.990	.0009	4.45	.005
34	.825	.994	.0006	4.73	.003
36	.827	.996	.0004	5.00	.002
38	.828	.998	.0002	5.28	.001
40	.829	.999	.0001	5.56	.001

If the chart reading for clear liquid was arbitrarily set at 0.000, then the reading for 0% transmittance was 0.830. The relative height of trace $= \frac{\text{height of trace}}{0.830}$.

The values of $E(\theta)$ in column 6 were obtained by normalizing the $C(\theta)$ curve given in column 4.

First Moment

In Table XI, $E(\theta)$ is given at non-integral values of θ. $E(\theta)$ was plotted as a function of θ and values were read off at integral values of θ. These values of $E(\theta)$, along with other quantities used in calculating the first moment and conversion, are given in Table XII, which has the following column headings.

Column	Description
1	θ = The number of residence times.
2	$k\tau\theta$ where k = the reaction rate constant. $\tau = \frac{V}{v}$, the length of 1 residence time θ = the number of residence times.
3	$e^{-k\tau\theta}$
4	$E(\theta) = \frac{vC(\theta)}{Q}$
5	$\theta \Delta \theta$

The first moment of the distribution function was calculated from $E(\theta)$ in column 4 and $\theta\Delta\theta$ in column 5 of Table XII.

$$\lim_{\theta \to \infty} \int_0^{\theta} \theta E(\theta)\, d\theta \cong \sum_0^{\infty} E\theta\Delta\theta$$

For run 45 the first moment was 1.044.

TABLE XII

SAMPLE CALCULATION OF THE FIRST MOMENT AND CONVERSION

1	2	3	4	5
θ	$k\tau\theta$	$e^{-k\tau\theta}$	$E(\theta)$	$\theta\Delta\theta$
.025	.023	.977	.000	.0012
.1	.092	.912	.332	.01
.2	.183	.834	.479	.02
.3	.275	.759	.572	.03
.4	.366	.693	.635	.04
.5	.458	.633	.676	.05
.6	.550	.577	.706	.06
.7	.641	.527	.695	.07
.8	.733	.480	.665	.08
.9	.824	.438	.621	.09
1.0	.915	.400	.566	.10
1.1	1.01	.364	.511	.11
1.2	1.10	.333	.459	.12
1.3	1.19	.304	.410	.13
1.4	1.28	.278	.362	.14
1.5	1.37	.254	.322	.15
1.6	1.47	.230	.280	.16
1.7	1.56	.210	.243	.17
1.8	1.65	.192	.201	.27
2.0	1.83	.160	.160	.40
2.2	2.02	.133	.120	.44
2.4	2.20	.111	.082	.48
2.6	2.38	.093	.061	.52
2.8	2.56	.077	.041	.56
3.0	2.75	.064	.030	.60
3.2	2.93	.053	.021	.64
3.4	3.11	.045	.016	.68
3.6	3.30	.037	.011	.72
3.8	3.48	.031	.009	.76
4.0	3.66	.026	.007	.80
4.2	3.85	.021	.006	.84
4.4	4.03	.018	.005	.88
4.6	4.21	.015	.004	.92
4.8	4.40	.012	.003	.96
5.0	4.58	.010	.002	1.00
5.2	4.76	.009	.001	1.04
5.4	4.95	.007	.001	1.08

As discussed on page 7 the first moment or internal material balance served as a check of a measured distribution function.

Conversion Calculated by the Measured Distribution of Residence Times

The conversion as calculated by the measured distribution of residence times was given by Equation (6).

$$f_{M.D.} = 1 - \lim_{\theta \to \infty} \int_0^{\theta} e^{-k\tau\theta} \; E(\theta) \, d\theta$$

$$\cong 1 - \sum_0^{\infty} e^{-k\tau\theta} \; E(\theta) \, \Delta\theta$$

For this run $f_{M.D.} = 0.5452$

Calculated Reaction Rate Constant

It was shown on page 73 that a mean reaction rate constant could be used without introducing error.

$$T_{mean} = \frac{25.05 + 25.19}{2} = 25.12°C$$

$$C_{ETOH} = .6539$$

Upon making these substitutions in Equation (10).

$$\log k_{.088} = 15.9501 - 5.0223\,(.6539) - 4{,}641.22 / (273.1 + 25.12)$$

$$k_{.088} = .001267 \text{ sec.}^{-1}$$

where $k_{.088}$ was the reaction rate constant for an initial concentration of tertiary-butyl-bromide of .088 moles/liter. For an initial concentration of .0696 moles/liter, by Equation (11).

$$k_{.0696} - k_{.088} = .001268\ (.580)(.0880 - .0696)$$

$$k_{.0696} = .001281\ \text{sec.}^{-1}$$

Conversion Calculated by the Perfectly-mixed Distribution

$$f_{P.M.D.} = \frac{k\tau}{1 + k\tau} = \frac{11.91 \times 60 \times .001281}{1 + 11.91 \times 60 \times .001281} = .4779$$

Conversion Calculated by the Slug Flow Distribution

$$f_{S.F.D.} = 1 - e^{-k\tau} = .5998$$

Relative Conversion Difference Based Upon the Measured Distribution Function

$$F_{M.D} = \frac{f - f_{M.D.}}{f_{S.F.D.} - f_{P.M.D.}} \quad \frac{.5676 - .5452}{.5998 - .4779} = .184$$

Sample Calculations for Statistical Tests

Effect of Dye

The relative conversion difference data in Table VI was tested to determine whether dye had an effect upon conversion. The null hypothesis was that the difference between relative conversion differences in the presence and absence of dye was zero. Let 1 and 2 be subscripts denoting the presence and absence of dye respectively.

For the data in Table VI

$\bar{F}_1 = .06004$ $\qquad$ $\bar{F}_2 = .04902$

$N_1 = 12$ $\qquad$ $N_2 = 19$

$\sigma_1^2 = .00272$ $\qquad$ $\sigma_2^2 = .00227$

The variances were close enough to being equal to assume that the variances for the two universes were equal. Since the samples were small the t-test described by Duncan(14), page 394, was used.

$$S = \sqrt{\frac{N_1\sigma_1^2 + N_2\sigma_2^2}{N_1 + N_2 - 2}} = .0510$$

$$t = \frac{(\bar{F}_1 - \bar{F}_2) - 0}{S\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} = .585$$

Using a two-tailed test and a 5% significance level the critical t was 2.045. Therefore the hypothesis was not rejected and the data did not indicate that dye had a significant effect upon conversion.

$\bar{X}$ - Chart

The tests described on page 60 were then performed upon all the data used in the previous section.

The null hypothesis was that the means of all runs were the same

$$\bar{\bar{F}} = .0533$$

$$\sigma_{\bar{F}} = .0359$$

Hence an unbiased estimate of the standard error $\hat{\sigma}_{\bar{F}} = .0398$

$$N = 31$$

The upper limit was

$$\bar{\bar{F}} + \frac{3\hat{\sigma}_{\bar{F}}}{\sqrt{N}} = .1130$$

The lower limit was

$$\bar{\bar{F}} - \frac{3\hat{\sigma}_{\bar{F}}}{\sqrt{N}} = -.0063$$

None of the means for the runs were outside this interval. Therefore, the hypothesis was not rejected.

Barlett's Test

Bartlett's Test which was described on page 61 , was used to test for constant variability. The null hypothesis was that the variances for the individual runs were a homogeneous set.

TABLE XIII

SAMPLE CALCULATIONS FOR BARTLETT'S TEST

Run Number	σ^2	log σ^2
11	.001859	7.2693 - 10
12	.000511	6.7084 - 10
13	.000891	6.9500 - 10
14	.001941	7.2880 - 10
15	.000642	6.8075 - 10
16	.000147	6.1673 - 10
17	.002129	7.3282 - 10
33	.001025	7.0107 - 10

Arithmetic mean = $\bar{\sigma}^2$ = .0011437

log $\bar{\sigma}^2$ = 7.05832 - 10

log geometric mean = 6.94117 - 10

Let p = the number of variances

Then p = 8 and n = N-1 = 3

$$G = 2.3026\ pn\ (\text{log arithmetic mean} - \text{log geometric mean}) \qquad (14)$$

$$= 6.474$$

$$H = 1 + \frac{p+1}{3np} = 1.125 \qquad (15)$$

$$\frac{G}{H} = 5.755$$

For n = 7

$$\chi^2_{.05} = 16.0$$

The hypothesis was not rejected

χ^2 Test of Normality

From the results of the last two tests it was reasonable to assume that the means of the runs could be used to estimate a universe mean and the variance of the runs could be used to estimate a universe variance.

The null hypothesis was that the data were normally distributed with $\overline{\overline{F}} = .0533$ and $\sigma' = .052$

$$N = 31$$

Let Y = the theoretical frequency

and y = the actual frequency

TABLE XIV

SAMPLE CALCULATIONS FOR THE TEST OF NORMALITY

Upper limit of class	Z	Y	y	$\frac{(Y-y)^2}{Y}$
.00	-1.05	4.557	4	.068
.03	- .46	5.766	8	.865
.06	.13	6.789	7	.007
.09	.73	6.665	5	.416
.12	1.32	4.340	4	.027
∞	∞	2.883	3	.005

$$\Sigma \frac{(Y - y)^2}{Y} = 1.39$$

For 3 degrees of freedom

$$\chi^2_{.05} = 7.82$$

The hypothesis was not rejected.

Significance of the Mean

The previous test had shown that the data can reasonably be assumed to be approximately normally distributed. The null hypothesis for this test was that the mean, $\overline{F}$, of the relative conversion differences based upon the perfectly-mixed distribution was zero.

$$N = 31$$

$$\overline{F} = .0533$$

$$\sigma' = .0520$$

$$Z = \frac{\overline{F}\sqrt{N}}{\sigma'} = 5.7$$

For a 5 percent significance level Z = 1.96.

The hypothesis was rejected and it was concluded that the relative conversion differences were significantly different from zero.

Confidence Interval for the Mean

The 95 percent confidence interval for $\overline{F}$ is

$$\overline{F}' \pm \frac{1.96\ \sigma'}{\sqrt{N}} = .0533 \pm .0183$$

But $\overline{f}_{M.} - \overline{f}_{P.M.D.} = .0052$

Therefore the 95 percent confidence interval for $\overline{f}_{M.} - \overline{f}_{P.M.D.}$

$$= .0052 \pm \frac{.0183 \times .0052}{.0533}$$

$$= (0.5 \pm 0.2)\%$$

APPENDIX III

CALIBRATIONS

Dye Concentration as a Function of Colorimeter Reading

The amount of dye in the stream leaving the reactor was measured by a colorimeter which was calibrated by solutions of dyes mixed up to desired concentrations. A calibration curve for "Pontachrome" blue black r.m. conc. in aqueous ethyl alcohol containing .0575 moles of HBr per liter is shown in Figure 24. The calibration followed Beer's Law very closely

$$\log \frac{I}{I_o} = -K\,C$$

where

I_o = the intensity of incident light

I = the intensity of emergent light

C = the concentration of dye

K = the absorption coefficient

Thermometer Corrections

The thermometers when totally immersed in liquid were calibrated against thermometers which had been calibrated by the National Bureau of Standards. The calibrations are presented in Table XV and are shown in Figure 25. The standard thermometer for readings 1 through 9 was PRINCO 460641 and for readings 9 through 15 was PRINCO 461707. In Table XV correction was true temperature minus the thermometer reading.

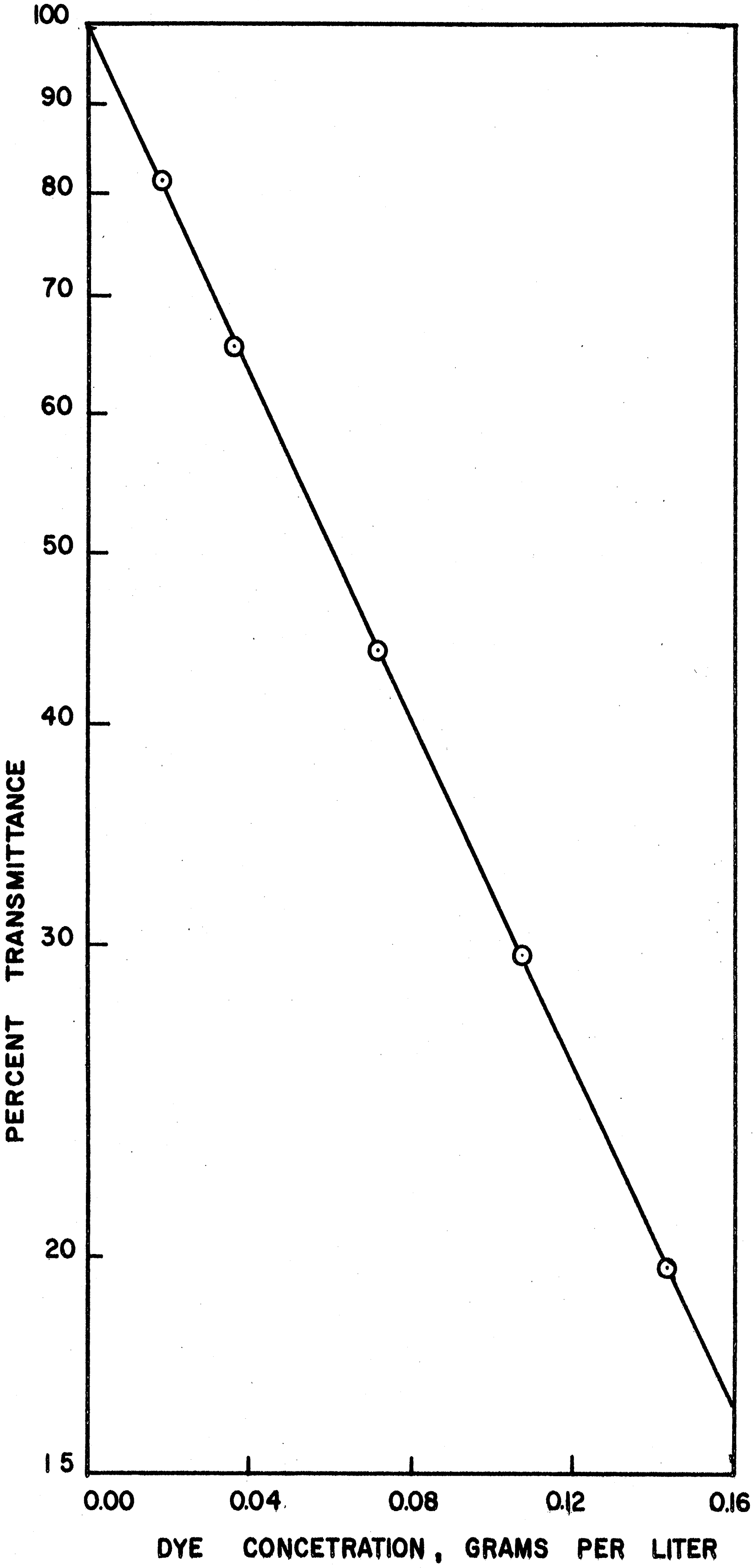


Figure 24. Calibration of Blue Black in Aqueous Ethyl Alcohol Reaction Mixtures.

TABLE XV

THERMOMETER CALIBRATIONS

Reading Number	Temperature °C	Corrections °C AMINCO 4002	PRINCO 224273	EXAX 7478	EXAX 7375	EXAX 7601
1	16.32			-.07	-.13	-.07
2	16.59		+.13			
3	19.67			-.04	-.06	-.02
4	24.93			-.04	-.02	-.04
5	25.12		+.07			
6	29.38			-.03	+.05	-.02
7	35.76		+.10			
8	45.69		+.03			
9	51.63	-.05	-.04			
10	50.51	-.04				
11	59.81	-.04				
12	70.30	-.13				
13	79.97	-.12				
14	90.10	-.15				
15	99.26	+.06				

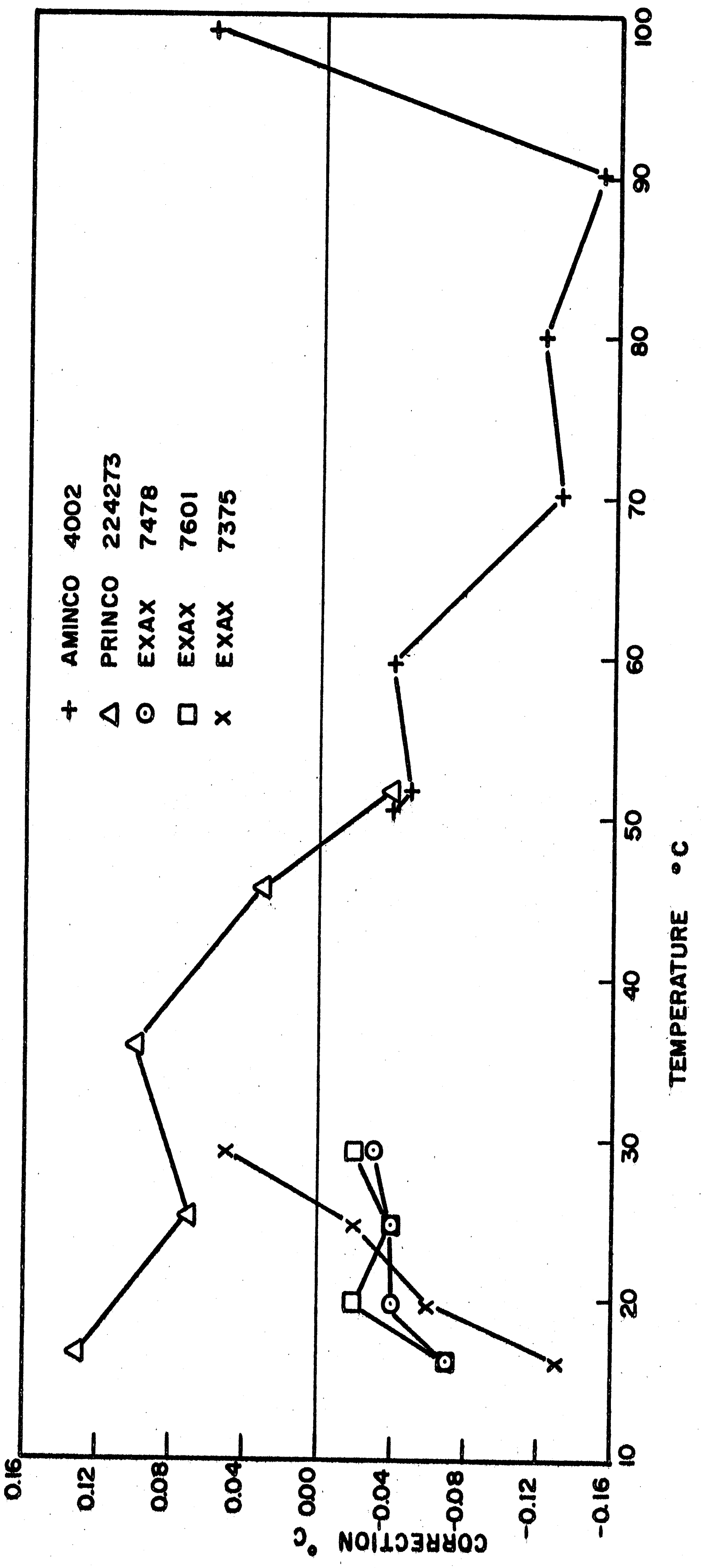


Figure 25. Thermometer Calibrations.

Aqueous Ethyl Alcohol Feed Bottles

The volumes of the aqueous ethyl alcohol feed bottles were calibrated in terms of liquid level. These data are presented in Table XVI and are shown in Figure 26.

TABLE XVI

CALIBRATION OF THE AQUEOUS ETHYL ALCOHOL FEED BOTTLES

Volume Liters	Liquid Level		
	3 gal. bottle	5 gal. bottle	12 gal. bottle
1	3.92	3.60	
2	6.60	5.64	7.8
3	9.25	7.58	
4	11.91	9.39	9.6
5	14.53	11.28	
6	17.14	13.09	11.4
7	19.78	14.90	
8	22.39	16.71	13.1
9	24.99	18.55	
10	27.59	20.37	14.7
11	30.56	22.19	
12		24.02	16.4
13		25.85	
14		27.67	18.0
15		29.51	
16		31.30	19.6
17		33.20	
18		35.23	21.3
19		38.63	
20			22.9
22			24.5
24			26.1
26			27.7
28			29.3
30			30.9
32			32.5
34			34.1
36			35.7
38			37.4
40			39.2
42			41.4

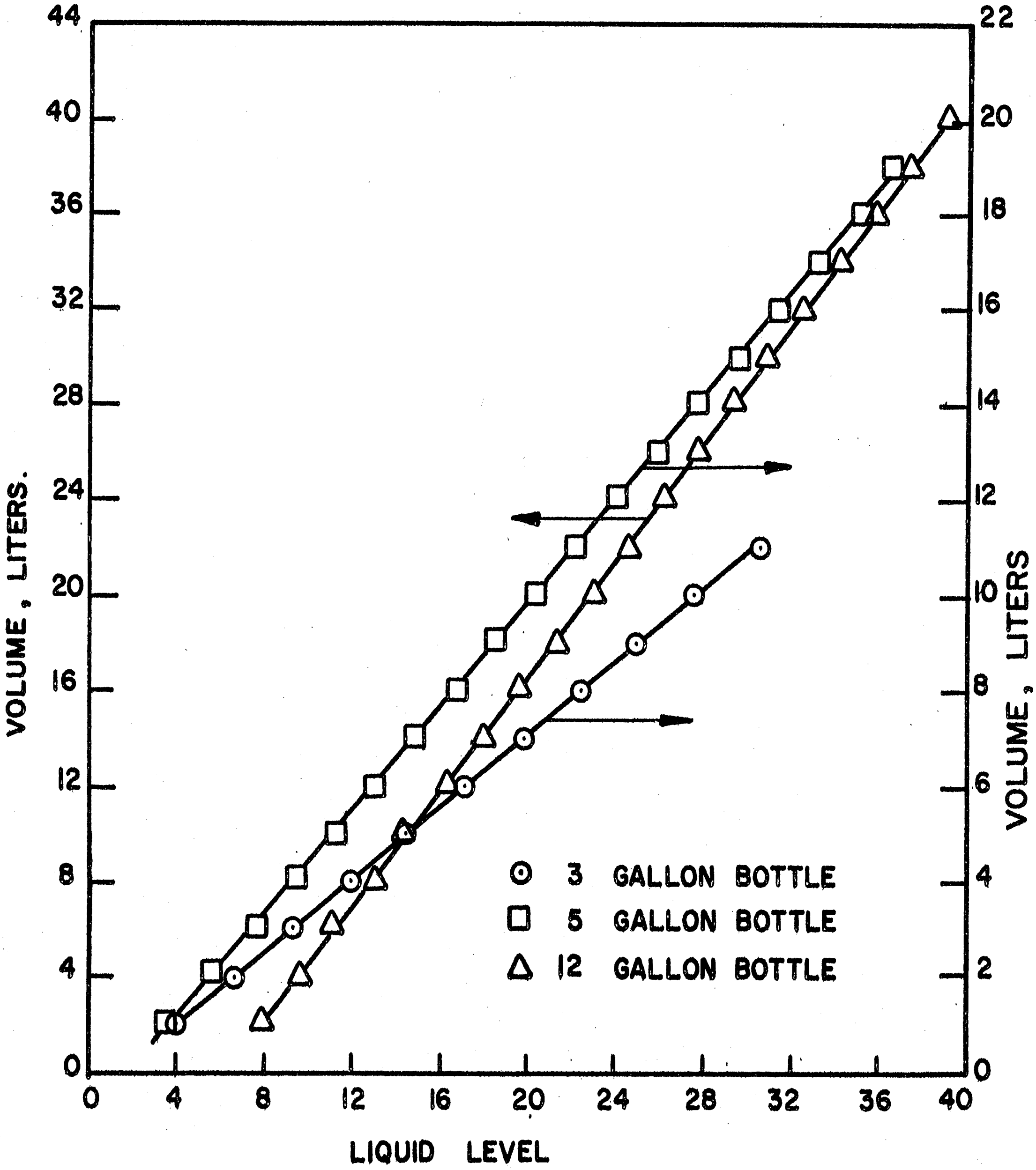


Figure 26. Volumes of the Alcohol Feed Bottles.

Tertiary-Butyl-Bromide Feed Bottle

The volume of the tertiary-butyl-bromide feed bottle was calibrated in terms of liquid level. These data are presented in Table XVII and are shown in Figure 27. The volume level relation was found to be linear and the slope was 16.64 ml./cm.

TABLE XVII

CALIBRATION OF THE TERTIARY-BUTYL-BROMIDE FEED BOTTLE

Liquid Level Cm.	Volume Ml.
25.56	505.1
24.00	478.1
22.73	457.1
21.02	429.4
19.80	409.3
18.27	382.3
16.88	359.3
15.59	337.1
14.09	313.2
12.43	283.8
11.18	263.2
9.70	238.8
8.35	216.7
6.77	188.9
5.41	166.5

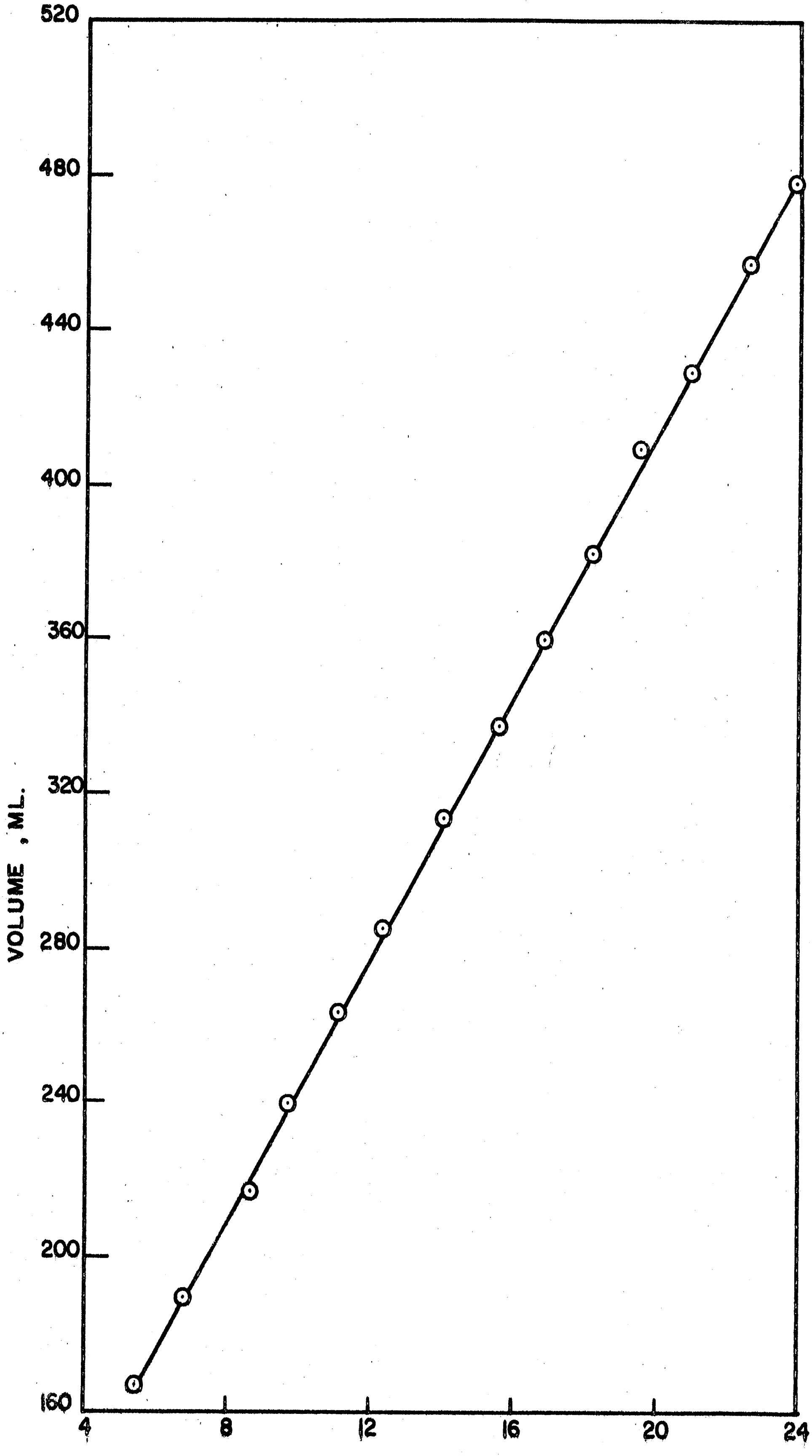


Figure 27. Volume of the Tertiary-Butyl-Bromide Feed Bottle.

Two-Compartment Reactor Volume

The liquid level in the reactors was measured by an inclined manometer. The reactor volumes were measured as a function of liquid level. For the two-compartment reactor the calibration is presented in Table XVIII and shown in Figure 28.

TABLE XVIII

VOLUME OF THE TWO-COMPARTMENT REACTOR

Liquid Level	Reactor Volume, Ml.
39.9	1930
42.8	1962
44.0	1979
48.1	2025
49.7	2041
57.0	2116
57.2	2119

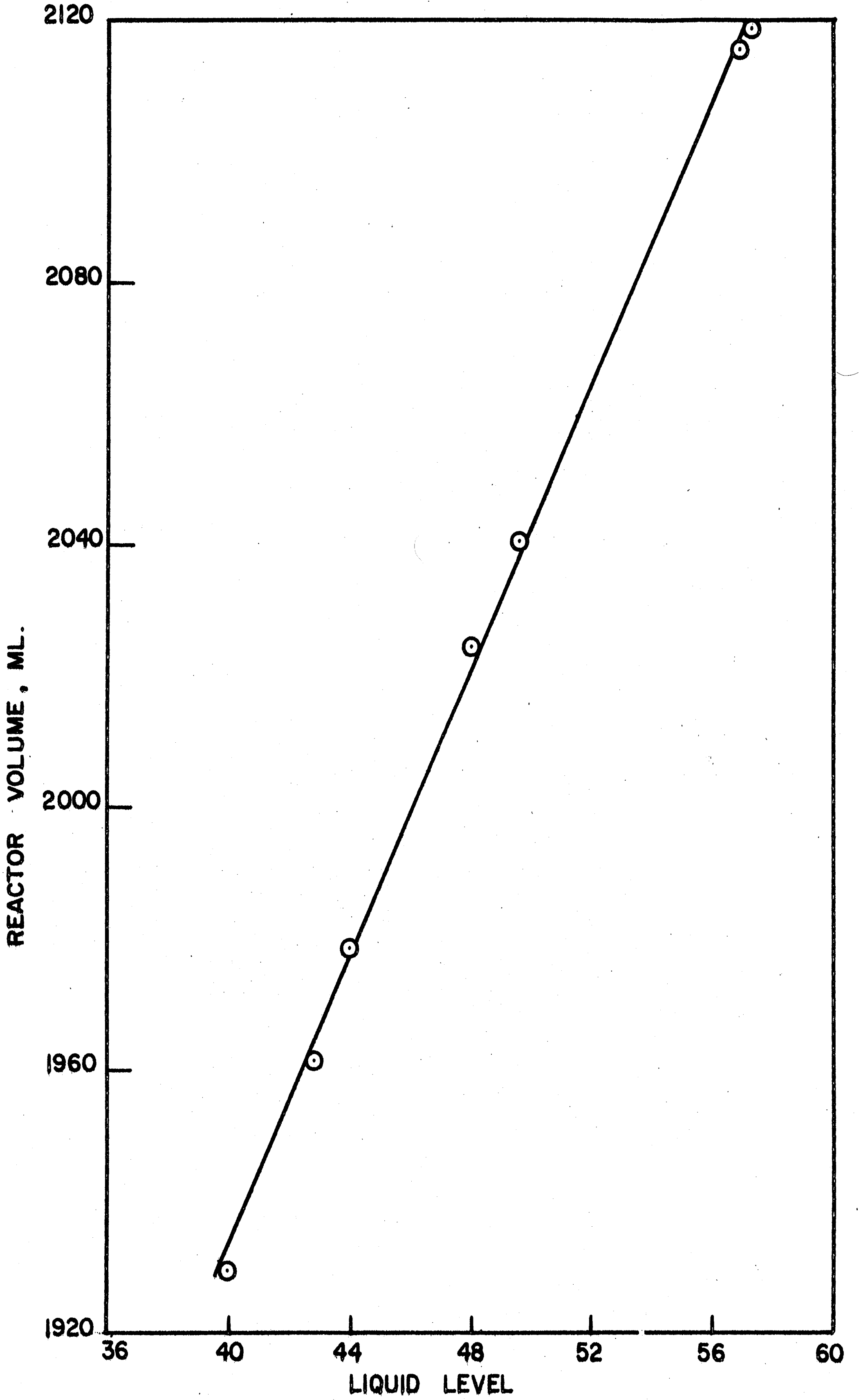


Figure 28. Two-Compartment Reactor Volume Calibration.

NOMENCLATURE

A, A', A'', A'''	Constants
B, B'	Constants
C_o	Initial Concentration of tertiary-butyl-bromide, moles/l.
C_{ETOH}	Mass fraction of alcohol in the aqueous ethyl alcohol
$C(\theta)$	Concentration of tracer in the exit stream for a pulse experiment, grams/ml.
D	Constant
E	Activation energy, cal./mole
$E(\theta)$	Non-cumulative distribution function for the outlet stream, dimensionless
f	Measured fractional conversion, dimensionless
f_D	Fractional conversion calculated by using any distribution of residence times, dimensionless
$f_{M.D.}$	Fractional conversion calculated by using a measured distribution of residence times, dimensionless
$f_{P.M.D.}$	Fractional conversion calculated by using the perfectly-mixed distribution of residence times, dimensionless
$f_{S.F.D.}$	Fractional conversion calculated by using the slug-flow distribution of residence times, dimensionless
F_i	Relative conversion difference based upon the distribution function i, dimensionless
$F(\theta)$	Cumulative distribution function for the outlet stream, dimensionless
G	Defined by Equation (14)
H	Defined by Equation (15)
I	Intensity of the emergent light beam

I_o	Intensity of the incident light beam
$I(\theta)$	Non-cumulative distribution function for the reactor, dimensionless
k	First-order reaction rate constant, sec.$^{-1}$
k_{C_o}	First-order reaction rate constant in a solution whose initial concentration of tertiary-butyl-bromide is C_o moles/l., sec.$^{-1}$
K	Absorption coefficient
n	Degrees of freedom
N	Sample size
p	Number of variances
Q	Quantity of tracer injected in the pulse, grams
$r_{i \cdot jk}$	Multiple correlation coefficient
R	Gas constant, 1.987 cal./mole °K.
t	Time measured from the introduction of the signal in a tracer experiment, sec.
t	Deviation of a variable from its mean divided by an estimate of the universe standard deviation based on the sample standard deviation, dimensionless
t_α	α point of a t distribution, dimensionless
T	Temperature, °C
V	Volume of flow system, ml.
y	Actual frequency
Y	Theoretical frequency
Z	A variable measured from the universe mean in terms of the universe standard deviation

Other Symbols:

α	Level of significance
θ	Number of residence times, dimensionless
τ	Mean residence time, $\frac{V}{v}$ sec.
σ^2	Variance
σ'	Standard error
$\hat{\sigma}_{\bar{F}}$	An estimate of $\sigma'_{\bar{F}}$
$\sigma'_{\bar{F}}$	Standard error of $\bar{F}$
χ^2	Sample sum of squares divided by the universe variance
∞	Infinity

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