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## A study of the effect of a dielectric field on the solvolysis rate of tert-butyl bromide in a recycle reactor

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A STUDY OF THE EFFECT OF A DIELECTRIC  
FIELD ON THE SOLVOLYSIS RATE OF  
TERT-BUTYL BROMIDE IN A RECYCLE REACTOR

BY

ROJF L. BALL B.S.(CH.E.)

UNIVERSITY OF CAPE TOWN

A THESIS  
PRESENTED IN PARTIAL FULFILLMENT OF  
THE REQUIREMENT FOR THE DEGREE  
OF  
MASTER OF SCIENCE IN CHEMICAL ENGINEERING  
AT  
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey  
1972

APPROVAL OF THESIS

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FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

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FACULTY COMMITTEE

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CHAIRMAN

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Newark, New Jersey

April 1972

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SECTION 1

A B S T R A C T

Previous experiments at Newark College of Engineering have shown that a dielectric field can effect the rate of a chemical reaction. A theory was developed in this thesis to postulate how a dielectric field can increase the rate of a first order reaction whose rate determining step is an ionization. An experimental procedure was developed to measure the reaction rate constant of a tertiary alkyl halide with a solvent to test this theory. The solvolysis of tert-butyl bromide in aqueous ethanol (80%), aqueous dioxane (75%) and aqueous acetone (75%) solvent systems were the reactions selected for study. A total of 17 runs were carried out in a recycle reactor. A small increase was found in the reaction rate constant upon the application of the dielectric field using the aqueous ethanol (80%) solvent system. Small decreases in the reaction rate constants upon the application of the field were found using the other two solvent systems. All changes were too small to say with certainty that the dielectric field had any effect upon the reaction rate constants. Further experiments at higher field strengths are necessary to supplement the result of this thesis.



## SECTION 2

### INTRODUCTION

Experiments carried out at Newark College of Engineering during the Spring Semester in 1971 have shown that a dielectric field applied across the full length of a plug flow reactor has influenced the rate of the reaction taking place within the reactor<sup>(1)</sup>. The reaction studied was the saponification of ethyl acetate. The results of that investigation will be briefly discussed here as the topic of this master's thesis is a sequel to those experiments. The results of the experiments have shown that the dielectric field slowed the rate of reaction to a significant extent. It further demonstrated that the effect of the field on the reaction rate was more pronounced at lower Reynolds numbers and that the more intense the field, the more the rate of reaction was slowed. A hypothesis was developed to explain these observations.

The saponification of ethyl acetate with sodium hydroxide is a second order nucleophilic substitution reaction. The sodium hydroxide is first ionized and the nucleophilic hydroxide ion attacks the partially positively charged carbonyl carbon of the ester group<sup>(1,2)</sup>. The rate of reaction is proportional to the concentrations of both the base and the ester substrate.

The theory postulated for the decrease in reaction rate is that a degree of physical separation is obtained between the positive

INTRODUCTION (continued)

carbonyl ion and the negative hydroxide ions when the dielectric field is applied. Turbulence will mix the ions, thus the theory is further plausible because the effect of the field is the strongest at low Reynolds numbers where turbulence is least. The overall affect of applying the dielectric field is a segregation of ions slowing down their probability of collision with each other and hence decelerating their rate of reaction. This theory, however, is not correct as the ester does not ionize before reacting with the hydroxide ions.

Having thus established experimentally that the application of a dielectric field can have an affect on the rate of a reaction by a mechanism which has not been correctly postulated, the task was now to find a reaction that would be accelerated rather than slowed by the application of the same dielectric field. The aim of this thesis has been to develop a theory on how a dielectric field can accelerate the rate of a reaction and to test that theory by experiment.

A large group of unimolecular nucleophilic substitution reactions have an ionization step which is rate determining. The rate of reaction should hence be increased if the rate of ionization could be accelerated. A theory will now be developed to explain how the solvolysis rate of a tertiary alkyl halide should be increased by the application of a dielectric field.

INTRODUCTION (continued)

For a given halogen atom the order of reactivity of the alkyl halide is tertiary secondary primary. This may be explained as follows<sup>(11)</sup>. In the above-mentioned solvolysis reaction the covalently bound halogen atom is converted into a halogen ion as the first step of the overall reaction. It is, therefore, logical to suppose that, in the structure of the tertiary alkyl halide, any force which tends to increase the polarity of the carbon-halogen bond will actually weaken this bond. Furthermore, all experimental and theoretical work has shown that as the polarity of a bond increases, its length will also increase with a consequent decrease in strength. Therefore, the more ionic the character of the bond, the weaker the bond and the greater the reactivity of the halide atom.

Since alkyl groups are electron repelling or electron releasing, the more alkyl groups attached to the carbon atom of the carbon-halogen bond, the greater is the electron density on this carbon atom, and the greater is the repulsion of the electron pair towards the halogen atom of carbon-halogen bond. Any external force that can simulate this electron repelling effect of the carbon atom or increase the electron attracting effect of the halogen atom should increase the rate of ionization of the alkyl halide molecule by converting the halogen atom into a halogen ion.

The application of a dielectric field will cause the dipolar molecule to be oriented with their dipoles parallel to the direction of the

INTRODUCTION (continued)

field. Turbulence in the reaction tube will reduce this tendency so reactions were carried out in the laminar flow range. If the dielectric field is strong enough additional ionization should occur as the electrons are physically pulled towards the halogen atom of the molecule which is pointing towards the positive pole of the dielectric field. This will increase the electronegativity of the halogen atom and increase the positive charge on the central carbon atom. The application of the dielectric field, therefore, facilitates charge separation in the tert-alkyl halide molecule and induces additional polarization. The dielectric field, therefore, changes the average electron distribution in comparison with that of an identical molecule not subjected to the dielectric field. This means that polarization deforms both bonding and non-bonding electron clouds substantially. As the cleavage of the bonding electron clouds determines the rate of a reaction, a deformation of these clouds to weaken the bond will increase ionization and the rate of that reaction. The task set in this thesis is to prove that the application of a dielectric field across a plug flow reactor will increase the rate of a unimolecular nucleophilic substitution reaction, whose rate determining step is the ionization of the starting material. This reaction has a tertiary alkyl halide as its starting material.

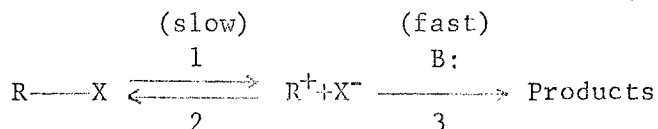
### SECTION 3

#### SELECTION OF REACTION SYSTEM

Having decided to use a unimolecular nucleophilic substitution reaction, the next step was the selection of a particular system.

In order to have a large excess of the other reactant or reactants, a solvolysis reaction was used. In this system one or more of the reactants also acts as the solvent and is present in a large excess. Solvolysis reactions of the above type are also very numerous so it was decided to use a system which is well known, has reasonable reaction times, does not cost too much per run, and is readily available. For these reasons the solvolysis of tert-butyl bromide in aqueous ethanol (80%), aqueous dioxane (75%), and aqueous acetone (75%) solvent systems was selected for study. The percentage figures are on a volume basis and the percentage refers to the non-aqueous component in each of the three systems. Furthermore, the reaction rate constant for the solvolysis of tert-butyl bromide in aqueous ethanol (80%) at 25°C is accurately known<sup>(7)</sup> and will be used to determine the accuracy of the experimental procedure.

The solvolysis of tert-butyl bromide is a first order reaction with the ionization step being rate controlling<sup>(3,4)</sup>. This  $S_N1$  mechanism consists of three steps: (1) a reversible ionization step; (2) a reversal of step 1; and (3) the reaction of the carbonium ion with a nucleophilic solvent molecule.

SELECTION OF REACTION SYSTEM (continued)

Where: R-X = tert-butyl bromide  
 $\text{R}^+$  = Carbonium ion  
 $\text{X}^-$  = Bromide ion  
 B: = the solvent molecule

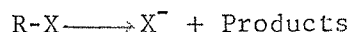
The application of the dielectric field should have a double effect on the overall reaction. It should speed up the ionization in step 1 and slow down the rate of step 2 by hindering the recombination of the  $\text{R}^+$  and  $\text{X}^-$  ions to reform the tert-butyl bromide molecule. Step 3 will not be accelerated but also not hindered by the application of the field. Although the carbonium ions will tend to migrate towards the negative plate of the dielectric field, they will be surrounded everywhere in the solvent by a large excess of nucleophilic solvent molecules, whether there is a dielectric field or not. The reaction will be carried out at all times in the region of laminar flow to keep mixing to an absolute minimum.

A great advantage in studying the solvolysis reaction chosen is the ease with which the disappearance of the tert-butyl bromide can be followed. The amount of bromide ion liberated is directly proportional to the amount of tert-butyl bromide reacted. The amount of bromide ion liberated can be titrated directly against a dilute

SELECTION OF REACTION SYSTEM (continued)

sodium hydroxide solution. The method is accurate because of the low concentration of bromide ion in the reaction system. At this concentration and temperature the vapor pressure of the bromide in solution is so low that essentially no bromide escapes from the reaction mass<sup>(5)</sup>.

The reaction is irreversible and may be presented as follows for kinetic purposes:



Where:            R-X        = tert-butyl bromide  
                   X<sup>-</sup>        = bromide ions  
                   Products = depends on solvent

and the reaction rate is given by<sup>(6)</sup>:

$$\text{Rate} = - \frac{d[RX]}{dt} = \frac{d[X^-]}{dt} = K [RX]$$

where:            [RX]        = Concentration of tert-butyl bromide  
                   [X<sup>-</sup>]        = Concentration of bromide ions  
                   K            = Reaction rate constant

The effect of the dielectric field on the reaction will be found by running the reaction under exactly the same conditions except for the presence of the field for each of the three solvent systems. The reaction rate constant is then found graphically, the actual slope being found by the least squares method.

#### SECTION 4

##### EXPERIMENTAL APPARATUS

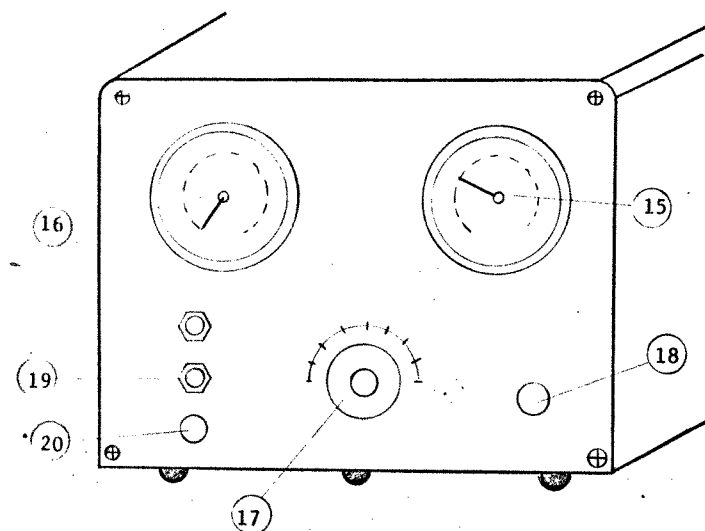
The investigations of the effect of the dielectric field on the saponification of ethyl acetate were carried out in a "once through" plug flow reactor<sup>(1)</sup>. This gives very low residence times resulting in low conversions. A small portion of total reaction could only be followed and different residence times were obtained by running at different flow rates. For the solvolysis of tert-butyl bromide a residence time of at least 90 minutes was required to follow about 90% of the total reaction<sup>(7)</sup>. For this reason the "once through" plug flow reactor was converted into a recycle reactor.

A recycle reactor behaves kinetically like a batch reactor and the reaction rate constant can be very easily found<sup>(6)</sup>. The system will also behave as a constant volume batch reactor if the samples, removed during the course of the reaction, are small compared to the total volume of the reactor. The recycle reactor system has the advantage of having the tubular reactor, with the possibility of applying the dielectric field, and being a batch reactor allowing for any desired residence time. Sampling was carried out in all runs for about 90% of the total conversion, making it possible for a complete picture of the reaction to be obtained.

When the dielectric field is applied to the tubular part of the reaction system it behaves like two batch reactors in series. An



DETAILS OF HIGH VOLTAGE GENERATOR



DETAIL VIEW OF REACTION TUBE WITH INSULATION REMOVED (not to scale)

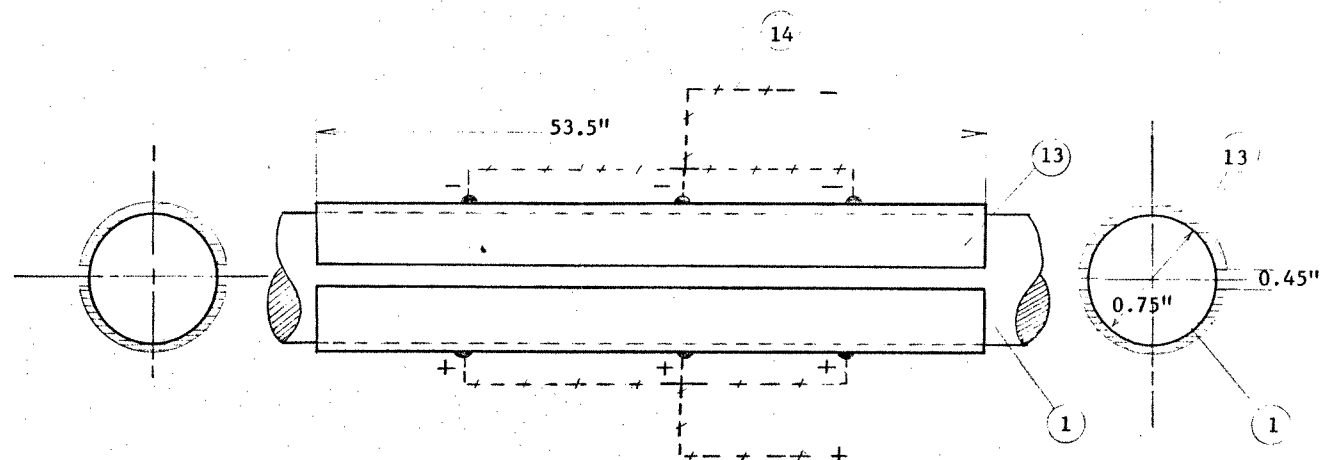
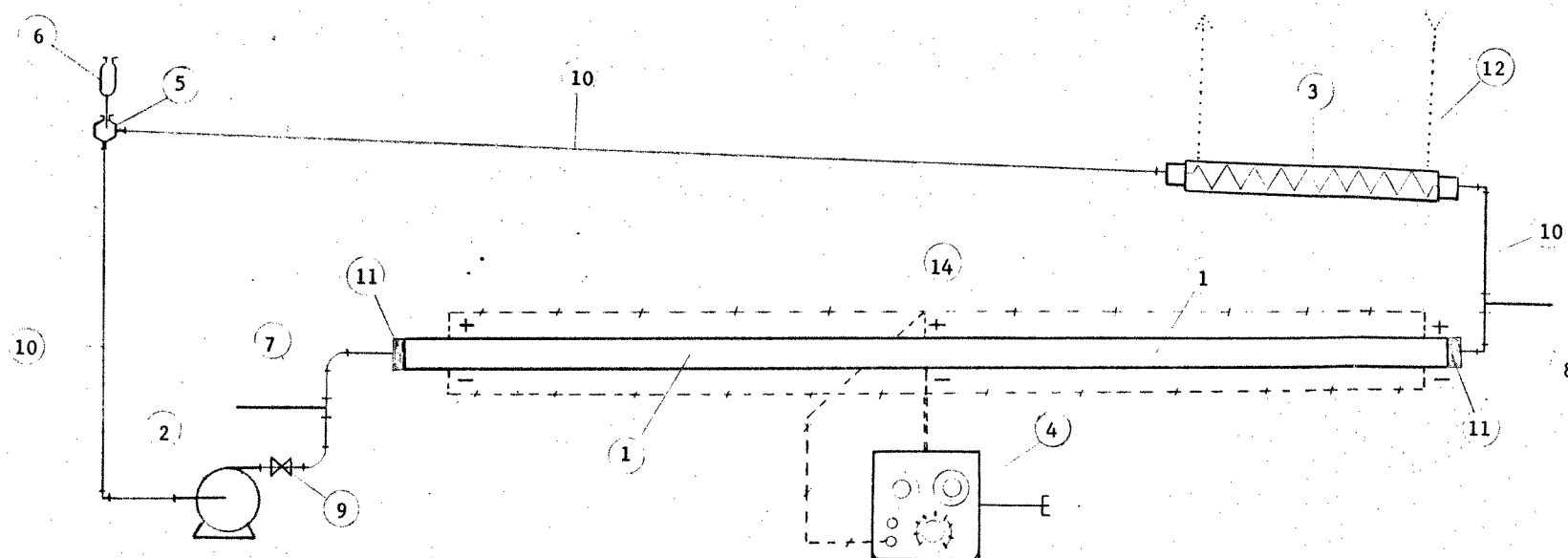


DIAGRAM OF REACTION SYSTEM (not to scale)



#	ITEM	MATERIAL
1	0.75" I.D. Reaction Tube	Glass
2	0.10 H.P. Cent. Pump	Penton
3	Water Cooler	Glass
4	Hi Voltage Generator	-
5	Sampling Well	Glass
6	Charging Funnel	Glass
7	Thermometer (1)	Alcohol
8	Thermometer (2)	Mercury
9	Pinch Clamp	S. Steel
10	0.25" O.D. Tubing	Glass
11	Stoppers	Rubber
12	Tubing for Cooling Water	Rubber
13	Plating for Dielectric Field	Copper
14	Electric Wiring	Copper
15	Kilovolt Indicator	-
16	Milliampere Indicator	-
17	Power Control	-
18	Power Indicating Light	-
19	Earth Connection (+)	-
20	Fuse	-

DRAWN BY: *Kelly L. Ball*

EXPERIMENTAL APPARATUS (continued)

adjustment has to be made that part of the reaction taking place outside the influence of the dielectric field. A new titration reading is calculated to simulate a recycle reactor completely under the influence of the dielectric field.

The main components of the experimental apparatus making up the reaction system are: (1) a 3/4" I.D. glass tube covered for 53½" by thin copper plating, heavily insulated; (2) a 0.10 H.P. pump with a penton impeller housing; (3) a glass condenser acting as a cooler; and (4) a high voltage generator. There are two calibrated thermometers in the system, one being just before and one just after the 3/4" I.D. glass tubing. All tubing connecting the major piece of apparatus are ½" O.D. glass. The reactants are charged and samples are taken from a small sampling well on the suction side of the pump. (See sketch of apparatus for details.)

The rate controlling ionization step is a heterolysis of the carbon-halogen bond. Since a covalent bond is being broken the reaction is endothermic<sup>(8)</sup>. The heat being removed from the system by the cooler, therefore, comes from the pump. This enters the reaction system at a steady rate and temperature control to within 1°C of the desired temperature is possible with experience. The flow within the system is kept in the laminar range (Reynolds Number approximately 500) by means of a pinch cock close to the pump in the discharge tube. The setting was kept constant throughout the runs insuring a consistent flow rate.

EXPERIMENTAL APPARATUS (continued)

There is a serious limitation in this reaction system as far as the application of the dielectric field is concerned. Arcing occurs between edges of the plates when a dielectric field above 9.0 kilovolts is applied. This is because there is only a 0.45" gap between the edges of the plates. Increasing the distance between the plates would mean decreasing the effective area of the plates. All runs were carried out at a 8.0 kilovolts potential difference. Even at this reading the insulation between the edges of the plates would break down with time and the strength of the field decayed. The insulation had to be changed several times during the course of the runs. As the tube is heavily insulated to prevent accidental discharge this was a painstaking operation.

SECTION 5

EXPERIMENTAL PROCEDURE

The disappearance of the tert-butyl bromide during the course of the reaction is best determined by measuring the rate of formation of the bromide ions. The bromide ions are present in a very low concentration but can be accurately measured by titration against a dilute sodium hydroxide solution. The titration is carried out in methanol or ethanol with phenolphthalein as indicator and gives a distinct end point<sup>(9)</sup>. The titration is completely quantitative as the moles of bromide ion determined by titration in the "time infinity" sample were found equal, within the limits of experimental error, to the moles of tert-butyl bromide weighed out. The reaction goes to completion at a 100% conversion of ter-butyl bromide when a large excess of the other reactants is present such as in a solvolysis reaction. Titration is carried out by means of a 10 ml micro-burette which allows titration values to be read accurately to two decimal places. A pre-determined blank is subtracted from each titration reading.

The experimental procedure consists of making up as accurately as possible a 0.1M solution of tert-butyl bromide in either aqueous ethanol (80%), aqueous dioxide (75%), or in aqueous acetone (75%).

The remainder of the procedure is the same for whatever solvent system is used. The solution is well mixed and charged to the reaction system through the charge funnel as rapidly as possible. The recycle pump is turned on as soon as charging begins. The temperature is adjusted

EXPERIMENTAL PROCEDURE (continued)

to 25°C by adjusting the cooling water flow to the cooler and kept as close as possible to 25°C throughout the reaction. Samples are taken at regular time intervals with a 1 ml syringe through the sampling well. The sample solution is immediately quenched into a preweighed quantity of pure methanol. This quenching action slows the reaction rate by about a factor of 10.<sup>(10)</sup>

The quench solution is weighed at once so that the weight of the sample is obtained before titration. Titration is carried out immediately after weighing against a 0.0206 N solution of sodium hydroxide. The total time from removal of sample till the end of titration takes about two minutes. Allowing for the factor of 10, the actual time elapsed till titration is about 12 seconds, a time too small to effect the accuracy of the readings. The titration readings increase from about 1 ml after 10 minutes to 4.5 ml when about 90% of the reaction is completed and the run is stopped. The "time infinity" sample is found by letting a portion of the reaction mass stand overnight and carrying out the titration on the next day. Since the moles of tert-butyl bromide reacted are inversely proportional to the amount of bromide ion formed and therefore to the titration readings, the progress of the reaction is followed from the titration readings. The reaction being of the first order, the reaction rate constant can be easily found graphically.<sup>(6)</sup> The tables and the graphs in the appendix give details of procedure.

EXPERIMENTAL PROCEDURE (continued)

A slight difficulty arises in determining the reaction rate constant when the dielectric field is applied to the 3/4" glass tube, which is only part of the total reaction system. The titration reading must be adjusted to take into account the part of the reading which is due to the bromide ion formed by the reaction outside the influence of the dielectric field. This is done by simulating the system to be two constant volume batch reactors in series. The average titration readings for each solvent system were plotted separately. This made it possible to obtain the average incremental titration reading for each time segment (see graphs 18-20). The time the reaction takes place away from and under the influence of the dielectric field is found by taking the volumes of the two simulated reactors. The volume of the reactor under the influence of the dielectric field stays at 371 ml while the other reactor outside the field is approximately 570 ml depending on just how full the reactor has been filled. The volume of the reaction system varied from 562 ml to 572 ml throughout runs 1 to 17.

Approximately two-thirds of the reaction takes place in the dielectric field and one-third outside it. The following equation was developed for adjusting the titration reading to give an equivalent reading for the whole reaction system under the influence of the dielectric field.

$$T_{n+1}(ad) = T_n(ad) + \left[ \frac{(T_{n+1}-T_n)Act - F(T_{n+1}-T_n)Ave}{(1 - F)} \right]$$

$$\text{and } F = 1 - \frac{371}{V}$$

EXPERIMENTAL PROCEDURE (continued)

where  $T_{n+1}(ad)$  = Adjusted titre for sample  $N+1$

$T_n(ad)$  = Adjusted titre for sample  $N$

$N$  = Sample number at time  $t$

$N+1$  = Following sample number at time  $t + \Delta t$

$Act$  = Actual values from run

$Ave$  = Average values from graphs 18-20

$F$  = Adjustment factor

$V$  = Average volume of reaction mass (given in tables  
for each run)

SECTION 6

SUMMARY OF RESULTS

A total of seventeen recorded runs were carried out. The details of each are presented in tabular form in the appendix. Table A gives a complete summary of the reaction rate constants. Nine runs were carried out using the aqueous ethanol (80%) system, four runs using the aqueous dioxane (75%) system, and four runs using the aqueous acetone (75%) system. All values of the reaction rate constant were close to each other within a particular solvent system. Each individual run gave points on a graph which made a good straight line. There were very few points which were far off the best straight line. Since it is known that the reaction is of the first order, the reaction system behaved as a constant volume batch reactor because it gave points which made a straight line. It showed that the analytical procedure is applicable and accurate<sup>(6)</sup> because it gives reaction rate constants very close to the literature value. The following is a summary of the runs.

Run #1: This gave a reaction rate constant of  $65.7 \times 10^{-5} \text{ sec.}^{-1}$ .

This is much too high as the reaction rate constant for aqueous ethanol (80%) solvent system is given as  $37.9 \times 10^{-5} \text{ sec.}^{-1}$  in the literature<sup>(7)</sup>. The reaction system was physically not in its final form for #1. The temperature was only measured at one point in the reaction system. As can be seen from Table #1 the temperature was high during most of the earlier part of this run.



TABLE A  
REACTION RATE CONSTANTS (K)

Run #	Solvent System (Volume Basis)	Field Strength (Kilovolts)	$10^5 \text{ K}$ sec. <sup>-1</sup>
1	Aqueous Ethanol (80%)	0.0	65.7
2	" " "	0.0	40.1
3	" " "	0.0	39.3
4	" " "	0.0	35.9
5	" " "	0.0	37.0
6	" " "	8.0	38.2
7	" " "	8.0	47.1
8	" " "	8.0	41.6
9	" " "	8.0	39.9
10	Aqueous Dioxane (75%)	0.0	26.5
11	" " "	0.0	27.6
12	" " "	8.0	26.4
13	" " "	8.0	25.8
14	Aqueous Acetone (75%)	0.0	28.7
15	" " "	0.0	29.9
16	" " "	8.0	29.1
17	" " "	8.0	28.5

NOTE: The percentages are on a volume basis and refer the non-aqueous component of the solvent system.

SUMMARY OF RESULTS (continued)

Run #2: The experimental equipment was improved for run #2 but still only one thermometer was installed in the system. Temperature control was better but since it was only read at one point it did not give a true picture of the overall temperature in the reaction system. The reaction rate constant of  $40.1 \times 10^{-5} \text{ sec.}^{-1}$  was nevertheless within about 5.8% of the literature value.

Run #3: The reaction system was in its final form for this run. Two calibrated thermometers were now installed at positions shown in the sketch. The reaction rate constant of  $39.3 \times 10^{-5} \text{ sec.}^{-1}$  found, is further in the right direction. Only one point is quite far off the straight line (see Graph 5).

Run #4: This run was carried out without any modification of the reaction system to confirm the result obtained in the previous run. A reaction rate of  $35.9 \times 10^{-5} \text{ sec.}^{-1}$  was obtained with all points forming a good straight line. Since this result was within 6.4% of the literature value it was decided that equipment and method was made as suitable as possible.

Run #5: This was to have been the first run using the dielectric field. A field strength of 8.0 kilovolts was recorded over the first 10 minutes of the run. When taking the reading at 20 minutes, the field had decayed as no voltage indication was obtained. The run was continued without the field.

SUMMARY OF RESULTS (continued)

Run #5: (continued)

A value of  $37.0 \times 10^{-5} \text{ sec.}^{-1}$  was obtained for the reaction rate constant which was the closest yet to the literature value of  $37.9 \times 10^{-5} \text{ sec.}^{-1}$ .

Run #6: This was the first run completely carried out under the influence of the field. The field, however, did not influence the reaction rate constant, which was found to be  $38.2 \times 10^{-5} \text{ sec.}^{-1}$  and very close to the literature value of  $37.9 \times 10^{-5} \text{ sec.}^{-1}$ . It should be noted that a considerable amount of undercooling took place. This took place because the new pump was used for the first time, which as it turned out, does not heat up the system as much as the pump previously used. Having no provision for heating the reaction mass in the system, it took some time to reach  $25^{\circ}\text{C}$  (see Table #6). However, the points were still all in a good straight line, so the effect of the  $2^{\circ}\text{C}$  undercooling must have been very small.

Run #7: The field seemed to have a definite effect on the reaction rate constant in this run. The reaction rate constant obtained was  $47.1 \times 10^{-5} \text{ sec.}^{-1}$ . This effect was not confirmed in the next two runs, therefore, there must have been some experimental error in the run. This run was

SUMMARY OF RESULTS (continued)

Run #7: (continued)

carried out just before the electronic calculators were moved from the old chemical engineering building. The calculations on this run were carried out about one month later when a new electronic calculator was found. At that stage it could not be ascertained whether the blank had been subtracted from the titration readings. It now seems, that it had not. Subtracting the blank from each reading would give normal titration readings and a much lower reaction rate constant.

Run #8: This gave a reaction rate constant of  $41.6 \times 10^{-5} \text{ sec.}^{-1}$ .

This is a little higher than the literature value but does not confirm the high value of  $47.1 \times 10^{-5} \text{ sec.}^{-1}$  from the previous run. Since the situation was inconclusive at this point it was decided to make another run using the field with the aqueous ethanol (80%) solvent system.

Run #9: Another inconclusive run giving a reaction rate constant of  $39.9 \times 10^{-5} \text{ sec.}^{-1}$ . This is again higher than the literature value of  $37.9 \times 10^{-5} \text{ sec.}^{-1}$  but not enough to say with certainty that the dielectric field has had a definite effect.

SUMMARY OF RESULTS (continued)

Runs # 10 and 11: These were the first two runs using a different solvent system namely aqueous dioxane (75%). No dielectric field was applied for these two runs. The reaction rate constant values of  $26.5 \times 10^{-5} \text{ sec.}^{-1}$  and  $27.6 \times 10^{-5} \text{ sec.}^{-1}$  were close enough to each other to be used as the base for this system. The points on the graphs, however, were not as good as the aqueous ethanol (80%) system.

Runs # 12 and 13: These runs were using the aqueous dioxane (75%) solvent system with the application of the field at 8.0 kilovolts. The reaction rate constants obtained were  $25.4 \times 10^{-5} \text{ sec.}^{-1}$  and  $25.8 \times 10^{-5} \text{ sec.}^{-1}$  respectively. These are both a little below the values without field, but being on an average only about 3% different, it cannot be stated with certainty that the field had any effect.

Runs #14 and 15: Both these two runs used aqueous acetone (75%) as the solvent system. No dielectric field was applied for these two runs. The reaction rate constant of  $28.7 \times 10^{-5} \text{ sec.}^{-1}$  and  $29.9 \times 10^{-5} \text{ sec.}^{-1}$  were

SUMMARY OF RESULTS (continued)

Runs # 14 and 15: (continued)

close enough to each other to act as a base for this system. The points on the graphs formed a better straight line than the aqueous dioxane (75%) system but not as good as the aqueous ethanol (75%) system. Temperature control was very good for both runs.

Runs # 16 and 17: These were the last two runs made. The solvent system was aqueous acetone (75%) with the application of the dielectric field at 8.0 kilovolts. The reaction rate constants obtained were  $29.1 \times 10^{-5} \text{ sec.}^{-1}$  and  $27.5 \times 10^{-5} \text{ sec.}^{-1}$ . They are both a little below the values obtained without the field. They are, however, on the average less than 2% different. This is too small to state that the field had any influence.

SECTION 7

DISCUSSION OF RESULTS

The values of the reaction rate constants obtained showed that the reaction system behaved as a constant volume batch reactor and that the experimental procedure was capable of giving consistent results. Three consecutive runs, #3, #4 and #5, gave reaction rate constants with a maximum deviation of less than 4.0% from their average value. The deviation of the average value was also less 1.5% of the literature value<sup>(7)</sup>. Considering the reaction system is not, strictly speaking, a constant temperature reactor, the results are better than were expected. The main sources of error in the procedure were 1) the difficulty of getting an end point deviating less than 2% from the correct value and 2) the difficulty of getting exactly the best straight line through the graphical points, especially if they are a bit scattered as in the aqueous dioxane (75%) solvent system. The latter difficulty was overcome by finding the actual slope by the method of least squares. It should, therefore, be assumed that reaction rate constant differences of less than 4.0% have no significance unless these are based on many consecutive runs. The reaction system and the reaction procedure is, therefore, suitable for carrying out original investigations, and obtaining accurate results.

DISCUSSION OF RESULTS (continued)

An average value of the reaction rate constant is given for each solvent system, with and without the field, in tabular form below:

Run #'s	Solvent System (volume Basis)	Average K 0.0 Kilovolts	Average K 8.0 Kilovolts	Increase
3,4,5 6,8,9	Aqueous Ethanol (80%)	$37.4 \times 10^{-5} \text{ sec.}^{-1}$	$39.9 \times 10^{-5} \text{ sec.}^{-1}$	+7.3%
10,11 12,13	Aqueous Dioxane (75%)	$27.0 \times 10^{-5} \text{ sec.}^{-1}$	$26.1 \times 10^{-5} \text{ sec.}^{-1}$	-3.3%
14,15 16,17	Aqueous Acetone (75%)	$29.3 \times 10^{-5} \text{ sec.}^{-1}$	$28.8 \times 10^{-5} \text{ sec.}^{-1}$	-1.7%

With the aqueous alcohol (80%) solvent system the average value of the reaction rate constant obtained for the runs using the dielectric field is 7.3% higher than those without the field. Assuming that the slightly higher values were due to the influence of the field, it would seem that at 8.0 kilovolts the field is just beginning to exert an influence on the rate of reaction. A considerably higher field strength should be used to enlarge these results.

A slightly lower average reaction rate constant was found for runs using the dielectric field with the aqueous dioxane (75%) solvent system. This difference was only 3.3% and is well within the accuracy limits of the



DISCUSSION OF RESULTS (continued)

experimental procedures which has been set at 4%. The points on the graphs are a little scattered so it is difficult to determine which is exactly the correct straight line through all the points. This takes away from the accuracy of the experimental procedure especially for this solvent system. The maximum deviation of any value of the reaction rate constant from the average of all the runs using the aqueous dioxane system (75%) was only 3.8%. The dielectric field can safely be said to have had no effect on the rate of this reaction.

A slightly lower average reaction rate constant was also found using the dielectric field with the aqueous acetone solvent system. This difference was only 1.7% and is well within the accuracy limits of the experimental procedures which has been set at 4%. The maximum deviation of any value of the reaction rate constant from the average of all the runs using the aqueous acetone (75%) solvent system was only 2.8%. Therefore, the dielectric field can safely be said not to have had any influence on the rate of this reaction.

It may also be seen from the plots of the reaction rate constants (see graphs #1-#17) that most of the points for the aqueous ethanol system (75%) are in a much better straight line than for the other two solvent systems. The values obtained for the reaction rate constants are much more accurate in system. The increase of the reaction

DISCUSSION OF RESULTS (continued)

rate constant for this system is of much greater significance than the decrease in the other two systems. The 7.3% increase, therefore, has a good possibility of being the result of the field rather than being due to the normal distribution of values in experimental results.

Assuming this to be true, the obvious conclusion would have been to increase the strength of the dielectric field. The voltage generator has a rating up to 50 kilovolts so power supply was no problem.

However, there is electrical discharge between the edges of the plates above 9.0 kilovolts. Since it was only discovered after many runs and much time that 8.0 kilovolts was not powerful enough to effect the rate of the reaction more than slightly, there was no time or money to construct a newly shaped reactor and make a series of new runs. This must regretfully be left to future investigators.

SECTION 8

A P P E N D I X

Table 1 - 17	-	Details of Runs
Graphs 1 - 17	-	Reaction Rate Constants
Graphs 18 - 20	-	Average Titration Values
Table 18	-	Sample Weights
Table 19	-	Equipment Details
Table 20	-	Reagent Details
Table 21	-	Abbreviations
References	-	Literature cited

TABLE # 1

Run: #1

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	-	27	-	-	-	-	-	6.27	0.000
1	10	-	28	-	2.57	1.058	2.43	-	3.84	0.490
2	17	-	30	-	3.04	1.055	2.88	-	3.39	0.615
3	26	-	28	-	4.16	1.037	4.01	-	2.26	1.020
4	33	-	26	-	4.94	1.065	4.64	-	1.63	1.347
5	41	-	25	-	5.33	1.053	5.06	-	1.21	1.645
6	50	-	25	-	5.65	1.052	5.37	-	0.90	1.941
7	60	-	26	-	5.89	1.039	5.67	-	0.60	2.346
8	$\infty$	-	26	-	6.65	1.060	6.27	-	0.00	$\infty$

Room Temperature: 26°C

C. Water Temperature: 17°C

Volume of Reaction Mass: 565 ml

Initial Concentration of RX: 0.2615 gm. moles/litre (weight)

Final Concentration of X: 0.2620 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0418 gm. moles/litre

Weight of t-Butyl Bromide: 21.5050 gms.

Density of Reaction Mass: 0.860 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $65.7 \times 10^{-5} \text{ sec.}^{-1}$

Run: #1

Solvent: Aqueous Ethanol (80%)

Field Strength: 0.0 Kilovolts

GRAPH # 1

Reaction Rate Constant (K):  $65.7 \times 10^{-5} \text{ sec.}^{-1}$

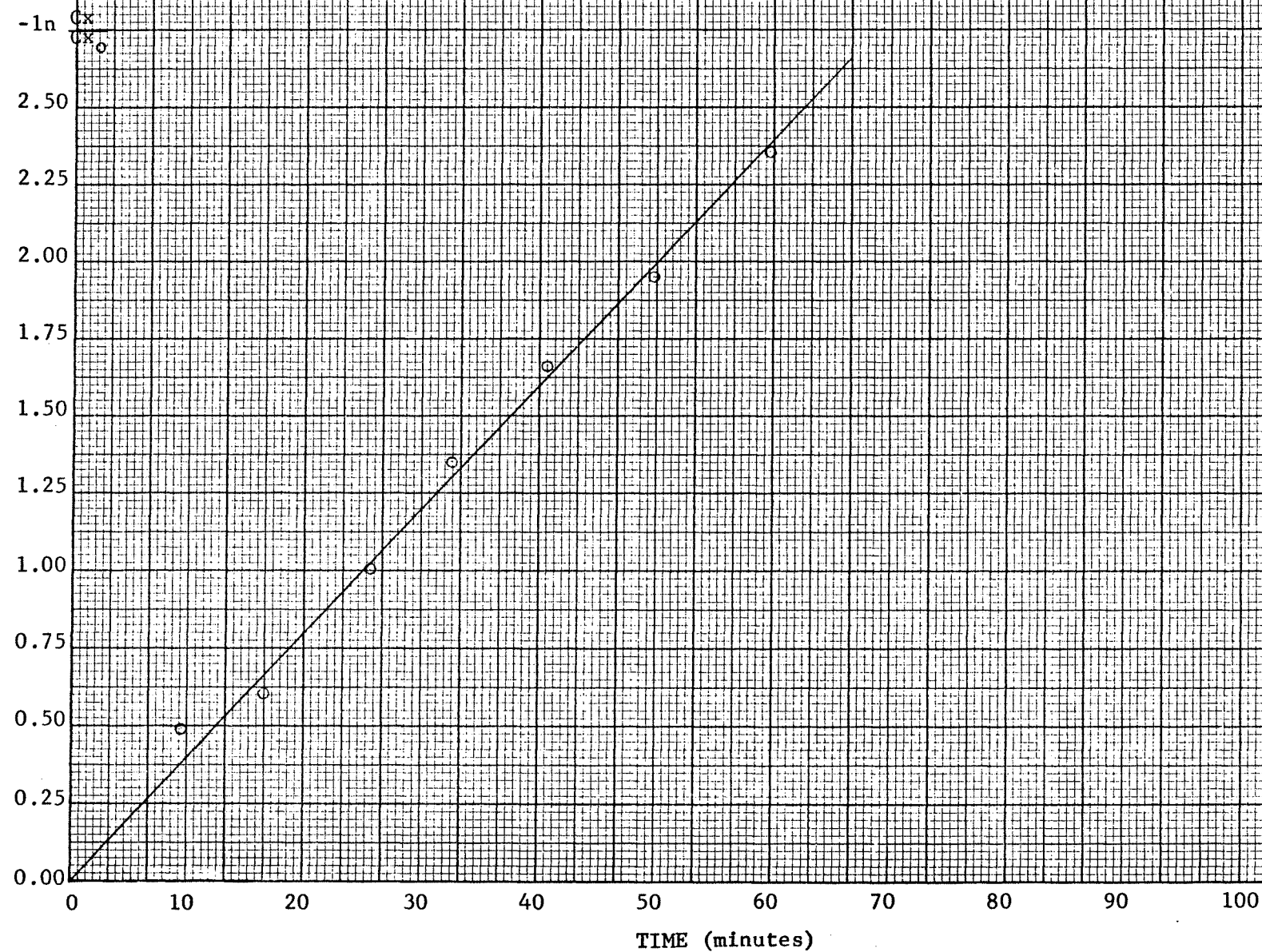


TABLE # 2

Run: #2

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x_0}}$
0	-	-	25	-	-	-	-	-	5.76	0.000
1	10	-	25	-	1.55	1.086	1.43	-	4.33	0.285
2	15	-	25	-	2.06	1.039	1.98	-	3.68	0.448
3	20	-	25	-	2.75	1.064	2.58	-	3.18	0.552
4	25	-	24	-	3.11	1.087	2.86	-	2.90	0.686
5	30	-	25	-	3.25	1.043	3.11	-	2.65	0.776
6	36	-	25	-	3.68	1.048	3.51	-	2.25	0.940
7	45	-	25	-	4.17	1.079	3.86	-	1.90	1.109
8	55	-	25	-	4.46	1.047	4.26	-	1.50	1.345
9	70	-	24	-	5.05	1.071	4.71	-	1.05	1.702
10	85	-	25	-	5.25	1.056	4.97	-	0.79	1.986
11	105	-	25	-	5.60	1.064	5.26	-	0.50	2.444
12	$\infty$	-	25	-	6.15	1.068	5.76	-	0.00	$\infty$

Room Temperature: 26°C

C. Water Temperature: 18°C

Volume of Reaction Mass: 570 ml

Initial Concentration of RX: 0.1150 gm. moles/litre (weight)

Final Concentration of X: 0.1175 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 9.4480 gms.

Density of Reaction Mass: 0.850 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $40.1 \times 10^{-5} \text{ sec.}^{-1}$

Run: #2

Solvent: Aqueous Ethanol (80%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $40.1 \times 10^{-5} \text{ sec.}^{-1}$

GRAPH # 2

$\ln \frac{C_x}{C_0}$

2.50

2.25

2.00

1.75

1.50

1.25

1.00

0.75

0.50

0.25

0.00

0

10

20

30

40

50

60

70

80

90

100

TIME (minutes)

K&E 10 X 10 TO 1/2 INCH  
46 1320  
MADE IN U.S.A.  
KEUFFEL & ESSER CO.

TABLE # 3

Run: #3

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	-	-	25.0	25.0	-	-	-	-	4.92	0.000
1	10	-	24.8	24.9	1.02	1.063	0.96	-	3.96	0.222
2	20	-	25.2	25.5	1.92	1.080	1.77	-	3.15	0.457
3	30	-	25.5	25.9	2.77	1.082	2.56	-	2.36	0.757
4	40	-	25.3	25.6	3.09	1.057	2.92	-	2.00	0.930
5	50	-	25.5	25.5	3.37	1.075	3.13	-	1.79	1.053
6	60	-	25.5	25.8	3.91	1.068	3.66	-	1.26	1.424
7	75	-	25.0	25.3	4.30	1.068	4.03	-	0.89	1.815
8	90	-	24.5	24.8	4.58	1.078	4.25	-	0.67	2.135
9	$\infty$	-	24.4	24.7	5.28	1.067	4.92	-	0.00	$\infty$

Room Temperature: 25°C

C. Water Temperature: 15°C

Volume of Reaction Mass: 565 ml

Initial Concentration of RX: 0.1003 gm. moles/litre (weight)

Final Concentration of X: 0.1009 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2472 gms.

Density of Reaction Mass: 0.848 gms./ml.

Adjustment Factor (F): -

Reaction Rate Constant:  $39.3 \times 10^{-5} \text{ sec.}^{-1}$



Run: #3

Solvent: Aqueous Ethanol (80%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $39.3 \times 10^{-5} \text{ sec}^{-1}$ 

GRAPH #3

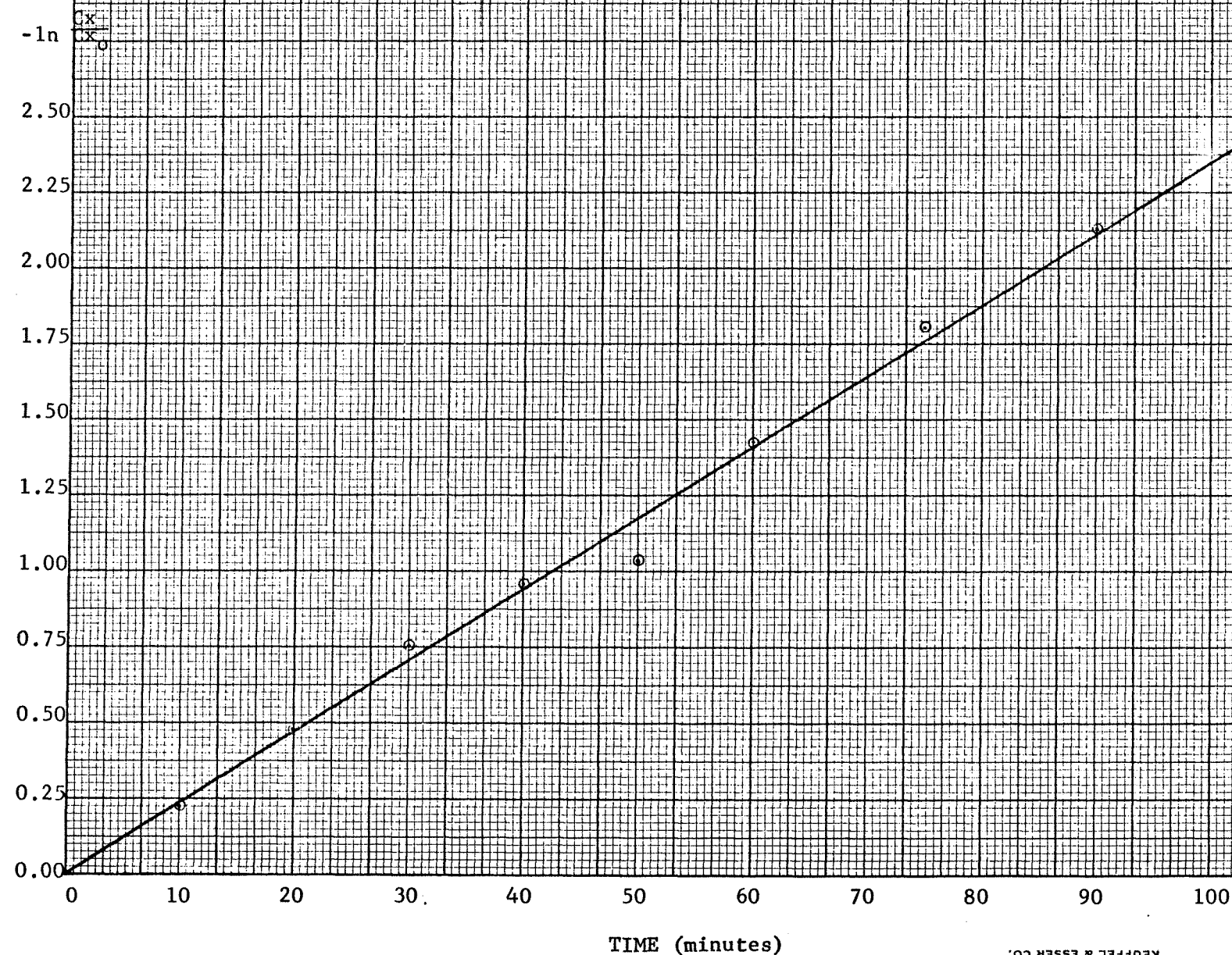


TABLE # 4

Run: #4

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	-	24.4	25.1	-	-	-	-	4.98	0.000
1	15	-	25.0	25.5	1.40	1.050	1.33	-	3.65	0.311
2	25	-	25.0	24.7	2.17	1.056	2.05	-	2.93	0.530
3	35	-	25.2	25.7	2.75	1.045	2.63	-	2.35	0.758
4	45	-	24.4	24.7	3.25	1.058	3.07	-	1.91	0.958
5	55	-	24.5	25.0	3.60	1.033	3.48	-	1.50	1.200
6	65	-	25.0	25.4	3.92	1.035	3.78	-	1.20	1.420
7	75	-	25.0	25.3	4.23	1.062	3.98	-	1.00	1.605
8	90	-	24.8	25.0	4.46	1.047	4.26	-	0.72	1.934
9	$\infty$	-	25.2	25.5	5.22	1.048	4.98	-	0.00	$\infty$

Room Temperature: 25.5°C

C. Water Temperature: 21°C

Volume of Reaction Mass: 572 ml

Initial Concentration of RX: 0.0998 gm. moles/litre (weight)

Final Concentration of X: 0.1025 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2053 gms.

Density of Reaction Mass: 0.850 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $35.9 \times 10^{-5} \text{ sec.}^{-1}$

Run: #4

Solvent: Aqueous Ethanol (80%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $35.9 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 4

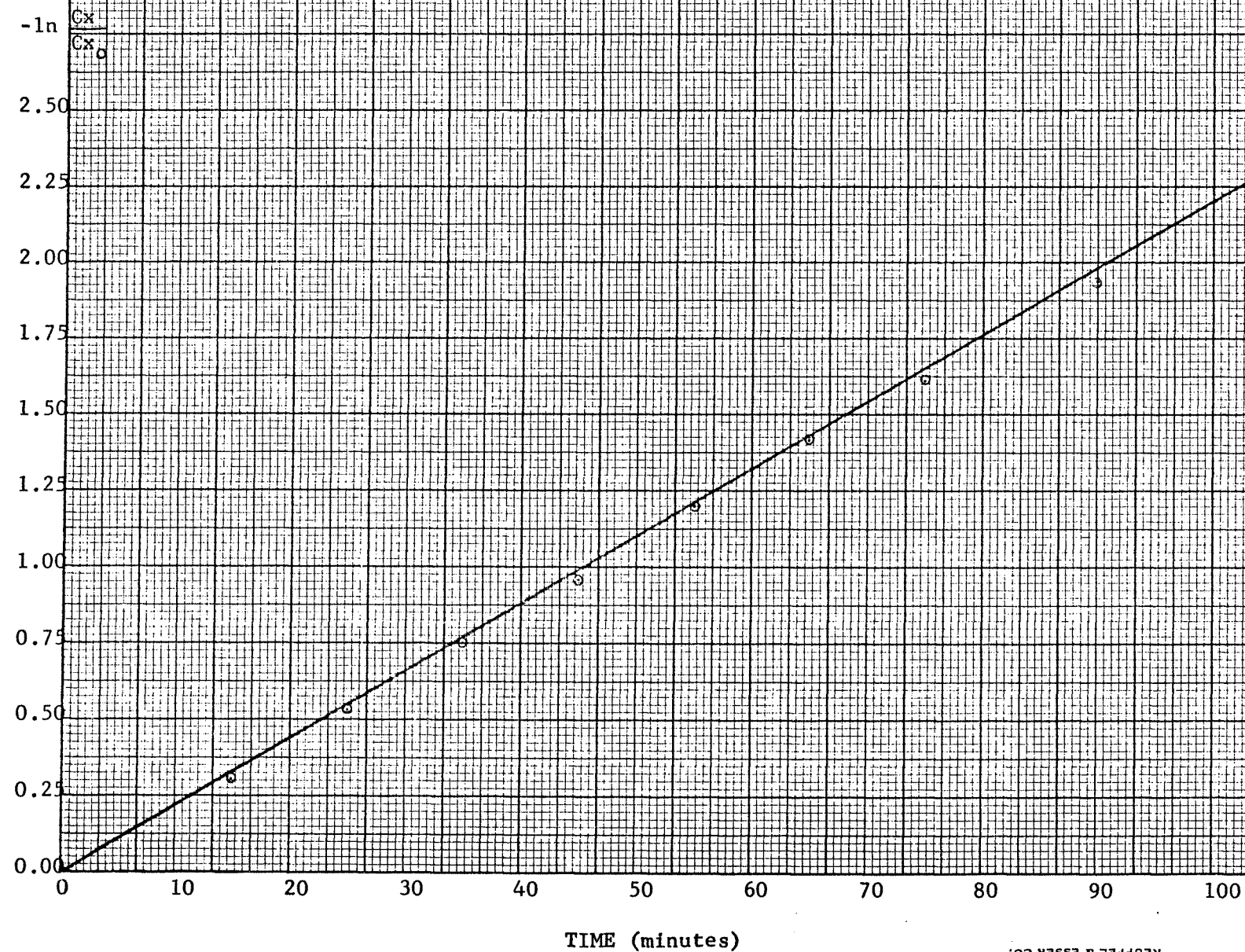


TABLE # 5

Run: #5

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	24.6	25.0	-	-	-	-	5.01	0.000
1	10	8.0	24.8	25.3	1.27	1.063	1.19	-	3.82	0.271
2	20	-	25.1	25.5	1.94	1.052	1.84	-	3.17	0.451
3	30	-	25.2	25.5	2.61	1.045	2.50	-	2.51	0.691
4	40	-	25.0	25.4	3.16	1.011	3.12	-	1.89	0.974
5	55	-	25.0	25.2	3.65	1.027	3.55	-	1.46	1.233
6	70	-	24.7	25.0	4.00	1.028	3.89	-	1.12	1.498
7	85	-	24.5	24.8	4.35	1.041	4.18	-	0.83	1.797
8	135	-	25.2	24.9	4.80	1.014	4.73	-	0.24	3.038
9	$\infty$	-	-	-	5.20	1.038	5.01	-	0.00	$\infty$

Room Temperature: 25°C

C. Water Temperature: 14°C

Volume of Reaction Mass: 568 ml

Initial Concentration of RX: 0.1009 gm. moles/litre (weight)

Final Concentration of X: 0.1029 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2974 gms.

Density of Reaction Mass: 0.849 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $37.0 \times 10^{-5} \text{ sec.}^{-1}$

Run: #5

Solvent: Aqueous Ethanol (80%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $37.0 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 5

 $-\ln \frac{C_x}{C_0}$ 

2.50

2.25

2.00

1.75

1.50

1.25

1.00

0.75

0.50

0.25

0.00

0

10

20

30

40

50

60

70

80

90

100

TIME (minutes)

TABLE # 6

Run: #6

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x_0}}$
0	0	8.0	24.5	24.8	-	-	-	-	4.92	0.000
1	10	8.0	23.9	24.2	1.14	1.036	1.10	1.14	3.78	0.261
2	20	8.0	23.1	23.4	1.95	1.056	1.85	1.85	3.07	0.472
3	30	8.0	23.8	24.1	2.59	1.050	2.47	2.48	2.44	0.703
4	40	8.0	24.5	24.8	3.07	1.045	2.94	2.94	1.98	0.910
5	50	8.0	24.8	25.1	3.51	1.044	3.42	3.46	1.46	1.214
6	60	8.0	25.3	25.5	3.66	1.027	3.68	3.69	1.23	1.386
7	70	8.0	25.0	25.5	4.10	1.056	3.88	3.88	1.04	1.551
8	80	8.0	25.1	25.6	4.33	1.050	4.12	4.12	0.80	1.820
9	90	8.0	24.8	25.2	4.52	1.055	4.28	4.27	0.65	2.025
10	100	8.0	25.1	25.5	4.68	1.056	4.43	4.44	0.48	2.323
11	$\infty$	8.0	26.0	26.3	5.05	1.027	4.92	4.92	0.00	$\infty$

Room Temperature: 23°C

C. Water Temperature: 18°C

Volume of Reaction Mass: 570 ml

Initial Concentration of RX: 0.1000 gm. moles/litre (weight)

Final Concentration of X: 0.1013 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2254 gms.

Density of Reaction Mass: 0.850 gms/ml

Adjustment Factor (F): 0.343

Reaction Rate Constant:  $38.2 \times 10^{-5} \text{ sec.}^{-1}$



Run: #6

Solvent: Aqueous Ethanol (80%)

Field Strength: 8.0 kilovolts

Reaction Rate Constant (K):  $38.2 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH #6

 $-\ln \frac{C_x}{C_{x_0}}$ 

2.50

2.25

2.00

1.75

1.50

1.25

1.00

0.75

0.50

0.25

0.00

TIME (minutes)

TABLE # 7

Run: #7

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	24.8	25.1	-	-	-	-	4.92	0.000
1	10	8.0	24.8	25.1	1.41	1.033	1.36	1.57	3.35	0.383
2	20	8.0	25.2	25.5	2.04	1.028	1.98	2.10	2.82	0.557
3	30	8.0	25.3	25.6	2.71	1.053	2.57	2.68	2.24	0.787
4	40	8.0	25.6	25.9	3.21	1.030	3.15	3.30	1.62	1.109
5	50	8.0	24.9	25.2	3.55	1.039	3.56	3.71	1.21	1.402
6	60	8.0	24.8	25.1	3.80	1.043	3.91	4.08	0.84	1.766
7	70	8.0	25.2	25.3	4.08	1.032	4.12	4.27	0.65	2.025
8	80	8.0	25.4	25.7	4.25	1.049	4.26	4.38	0.54	2.207
9	$\infty$	8.0	25.1	25.4	5.12	1.042	4.92	4.92	0.00	$\infty$

Room Temperature: 25°C

C. Water Temperature: 20°C

Volume of Reaction Mass: 564 ml

Initial Concentration of RX: 0.1009 gm. moles/litre (weight)

Final Concentration of X: 0.1013 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2958 gms.

Density of Reaction Mass: 0.850 gms./ml

Adjustment Factor (F): 0.342

Reaction Rate Constant:  $47.1 \times 10^{-5} \text{ sec.}^{-1}$



Run: #7  
Solvent: Aqueous Ethanol (80%)  
Field Strength: 8.0 Kilovolts

GRAPH # 7

Reaction Rate Constant (K):  $47.1 \times 10^{-5} \text{ sec.}^{-1}$

$-\ln \frac{C_x}{C_0}$

2.50

2.25

2.00

1.75

1.50

1.25

1.00

0.75

0.50

0.25

0.00

0 10 20 30 40 50 60 70 80 90 100

TIME (minutes)

TABLE # 8

Run: #8

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	25.0	25.3	-	-	0.00	0.00	4.85	0.000
1	10	8.0	25.5	25.8	1.46	1.027	1.42	1.64	3.21	0.412
2	20	8.0	25.5	25.8	2.17	1.029	2.11	2.28	2.57	0.613
3	30	8.0	25.0	25.3	2.63	0.995	2.65	2.77	2.08	0.844
4	40	8.0	24.5	24.8	3.19	1.032	3.09	3.18	1.67	1.067
5	50	8.0	25.0	25.3	3.53	1.026	3.43	3.49	1.36	1.269
6	60	8.0	25.2	25.5	3.88	1.039	3.73	3.80	1.05	1.523
7	70	8.0	24.3	24.7	4.03	1.014	3.98	4.03	0.82	1.777
8	80	8.0	24.5	24.9	4.12	1.002	4.11	4.13	0.72	1.904
9	90	8.0	24.5	24.8	4.35	1.019	4.27	4.30	0.55	2.171
10	$\infty$	8.0	26.0	26.3	4.95	1.021	4.85	4.85	0.00	$\infty$

Room Temperature: 26°C

C. Water Temperature: 18°C

Volume of Reaction Mass: 564 ml

Initial Concentration of RX: 0.0996 gm. moles/litre (weight)

Final Concentration of X: 0.1000 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.1912 gms.

Density of Reaction Mass: 0.850 gms./ml

Adjustment Factor (F): 0.342

Reaction Rate Constant:  $41.6 \times 10^{-5} \text{ sec}^{-1}$

Run: #8

Solvent: Aqueous Ethanol (80%)

Field Strength: 8.0 Kilovolts

Reaction Rate Constant (K):  $41.6 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 8

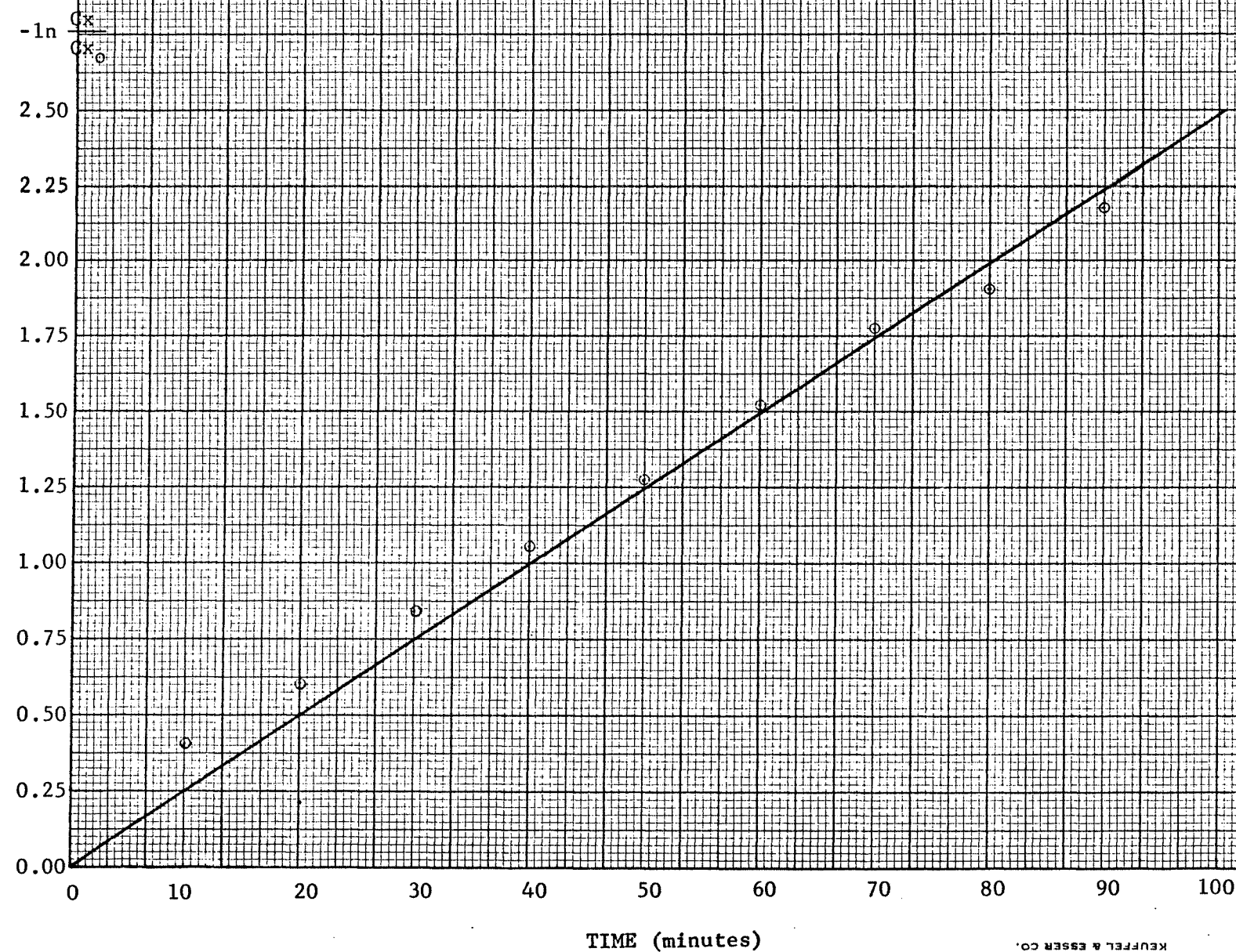


TABLE # 9

Run: #9

Solvent: Aqueous Ethanol (80%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	25.5	25.8	0.00	-	-	-	3.86	0.000
1	10	8.0	25.8	26.1	1.07	1.070	1.00	1.08	2.78	0.329
2	20	8.0	25.5	28.8	1.48	1.059	1.40	1.35	2.51	0.431
3	30	8.0	25.0	25.3	2.07	1.055	1.96	1.94	1.92	0.701
4	40	8.0	25.2	25.5	2.44	1.010	2.42	2.44	1.42	1.000
5	50	8.0	25.5	25.8	2.73	1.019	2.68	2.70	1.16	1.204
6	60	8.0	25.0	25.3	3.00	1.035	2.90	2.90	0.96	1.390
7	70	8.0	24.9	25.2	3.30	1.055	3.13	3.14	0.72	1.682
8	80	8.0	25.0	25.3	3.42	1.039	3.29	3.31	0.55	1.952
9	90	8.0	25.2	25.5	3.51	1.034	3.39	3.40	0.46	2.128
10	$\infty$	8.0	25.8	26.1	4.03	1.045	3.86	3.86	0.00	$\infty$

Room Temperature: 26°C

C. Water Temperature: 20°C

Volume of Reaction Mass: 562 ml

Initial Concentration of RX: 0.1000 gm. moles/litre (weight)

Final Concentration of X: 0.0992 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0257 gm. moles/litre

Weight of t-Butyl Bromide: 8.2215 gms.

Density of Reaction Mass: 0.849 gms./ml

Adjustment Factor (F): 0.340

Reaction Rate Constant:  $39.9 \times 10^{-5} \text{ sec.}^{-1}$

Run: #9

Solvent: Aqueous Ethanol (80%)

Field Strength: 8.0 Kilovolts

Reaction Rate Constant (K):  $39.9 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 9

 $-\ln \frac{C_x}{C_{x_0}}$ 

2.50

2.25

2.00

1.75

1.50

1.25

1.00

0.75

0.50

0.25

0.00

TIME (minutes)

TABLE # 10

Run: #10

Solvent: Aqueous Dioxane (75%) (V/V)

#	Time	V	Temp.1	Temp.2	Titre	Sample	Tit/ml	Tit(ad)	$T_{\infty} - T_t$	$-\ln \frac{C_x}{C_{x0}}$
0	0	-	25.8	26.1	0.00	-	-	-	4.90	0.000
1	10	-	24.8	25.1	0.98	1.071	0.92	-	3.98	0.208
2	20	-	24.0	24.3	1.50	1.051	1.43	-	3.47	0.342
3	30	-	25.0	25.4	2.02	1.085	1.86	-	3.04	0.418
4	40	-	24.8	25.2	2.39	1.062	2.25	-	2.65	0.614
5	60	-	25.3	25.5	3.20	1.052	3.04	-	1.86	0.970
6	80	-	25.8	26.1	3.55	1.069	3.32	-	1.58	1.133
7	100	-	25.0	25.3	4.06	1.065	3.81	-	1.09	1.505
8	120	-	25.5	25.8	4.31	1.034	4.17	-	0.73	1.904
9	135	-	25.2	25.5	4.56	1.035	4.41	-	0.49	2.304
10	$\infty$	-	25.1	25.4	5.14	1.050	4.90	-	0.00	$\infty$

Room Temperature: 24°C

C. Water Temperature: 21°C

Volume of Reaction Mass: 565 ml

Initial Concentration of RX: 0.1009 gm. moles/litre (weight)

Final Concentration of X: 0.1010 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2920 gms.

Density of Reaction Mass: 1.032 gms./ml

Adjustment Factor (F):

Reaction Rate Constant:  $26.5 \times 10^{-5} \text{ sec.}^{-1}$



Run: #10

Solvent: Aqueous Dioxane (75%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $26.5 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 10

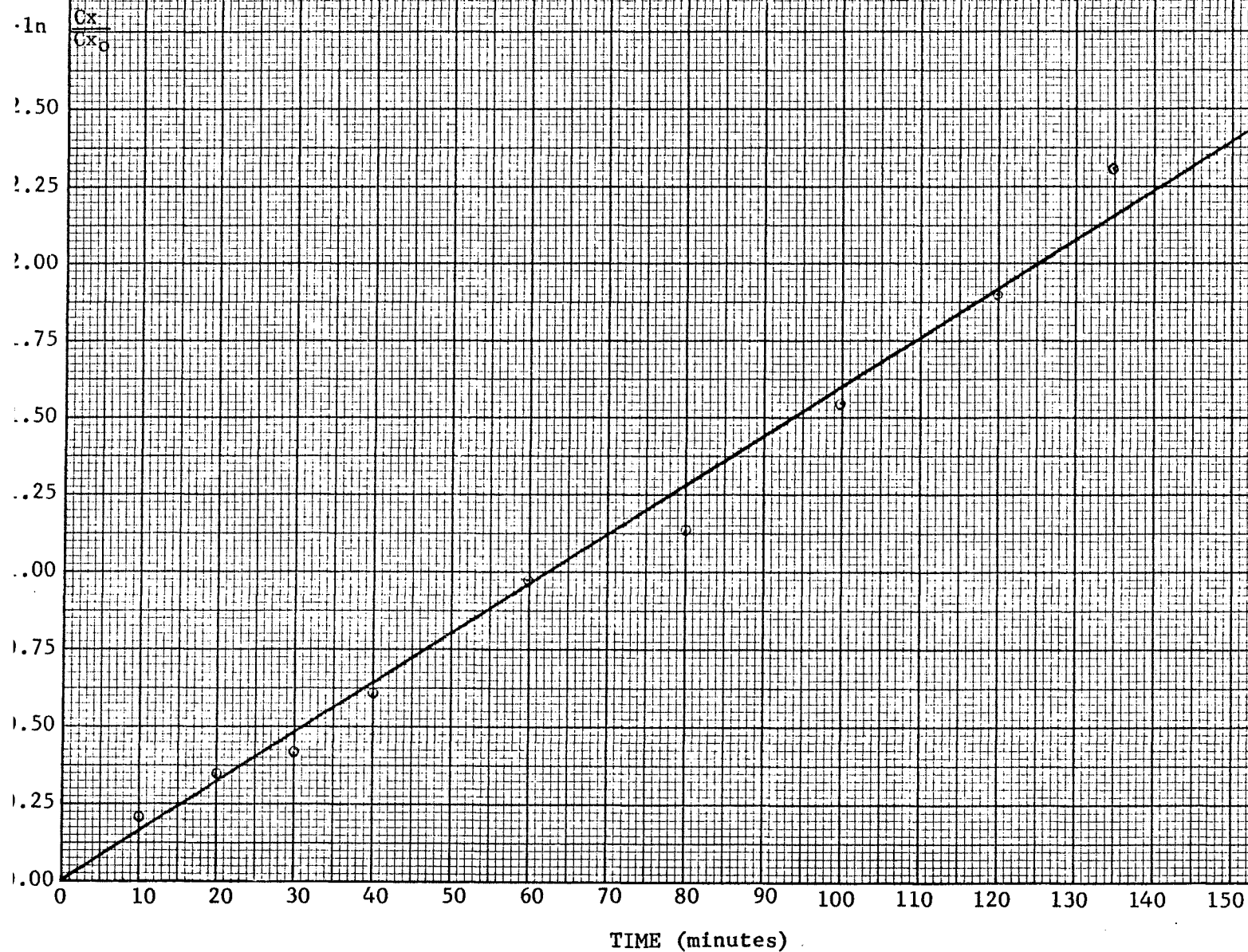


TABLE # 11

Run: #11

Solvent: Aqueous Dioxane (75%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	-	23.2	23.5	0.00	-	-	-	4.86	0.000
1	15	-	24.8	25.1	1.20	1.043	1.15	-	3.71	0.256
2	30	-	25.5	25.8	1.87	1.052	1.78	-	3.08	0.454
3	45	-	24.8	25.1	2.47	1.049	2.35	-	2.51	0.662
4	60	-	25.3	25.6	2.98	1.017	2.93	-	1.93	0.926
5	75	-	24.7	25.0	3.46	1.054	3.28	-	1.58	1.124
6	90	-	24.8	25.1	3.81	1.050	3.63	-	1.23	1.374
7	105	-	25.0	25.3	4.21	1.037	4.06	-	0.80	1.801
8	120	-	25.1	25.4	4.40	1.037	4.24	-	0.62	2.056
9	135	-	25.0	25.4	4.68	1.054	4.44	-	0.42	2.353
10	$\infty$	-	25.2	25.5	5.20	1.072	4.86	-	0.00	$\infty$

Room Temperature: 23°C

C. Water Temperature: 15°C

Volume of Reaction Mass: 570 ml

Initial Concentration of RX: 0.1000 gm. moles/litre (weight)

Final Concentration of X: 0.1001 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2256 gms.

Density of Reaction Mass: 1.035 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $27.6 \times 10^{-5} \text{ sec.}^{-1}$



GRAPH #11

Run: #11

Solvent: Aqueous Dioxane (75%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $27.6 \times 10^{-5} \text{ sec.}^{-1}$

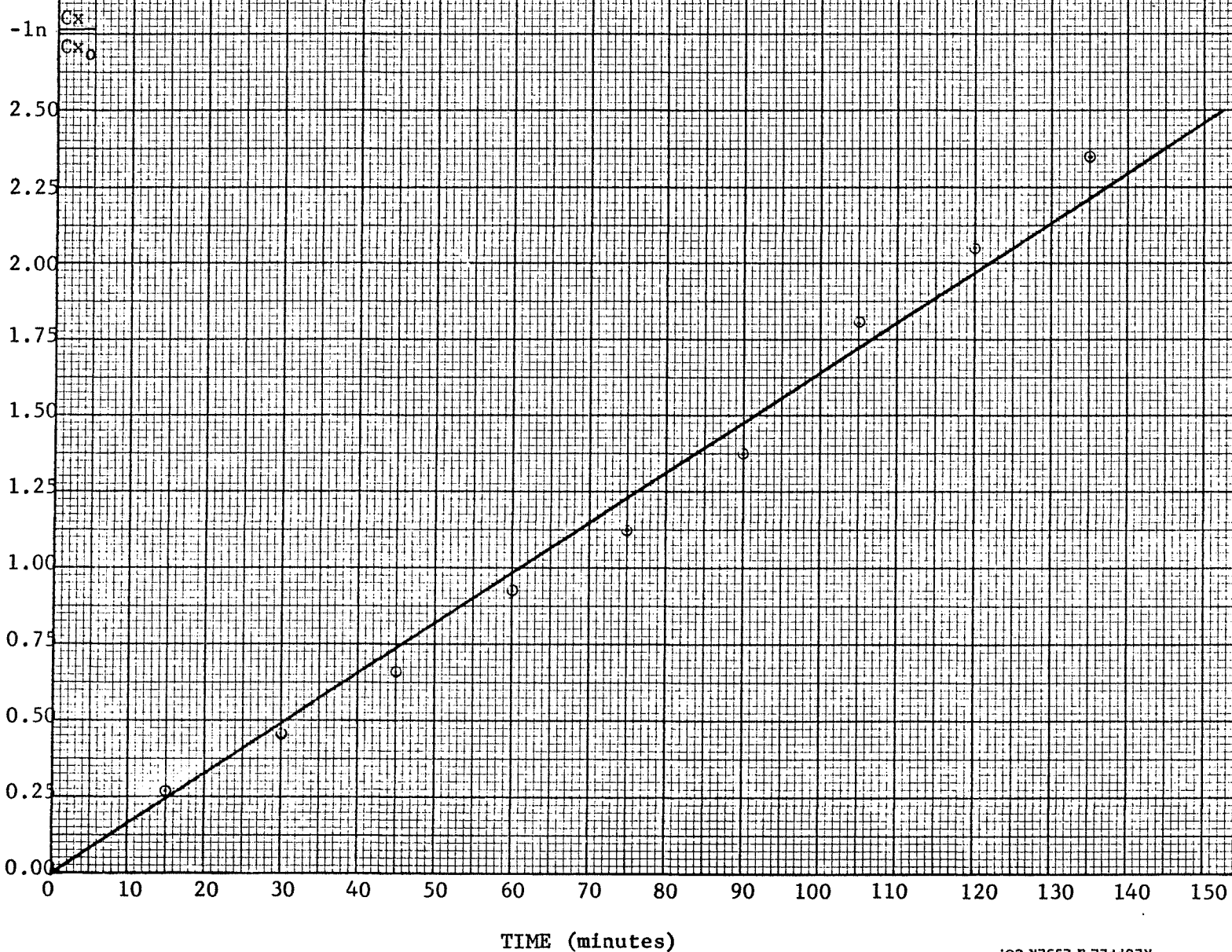


TABLE # 12

Run: #12

Solvent: Aqueous Dioxane (75%) (V/V)

#	Time mins	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-1 \ln \frac{C_x}{C_{x0}}$
0	0	8.0	24.2	24.5	0.00	-	-	-	4.96	0.000
1	10	8.0	25.1	25.4	0.92	1.055	0.87	0.87	4.09	0.195
2	30	8.0	25.0	25.3	1.83	1.057	1.73	1.90	2.86	0.548
3	45	8.0	25.5	25.8	2.30	1.045	2.20	2.33	2.63	0.634
4	60	8.0	25.4	25.7	2.89	1.053	2.75	2.76	2.20	0.814
5	75	8.0	25.6	25.9	3.35	1.056	3.17	3.09	1.87	1.087
6	90	8.0	25.2	25.5	3.91	1.048	3.73	3.77	1.19	1.427
7	105	8.0	25.5	25.8	4.15	1.055	3.93	3.91	1.05	1.551
8	120	8.0	25.5	25.8	4.39	1.067	4.23	4.23	0.73	1.917
9	135	8.0	25.0	25.3	4.53	1.046	4.33	4.31	0.65	2.032
10	$\infty$	8.0	25.4	25.7	5.14	1.049	4.90	4.96	0.00	$\infty$

Room Temperature: 25°C

C. Water Temperature: 19°C

Volume of Reaction Mass: 570 ml

Initial Concentration of RX: 0.1004 gm. moles/litre (weight)

Final Concentration of X: 0.1009 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2554 gms.

Density of Reaction Mass: 1.034 gms./ml

Adjustment Factor (F): 0.350

Reaction Rate Constant:  $26.4 \times 10^{-5} \text{ sec.}^{-1}$

Run: #12  
Solvent: Aqueous Dioxane (75%)  
Field Strength: 8.0 Kilovolts

Reaction Rate Constant (K):  $26.4 \times 10^{-5} \text{ sec.}^{-1}$

GRAPH # 12

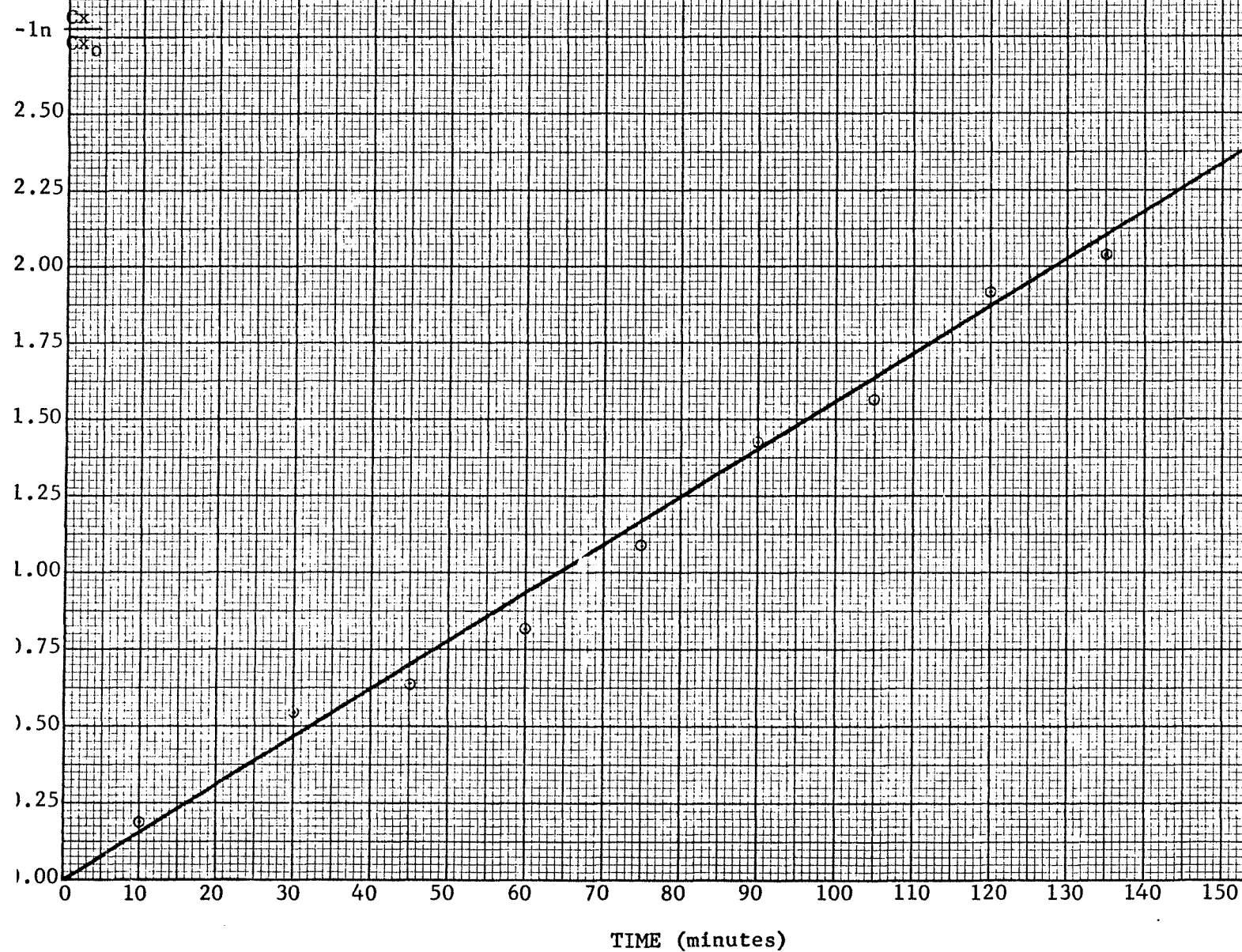


TABLE # 13

Run: #13

Solvent: Aqueous Dioxane (75%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	24.5	24.8	0.00	-	-	-	4.88	0.000
1	10	8.0	25.8	25.1	0.89	1.050	0.85	0.84	4.04	0.191
2	30	8.0	25.2	25.5	1.85	1.052	1.76	1.70	3.18	0.431
3	45	8.0	25.4	25.7	2.25	1.056	2.13	1.98	2.90	0.521
4	60	8.0	25.2	25.5	2.94	1.053	2.79	2.73	2.15	0.819
5	75	8.0	25.0	25.3	3.30	1.055	3.19	3.11	1.77	1.011
6	90	8.0	24.9	25.2	3.95	1.053	3.75	3.78	1.10	1.487
7	105	8.0	24.7	25.0	4.11	1.055	3.90	3.84	1.04	1.546
8	120	8.0	25.0	25.3	4.45	1.052	4.23	4.21	0.67	1.980
9	135	8.0	25.2	25.5	4.58	1.051	4.36	4.33	0.55	2.180
10	$\infty$	8.0	25.5	25.8	5.14	1.055	4.88	4.88	0.00	$\infty$

Room Temperature: 26°C

C. Water Temperature: 19°C

Volume of Reaction Mass: 568 ml

Initial Concentration of RX: 0.1006 gm. moles/litre (weight)

Final Concentration of X: 0.1005 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2610 gms.

Density of Reaction Mass: 1.034 gms./ml

Adjustment Factor (F): 0.345

Reaction Rate Constant:  $25.8 \times 10^{-5} \text{ sec.}^{-1}$

Run: #13

Solvent: Aqueous Dioxane (75%)

Field Strength: 8.0 Kilovolts

Reaction Rate Constant (K):  $25.8 \times 10^{-5} \text{ sec.}^{-1}$

GRAPH # 13

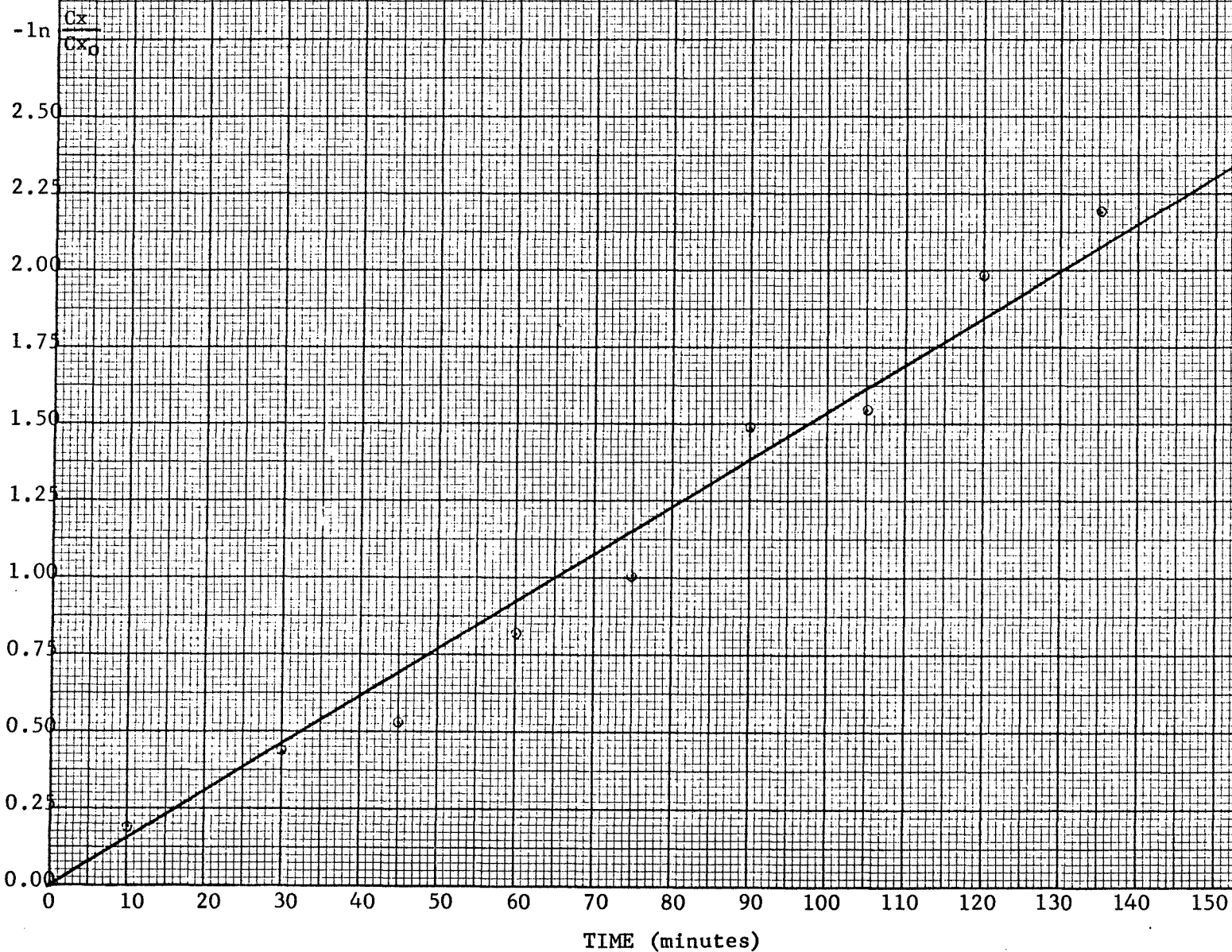


TABLE # 14

Run: #14

Solvent: Aqueous Acetone (75%) (v/v)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	-	25.0	25.3	0.00	-	-	-	4.83	0.000
1	15	-	25.0	25.3	1.16	1.054	1.10	-	3.73	0.259
2	30	-	25.2	25.5	2.07	1.048	1.98	-	2.85	0.545
3	45	-	25.0	25.3	2.73	1.052	2.60	-	2.23	0.772
4	60	-	25.3	25.6	3.33	1.036	3.21	-	1.62	1.094
5	75	-	25.2	25.5	3.77	1.058	3.56	-	1.27	1.336
6	90	-	25.0	25.3	4.00	1.037	3.86	-	0.97	1.604
7	105	-	25.3	25.6	4.07	1.030	3.95	-	0.88	1.704
8	120	-	25.9	25.3	4.33	1.052	4.16	-	0.67	1.973
9	135	-	25.0	25.3	4.50	1.025	4.39	-	0.44	2.384
10	$\infty$	-	25.2	25.3	5.05	1.046	4.83	-	0.00	$\infty$

Room Temperature: 24°C

C. Water Temperature: 18°C

Volume of Reaction Mass: 570ml

Initial Concentration of RX: 0.1001 gm. moles/litre (weight)

Final Concentration of X: 0.0995 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2306 gms.

Density of Reaction Mass: 0.868 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $28.7 \times 10^{-5} \text{ sec.}^{-1}$



Run: #14

Solvent: Aqueous Acetone (75%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $28.7 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 14

 $-\ln \frac{C_x}{C_0}$ 

2.50

2.25

2.00

1.75

1.50

1.25

1.00

0.75

0.50

0.25

0.00

TIME (minutes)

TABLE # 15

Run: #15

Solvent: Aqueous Acetone (75%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	-	24.5	24.8	0.00	-	-	-	4.82	0.000
1	15	-	25.8	25.1	1.20	1.056	1.14	-	3.68	0.269
2	30	-	25.1	25.4	2.11	1.051	2.01	-	2.81	0.538
3	45	-	25.0	25.3	2.69	1.052	2.56	-	2.26	0.757
4	60	-	24.9	25.2	3.35	1.038	3.23	-	1.59	1.121
5	75	-	25.1	25.4	3.74	1.057	3.54	-	1.28	1.328
6	90	-	25.2	25.5	3.98	1.036	3.84	-	0.98	1.594
7	105	-	24.8	25.1	4.15	1.033	4.02	-	0.80	1.796
8	120	-	25.0	25.3	4.30	1.053	4.08	-	0.55	2.160
9	135	-	25.1	25.4	3.54	1.027	4.42	-	0.40	2.489
10	$\infty$	-	25.5	23.8	4.98	1.034	4.82	-	0.00	$\infty$

Room Temperature: 24°C

C. Water Temperature: 17°C

Volume of Reaction Mass: 565 ml

Initial Concentration of RX: 0.1000 gm. moles/litre (weight)

Final Concentration of X: 0.0993 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2250 gms.

Density of Reaction Mass: 0.868 gms./ml

Adjustment Factor (F): -

Reaction Rate Constant:  $29.9 \times 10^{-5} \text{ sec.}^{-1}$



Run: #15

Solvent: Aqueous Acetone (75%)

Field Strength: 0.0 Kilovolts

Reaction Rate Constant (K):  $29.9 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 15

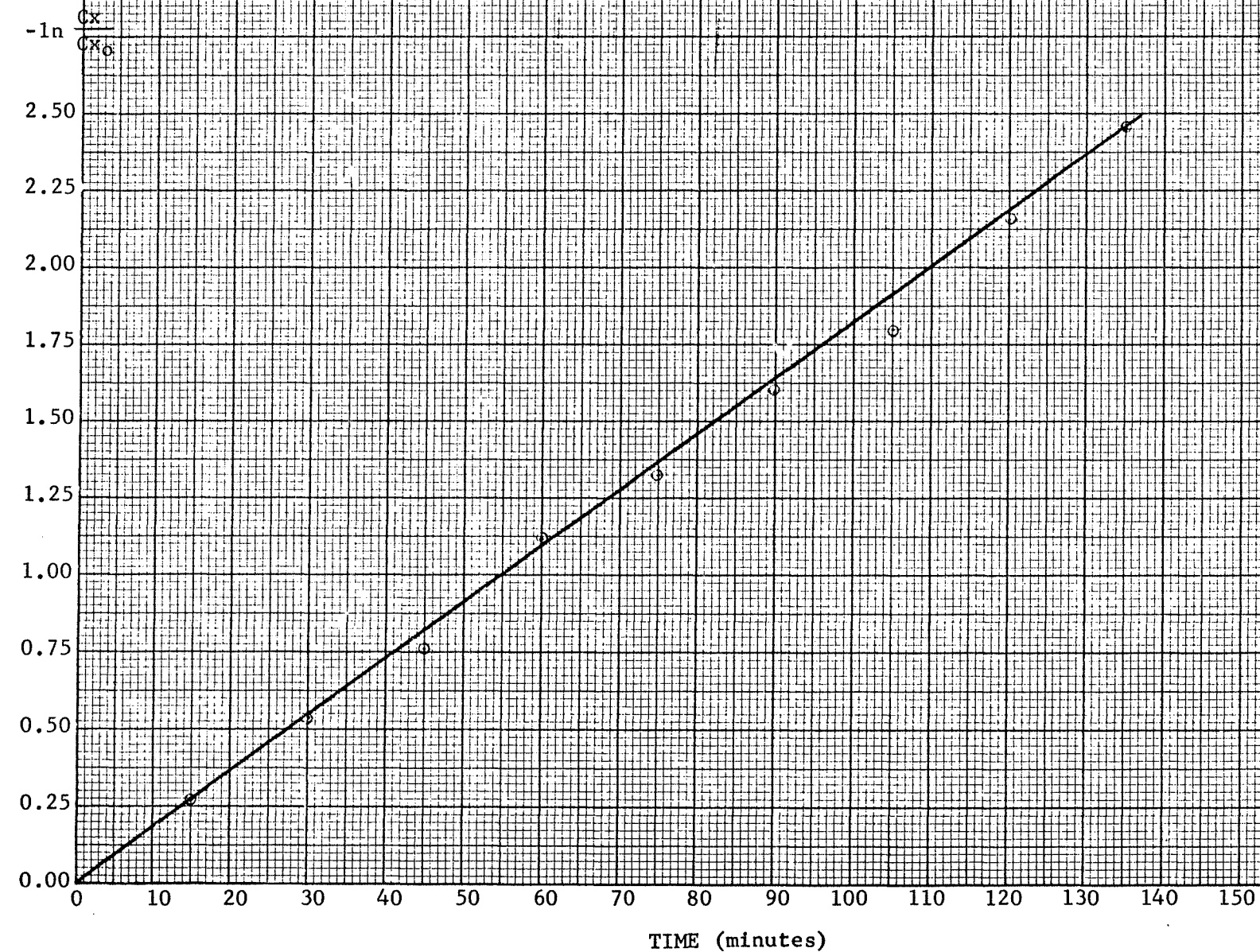


TABLE # 16

Run: #16

Solvent: Aqueous Acetone (75%) (v/v)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	24.2	24.5	0.00	-	-	-	4.82	0.000
1	15	8.0	24.8	25.1	1.18	1.052	1.12	1.14	3.68	0.270
2	30	8.0	24.9	25.2	2.05	1.046	1.96	1.93	2.89	0.512
3	45	8.0	25.2	25.5	2.75	1.040	2.64	2.59	2.23	0.770
4	60	8.0	25.3	25.6	3.31	1.036	3.19	3.17	1.65	1.073
5	75	8.0	25.0	25.3	3.81	1.038	3.67	3.70	1.12	1.457
6	90	8.0	24.8	25.1	4.02	1.054	3.81	3.76	1.06	1.514
7	105	8.0	24.9	25.2	4.21	1.044	4.03	3.99	0.83	1.760
8	120	8.0	25.0	25.3	4.38	1.035	4.23	4.23	0.59	2.104
9	135	8.0	25.2	25.5	4.50	1.032	4.36	4.37	0.45	2.364
10	$\infty$	8.0	25.5	25.8	5.05	1.047	4.82	4.82	0.00	$\infty$

Room Temperature: 24°C

C. Water Temperature: 18°C

Volume of Reaction Mass: 565 ml

Initial Concentration of RX: 0.1000 gm. moles/litre (weight)

Final Concentration of X: 0.0993 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2258 gms.

Density of Reaction Mass: 0.868 gms./ml

Adjustment Factor (F): 0.343

Reaction Rate Constant:  $29.1 \times 10^{-5} \text{ sec.}^{-1}$

Run: #16

Solvent: Aqueous Acetone (75%)

Field Strength: 8.0 Kilovolts

Reaction Rate Constant (K):  $29.1 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 16

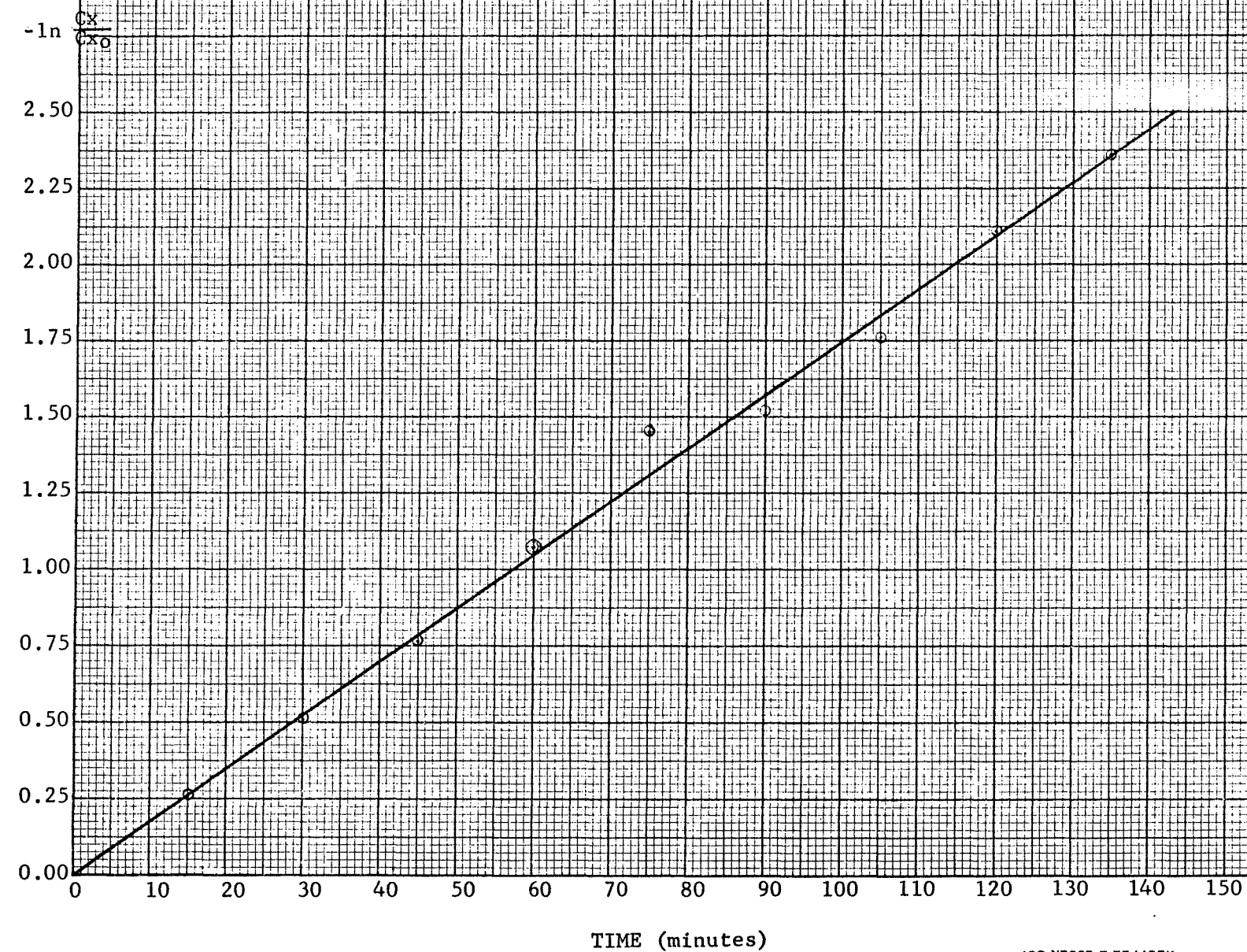


TABLE # 17

Run: #17

Solvent: Aqueous Acetone (75%) (V/V)

#	Time mins.	V KV	Temp.1 °C	Temp.2 °C	Titre ml.	Sample ml.	Tit/ml ml.	Tit(ad) ml.	$T_{\infty} - T_t$ ml.	$-\ln \frac{C_x}{C_{x0}}$
0	0	8.0	24.5	24.8	0.00	-	-	-	4.96	0.000
1	15	8.0	25.9	25.2	1.15	1.043	1.10	1.11	3.85	0.251
2	30	8.0	25.2	25.5	2.01	1.035	1.94	1.89	3.07	0.478
3	45	8.0	25.0	25.3	2.70	1.051	2.57	2.47	2.49	0.689
4	60	8.0	24.9	25.2	3.29	1.032	3.19	3.16	1.80	1.013
5	75	8.0	24.8	25.1	3.76	1.049	3.58	3.56	1.40	1.262
6	90	8.0	25.0	25.3	4.00	1.043	3.83	3.79	1.17	1.444
7	105	8.0	25.2	25.5	4.25	1.052	4.04	4.00	0.96	1.640
8	120	8.0	25.1	25.4	4.45	1.036	4.30	4.33	0.63	2.064
9	135	8.0	25.9	25.1	4.55	1.031	4.42	4.45	0.51	2.271
10	$\infty$	8.0	25.5	25.8	5.09	1.038	4.96	4.96	0.00	$\infty$

Room Temperature: 24°C

C. Water Temperature: 18°C

Volume of Reaction Mass: 568 ml

Initial Concentration of RX: 0.1008 gm. moles/litre (weight)

Final Concentration of X: 0.1022 gm. moles/litre (titre)

Normality of Sodium Hydroxide: 0.0206 gm. moles/litre

Weight of t-Butyl Bromide: 8.2856 gms.

Density of Reaction Mass: 0.868 gms./ml

Adjustment Factor (F): 0.345

Reaction Rate Constant:  $28.5 \times 10^{-5} \text{ sec.}^{-1}$

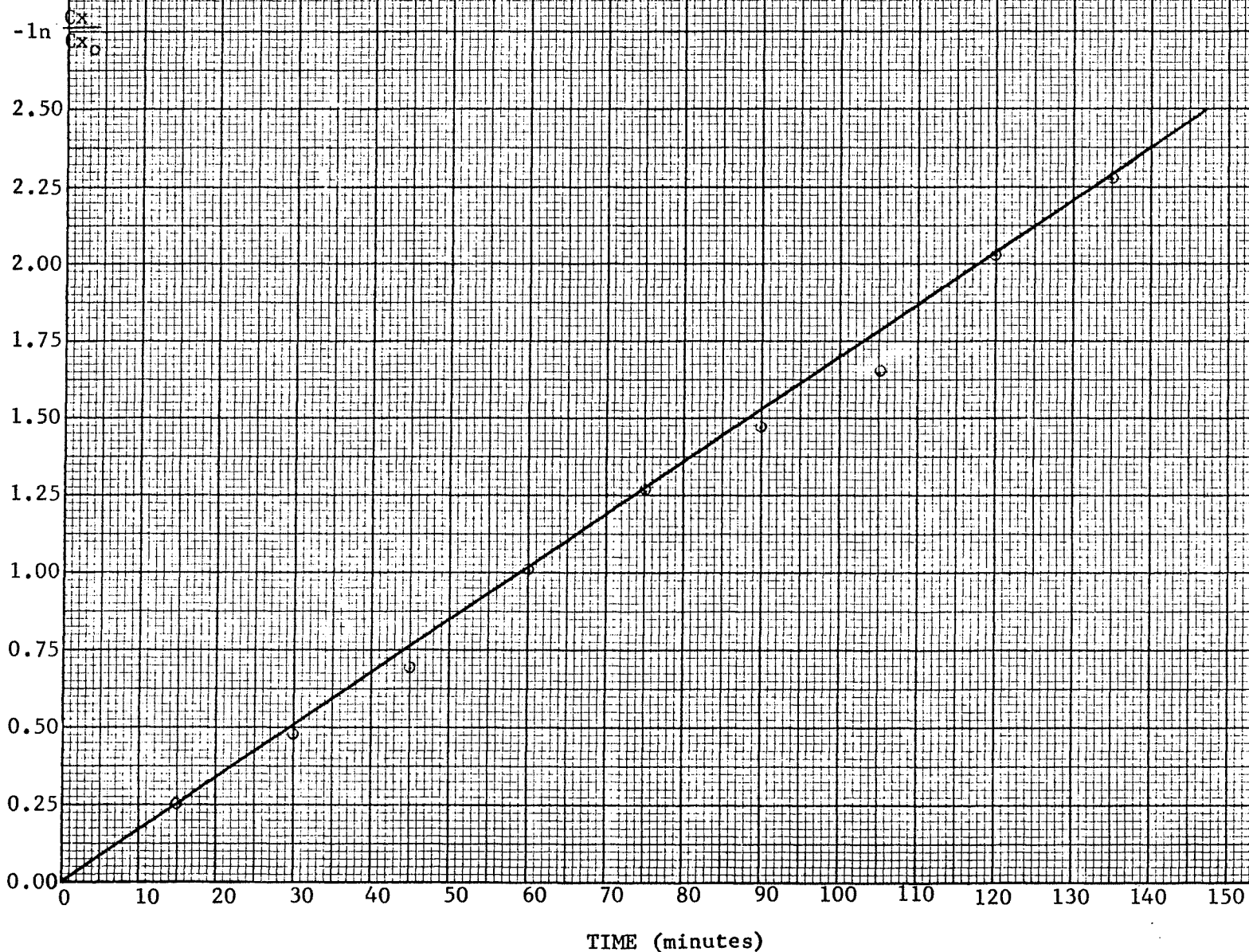
Run: #17

Solvent: Aqueous Acetone (75%)

Field Strength: 8.0 Kilovolts

Reaction Rate Constant (K):  $28.5 \times 10^{-5} \text{ sec.}^{-1}$ 

GRAPH # 17





Plot of average Titre/ml sample vs. Time  
Solvent: Aqueous Ethanol (80%)

GRAPH # 18

Titre/ml

5.0

4.0

3.0

2.0

1.0

10

20

30

40

50

60

70

80

90

100

110

120

130

140

TIME (minutes)

Note: Based on runs 3, 4 and 5

Plot of average Titre/ml sample vs. Time  
Solvent: Aqueous Dioxane (75%)

GRAPH # 19

Titre/ml

5.0

4.0

3.0

2.0

1.0

10 20 30 40 50 60 70 80 90 100 110 120 130 140

Note: Based on runs 10 and 11

Plot of average Titre/ml sample vs. Time  
Solvent: Aqueous Acetone (75%)

GRAPH # 20

Titre/ml

5.0

4.0

3.0

2.0

1.0

10

20

30

40

50

60

70

80

90

100

110

120

130

140

TIME (minutes)

Note: Based on runs 14 and 15



TABLE # 18  
SAMPLE WEIGHTS

Run: #1

Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
88.4099	87.8009	90.3391	87.0690	91.3656	99.0719
<u>87.4994</u>	<u>86.8929</u>	<u>89.4467</u>	<u>86.1527</u>	<u>90.4595</u>	<u>98.1670</u>
<u>0.9105</u>	<u>0.9080</u>	<u>0.8924</u>	<u>0.9163</u>	<u>0.9061</u>	<u>0.9049</u>
7	8	9	$\infty$	Rx	d
104.7287	105.9854	91.2768	92.9742	86.8273	88.8356
<u>103.8345</u>	<u>105.0735</u>	<u>90.3628</u>	<u>92.0861</u>	<u>65.3223</u>	<u>67.3235</u>
<u>0.8942</u>	<u>0.9119</u>	<u>0.9140</u>	<u>0.8881</u>	<u>21.5050</u>	<u>21.5121</u>

Run: #2

Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
84.7475	87.4861	84.2610	83.7870	85.3640	90.7950
<u>83.8240</u>	<u>86.6020</u>	<u>83.3560</u>	<u>82.8620</u>	<u>84.4769</u>	<u>89.9035</u>
<u>0.9235</u>	<u>0.8841</u>	<u>0.9050</u>	<u>0.9250</u>	<u>0.8871</u>	<u>0.8915</u>
7	8	9	$\infty$	Rx	d
86.2898	85.4444	83.0410	86.9308	74.7520	88.5068
<u>85.3719</u>	<u>84.5540</u>	<u>82.1300</u>	<u>86.0256</u>	<u>65.3040</u>	<u>67.3103</u>
<u>0.9179</u>	<u>0.8904</u>	<u>0.9110</u>	<u>0.9052</u>	<u>9.4480</u>	<u>21.1965</u>

Run: #3

Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
85.8970	87.2841	88.9852	87.4020	88.7168	93.2824
<u>84.9980</u>	<u>86.3710</u>	<u>88.0699</u>	<u>86.5086</u>	<u>87.8079</u>	<u>92.3796</u>
<u>0.8990</u>	<u>0.9131</u>	<u>0.9153</u>	<u>0.8934</u>	<u>0.9089</u>	<u>0.9028</u>
7	8	$\infty$	Rx	d	
75.7926	74.8299	86.4132	63.2694	79.1158	
<u>74.8893</u>	<u>73.9180</u>	<u>85.5108</u>	<u>55.0222</u>	<u>57.9772</u>	
<u>0.9033</u>	<u>0.9119</u>	<u>0.9024</u>	<u>8.2472</u>	<u>21.1386</u>	

NOTE: All numbers are in gms.

Run: #4  
Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
84.0200	83.9248	81.5512	84.4566	87.7975	87.2596
<u>83.1294</u>	<u>83.0291</u>	<u>80.6648</u>	<u>83.5589</u>	<u>86.9213</u>	<u>86.3819</u>
<u>0.8906</u>	<u>0.8957</u>	<u>0.8864</u>	<u>0.8971</u>	<u>0.8762</u>	<u>0.8777</u>
7	8	$\infty$	Rx	d	
75.2118	86.0061	88.1108	63.2220	88.6061	
<u>74.3113</u>	<u>85.1184</u>	<u>87.2222</u>	<u>55.0167</u>	<u>67.3412</u>	
<u>0.9005</u>	<u>0.8877</u>	<u>0.8886</u>	<u>8.2053</u>	<u>21.2649</u>	

Run: #5  
Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
83.5191	82.5085	83.4951	80.8779	83.1737	88.4602
<u>82.6177</u>	<u>81.6156</u>	<u>82.6090</u>	<u>80.0201</u>	<u>82.3024</u>	<u>87.5882</u>
<u>0.9014</u>	<u>0.8929</u>	<u>0.8861</u>	<u>0.8578</u>	<u>0.8713</u>	<u>0.8720</u>
7	8	$\infty$	Rx	d	
83.8423	74.1951	83.0310	63.3270	80.3468	
<u>82.9593</u>	<u>73.3348</u>	<u>82.1565</u>	<u>55.0296</u>	<u>59.1261</u>	
<u>0.8830</u>	<u>0.8603</u>	<u>0.8805</u>	<u>8.2974</u>	<u>21.2207</u>	

Run: #6  
Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
77.3627	84.4424	80.2277	79.4135	80.7195	83.6971
<u>76.4832</u>	<u>83.5444</u>	<u>79.3366</u>	<u>78.5268</u>	<u>79.8330</u>	<u>82.8252</u>
<u>0.8795</u>	<u>0.8980</u>	<u>0.8911</u>	<u>0.8867</u>	<u>0.8865</u>	<u>0.8719</u>
7	8	9	$\infty$	Rx	d
83.2120	72.0125	83.5352	82.8081	63.8553	88.6449
<u>82.3158</u>	<u>71.1208</u>	<u>82.6397</u>	<u>81.9361</u>	<u>55.6299</u>	<u>67.3831</u>
<u>0.8962</u>	<u>0.8917</u>	<u>0.8955</u>	<u>0.8720</u>	<u>8.2254</u>	<u>21.2618</u>

NOTE: All numbers are in gms.

Run: #7  
Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
83.9327	82.5425	80.2440	81.2400	81.3788	85.5169
<u>83.0558</u>	<u>81.6700</u>	<u>79.3505</u>	<u>80.3654</u>	<u>80.4969</u>	<u>84.6316</u>
<u>0.8769</u>	<u>0.8725</u>	<u>0.8935</u>	<u>0.8746</u>	<u>0.8819</u>	<u>0.8853</u>
7	8	$\infty$	Rx	d	
83.1148	73.4268	91.8611	63.9304	76.9852	
<u>82.2390</u>	<u>72.5362</u>	<u>90.9765</u>	<u>55.6346</u>	<u>55.6970</u>	
<u>0.8758</u>	<u>0.8906</u>	<u>0.8846</u>	<u>8.2958</u>	<u>21.2882</u>	

Run: #8  
Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
88.7155	90.5769	89.9418	84.4013	84.8820	91.2316
<u>87.8215</u>	<u>89.6790</u>	<u>89.0957</u>	<u>83.4940</u>	<u>83.9898</u>	<u>90.3187</u>
<u>0.8940</u>	<u>0.8979</u>	<u>0.8461</u>	<u>0.9073</u>	<u>0.8922</u>	<u>0.9129</u>
7	8	9	$\infty$	Rx	d
91.1272	74.1487	86.9127	87.6562	63.8221	76.9723
<u>90.2554</u>	<u>73.2937</u>	<u>86.0256</u>	<u>86.7740</u>	<u>55.6309</u>	<u>55.6922</u>
<u>0.8718</u>	<u>0.8550</u>	<u>0.8871</u>	<u>0.8822</u>	<u>8.1912</u>	<u>21.2801</u>

Run: #9  
Solvent: Aqueous Ethanol (80%)

1	2	3	4	5	6
86.1672	87.9121	81.7530	81.0721	84.1597	87.8402
<u>85.2584</u>	<u>87.0130</u>	<u>80.8572</u>	<u>80.2147</u>	<u>83.2944</u>	<u>86.9609</u>
<u>0.9088</u>	<u>0.8991</u>	<u>0.8958</u>	<u>0.8574</u>	<u>0.8653</u>	<u>0.8793</u>
7	8	9	$\infty$	Rx	d
87.1620	77.0587	75.2447	88.5013	63.8416	89.5515
<u>86.2660</u>	<u>76.1767</u>	<u>74.3667</u>	<u>87.6151</u>	<u>55.6201</u>	<u>68.3215</u>
<u>0.8960</u>	<u>0.8820</u>	<u>0.8780</u>	<u>0.8862</u>	<u>8.2215</u>	<u>21.2300</u>

NOTE: All numbers are in gms.

Run: #10

Solvent: Aqueous Dioxane (75%)

1	2	3	4	5	6
86.3931	87.1211	85.3751	81.5097	93.1356	87.2937
<u>85.2874</u>	<u>86.0365</u>	<u>84.2551</u>	<u>80.4135</u>	<u>92.0321</u>	<u>86.2062</u>
<u>1.1057</u>	<u>1.0846</u>	<u>1.1200</u>	<u>1.0962</u>	<u>1.1035</u>	<u>1.0875</u>
7	8	9	$\infty$	Rx	d
85.1953	75.8470	85.8479	106.7422	63.9091	81.4456
<u>84.0960</u>	<u>74.7801</u>	<u>84.7800</u>	<u>105.6821</u>	<u>55.6171</u>	<u>55.6354</u>
<u>1.0993</u>	<u>1.0669</u>	<u>1.0679</u>	<u>1.0601</u>	<u>8.2920</u>	<u>25.8102</u>

Run: #11

Solvent: Aqueous Dioxane (75%)

1	2	3	4	5	6
85.4819	84.8270	83.3723	81.4632	82.3562	87.4962
<u>84.4019</u>	<u>83.7378</u>	<u>82.2860</u>	<u>80.4103</u>	<u>81.2650</u>	<u>86.4093</u>
<u>1.0800</u>	<u>1.0892</u>	<u>1.0863</u>	<u>1.0529</u>	<u>1.0912</u>	<u>1.0869</u>
7	8	9	$\infty$	Rx	d
87.5861	73.5473	71.4271	85.0745	63.8634	85.1540
<u>86.5127</u>	<u>72.4740</u>	<u>70.3358</u>	<u>83.9910</u>	<u>55.6378</u>	<u>59.2630</u>
<u>1.0734</u>	<u>1.0733</u>	<u>1.0913</u>	<u>1.0835</u>	<u>8.2256</u>	<u>25.8910</u>

Run: #12

Solvent: Aqueous Dioxane (75%)

1	2	3	4	5	6
83.7992	84.2175	81.3733	81.2291	83.8415	88.8165
<u>82.7087</u>	<u>83.1255</u>	<u>80.2908</u>	<u>80.1412</u>	<u>82.7500</u>	<u>87.7335</u>
<u>1.0905</u>	<u>1.0920</u>	<u>1.0825</u>	<u>1.0879</u>	<u>1.0915</u>	<u>1.0830</u>
7	8	9	$\infty$	Rx	d
88.1461	75.1718	75.5648	89.9577	63.8885	85.1527
<u>87.0560</u>	<u>74.0685</u>	<u>74.4834</u>	<u>88.8733</u>	<u>55.6335</u>	<u>59.3132</u>
<u>1.0901</u>	<u>1.1033</u>	<u>1.0814</u>	<u>1.0844</u>	<u>8.2550</u>	<u>25.8395</u>

NOTE: All numbers are in gms.

Run: #13

Solvent: Aqueous Dioxane (75%)

1	2	3	4	5	6
88.6728	86.3232	84.2494	86.0761	86.9543	88.6250
<u>87.5873</u>	<u>85.2356</u>	<u>83.1579</u>	<u>84.9872</u>	<u>85.8642</u>	<u>87.5365</u>
<u>1.0855</u>	<u>1.0876</u>	<u>1.0910</u>	<u>1.0889</u>	<u>1.0901</u>	<u>1.0885</u>
7	8	9	$\infty$	Rx	d
89.8782	74.9410	73.0616	89.2262	63.8873	85.2031
<u>88.7872</u>	<u>73.8530</u>	<u>71.9753</u>	<u>88.1357</u>	<u>55.6263</u>	<u>59.3579</u>
<u>1.0910</u>	<u>1.0880</u>	<u>1.0863</u>	<u>1.0905</u>	<u>8.2610</u>	<u>25.8452</u>

Run: #14

Solvent: Aqueous Acetone (75%)

1	2	3	4	5	6
85.6765	86.5010	86.4116	83.1032	87.2178	88.3871
<u>84.7616</u>	<u>85.5908</u>	<u>85.4980</u>	<u>82.2037</u>	<u>86.2989</u>	<u>87.4868</u>
<u>0.9149</u>	<u>0.9102</u>	<u>0.9136</u>	<u>0.8995</u>	<u>0.9189</u>	<u>0.9003</u>
7	8	9	$\infty$	Rx	d
85.2894	71.6580	71.7677	94.9237	63.8562	92.4341
<u>84.3947</u>	<u>70.7535</u>	<u>70.8775</u>	<u>94.0151</u>	<u>55.6256</u>	<u>70.7271</u>
<u>0.8947</u>	<u>0.9045</u>	<u>0.8902</u>	<u>0.9086</u>	<u>8.2306</u>	<u>21.7070</u>

Run: #15

Solvent: Aqueous Acetone (75%)

1	2	3	4	5	6
85.6775	84.5640	82.4560	83.3355	86.7941	87.8216
<u>84.7612</u>	<u>83.6523</u>	<u>81.5434</u>	<u>82.4345</u>	<u>85.8767</u>	<u>86.9223</u>
<u>0.9163</u>	<u>0.9117</u>	<u>0.9126</u>	<u>0.9010</u>	<u>0.9174</u>	<u>0.8993</u>
7	8	9	$\infty$	Rx	d
90.1336	71.0494	71.8541	94.8850	63.8536	93.3464
<u>89.2376</u>	<u>70.1357</u>	<u>70.9630</u>	<u>93.9753</u>	<u>55.6283</u>	<u>71.6512</u>
<u>0.8960</u>	<u>0.9137</u>	<u>0.8911</u>	<u>0.9097</u>	<u>8.2253</u>	<u>21.6952</u>

NOTE: All numbers are in gms.

Run: #16

Solvent: Aqueous Acetone (75%)

1	2	3	4	5	6
85.2699	88.1954	84.2624	86.1451	87.2820	89.1581
<u>84.3567</u>	<u>87.2872</u>	<u>83.3597</u>	<u>85.2459</u>	<u>86.3812</u>	<u>88.2431</u>
<u>0.9132</u>	<u>0.9082</u>	<u>0.9027</u>	<u>0.8992</u>	<u>0.9008</u>	<u>0.9150</u>
7	8	9	$\infty$	Rx	d
83.0411	72.1876	72.2536	85.0465	63.8560	94.2317
<u>82.1346</u>	<u>71.2896</u>	<u>71.3581</u>	<u>84.1375</u>	<u>55.6302</u>	<u>72.5322</u>
<u>0.9065</u>	<u>0.8980</u>	<u>0.8955</u>	<u>0.9090</u>	<u>8.2258</u>	<u>21.6995</u>

Run: #17

Solvent: Aqueous Acetone (75%)

1	2	3	4	5	6
86.2307	88.7597	90.0437	83.6123	86.0346	84.4669
<u>85.3251</u>	<u>87.8612</u>	<u>89.1312</u>	<u>82.7161</u>	<u>85.1241</u>	<u>83.5617</u>
<u>0.9056</u>	<u>0.8985</u>	<u>0.9125</u>	<u>0.8962</u>	<u>0.9105</u>	<u>0.9052</u>
7	8	9	$\infty$	Rx	d
85.2274	77.4381	76.0815	83.1530	63.9139	91.8553
<u>84.3142</u>	<u>76.5389</u>	<u>75.1865</u>	<u>82.2520</u>	<u>55.6283</u>	<u>70.1532</u>
<u>0.9132</u>	<u>0.8992</u>	<u>0.8950</u>	<u>0.9010</u>	<u>8.2856</u>	<u>21.7021</u>

NOTE: All numbers are in gms.

TABLE 19  
EQUIPMENT DETAILS

1. 0.10 HP 3250 RPM Centrifugal Pump, Eastern Model P-6, Penton  
body construction with 316 S.S. shaft and impeller. (2)
2. 0.75" I.D. Glass Tube covered by two copper plates each 1"  
wide, 53.5" long and 0.45" apart. (1)
3. High Voltage Power Supply (0.50 kilovolts) - Industrial  
Instruments Inc. (4)
4. Calibrated Alcohol Thermometer ( $\pm 50^{\circ}\text{C}$ ) for Temp. 1 (7)
5. Calibrated Mercury Thermometer ( $-10^{\circ}\text{C} + 260^{\circ}\text{C}$ ) for Temp. 2 (8)
6. 10 ml Exac microburette
7. 250 ml Pyrex Extraction Funnel (6)
8. Glass Condenser (used as cooler). (3)
9. Electric Balance (0-200 gms) Sagatorius

NOTE: The numbers in brackets are the numbers used for each piece  
of equipment in the equipment diagrams.

TABLE 20

DETAILS OF REAGENTS

1. Tert-Butyl Bromide (BP.72-74°C) MCB# BX1345
2. Sodium Hydroxide solution 0.2N (Reagent Grade) Fischer Lot #781248
3. Methanol (Reagent Grade) MCB# MK485
4. Ethanol (Anhydrous Denatured) MCB# EX285
5. p-Dioxane (Practical) MCB# DX2105
6. Acetone (Reagent Grade) Merck MCB# AX120

Note: MCB# - is Matheson Coleman and Bell catalog order number



TABLE 21

LIST OF ABBREVIATIONS

This list of abbreviations applies to the Appendix only. All other abbreviations have been identified immediately after use.

$C_x$	=	Concentration of tert-butyl bromide at time $t = t$
$C_{x0}$	=	Initial concentration of tert-butyl bromide at time $t = 0$
Temp. 1	=	Temperature measured before reaction tube (see sketch)
Temp. 2	=	Temperature measured after reaction tube (see sketch)
V	=	Voltage across dielectric field
Titre	=	Titration reading
Tit/ml	=	Titration reading per ml of sample
Tit(ad)	=	Titration reading per ml of sample after adjustment
$T_\infty$	=	Titration reading after completed reaction
$T_t$	=	Titration reading at time $t$ which is equal to Tit(ad)

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