IODIDE EXCHANGE IN ACETONITRILE

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THE IODIDE EXCHANGE REACTION IN ACETONITRILE

THE INITIAL OBJECTIVES OF THIS RESEARCH WERE TO INVESTIGATE THE DEPENDENCE OF THE RATE CONSTANT OF THE EXCHANGE REACTION

$$RI + I^{*-} \xrightarrow{K} RI^{*} + I^{-}$$

UPON:

A. TEMPERATURE
B. IONIC STRENGTH AND NaI CONCENTRATION
C. ALKYL IODIDE CONCENTRATION
D. ALKYL IODIDE

BECAUSE OF THE LARGE ERRORS AT FIRST PRESENT AND ALSO DUE TO A LACK OF TIME, NO DATA WAS GATHERED RELATING EITHER TO A. OR D. THAT GATHERED ON B. AND C. WAS EITHER TOO SCANTY OR TOO INACCURATE TO DRAW MANY CONCLUSIONS FROM. HENCE I SHALL RESTRICT THIS PAPER TO A DISCUSSION MAINLY OF THE THEORY WITH A FEW REMARKS ABOUT THE DATA.

THE RATE EQUATION

AS METHODS OF REACTION, LET US CONSIDER THE FOLLOWING POSSIBLE REACTION SCHEMES:

A. A SECOND ORDER SCHEME INVOLVING RI AND I^- WITH RATE CONSTANT K_2

$$RI + I^{*-} \xrightarrow{K_2} RI^* + I^-$$

$$RI^* + I^- \xrightarrow{K_2} RI + I^{*-}$$

B. A SECOND ORDER SCHEME INVOLVING RI AND NaI (UNDISSOCIATED) WITH RATE CONSTANT K_2'

$$RI + NaI^* \xrightarrow{k_2'} RI^* + Na^+ + I^-$$

$$RI^* + NaI \xrightarrow{k_2'} RI + Na^+ + I^{*-}$$

THE REACTION MECHANISM FOR THIS PARTICULAR SCHEME WOULD PROBABLY BE SOMETHING LIKE:

$$Na\text{-}I^* + R\text{-}I \longrightarrow Na\cdots I^*\cdots R\cdots I \longrightarrow Na^+ + I^*R + I^-$$

C. A FIRST ORDER SCHEME INVOLVING RI (AND LATER EITHER I^- OR NaI) WITH RATE CONSTANT K_1

$$RI \xrightarrow{K_1} R^+ + I^-$$

then

$$R^+ + \underset{\text{or } NaI}{I^-} \xrightarrow{\text{fast}} RI$$

$$R^+ + \underset{\text{or } NaI^*}{I^{*-}} \xrightarrow{\text{fast}} RI^*$$

$$RI^* \xrightarrow{K_1} R^+ + I^{*-}$$

then

$$R^+ + \underset{\text{or } NaI}{I^-} \xrightarrow{\text{fast}} RI$$

$$R^+ + \underset{\text{or } NaI^*}{I^{*-}} \xrightarrow{\text{fast}} RI^*$$

NOTE THAT SINCE $$\frac{[I^{*-}]}{[I^{*-}]+[I^-]} = \frac{[NaI^*]}{[NaI^*]+[NaI]}$$

THAT THE FRACTION OF R^+ IONS WHICH FORM RI^* IS JUST $\frac{[I^{*-}]}{[I^{*-}]+[I^-]}$ WHETHER OR NOT THE I^* WAS ORIGINALLY AN ION OR NaI^*.

THESE THREE REACTION SHCEMES LEAD TO THE FOLLOWING DIFFERENTIAL EQUATION:

$$\frac{d[I^{*-}]}{dt} = K_2\left([RI^*][I^-] - [RI][I^{*-}]\right) + K_2'\left([RI^*][NaI] - [RI][NaI^*]\right) + K_1\left([RI^*]\cdot\frac{[I^-]}{[I^{*-}]+[I^-]} - [RI]\cdot\frac{[I^{*-}]}{[I^{*-}]+[I^-]}\right)$$

NOTE: THE FIRST ORDER FORWARD REACTION CONTRIBUTES I^{*-} AT THE RATE $K_1[RI^*]$; HOWEVER WHEN THE R^+ RECOMBINES, ONLY THE FRACTION $\frac{[I^-]}{[I^{*-}]+[I^-]}$ WILL AVOID REMOVING THAT I^{*-} FROM SOLUTION. HENCE THE ACTUAL CONTRIBUTION OF THE FORWARD FIRST ORDER REACTION IS $$K_1\cdot[RI^*]\cdot\frac{[I^-]}{[I^{*-}]+[I^-]}$$

ALSO, IF K_D IS THE DISSOCIATION CONSTANT FOR THE REACTION

$$NaI \underset{}{\overset{K_D}{\rightleftharpoons}} Na^+ + I^- \qquad K_D = \frac{[Na^+][I^-]}{[NaI]}$$

THEN

$$[NaI] = \frac{[Na^+][I^-]}{K_D}$$

THE DIFFERENTIAL EQUATION CAN NOW BE WRITTEN:

$$\frac{d[I^{*-}]}{dt} = \left(K_2 + \frac{K_2'}{K_D}\cdot[Na^+] + K_1\cdot\frac{1}{[I^{*-}]+[I^-]}\right)\left([RI^*][I^-] - [RI][I^{*-}]\right)$$

$$= K\left([RI^*][I^-] - [RI][I^{*-}]\right)$$

$$K = K_2 + \frac{K_2'}{K_D}\cdot[Na^+] + K_1\cdot\frac{1}{[I^{*-}]+[I^-]}$$

WE NOW MAKE THE FOLLOWING SUBSTITUTIONS:

	$[RI]$	$[RI^*]$	$[I^-]$	$[I^{*-}]$	$[Na^+]$	$[NaClO_4]$
time = 0	A	0	B	C	B+C+Z	Z
time = t	A-x	x	B+x	C-x	B+C+Z	Z

NOTE: $B+C = I^-_{TOTAL}$ ONLY IF $K_D = \infty$. ALSO, IT HAS BEEN ASSUMED THAT $NaClO_4$ IS COMPLETELY DISSOCIATED IN ACETONITRILE.

THE DIFFERENTIAL EQUATION CAN NOW BE REWRITTEN:

$$-\frac{dx}{dt} = K\left([x][B+x] - [A-x][C-x]\right)$$

$$= K\left([A+B+C]x - AC\right)$$

THEN:

$$\int_{t_1}^{t_2} K\,dt = -\int_{x_1}^{x_2} \frac{dx}{[A+B+C]x - AC}$$

$$K(t_2-t_1) = \frac{-1}{[A+B+C]} \ln\left([A+B+C]x - AC\right)\Big|_{x_1}^{x_2}$$

$$K = \frac{2.303}{[A+B+C](t_2-t_1)} \log\left[\frac{\left(\frac{C-x_1}{C}\right)(A+B+C) - (B+C)}{\left(\frac{C-x_2}{C}\right)(A+B+C) - (B+C)}\right]$$

$$K = \frac{2.303}{\left([RI]+[I^-]+[I^{*-}]\right)(t_2-t_1)} \log\left[\frac{\frac{[I^{*-}]_{t_1}}{[I^{*-}]_0}\left([RI]+[I^-]+[I^{*-}]\right) - \left([I^-]+[I^{*-}]\right)}{\frac{[I^{*-}]_{t_2}}{[I^{*-}]_0}\left([RI]+[I^-]+[I^{*-}]\right) - \left([I^-]+[I^{*-}]\right)}\right]$$

ERROR ANALYSIS

LET c_i = CPM OF THE SAMPLE TAKEN AT TIME t_i WITH $c_i > c_j$ IF $t_i < t_j$

$A_1 = [RI]$ $\quad A_2 = [I^-] + [I^{*-}]$

THEN

$$K = \frac{2.303}{(A_1+A_2)(t_j - t_i)} \log \left[\frac{\frac{c_j}{c_0}(A_1+A_2) - A_2}{\frac{c_i}{c_0}(A_1+A_2) - A_2} \right]$$

PARTIAL DIFFERENTIATION WITH RESPECT TO THE PROPER VARIABLES YIELDS THE FOLLOWING FIRST ORDER APPROXIMATION TO THE ERROR IN K:

$$\Delta K = -K \cdot \frac{\Delta(t_j - t_i)}{(t_j - t_i)} + \frac{A_2}{(t_j - t_i)} \cdot \frac{\left(\frac{c_j}{c_0} - \frac{c_i}{c_0}\right)}{\left(\frac{c_i}{c_0}(A_1+A_2) - A_2\right)\left(\frac{c_j}{c_0}(A_1+A_2) - A_2\right)} \cdot \frac{\Delta c_0}{c_0}$$

$$+ \frac{1}{t_j - t_i} \cdot \frac{\left(\frac{c_j}{c_0}\right)}{\left(\frac{c_i}{c_0}(A_1+A_2) - A_2\right.} \cdot \frac{\Delta c_i}{c_i} - \frac{1}{t_j - t_i} \cdot \frac{\left(\frac{c_j}{c_0}\right)}{\left(\frac{c_j}{c_0}(A_1+A_2) - A_2\right)} \cdot \frac{\Delta c_j}{c_j}$$

$$- K \cdot \frac{\Delta(A_1+A_2)}{(A_1+A_2)} + \frac{A_1 - A_2}{t_j - t_i} \cdot \frac{\left(\frac{c_i}{c_0} - \frac{c_j}{c_0}\right)}{\left(\frac{c_i}{c_0}(A_1+A_2) - A_2\right)\left(\frac{c_j}{c_0}(A_1+A_2) - A_2\right)} \cdot \frac{\Delta(A_1+A_2)}{(A_1+A_2)}$$

CALCULATION OF ERRORS DUE TO VARIATION IN THE COUNTING BASED ON THIS FORMULA COMPARE FAIRLY WELL WITH VALUES OBTAINED EMPIRICALLY. (SEE TABLES 1,2&3). HOWEVER, AS CAN BE SEEN, THERE IS SOME SECOND ORDER CONTRIBUTION TO ALL THE TRUE VALUES AND EVEN SOME THIRD ORDER CONTRIBUTIONS TOWARDS THE END. THESE VALUES ALSO REVEAL THAT CERTAIN MEASUREMENTS ARE MUCH MORE CRITICAL THAN OTHERS. IN PARTICULAR, THE FIRST AND LAST MEASUREMENTS ARE ESPECIALLY CRITICAL AS A 1% CHANGE IN ONE OF THEM CAN MAKE A 15 TO 20% CHANGE IN THE VALUE OF K. ALSO, IT CAN BE SEEN THAT SINCE ONE OF THE COEFFICIENTS IN THE ERROR TERM INVOLVING RI AND NaI IS SIMILAR TO THAT IN THE TERM FOR c_0, IF $A_1 - A_2$

IS OF THE SAME MAGNITUDE AS A_2 OR LARGER, THE ERROR DUE TO A SMALL ERROR IN EITHER THE RI OR NaI WILL BE OF THE SAME MAGNITUDE AS THE ERROR DUE TO A SIMILAR CHANGE IN c_o. THUS, IF AT ALL POSSIBLE, ONE SHOULD KEEP $A_1 \cong A_2$ TO MINIMIZE ERRORS. ALSO NOTICE THAT IF THE TIME INTERVALS ARE CHOSEN CORRECTLY, SOME OF THE ERRORS IN THE c_i's AND c_j's WILL BE OF EQUAL MAGNITUDE BUT OF OPPOSITE SIGN. THUS SOME OF THE ERRORS WILL CANCEL EACH OTHER OUT WHEN AN AVERAGE IS TAKEN.

ANOTHER SOURCE OF ERROR TO BE CONSIDERED IS THAT DUE TO THE FACT THAT IT TAKES A FINITE AMOUNT OF TIME FOR THE SAMPLE TO RUN INTO THE WATER WHICH QUENCHES THE REACTION. DUE TO THIS FACT, THE RADIOACTIVITY OF THE NaI WILL BE SLIGHTLY LOWER THAN WOULD BE FOUND IF THE SAMPLE WERE QUENCHED INSTANTANEOUSLY. IF WE MAKE THE APPROXIMATION THAT DURING THE SHORT TIME IT TAKES THE SAMPLE TO RUN INTO THE WATER, THE EXCHANGE RATE REMAINS CONSTANT, AND IF WE ALSO MAKE THE APPROXIMATION THAT THE REACTION MIXTURE RUNS OUT OF THE PIPET AT A CONSTANT RATE, THEN WE CAN GET AN IDEA OF THE MAGNITUDE OF THE ERROR AS FOLLOWS:

LET τ = CHANGE IN COUNTING RATE PER ML OF SOLUTION (APPROXIMATED AS A CONSTANT)
T = TOTAL NUMBER OF COUNTS LOST DUE TO THE TIME DELAY IN QUENCHING
t_1 = TIME AT WHICH QUENCHING BEGINS
t_2 = TIME AT WHICH THE PIPET IS FINALLY EMPTIED

THEN AT THE TIME WE ARE ABOUT TO QUENCH THE REACTION THE TOTAL CHANGE IN COUNTING RATE FOR THE 5ML SAMPLE WILL BE 5τ AND WE CAN WRITE:

$$T = \int_{t_1}^{t_2} 5\uparrow \left(1 - \frac{t - t_1}{t_2 - t_1}\right) dt$$

$$= \int_{t_1}^{t_2} 5\uparrow \left(\frac{t_2}{t_1 - t_2} - \frac{t}{t_1 - t_2}\right) dt$$

$$= \frac{5\uparrow}{t_2 - t_1}\left(t_2 t - \frac{t^2}{2}\right)\Bigg|_{t_1}^{t_2} = \frac{5\uparrow}{2(t_2 - t_1)}\left(t_2^2 - \frac{t_2^2}{2} - t_2 t_1 + \frac{t_1^2}{2}\right)$$

$$= \frac{5\uparrow}{2(t_2 - t_1)}\left(t_2^2 - 2t_2 t_1 + t_1^2\right) = \frac{5\uparrow}{2(t_2 - t_1)}(t_2 - t_1)^2$$

$$T = \frac{5}{2}\uparrow \cdot (t_2 - t_1)$$

USING SOME OF THE DATA FROM 18-1 WE OBTAIN THE FOLLOWING ESTIMATION OF THE ERRORINVOLVED FOR THE FIRST SAMPLE MEASURED.

$c_0 = 11818$ cpm $\qquad c_1 = 10792$ cpm $\qquad t_1 - t_0 = 300$ sec

$$5\uparrow \approx \frac{11818 - 10792}{300} = \frac{1026}{300}$$

$$T \approx \frac{1026}{2 \cdot 300} \cdot 10\,\text{sec} = 17.1 \text{ cpm}$$

THUS ASSUMING THAT IT TAKES 10 SECONDS TO DRAIN THE PIPET, WE FIND THAT THE COUNTING RATE FOR THIS FIRST SAMPLE, 10792 CPM, WOULD ACTUALLY BE LOW BY ABOUT 17 CPM, AN ERROR AMOUNTING TO APPROXIMATELY 0.16%. THIS ESTIMATE IS ACTUALLY A LITTLE BIT HIGH AS THE APPROXIMATION OF THE COUNTING RATE IS ALSO A LITTLE BIT TOO HIGH.

DISCUSSION OF DATA

CALCULATIONS BASED ON THE EQUATION DERIVED BY CONSIDERING THE THREE POSTULATED REACTION MECHANISMS YIELD THE COMPOSITE VALUE:

$$K = \left(k_2 + \frac{k_2'}{K_D} \cdot [Na^+] + \frac{K_1}{[I^-] + [I^{*-}]} \right)$$

THIS INDICATES THAT K SHOULD BE INDEPENDENT OF THE CONCENTRATION OF ALKYL IODIDE, SHOULD INCREASE WITH INCREASING SODIUM ION CONCENTRATION AND SHOULD INCREASE WITH DECREASING IODIDE ION CONCENTRATION. NOTE THAT AN INCREASE IN Na^+ WILL CAUSE A DECREASE IN I^-, HENCE THE ADDITION OF $NaClO_4$ SHOULD CAUSE AN INCREASE IN K. THE DATA, HOWEVER, CLEARLY INDICATES THAT THIS IS NOT THE CASE. HENCE SOME OTHER EFFECT WHICH HAS NOT BEEN CONSIDERED MUST BE AFFECTING THE REACTION. SPECULATION AS TO WHY THIS SHOULD HAPPEN YIELD THE FOLLOWING POSSIBILITIES. FIRST, AS WAS SHOWN BY EXPERIMENT, A VERY SMALL AMOUNT OF WATER (1ML IN 50ML OF SOLUTION) WAS ENOUGH TO CAUSE A VERY LARGE DECREASE IN THE RATE CONSTANT (30--40%). THE $NaClO_4$ USED CAME FROM A FRESHLY OPENED BOTTLE OF REAGENT GRADE MATERIAL; HOWEVER, IT IS POSSIBLE THAT IT HAD SOME WATER OF HYDRATION ALONG WITH IT. SECONDLY, THERE IS THE POSSIBILITY THAT THE ClO_4^- ION IS BECOMING PART OF THE SOLVENT CAGE SURROUNDING THE ALKYL IODIDE MOLECULE AND THAT ITS CHARGE PREVENTS THE IODIDE

ION FROM GETTING THROUGH TO REACT WITH THE ALKYL IODIDE. IF THIS EFFECT IS TAKING PLACE, ONE WOULD CONSIDER IT MOST LIKELY TO EXPECT TO FIND THE ClO_4^- ION AS FAR AWAY FROM THE IODIDE PART OF THE MOLECULE AS POSSIBLE, I.E., ON THE BACK SIDE OF THE MOLECULE, WHICH IS THE SPOT THE IODIDE ION ATTACKS IN THE BIMOLECULAR PROCESS. THE PRESENCE OF THE ClO_4^- IN THE SOLVENT CAGE WOULD ALSO BE EXPECTED TO HELP ACCELERATE THE UNIMOLECULAR REACTION BY HELPING TO PUSH THE IODIDE OFF OF THE ALKYL CATION. THUS IF THIS IS WHAT IS HAPPENING WE WOULD EXPECT THE S_{N_2} REACTION TO BE SLOWED DOWN AND THE S_{N_1} REACTION TO BE SPEEDED UP. FINALLY OF COURSE, THERE MAY BE SOME EFFECT OF INCREASED IONIC STRENGTH WHICH IS BEING OVERLOOKED.

I SHOULD ALSO NOTE AT THIS POINT THAT IN ONE OF THE EARLY EXPERIMENTS IN WHICH I ADDED FIRST 25mL AND THEN 50mL OF WATER, THE RATE APPEARED TO INCREASE BOTH TIMES, BUT UNFORTUNATELY, THE ACCURACY ON THE SECOND EXPERIMENT WAS VERY BAD AND NEITHER EXPERIMENT WAS EVER REPEATED. THIS SHOULD BE CHECKED INTO AGAIN.

FINALLY, IT IS INTERESTING TO NOTE THAT THEORETICALLY, WE COULD USE THIS REACTION TO DETERMINE THE DISSOCIATION CONSTANT FOR NaI IN ACETONITRILE. IF WE MEASURE ALL THE OTHER PARAMETERS VERY ACCURATELY, THEN WE CAN CONSIDER THE UNKNOWN VARIABLES IN THE EQUATION AS K, $[RI]$, AND $[I^-]$. THUS BY USING 3 CALCULATED VALUES OF K, AND THE KNOWN FORM OF THE ERROR EQUATION WE CAN SET UP A SYSTEM OF THREE EQUATIONS IN THREE UNKNOWNS AND ITERATE THIS SYSTEM TO OBTAIN ACCURATE VALUES OF K, $[RI]$, AND $[I^-]$. THIS INFORMATION, ALONG WITH THE KNOWLEDGE OF HOW MUCH NaI WAS

INITIALLY ADDED WOULD BE SUFFICIENT TO CALCULATE THE VLAUE OF K_D.

SOLUTIONS, APPARATUS, AND PROCEEDURES

Solutions

Acetonitirle--Matheson, Coleman, and Bell(tech grade)--ST2467 was distilled from anhydrous $CaSO_4$ and run through a chromatographic column containing Al_2O_3 which had been heated 4 days at 250°C. It was stored in a bottle with a squeeze bulb mechanism for delivery and protected by drying tubes containing "Drierite."

NaI--Baker and Adamson(reagent grade)--ST4619

$NaClO_4$--anhydrous from G.Fredric Smith Chem. Co.--ST4635

n-Butyl iodide--reagent grade--protected with mercury in the bottom of the container

CCl_4--reagent grade

H_2O--distilled water from the tap

Solutions were prepared by weighing into a volumetric flask the appropriate amount of NaI (and $NaClO_4$ when used). Acetonitrile was then added to make the solution up to the mark. The prepared solutions were kept in jars with ground glass stoppers.

Apparatus

A water bath equipped with a heater controlled by a thermoregulator, a Beckman thermometer graduated in 0.01°C., and a cooling coil.

The Cooling coil was supplied with water from an ice bath by a water circulating pump controlled by a variac transformer

A Nuclear Chicago Sintillation Counter

13--5ml pipets
12--4ml pipets
1--50ml pipet
1--7ml pipet
assorted micropipets ranging from .025ml to 1.0ml
1--automatic pipet filler bulb

MAGNETIC STIRRER AND SEVERAL LARGE STIRRING BARS
3--150ML ERLENMEYER FLASKS
3--60ML SEPARATORY FUNNELS
24 OR MORE SPECIAL LOW ADSORPTION GLASS TUBES OBTAINED FROM NUCLEAR CHICAGO

PROCEEDURES

STANDARD PRECAUCIONS WERE TAKEN IN THE HANDLING OF THE I^{131}. DISPOSABLE RUBBER GLOVES WERE WORN WHEN HANDLING RADIOACTIVE SOLUTIONS. THE GLOVES AND OTHER SUCH MATERIAL WERE DISCARDED IN A CLOSED, MARKED CONTAINER. RADIOACTIVE SOLUTIONS WERE DISCARDED INTO A PLASTIC BOTTLE AND THE GLASSWARE WHICH CONTAINED THESE SOLUTIONS WAS RINSED AT LEAST TWICE WITH 0.1 F KI SOLUTION. THESE RINSINGS WERE ALSO DISCARDED IN THE PLASTIC BOTTLE. WHEN THE BOTTLE WAS FILLED, THE SAFETY OFFICE WAS CALLED TO COME AND DISPOSE OF THE MATERIAL AND LEAVE A NEW BOTTLE.

THE PROCEEDURE FOLLOWED DURING THE RUNS WAS AS FOLLOWS: 50ML OF NaI SOLUTION WAS WITHDRAWN AND PIPETED INTO A 150ML ERLENMEYER FLASK. AN APPROPRIATE AMOUNT OF NaI* WAS ADDED TO GIVE A COUNTING RATE OF 10,000 TO 50,000 CPM. THE SOLUTION WAS THEN MIXED BY SWIRLING THE FLASK. TOWARDS THE END OF THE WORK, I SWITCHED TO A MAGNETIC STIRRER WHICH WORKED OUT MUCH BETTER. IT CAME IN VERY HANDY PARTICULARLY WHEN THE ALKYL IODIDE WAS ADDED. THE SOLUTION WITH THE RADIOACTIVE IODIDE ADDED WAS PLACED IN THE WATER BATH UNTIL THE SOLUTION REACHED THE WATER BATH TEMPERATURE. A 5ML SAMPLE WAS WITHDRAWN TO BE COUNTED FOR THE T=0 SAMPLE AND THEN THE FLASK WAS REMOVED AND THE ALKYL IODIDE WAS ADDED AND MIXED IN AS FAST AS POSSIBLE. THE

FLASK WAS THEN RETURNED TO THE WATER BATH. THE FLASK WAS KEPT STOPPERED WITH A RUBBER STOPPER EXCEPT WHEN THE REACTANTS WERE BEING ADDED AND SAMPLES WERE BEING WITHDRAWN. THIS PRECAUTION WAS TAKEN IN ORDER TO LIMIT THE ADSORPTION OF WATER BY THE SOLUTION. THE TIME T=0 WAS MARKED AT A CONSISTENT TIME DURING THE ADDITION OF THE ALKYL IODIDE FOR ALL THE RUNS. AT APPROPRIATE INTERVALS (RANGING FROM 5 TO 30 MINUTES) 5ML SAMPLES OF THE REACTION MIXTURE WERE WITHDRAWN TO BE COUNTED. COUNTING OF THE SAMPLES WAS DONE AFTER THE RUN WAS COMPLETED IN AS SHORT A TIME AS POSSIBLE IN ORDER TO MINIMIZE THE ERRORS DUE TO THE DECAY OF THE I^{*-}. A CORRECTION MUST BE APPLIED TO THE FIRST SAMPLE OF EACH RUN IN ORDER TO TAKE INTO ACCOUNT THE FACT THAT THE FIRST SAMPLE IS WITHDRAWN BEFORE THE ALKYL IODIDE IS ADDED. IF WE LET

VSI = VOLUME OF NaI IN ACETONITRILE WHICH WAS TAKEN
VSIR = VOLUME OF NaI* ADDED
VIMP = VOLUME OF IMPURITIES ADDED
VALKI = VOLUME OF ALKYL IODIDE ADDED
COUNTS = NUMBER OF COUNTS PER MINUTE OBTAINED FROM THE SAMPLE

THEN

$$(\text{Corrected counting rate}) = \text{COUNTS} \cdot \frac{VSI + VSIR + VIMP - VSAMP}{VSI + VSIR + VIMP + VALKI - VSAMP}$$

PREPARATION OF THE SAMPLE FOR COUNTING

5ML OF CCl_4 AND 7ML OF H_2O ARE PIPETED INTO A CLEAN, DRY 60ML SEPARATORY FUNNEL. THE FIVE ML SAMPLE OF THE REACTION MIXTURE IS PIPETED INTO THIS MIXTURE TO QUENCH THE REACTION, THE ALKYL IODIDE GOING INTO THE CCl_4 PHASE WHILE THE NaI GOES

INTO THE AQUEOUS PHASE. AS THE AQUEOUS PHASE INCREASED IN VOLUME TO SLIGHTLY OVER 8ML, A LITTLE MORE THAN 1ML OF THE ACETO-NITRILE MUST ALSO HAVE GONE INTO THE AQUEOUS PHASE WITH THE REMAINDER GOING INTO THE CCL_4 PHASE. (SHOULD THIS SEEM UNDESIRABLE, ONE MIGHT TRY OTHER NITRILES AS SOLVENTS SUCH AS PROPIONITRILE ETC.) THE SEPARATORY FUNNEL IS SHAKEN AND THE PHASES ARE ALLOWED TO SEPARATE. THE PROPORTION OF CCL_4 TO H_2O HAD BEEN PREVIOUSLY CHOSEN SO AS TO AVOID THE DIFFICULTIES ENCOUNTERED WITH THE FORMATION OF SLOWLY SEPARATING EMULSIONS. IN SOME CASES, HOWEVER, DIFFICULTIES WERE STILL ENCOUNTERED. IN THESE CASES IT WAS FOUND THAT IF THE SEPARATORY FUNNEL WAS SHAKEN GENTLY, THE EMULSION DID NOT FORM. AFTER THE MIXTURE HAS SEPARATED, THE BOTTOM CCL_4 PHASE IS RUN OFF AND DISCARDED IN THE WASTE CONTAINER. FROM THE REMAINING AQUEOUS PHASE, TWO 4ML SAMPLES WERE WITHDRAWN BY PIPET AND EACH WAS RUN INTO ONE OF THE SPECIAL GLASS TUBES. THESE TUBES HAVE A PLASTIC SCREW CAP WHICH WAS THEN SCREWED IN PLACE. THE TUBES CAN NOW EITHER BE COUNTED DIRECTLY OR IF THERE IS DIFFICULTY WITH DROPS OF LIQUID CLINGING TO THE SIDES OF THE TUBE (AFFECTING THE GEOMETRY OF THE SAMPLE IN THE COUNTER) THE TUBES CAN BE CENTRIFUGED AT LOW SPEEDS FOR ABOUT A MINUTE TO GET ALL THE LIQUID DOWN IN THE BOTTOM OF THE TUBE AND THEN COUNTED. (THE TUBES DO NOT FIT PROPERLY IN THE CENTRIFUGE AND AT HIGH SPEEDS THEY SHATTER.)

TABLES 1,2&3 CONTAIN THE FOLLOWING INFORMATION AND ARE ARRANGED IN THE FOLLOWING FORMAT. TABLE 1 CONTAINS THE FACTORS INVOLVED IN THE ERROR FORMULA FOR C_o , C_i , AND C_j AS CALCULATED FROM THAT FORMULA. TABLES 2 AND 3 CONTAIN THE SAME INFORMATION CALCULATED EMPIRICALLY BY ONE AT A TIME MAKING A 1% ERROR IN EACH OF THE COUNTING RATES. TABLE 2 IS FOR A POSITIVE ERROR AND TABLE 3 IS FOR A NEGATIVE ERROR. ALL THE TABLES ARE BASED ON THE DATA FROM RUN 18-1. THE DATA IS ARRANGED IN MATRIX FORM WITH EITHER THREE OR FOUR ENTRIES APPEARING IN EACH SLOT. THE FIRST OF THESE ENTRIES GIVES THE FACTOR FOR THE C_o ERROR TERM. THE SECOND IS THE FACTOR FOR THE C_i ERROR TERM, AND THE THIRD IS THE FACTOR OF THE C_j ERROR TERM. NOTE THAT IN THE FIRST COLUMN THE C_i ERROR TERM AND THE C_o ERROR TERM MUST BE COMBINED SINCE FOR THIS COLUMN $C_o = C_i$. THE FOURTH ENTRY IN TABLE 1 IS THE FACTOR FOR THE A_1+A_2 ERROR TERM WHICH WAS NOT CALCULATED IN THE THE OTHER TWO TABLES. THE DATA FOR RUN 18-1 IS LISTED BELOW.

18-1

C_i's	11818	10792	9611.8	8671.8	8364.7	8149.9	cpm
t_i's	0	300	1200	2100	3000	3900	sec

$K \cdot 10^3$

	t_0	t_1	t_2	t_3	t_4
t_1	3.5200				
t_2	2.4099	2.0398			
t_3	2.7304	2.5988	3.1578		
t_4	2.5361	2.4268	2.6203	2.0828	
t_5	2.5755	2.4968	2.6491	2.3948	2.7069

TABLE 1

	T_0	T_2	T_3	T_4	T_5
T_1	.043356				

	.043356				
	-.004324				
T_2	.016476	.007515			
	-------	.014452			
	.016476	.021968			
	-.003966	-.003847			
T_3	.019432	.015442	.023374		
	-------	.007226	.021968		
	.019432	.022671	.045342		
	-.007500	-.007906	-.011966		
T_4	.022653	.020350	.026771	.030166	
	-------	.004817	.010984	.045342	
	.022653	.025170	.037755	.075510	
	-.009810	-.010418	-.013705	-.015443	
T_5	.034496	.033752	.042505	.052070	.073980
	-------	.003656	.007323	.022671	.075510
	.034496	.037370	.049827	.074741	.149482
	-.016285	-.017279	-.021760	-.026656	-.037873

AVERAGE OF ERRORS FOR C_o FROM COLUMN 1 .027283

AVERAGE OF ERRORS FOR C_o FROM WHOLE TABLE .030823

TABLE 2

	T_0	T_1	T_2	T_3	T_4
T_1	.04482				

	.04371				
T_2	.01721	.00801			
	------	.01457			
	.01651	.02201			
T_3	.02099	.01702	.02603		
	------	.00728	.02201		
	.01896	.02212	.04424		
T_4	.02562	.02349	.03123	.03643	
	------	.00486	.01100	.04423	
	.02135	.02372	.03558	.07116	
T_5	.04457	.04455	.05673	.07208	.10772
	------	.00364	.00734	.02212	.07115
	.03002	.03252	.04336	.06505	.13010

TABLE 3

	T_0	T_1	T_2	T_3	T_4
T_1	.04401				

	.04544				
T_2	.01657	.00741			
	-----	.01515			
	.01751	.02336			
T_3	.01897	.01479	.02217		
	-----	.00758	.02336		
	.02145	.02502	.05004		
T_4	.02132	.01880	.02450	.02682	
	-----	.00505	.01168	.05005	
	.02626	.02918	.04376	.08753	
T_5	.02997	.02880	.03593	.04281	.05881
	-----	.00379	.00778	.02502	.08754
	.04590	.04973	.06631	.09946	.19891

THE FORMAT OF THE FOLLOWING TABLES LABLED DATA I, II, III, AND IV IS AS FOLLOWS. DATA I AND II GIVE THE VALUES OF K CALCULATED BY THE COMPUTER ALONG WITH THE STANDARD DEVIATIONS AND PERCENT ERROR. THE FIRST COLUMN GIVES THE AVERAGE OF ALL THE K VALUES CALCULATED WITH THE ASSOCIATED STANDARD DEVIATIONS AND PERCENT ERRORS IMMEDIATELY AFTER. THE SECOND THREE COLUMNS GIVE THE SAME DATA FOR THE CASE WHERE $c_i = c_o$. FOR EASE IN HANDLING, THE VALUES OF K AND THE STANDARD DEVIATION HAVE BEEN MULTIPLIED BY A FACTOR OF 1000. DATA III AND IV GIVE THE CONCENTRATIONS OF THE REACTANTS. THE COLUMN FOR H_2O GIVES THE NUMBER OF ML OF WATER ADDED TO THE REACTION MIXTURE. THE OTHER THREE COLUMNS GIVE THE CONCENTRATIONS IN MOLES PER LITER AND HAVE BEEN MULTIPLIED BY A FACTOR OF 100 FOR EASE OF HANDLING. WHERE VALUES HAVE NOT BEEN LISTED IN A COLUMN, THEY ARE THE SAME AS THE LAST VALUE LISTED, AND THE SPACE HAS IN SOME CASES BEEN USED FOR OTHER COMMENTS.

DATA I

RUN	K_{MATRIX}	ST.DEV.	%	$K_{1ST\ COL.}$	ST.DEV.	%
6-1	1.10	0.14				
7-1	1.93	0.28				
7-2	2.03	0.20				
9-1	2.74	0.11				
9-2	3.06	0.11				
9-3	3.55	0.67				
12-1	2.55	0.15	4.2	2.56	0.06	2.4
12-2	2.39	0.08	3.6	2.43	0.06	2.7
12-3	3.60	1.43	39.8	3.05	0.61	20.0
14-1	2.42	0.59	24.2	2.54	0.20	7.8
14-2	2.74	0.42	15.3	2.74	0.14	5.1
14-3	2.56	0.24	9.2	2.75	0.17	6.0
14-4	2.60	0.41	15.6	2.73	0.13	5.1
18-1	2.60	0.37	14.2	2.75	0.44	16.1
18-12	2.68	0.67	25.2	2.69	0.22	8.2
18-13	2.51	0.29	11.5	2.57	0.23	9.0
18-14	2.61	0.17	6.6	2.64	0.13	5.0
18-2	2.45	0.48	19.5	2.64	0.23	8.8
18-22	2.20	0.31	14.2	2.36	0.21	9.1
20-1	2.90	0.05	1.8	2.88	0.07	2.5
20-12	2.72	0.28	10.3	2.87	0.16	5.7
20-2	2.82	0.20	7.1	2.89	0.14	4.9
20-22	2.60	0.36	13.9	2.74	0.22	8.0
21-1	2.74	0.31	11.5	2.92	0.20	6.8
21-2	2.49	0.50	20.2	2.79	0.37	13.1
21-3	2.77	0.38	13.6	2.97	0.20	6.7
21-41	3.55	0.25	7.0	3.71	0.23	6.3

DATA II

RUN	K_{MATRIX}	ST.DEV.	%	$K_{1ST\ COL.}$	ST.DEV.	%
24-10	1.87	0.11	5.8	1.88	0.06	3.0
24-11	1.80	0.18	10.2	1.71	0.16	9.2
24-12	1.87	0.20	10.7	1.90	0.07	3.6
24-13	1.86	0.13	7.2	1.94	0.08	4.3
24-14	1.80	0.25	13.7	1.93	0.15	7.9
24-15	1.86	0.23	12.6	1.89	0.08	4.3
24-16	1.90	0.28	14.6	2.04	0.14	6.3
24-17	1.95	0.23	10.5	2.11	0.18	8.3
24-18	1.93	0.08	4.4	1.99	0.09	4.4
24-19	1.80	0.19	10.5	1.75	0.12	6.8
25-10	0.972	0.061	6.2	0.940	0.048	5.2
25-11	1.00	0.10	10.4	0.925	0.072	7.9
25-12	1.04	0.12	11.3	0.968	0.128	13.2
25-13	1.04	0.11	10.9	0.953	0.148	15.6
25-14	1.03	0.10	9.3	1.01	0.04	4.1
25-15	0.996	0.078	7.8	0.932	0.101	10.9
26-10	1.71	0.15	9.2	1.77	0.06	3.5
26-11	1.75	0.06	3.2	1.77	0.02	1.3
26-12	1.80	0.04	2.2	1.82	0.03	1.6
26-20	1.01	0.04	4.1	1.01	0.03	3.3
26-21	1.04	0.05	5.2	1.07	0.04	3.3
26-22	1.03	0.05	4.9	1.07	0.05	4.8
26-40	1.87	0.09	4.9	1.95	0.09	4.8
26-41	1.87	0.09	4.6	1.93	0.06	3.3
26-42	1.89	0.07	4.0	1.94	0.06	3.2
26-43	1.95	0.06	3.3	1.99	0.06	3.1
26-50	1.92	0.05	2.8	1.97	0.06	3.3
26-51	1.92	0.08	4.3	1.99	0.10	5.0

DATA III

RUN	RI	SI	H_2O	$NaClO_4$
6-1	7.91	9.10	0	0
7-1	8.69	9.89		
7-2				
9-1	9.64	9.89		
9-2			0.025ML	
9-3	9.63		0.05ML	

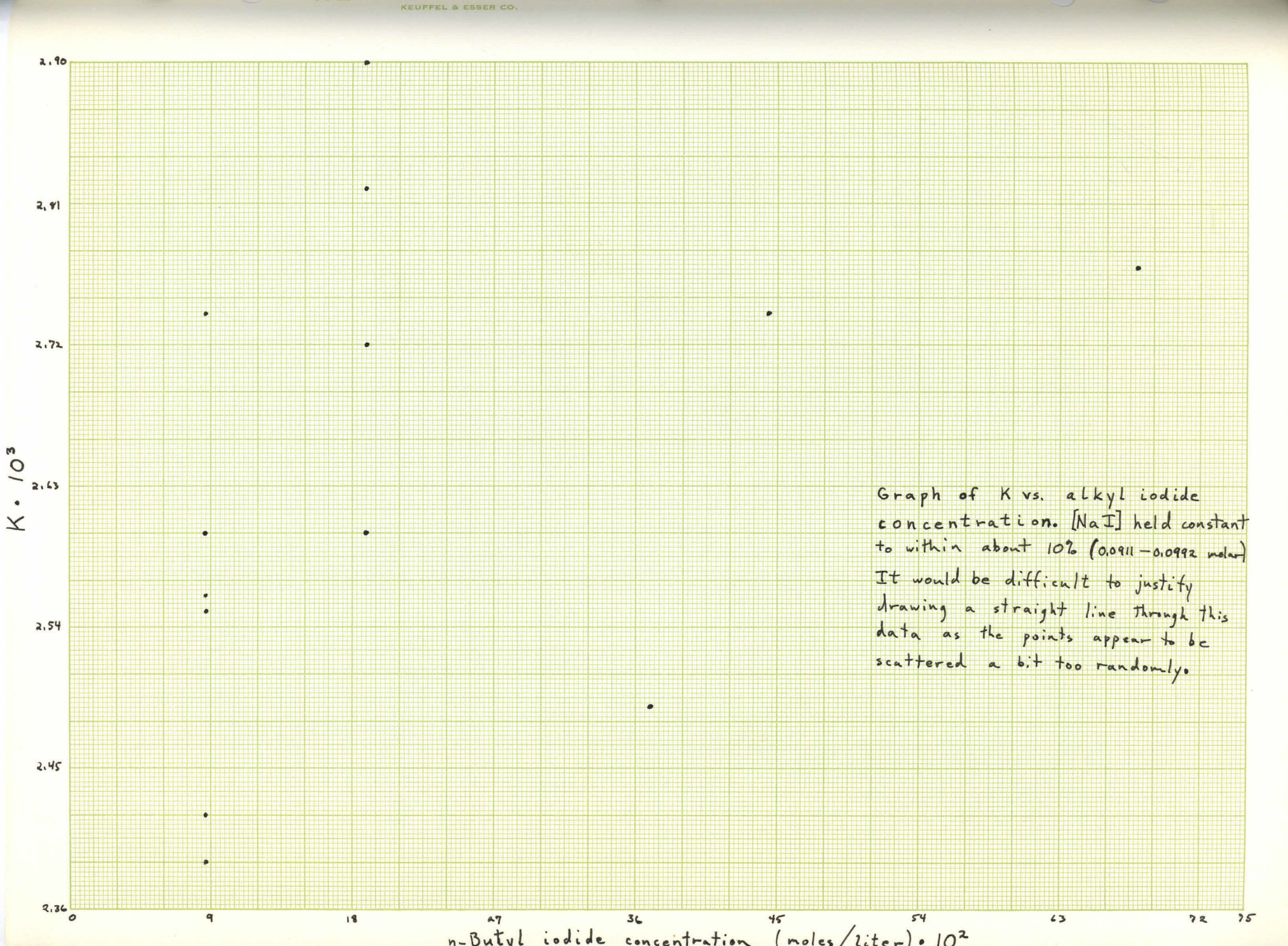
NaI SOLUTION USED IN RUNS 6-1 TO 9-3 WAS OF UNKNOWN ORIGIN AND WAS REPUTED TO BE 0.1 N. THE NaI* HAD H_2O IN IT. 5ML OF NaI* WERE ADDED TO 6-1 WHILE 0.05 ML WERE USED IN RUNS 7-1 TO 9-3. TEMPERATURE OF 6-1 WAS 22.8°C. WHILE THAT OF 7-1&2 WAS ABOUT 23°C. TEMPERATURE OF 9-1 TO 9-3 WAS 25-27°C. ALL FURTHER RUNS WERE CONDUCTED IN A WATER BATH KEPT AT 25.35° ± 0.05°C.

12-1	8.695	9.916	0	0
12-2				
12-3	IF VALUES CORBESPONDING TO $t=90$ ARE THROWN OUT YOU GET $K=(2.54\pm0.37)\cdot 10^{-3}$			
14-1	8.682	9.921		
14-2				
14-3	8.673	9.911	SAMPLES WASHED TWICE WITH CCl_4	
14-4				
18-1	9.550	19.57		
18-12				
18-13				
18-14				
18-2				
18-22				
20-1	18.90	9.698		
20-12				
20-2				
20-22				
21-1	41.35	9.444		
21-2	36.99	9.494		
21-3	71.00	9.110		
21-41	PROBABLE ERROR IN MEASUREMENT OF TIME			

DATA IV

RUN	RI	SI	H_2O	$NaClO_4$	
24-10	19.06	9.798	0	87.96	COUNTED 4:45 PM
24-11					COUNTED 7:00 PM
24-12					COUNTED 9:00 PM
24-13	CENTRIFUGED				COUNTED 9:30 PM
24-14					COUNTED NEXT DAY
24-15	SHOOK SAMPLE TUBES BEFORE COUNTING				
24-16	CENTRIFUGED				
24-17	SHOOK SAMPLE TUBES BEFORE COUNTING				
24-18	CENTRIFUGED				
24-19					
25-10	18.66	9.602	1.0ML	86.28	3HR. WAIT BEFORE COUNTING
25-11	CENTRIFUGED				
25-12	NEXT DAY--COUNTER LEFT ON OVER NIGHT				
25-13	TWO TUBES REPLACED IN COUNTER--COUNTED THREE HOURS LATER				
25-14					
25-15					
26-10	19.02	9.770	0	87.79	
26-11					
26-12	CENTRIFUGED ONE DAY AND COUNTED THE NEXT				
26-20	18.62	9.584	1.0ML	86.12	
26-21					
26-22	CENTRIFUGED ONE DAY AND COUNTED THE NEXT				
26-40	37.23	9.563	0	85.93	
26-41	CENTRIFUGED				
26-42	COUNTED THE NEXT DAY				
26-43					
26-50					
26-51	CENTRIFUGED				

A MAGNETIC STIRRER WAS USED IN RUNS 26-40 TO 26-51



Graph of K vs. alkyl iodide concentration. [NaI] held constant to within about 10% (0.0911 – 0.0992 molar) It would be difficult to justify drawing a straight line through this data as the points appear to be scattered a bit too randomly.

Graph of K vs. alkyl iodide concentration. [NaI] held constant to within about 2%. (0.0956–0.0980 molar). $NaClO_4$ was added to make the solution approximately 2 molar in ionic strength.