

A STUDY OF THE CATALYTIC DECOMPOSITION
OF
POTASSIUM CHLORATE
AND
POTASSIUM PERCHLORATE

A Thesis
by
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A STUDY OF THE CATALYTIC DECOMPOSITION OF POTASSIUM CHLORATE AND POTASSIUM PERCHLORATE.

Introduction

Although every student of Chemistry has generated oxygen by heating potassium chlorate, has written the equation, $2 \text{KClO}_3 = 2 \text{KCl} + 3 \text{O}_2$, and has noted the accelerating influence of catalysts on the evolution of gas, as yet the kinetics of the reactions involved have never been completely investigated. The present work is a study of the decomposition of potassium chlorate and potassium perchlorate. Because ferric oxide can be obtained in a purer state than the usually employed catalyst, manganese dioxide, it was decided to use only the former as catalyst. Since it is generally conceded that the decomposition of potassium perchlorate is a simpler change than that of potassium chlorate (the latter being partly simultaneously converted to potassium perchlorate) it was deemed advisable to limit the study of the catalytic effects of Fe_2O_3 to the former change, namely, $\text{KClO}_4 = \text{KCl} + 2 \text{O}_2$. The formation of potassium perchlorate from the chlorate was found to be auto-catalyzed by the potassium chloride formed from the two reactions:



Hence, experiments were tried in which some of the latter

was initially present. Also it was hoped that some indication of the nature of an intermediate compound between the decomposing substance and the catalyst might be gained from the results of this work.

It is customary to study the kinetics of a reaction in dilute solutions. At temperatures of 400° - 600° C fused salts are the only feasible solvents, and in fact, potassium nitrate was used as such in Scobai's research on the decomposition of potassium chlorate, which will be discussed later. To eliminate any possible catalytic effect, no solvent for the potassium chlorate and perchlorate has been used in the present investigation. This, of course, is not an entirely new procedure since an analogous research without solvent was conducted by Bruner⁽¹⁾ on the bromination of benzene in which the small amounts of 1 gm. of bromine and 1.65 cc. of benzene were used.

Historical

The historical review on the decomposition of these salts will be taken up in the following order: uncatalyzed potassium chlorate; catalyzed potassium chlorate; other chlorates; potassium perchlorate; other perchlorates.

In the decomposition of potassium chlorate by

heat it has been reported that chlorine also is evolved, and that an increase in temperature⁽²⁾, or a sudden rise in temperature⁽³⁾ causes an increase in the proportion of chlorine. This was explained by Sodeau⁽⁴⁾ from the consideration that the reaction, $\text{KClO}_3 = \text{KCl} + 3/2 \text{O}_2$, is exothermic while its change to chlorine and potassium oxide is endothermic. Reduced pressure did not affect the proportion of chlorine, potassium chloride and potassium perchlorate formed.⁽⁵⁾⁽²⁾ In a controversy of some length Brunck and McLeod⁽⁶⁾ produced experimental data to indicate the nature of the gas evolved which liberated iodine from potassium iodide solution. If it is true that chlorine is evolved during the decomposition, it follows that the solution of the residue must be alkaline and in fact this observation was made by Warren⁽⁷⁾ and McLeod⁽⁸⁾. On the other hand Sodeau⁽⁵⁾ maintains that the residues are slightly acid, requiring 0.05 - 0.3 cc. of N/500 potassium hydroxide to effect neutralization. No chlorine or other gas liberating iodine was obtained by Wagner⁽⁹⁾ when pure potassium chlorate was used and Sodeau⁽²⁾ states that no chlorine is evolved when the reaction is carried on in platinum vessels. Hence it is to be assumed that the evolution of chlorine is due either to the presence of impurities or to the influence of the walls of the vessel in which the reaction is carried out.

Due to varying conditions the proportional yields of oxygen, potassium chlorate and potassium perchlorate

have differed and investigators who proceeded on the theory that a single reaction gave all three products were very much puzzled. Several⁽¹⁰⁾⁽¹¹⁾⁽¹²⁾⁽¹³⁾⁽⁵⁾ have expressed their own results in specific chemical equations. In as much as the manufacture of potassium perchlorate is involved in this reaction, it will be interesting to tabulate the largest yields which have been obtained.

Serullas	44%	year 1831	(14)
Liebig	50 - 53%	1844	(15)
Marignac	65 - 66%	1843	(16)
Blau and Weingand	69%	1921	(17)

The effect of additions of oxides of manganese on the decomposition of potassium chlorate has been studied by Sodeau⁽⁵⁾, Hodgkinson and Lowndes⁽¹⁸⁾, Fowler and Grant⁽¹⁹⁾, McLeod⁽²⁰⁾, Mills and Donald⁽²¹⁾ and Widerhold⁽²²⁾. The last has found that manganese dioxide reduces the temperature of oxygen evolution to 200°C. Sodeau and Fowler and Grant found that chlorine was given off under these conditions although Hodgkinson and Lowndes observed none when the mass was heated moderately. McLeod reported that Mn_2O_4 had very little catalytic effect.

The effect of Silicon dioxide or powdered glass was found to be negligible by Teed⁽¹⁰⁾, although Fowler and Grant⁽¹⁹⁾ state that it increased the amount of chlorine evolved. Frankland and Dingwald⁽¹²⁾ and Blau and Weingand⁽¹⁷⁾ found that it caused a better yield of potassium perchlorate.

The catalytic effect of many other oxides has been investigated by Fowler and Grant⁽¹⁹⁾, including ferric oxide, the catalyst selected for the present research. These authors say the presence of small amounts of this oxide increases the evolution of chlorine, though with larger proportions of catalyst this is decreased. In the present research no chlorine was detected as will be noted later. Mills and Donald⁽²¹⁾ have derived a mathematical equation which expresses their observations on the use of ferric oxide as catalyst for this reaction. They reject the idea of contact action. The temperature at which oxygen is evolved under these conditions is stated by Widerhold⁽²²⁾ to be 110 - 120° C.

Veley⁽²³⁾ claims that any inert finely divided substance will act as catalyzer for this reaction. Sodeau⁽²⁴⁾ thinks that the substance Veley used for experimentation (BaSO_4) cannot be said to be wholly inert.

Marignac⁽¹⁶⁾ working with open tubes and no temperature regulation found that potassium chlorate and potassium perchlorate decreased the yield of perchlorate from potassium chlorate in the time in which equal amounts of oxygen had been evolved from the tube of pure potassium chlorate and the one to which additions of the above salts had been made. Scobai⁽²⁵⁾ found potassium perchlorate to have no influence on the transformation. His mixtures of potassium chlorate and potassium chloride solidified quickly and he did not attempt any further work with them. This omission by Scobai has been investigated to some extent in

the present work.

A brief summary of work on the decomposition of other chlorates should be noted. Reduced pressure increased the evolution of chlorine from lead and silver chlorates⁽⁵⁾ and affected the proportion of chloride and perchlorate formed from barium chlorate⁽²⁾. The effect of temperature on barium, lithium and strontium chlorates has been studied by Potilitzin⁽²⁶⁾. When aluminum chlorate is cautiously heated to 100° it explodes. On the other hand, rapid heating to above 100° causes it to evolve chlorine leaving a basic "chlorate" $\text{Al}_2(\text{ClO}_4)_6 \cdot \text{Al}_2\text{O}_3$ ⁽²⁷⁾. (The formula of a perchlorate is given in the abstract.) Sodeau⁽²⁸⁾ observed the formation of lead dioxide when lead chlorate was heated. In another article he states that silver chlorate explodes at 345°⁽²⁹⁾. The decomposition of many chlorates in the presence of various catalysts was studied by Spring and Prost⁽³⁾.

With reference to the decomposition studies of potassium perchlorate the loss in weight on heating to 395° was found negligible by Scobai⁽²⁵⁾. On heating for 56 hours in sulphur vapor Frankland and Dingwald⁽¹²⁾ reported a loss of 0.3% by weight. McLeod⁽²⁰⁾ states that it does not decompose at the boiling point of mercury in the presence of manganese dioxide.

The presence of chlorate in residues of moderately heated perchlorate was observed by Millon⁽³⁰⁾, Teed⁽¹⁰⁾ and Frankland and Dingwald⁽¹²⁾, the latter claiming its

separation by fractional crystallization. Scobai occasionally found traces of chlorate. None of these investigators have found chlorate in perchlorate residues when manganese dioxide was used as catalyst.

Anomalously Potilitzin⁽²⁶⁾ (in abstract) reports that the rate of decomposition of lithium perchlorate is greatest at 368° and that decomposition begins at 380° .

From this brief historical survey it is quite evident that there is no settled opinion as to the exact nature of the decomposition of potassium chlorate and perchlorate either with, or without the presence of catalyst.

Theoretical

For some time after the discovery that the products obtained on heating potassium chlorate were potassium perchlorate, potassium chloride and oxygen, various investigators attempted to represent the reaction by suitable equations, thus;

Th. Graham⁽³¹⁾ wrote $2 \text{KClO}_3 = \text{KClO}_4 + \text{KCl} + \text{O}_2$;

Frankland and Dingwald⁽¹²⁾, $8 \text{KClO}_3 = 5 \text{KClO}_4 + 3 \text{KCl} + 2 \text{O}_2$;

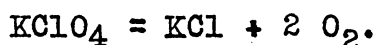
Teed⁽¹⁰⁾, $22 \text{KClO}_3 = 14 \text{KClO}_4 + 8 \text{KCl} + 5 \text{O}_2$.

None of these equations will fit the facts under more than one set of conditions, and it is now generally conceded that two simultaneous and independent chemical changes proceed instead of a single reaction. Thus potassium chlorate by one reaction gives potassium perchlorate and potassium chloride; by the other it loses oxygen leaving potassium

chloride. These reactions are represented by the simple equations (1) $4 \text{KClO}_3 = 3 \text{KClO}_4 + \text{KCl}$

and (2) $2 \text{KClO}_3 = 2 \text{KCl} + 3 \text{O}_2$,

which are not intended to indicate in any way the mechanism of the change. Equation 1 according to some investigators is reversible (cf Historical Part). Thus, when potassium perchlorate is heated, in addition to the decomposition into potassium chloride and oxygen, a reaction would take place by which potassium chlorate would be formed. This potassium chlorate would immediately begin to decompose and therefore in heating potassium perchlorate the concentration of potassium chlorate naturally would soon become almost constant. But in the present investigation, as will be shown later, no chlorate was found in the perchlorate residues. In case potassium chlorate is formed, its concentration would probably be constant after the initial heating disturbances and hence its formation would not affect the calculations for the velocity coefficient of the equation



In all the calculations of this research, the concentration of the original pure substance has been taken equal to one. Hence, the weight of the original substance equivalent to the weight of any product formed, divided by the initial weight of material, will express the concentration of the product. Therefore, the fractional amount changed or unchanged at any time, or for brevity written simply as amount, will be considered from now on as synonymous with the concentration of the product or reacting substance respectively.

The above equation admits of very easy kinetic treatment. According to the mass law for a monomolecular reaction,

$$dx/dt = k(a - x),$$

where t is time, a the initial concentration of reacting substance, x the fractional amount already transformed and k the proportionality constant or velocity coefficient. Integrating and solving this equation for k, it is seen that k can be calculated from finite values of t, a and x.

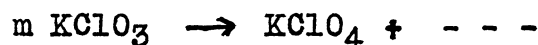
$$k = 1/t \log a/(a - x).$$

To eliminate the initial disturbances mentioned above, k can be calculated between any two observations of (a - x) of the experiment. In this case the equation is

$$k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2},$$

where t₁ and x₁, and t₂ and x₂ are simultaneous observations, respectively.

If the decomposition of potassium chlorate is expressed as follows,



a general differential equation for the combined side reactions is deducible, but can not be integrated without assuming values for n and m. Since these equations lead to differential equations with somewhat complicated solutions, not generally given in textbooks, the entire derivation is included here.

In the time t let the amount of potassium chlorate changed into potassium perchlorate be y and let z be the amount of potassium chlorate changed into oxygen.

Then $dy/dt = k_1(a - y - z)^m$

and $dz/dt = k_2(a - y - z)^n$

Let x be the total amount changed in the time t .

That is, $x = y + z$

$$dx/dt = dy/dt + dz/dt$$

$$dx/dt = k_1(a - x)^m + k_2(a - x)^n$$

let $(a - x) = C$

$$- dx/dt = dC/dt$$

$$- dC/dt = k_1 C^m + k_2 C^n$$

$$\frac{dC}{k_1 C^m + k_2 C^n} = - dt$$

$$\frac{dC}{C^m + \frac{k_2}{k_1} C^n} = - k_1 dt$$

Let $k_2/k_1 = K$ and $-k_1 t = s$

Then $-k_1 dt = ds$

Substituting $\frac{dC}{C^m + KC^n} = ds$

or $\frac{dC}{C^n(C^{m-n} + K)} = ds$

By partial fractions

$$\frac{1}{C^n(C^{m-n} + K)} = \frac{1/K}{C^n} + \frac{-1/KC \cdot C^{m-2n}}{C^{m-n} + K}$$

whence $\left[\frac{1}{C^n} - \frac{C^{m-2n}}{C^{m-n} + K} \right] dC = K ds$

At this point m and n must be evaluated. Since it is probable that four molecules of potassium chlorate react together to form three molecules of potassium perchlorate with the elimination of one molecule of potassium chloride and another molecule of potassium chlorate yields 3 atoms of oxygen, which then, by a very fast consecutive reaction forms molecules of oxygen,

let us suppose $m = 4$ and $n = 1$.

Then,
$$\left[\frac{1}{C^2} - \frac{C^2}{C^3 + K} \right] dC = K ds$$

Integrating, $\log C - 1/3 \log (C^3 + K) = Ks + F$

Substituting for C , s and K their former values,

$$\log \frac{a-x}{[(a-x)^3 + k_2/k_1]}^{1/3} = -k_2 t + F$$

Evaluating the integration constant F by letting $t = 0$,

whence $x = 0$,

$$\log \frac{a}{(a^3 + k_2/k_1)}^{1/3} = F$$

Substituting for F its value,

$$\log \frac{a-x}{[(a-x)^3 + k_2/k_1]}^{1/3} = -k_2 t + \log \frac{a}{(a^3 + k_2/k_1)}^{1/3}$$

Solving for $k_2 t$

$$k_2 t = \log \frac{a}{a-x} \left[\frac{(a-x)^3 + k_2/k_1}{a^3 + k_2/k_1} \right]^{1/3}$$

Cubing

$$\left(\frac{a-x}{a} e^{k_2 t} \right)^3 = \frac{k_1(a-x)^3 + k_2}{k_1 a^3 + k_2}$$

Multiplying by $k_1 a^3 + k_2$,

$$(k_1 a^3 + k_2) \left(\frac{a-x}{a} e^{k_2 t} \right)^3 = k_1(a-x)^3 + k_2$$

Multiplying and assembling coefficients of k_1 and k_2 ,

$$k_1 [(a-x)^3 e^{3k_2 t} - (a-x)^3] = k_2 \left[1 - \left(\frac{a-x}{a} e^{k_2 t} \right)^3 \right]$$

Solving for k_1 ,

$$k_1 = k_2 \frac{1 - \left(\frac{a-x}{a} e^{k_2 t} \right)^3}{(a-x)^3 (e^{3k_2 t} - 1)}$$

This equation only gives a relation between k_1 and k_2 , and

accordingly k_2 must be determined by other means. The differential formula $\Delta z/\Delta t = k_2(a - x)$ was used. The corresponding equation for the other side reaction $\Delta y/\Delta t = k_1(a - x)$ was employed in a few calculations when the value for k_2 , due to experimental error, was obviously wrong. The difficulty in the use of these formulae lies in the determination of the tangents $\Delta z/\Delta t$ and $\Delta y/\Delta t$ on the z, t and y, t curves. The tangents, however, were determined (this detail will be explained later) with at least as great an accuracy as the plotting of the curves permitted.

The quantities a and a - x in the above equations are directly measurable, but the separate quantities y and z whose sum is x can not be measured directly. The oxygen is evolved not only from the chlorate, but from the perchlorate which has been formed during the process. Hence the true values of y and z can be obtained by subtracting from the apparent z and adding to the apparent y a correction, which is calculated from these apparent values and the velocity coefficient for the decomposition of pure potassium perchlorate. The apparent y (y'') is the amount of perchlorate formed minus the amount decomposed. Hence, it may be assumed that in a given interval the average amount of perchlorate present has decomposed according to the velocity coefficient of pure potassium perchlorate at that temperature. Since this decomposition is of the first order, no account need be taken of the fact that its concentration here is lower than when initially pure potassium perchlorate was

decomposed. The weight of perchlorate (w) which would be decomposed if the average amount present in each interval $\frac{y_n'' + y_{n+1}''}{2}$ were held at the condition of the experiment, was calculated.

$$w = \frac{y_n'' + y_{n+1}''}{2} \left(1 - \frac{1}{10^{k(t_{n+1} - t_n)}} \right)$$

(n is the number of the observation.) This weight is then added to y_{n+1}'' and all subsequent values of y'' , making a series of values y' , which are the apparent values, once corrected. These values of y' were again corrected in the same manner and, if the second corrections were so small that it was obvious that a third correction was unnecessary, the values obtained were called $\underline{y}$. The difference between y'' and y was then subtracted from z'' giving z . Then $\underline{y}$ and $\underline{z}$ could be used to make the y, t and z, t curves. For clearness, the conversion factor of potassium chlorate to potassium perchlorate and vice versa has been omitted in this explanation but was included in the calculations.

Since velocity coefficients are a function of temperature their evaluation according to the foregoing equations must be done at constant temperature. Otherwise, consistent results could not be expected. A relation between the velocity coefficients of reversible reactions at different temperatures has been deduced by van't Hoff and a similar relation has been found by Arrhenius⁽³²⁾ to

hold good for irreversible reactions. $\frac{d \log K}{dT} = \frac{Q}{RT^2}$

or $\log K = \frac{-Q}{RT} + B$ (van't Hoff), where Q is the heat of reaction, R the gas constant and B the constant of integration.

$$\log K = \frac{A}{T^2} + B \quad (\text{Arrhenius})$$

It is understood that A has no physical significance unless it is a relation between the number of "active" and "passive" molecules as postulated by Arrhenius.

Another phase of the present investigation was to ascertain what relation the velocity coefficient bore to the amount of catalyst present. Since the method of approach to this problem was that of cut and try, the discussion of the algebraic equations involved will be postponed until after the experimental data and necessary calculations have been given.

In all of these derivations and the applications of them in the present work, the following assumptions have been made:

- (1) That the Mass Law applies in concentrated solutions,
- (2) That the volume of the solid and liquid phases does not change during decomposition,
- (3) That the decomposition of potassium perchlorate (temperature correction applied) is the same, when dissolved in fused potassium chlorate, as when it itself is in the fused state,
- (4) That the particles of solid catalyst remain uniformly distributed during the experiment.

Criticism of Scobai's Work

The work which Scobai⁽²⁵⁾ under the direction of Wilhelm Ostwald has done upon the decomposition of potassium chlorate is open to criticism. In the first place, as can be seen by referring to Table 1, for the transformation of potassium chlorate to potassium perchlorate, Scobai employs the formula $K = \left(\frac{1}{3t} \frac{1}{(a-x)^3} - \frac{1}{a^3} \right)$ which should be used for a simple fourth order reaction. It takes no account of the potassium chlorate decomposing to give oxygen, which according to Scobai is small, but does in fact involve approximately 20% of the total amount of potassium chlorate.

Then for calculating the velocity of this decomposition to give oxygen, Scobai uses a differential formula

$$K = \frac{\Delta z / \Delta t}{C_m},$$

but $\Delta z / \Delta t$ instead of being as nearly an instantaneous value as possible is defined as the slope of a line drawn from a given point on the z, t curve to the origin and C_m is the concentration midway between the origin and the point in question. That is, $C_m = a - x/2$ if x is the amount of the initial substance $\frac{a}{2}$ which has decomposed in the time t . The formula by which he has calculated K is not $K = \frac{\Delta z / \Delta t}{C_m^n}$, but a formula derived from $z/t = K \frac{a + (a - x)}{2}$, namely, $K = \frac{z}{t} \left(\frac{1}{a - x/2} \right)^n$.

His constants have an average deviation of 22.5%.

In recalculations with these observations, the concentrations have been reduced to the basis of pure potassium

chlorate having a concentration of one instead of five. After correcting (Table 2) for the oxygen evolved from the potassium perchlorate, according to the method explained in the theoretical part of this thesis, the values of $\underline{x}$, $\underline{y}$ and $\underline{z}$ were plotted against time on Graph 1, page . From these curves the value of $a - x$, $\Delta y/\Delta t$ and $\Delta z/\Delta t$ were read at 10 hour intervals.

The latter tangents were determined by the following method. A fine straight scratch on the under side of a piece of celluloid was placed so that it intersected the y, t or z, t curve at equal distances from the given point along the t axis. This could be done with much greater precision than trying to place it as a tangent and gave practically the same figure. The slope of this line was then determined and recorded (Tables 3 and 4) as $\Delta y/\Delta t$ or $\Delta z/\Delta t$ although they are almost dy/dt and dz/dt .

If the log of the general formula $\Delta y/\Delta t = K(a-x)^n$ is taken, a straight line relation is obtained between $\log \Delta y/\Delta t$ and $\log (a-x)$.

$$\log \Delta y/\Delta t = n \log (a - x) + \log K$$

When the logs of the values calculated above are plotted (Graph 2, page), a straight line is obtained in which the slope is found to be 4. Hence the velocity coefficients were calculated by the formula,

$$K = \frac{\Delta y/\Delta t}{(a-x)^4}$$

The average value obtained was $3.532 \times 10^{-3} \pm 0.076 \times 10^{-3} =$

2.15%, while Scobai's average reduced to the basis of the initial concentration equalling one instead of five, is

$$4.600 \times 10^{-3} \pm 0.188 \times 10^{-3} = 4.1\%$$

The same operation (see Graph 3) applied to the other side reaction lead to the obviously incorrect value of $n = 10$, and accordingly the calculation of K from these data was not made. It was hoped that better data could be obtained for this computation.

Further in his paper Scobai, using fused potassium nitrate as solvent, does not employ the incorrect integrated formula as previously, but he still can be criticised for the value he assigns to C_m , $\Delta y/\Delta t$ and $\Delta z/\Delta t$.

Also he maintains that his experimental data give K the greatest constancy when $n = 4$. But, when his own results are plotted on a $\log \Delta y/\Delta t \cdot \log C_m$ curve, the slope obtained is not $+4$ but roughly -1 . (For data see Table 5 and Graph 4) And in fact the product $\Delta y/\Delta t \cdot C_m$ is nearly constant as shown in the last column of Table 5.

Thus, contrary to the law of Mass Action, the less potassium chlorate remaining, the faster it is transformed to potassium perchlorate. The general trend of these results is, however, in accord with the observations of the present research, but, as will be shown, it must be ascribed to autocatalysis.

TABLE 1.

Scobai's Observations and Calculations

Time hrs.	Wt. KClO ₃	Wt. KClO ₃ undec. per 5 gms. (a - x)	Evolved O ₂ per 5 gms.	$K = \frac{x(3a^2 - 3ax + x^2)}{3ta^3(a - x)^3}$
9	5.1862	4.797	.025	.0000392
24	5.2482	4.533	.0373	380
48	5.2528	4.245	.072	352
72	5.2163	3.959	.0954	376
96	5.2530	3.785	.113	362
120	5.2169	3.671	.1211	339
144	5.2243	3.455	.1274	377

Av. .0000368 $\pm$.0000015 (4.1%)

Time hrs.	Wt. left in tube KClO ₄ , KCl, KClO ₃ per 5 gms.	KCl formed	Wt. undec. KClO ₃ a - x	Wt. KClO ₄ y	KClO ₃ KClO ₄ y	KClO ₃ giving oxygen z	KClO ₃ $\rightleftharpoons$ KCl found minus that due to perchlorate z'
9	4.975	.047	4.797	.131	.1545	.0485	.0639
24	4.963	.078	4.533	.352	.4153	.0517	.0953
48	4.929	.154	4.245	.530	.6253	.1297	.1840
72	4.906	.248	3.959	.699	.8247	.2163	.2435
96	4.888	.293	3.785	.810	.9557	.2593	.2887
120	4.879	.308	3.671	.900	1.0620	.267	.3097
144	4.873	.371	3.454	1.048	1.236	.3100	.3255

Time	z	C _m	$k_1 = \frac{\Delta/\Delta t}{C_m}$
9	.0485	4.899	.00110
24	.0517	4.767	.000452
48	.1297	4.623	585
72	.2163	4.480	670
96	.2593	4.393	615
120	.267	4.336	513
144	.3100	4.227	509

Av. .000635 $\pm$.000143 (22.5%)

Note: Average Deviations are included and some of the reference letters are changed to conform with the present thesis.

TABLE 2.

Correcction for KClO_4 decomposed

(Recalculation of Scobai's work)

Time hrs.	Wt. KClO_3 undec. per 5 gm.	Total KClO_3 dec. per gm. x	Wt. O_2 evolved per 5 gm.	KClO_3 z O_2 evolved per gm. z"	KClO_3 z KClO_4 remain- ing y"	KClO_4 formed
9	4.797	.0406	.0250	.0128	.0278	.0236
24	4.533	.0934	.0373	.0191	.0743	.0630
48	4.245	.1510	.0720	.0368	.1142	.0968
72	3.959	.2082	.0954	.0487	.1595	.1352
96	3.785	.2430	.1130	.0578	.1852	.1570
120	3.671	.2658	.1211	.0618	.2040	.1730
144	3.455	.3090	.1274	.0651	.2439	.2068

Time	W_1	KClO_4 once cor- rected	W_2	KClO_4 twice cor- rected	KClO_3 form- ing KClO_4 y	KClO_3 form- ing O_2 z
9	.00002356	.0236	.0000236	.0236	.0278	.0128
24	.0001441	.0632	.0001444	.0632	.0745	.0189
48	.0004252	.0974	.0004273	.0974	.1149	.0361
72	.0006173	.1364	.0006221	.1364	.1609	.0473
96	.0007775	.1590	.0007860	.1590	.1875	.0555
120	.0008781	.1759	.0008914	.1759	.2075	.0583
144	.0010106	.2107	.0010286	.2107	.2485	.0605

GRAPH 1

Decomposition of KClO_3 (Scobai)

University of Cincinnati, College of Engineering

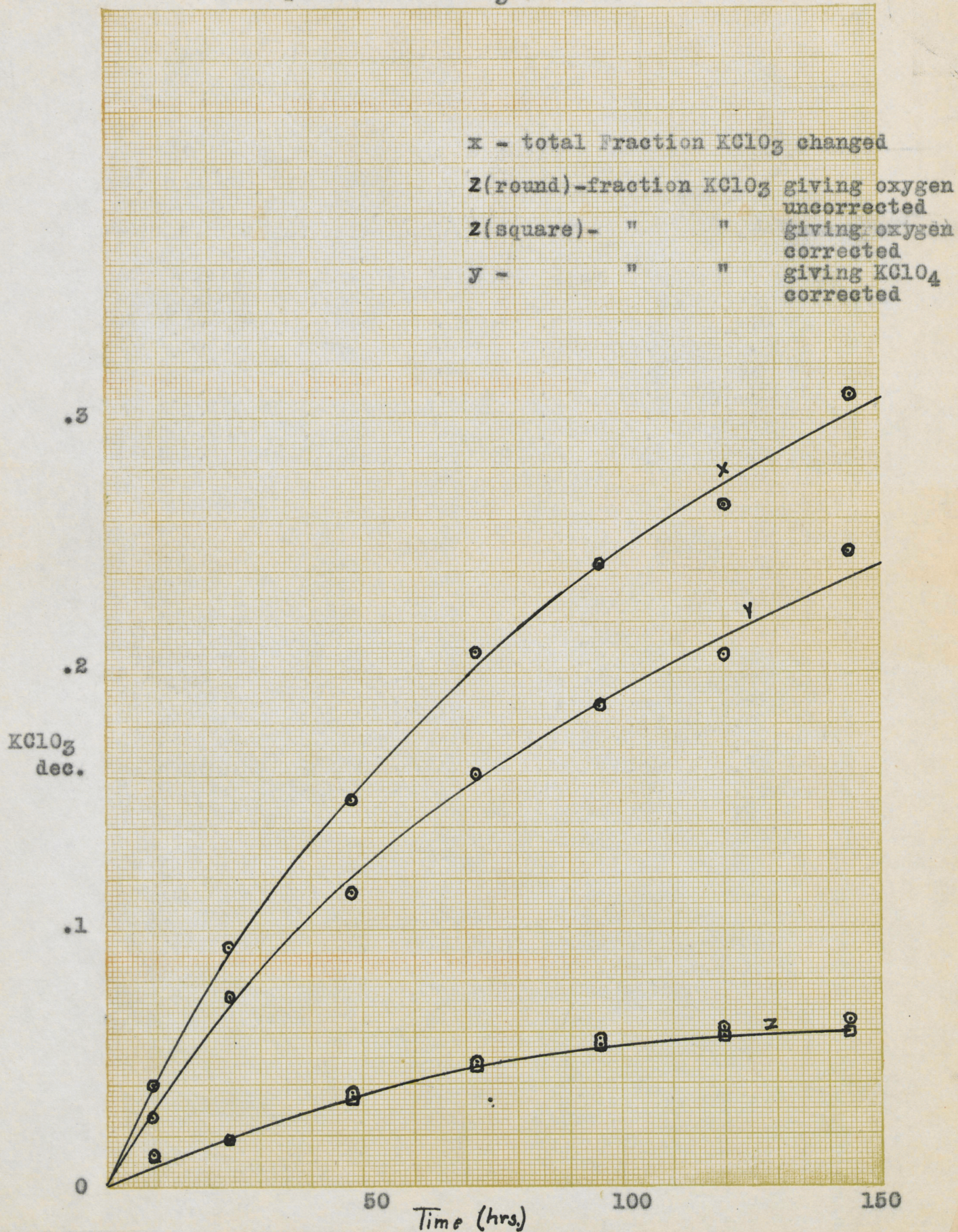


TABLE 3.

Transformation of KClO_3 to KClO_4

Scobai's Work Recalculated

Time hrs.	a - x	$\frac{\Delta y}{\Delta t}$	$\log(a-x)$	$\log \frac{\Delta y}{\Delta t}$	$k_1 = \frac{\Delta y / \Delta t}{(a-x)^4}$
10	.9567	.002954	-.01922	-2.52959	.003526
20	.9195	.002590	-.03645	-2.58670	.003623
30	.8900	.002266	-.05061	-2.64474	.003612
40	.8658	.001980	-.06258	-2.70333	.003524
50	.8433	.001728	-.07402	-2.76246	.003417
60	.8215	.001557	-.08539	-2.80771	.003419
70	.8015	.001402	-.09610	-2.85325	.003397
80	.7830	.001292	-.10624	-2.88874	.003437
90	.7660	.001199	-.11577	-2.92118	.003483
100	.7517	.001149	-.12396	-2.93968	.003599
110	.7388	.001058	-.13147	-2.97551	.003551
120	.7266	.001019	-.13870	-2.99183	.003654
130	.7151	.000956	-.14563	-3.01954	.003654
140	.7039	.000873	-.15249	-3.05899	.003556

Av. .003532 $\pm$.000076

2.15%

Scobai's Constant Reduced to a = 1 basis:

0.004600 $\pm$.0001875

4.1%

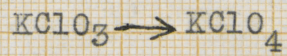
GRAPH 2

Transformation of KClO_3 to KClO_4 - Scobal

Recalc. by C.E.O.

Slope of this line (4) shows

the Reaction



to be of the

fourth order

 $\log \frac{\Delta y}{\Delta x}$

-2.55

-2.6

-2.65

-2.7

-2.75

-2.8

-2.85

-2.9

-2.95

-3.00

-0.15

-0.10

 $\log(a-x)$

-0.05

-0.01

TABLE 4.

Decomposition of KClO_3 to O_2

Scobai's Work Recalculated

Time hrs.	a - x	$\frac{\Delta z}{\Delta t}$	$\log(a - x)$	$\log \frac{\Delta z}{\Delta t}$
10	.9567	.000824	-.01922	-3.08407
20	.9195	.000780	-.03645	-3.10791
30	.8900	.000722	-.05061	-3.14146
40	.8658	.000640	-.06258	-3.19382
50	.8433	.000553	-.07402	-3.25727
60	.8215	.000474	-.08539	-3.32422
70	.8015	.0004095	-.09610	-3.38775
80	.7830	.0003345	-.10624	-3.47560
90	.7660	.0002403	-.11577	-3.61907
100	.7517	.0001770	-.12396	-3.75203
110	.7388	.0001560	-.13147	-3.80688
120	.7266	.0001311	-.13870	-3.88240
130	.7151	.0001020	-.14563	-3.99140
140	.7039	.0000827	-.15249	-4.08249

GRAPH 3

Decomposition of KClO_3 to O_2 - Scobai Inchmatt, College of Engineering

Recalc. by C. E. O.

Slope of straight line

is 10, which would

indicate that the

reaction $\text{KClO}_3 \rightarrow \text{O}_2$

is of the tenth

order

 $\log \frac{\Delta \bar{a}}{\Delta t}$

-3.5

-4.0

-0.15

 $\log (a - x)$

-0.05

-0.01

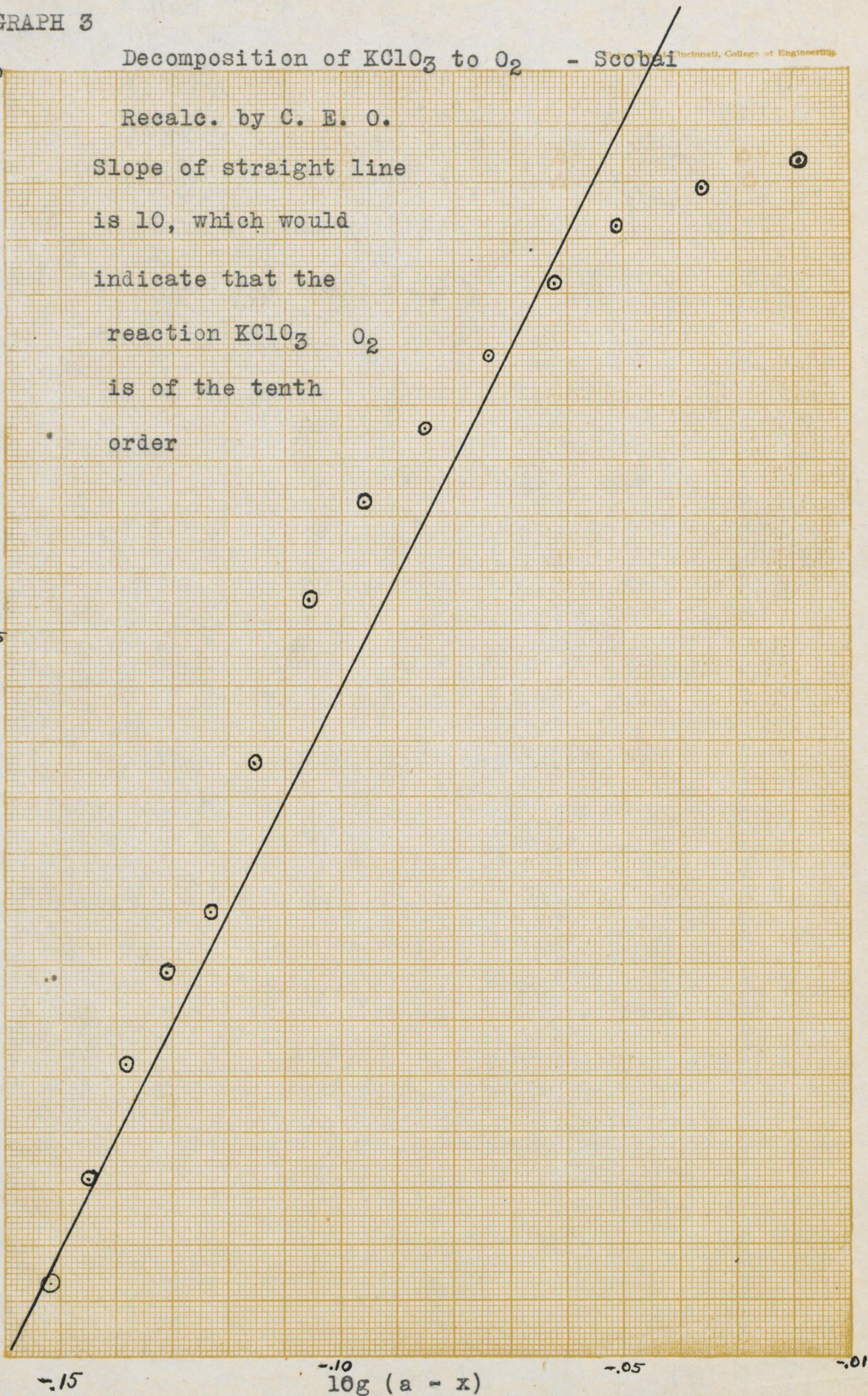


TABLE 5.

KClO₃ in KNO₃ - Scobai

Time	KClO ₃	C _m	$K = \frac{\Delta y}{\Delta t} 1/C_m^4$	$\log \frac{\Delta x}{\Delta t}$	$\log C_m$	$\frac{\Delta x}{\Delta t} C_m$
24	.1789	4.835	0.0000137	-2.1276	.6844	.003604
48	.4247	4.658	188	-2.0532	.6682	.4121
72	.6404	4.528	212	-2.0509	.6559	.4028
96	.8015	4.414	220	-2.0784	.6448	.3685
120	.9380	4.299	229	-2.1070	.6334	.3360
144	1.1450	4.157	267	-2.0996	.6188	.3305
168	1.9430	3.736	594	-1.9367	.5724	.4323
192	2.2500	3.518	765	-1.9311	.5463	.4123
216	2.5770	3.261	0.0001060	-1.9233	.5134	.003890

Note: First four columns are copied directly from Scobai's article.

Initial Concentration of KClO₃ is left equal to 5 and not reduced to 1 as in other data.

GRAPH 4.

 KClO_3 in KNO_3 - Scobai

University of Cincinnati, College of Engineering

Orig. data by Scobai plotted as logs
by C. E. O.

Scobai infers that these points
give a positive slope of 4, but as
can be seen they give approximately
a slope of minus 1.

 $\log \frac{\Delta y}{\Delta t}$

-1.9

-2.0

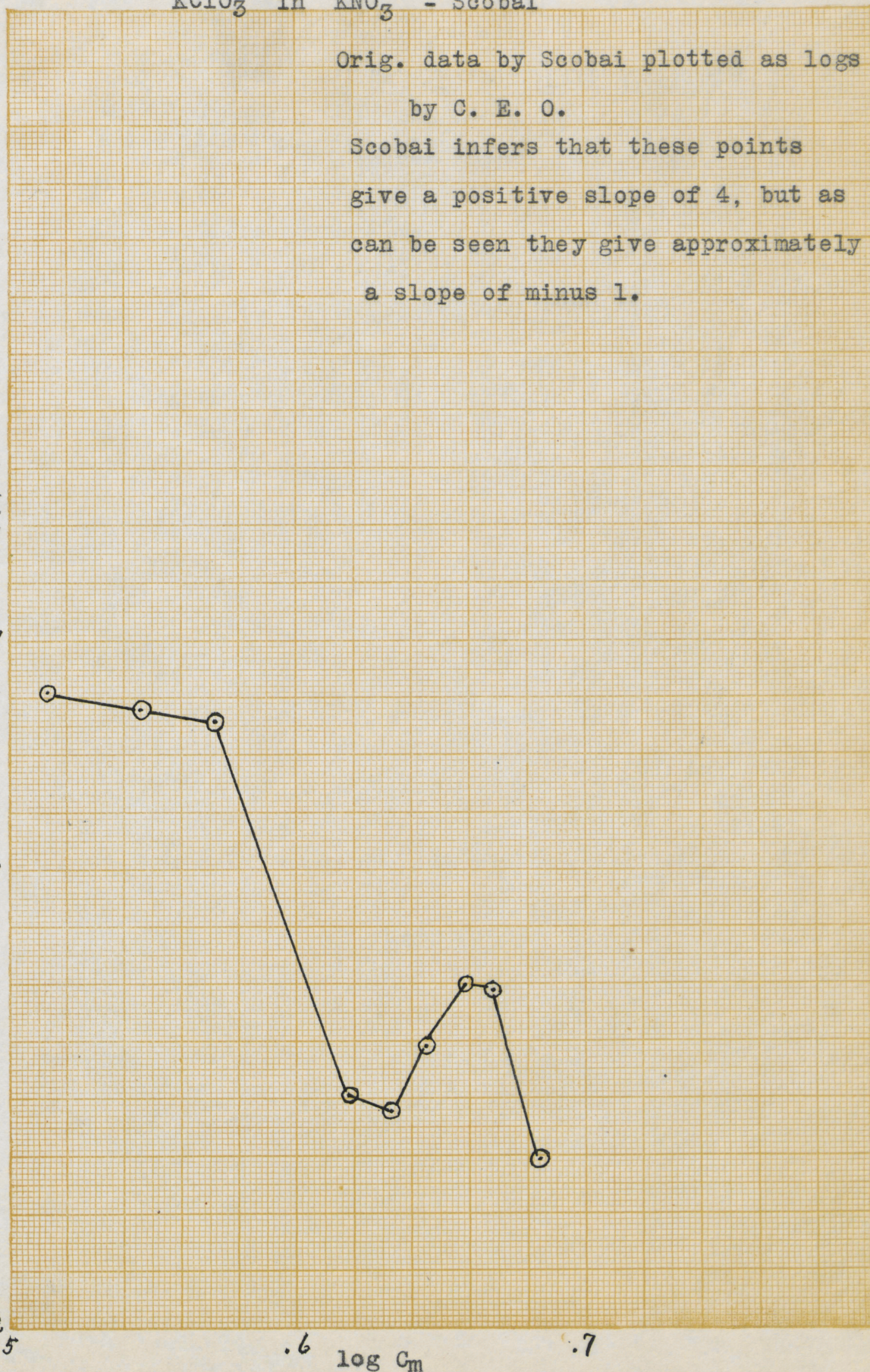
-2.1

-2.2
.5

.6

 $\log C_m$

.7



Experimental

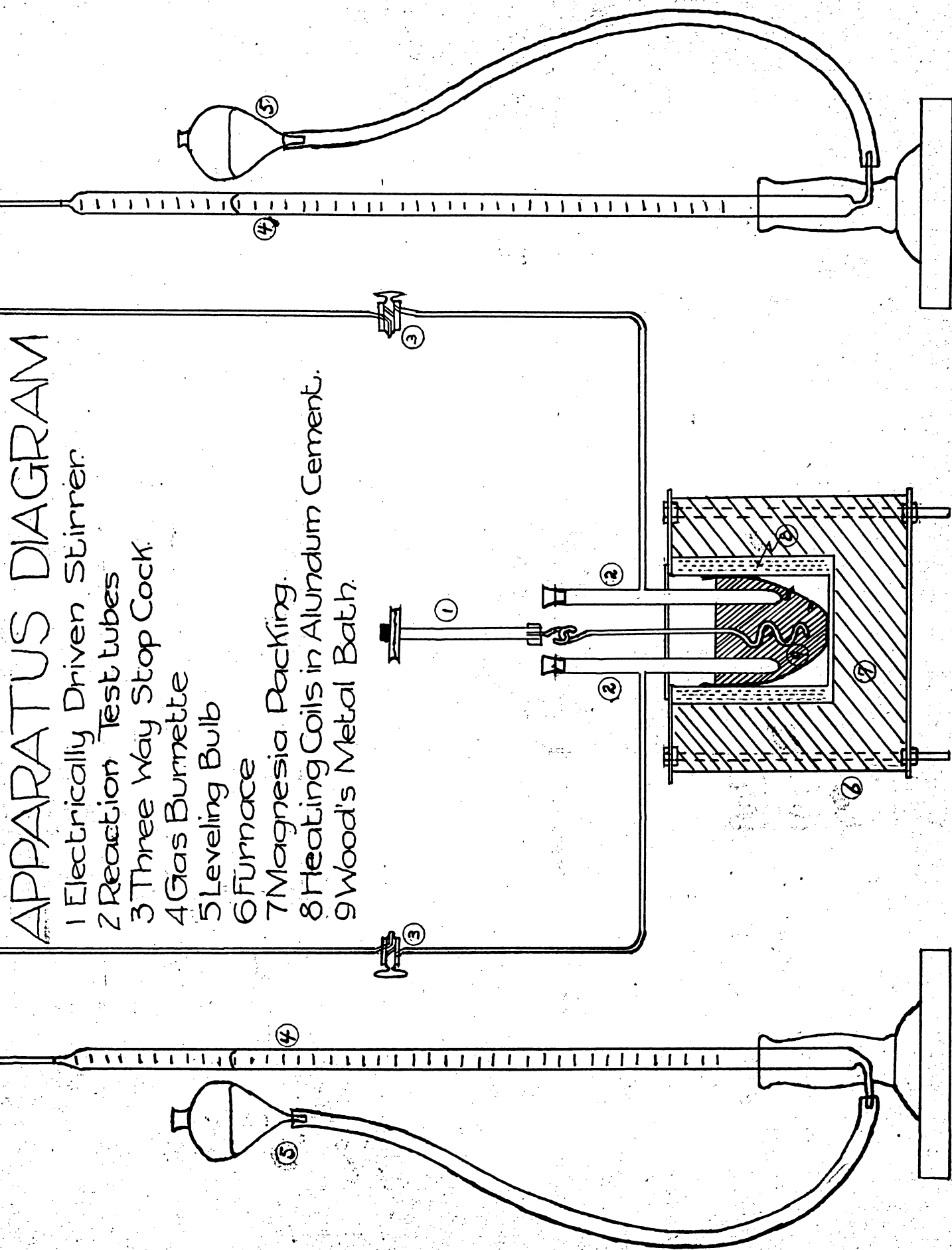
Apparatus

The apparatus which previous investigators have used has varied from the open tubes of Marignac to the air bath of Fowler and Grant, the self-regulating air bath of Scobai and the metal bath of Sodeau. Reaction vessels have been test tubes or flasks of glass, iron, or quartz.⁽¹⁷⁾ In case chlorine was found to be given off, adsorption towers of various fantastic shapes were included in the gas train. If the volume of evolved oxygen was desired, a gas burette was incorporated.

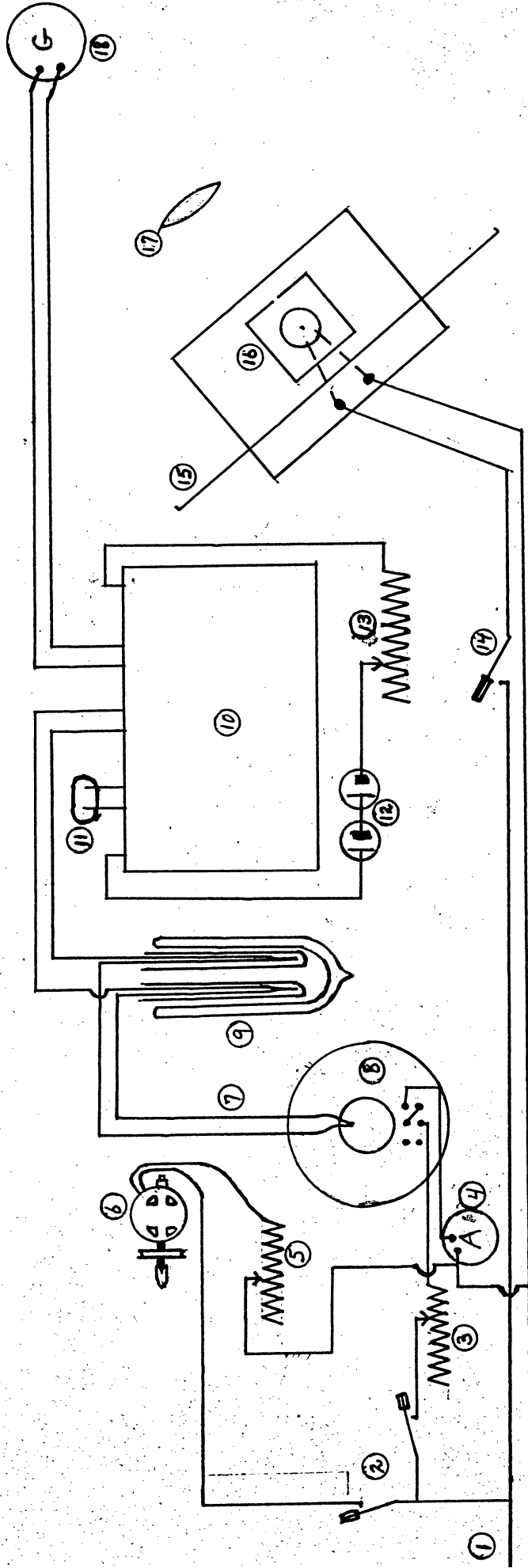
The details of the apparatus used in the present work are shown in diagrams I and II, pages 31 and 32. The first of these sketches shows the general assembling of the apparatus and the second shows the details in wiring. The electrical resistance furnace contained a bath of Wood's metal covered with charcoal to prevent oxidation. The contents were stirred by a centrally located rotating iron wire S-shaped in the bath and connected to an electric motor through a universal joint and pulley. The lid of the furnace contained openings for four reaction test tubes, two of which as shown in diagram I were connected by means of thick-walled capillary tubing to gas burettes with mercury levelling bulbs. All joints through which gas passed were sealed with shellac and tested each time before use with about ten centimeters of mercury pressure. A sixth hole in the furnace lid was for the insertion of an iron-constantan thermocouple contained in a

APPARATUS DIAGRAM

- 1 Electrically Driven Stirrer
- 2 Reaction Test tubes
- 3 Three Way Stop Cock
- 4 Gas Burnette
- 5 Leveling Bulb
- 6 Furnace
- 7 Magnesia Packing
- 8 Heating Coils in Alundum Cement.
- 9 Wood's Metal Bath.



WIRING DIAGRAM



- 1 110-Volt A.C. Main
- 2 Furnace & Stirring Motor Switches.
- 3 Furnace Rheostat
- 4 Ammeter
- 5 Stirrer Rheostat
- 6 Stirrer Motor
- 7 Thermocouple Leads.
- 8 Electric Furnace (2 Coils in Series)
- 9 Thermocouple Cold Junction

- 10 Type "K" Potentiometer
- 11 Standard Cell
- 12 Storage Cells
- 13 Potentiometer Rheostat
- 14 Galvanometer Light Switch
- 15 " " " " " "
- 16 Light & Slit
- 17 Focusing Lens.
- 18 Galvanometer

small iron tube sealed at the lower end and covered with layers of asbestos paper outside the furnace in order that the tube itself be maintained at the furnace temperature. The latter was regulated by hand by means of an external resistance. The asbestos covered thermocouple wires were run to an ice bath in a Dewar flask whence copper leads were connected to a Leeds and Northrup Type K potentiometer, which after calibration gave the temperature readings. The potentiometer, galvanometer, stirring motor, ammeter, etc., connections are evident in the wiring diagram, page 32.

Calibration of the Thermocouple

The thermocouple was calibrated for the lower temperatures by immersion in the Wood's metal bath along with a mercury thermometer which was previously checked with a standard thermometer. Corrections for stem exposure were applied. The freezing points of lead, aluminium and antimony and the boiling point of sulphur were also used in the calibration.

Preparation of Materials

Naturally, an investigation of the effect of catalysts upon given reagents, demands that all substances employed be of the highest purity possible.

Potassium perchlorate. Kahlbaum's K Analyzed Potassium Perchlorate was dried at $105-110^{\circ}$ C and found free from chloride and chlorate. Portions were heated alone or in the presence of chloride-free sodium carbonate and potas-

sium nitrate in a platinum crucible and were found on complete decomposition to give the theoretical amount of potassium chloride. After grinding, a portion was sifted in order to determine the average size of the particles with the following results:

Larger than 60 mesh	28%
Between 60 and 80 mesh	4%
Smaller than 80 mesh	68%

Potassium Chlorate. Kahlbaum's "K" Analyzed Potassium Chlorate after drying was found to be free from chloride and upon reduction with ferrous sulphate to give the theoretical amount of chloride. The size of the particles after drying was found to be:

Larger than 60 mesh	28%
Between 60 and 80 mesh	6%
Smaller than 80 mesh	66%

Potassium Chloride. Since this salt was used as catalyst in the transformation of potassium chlorate to potassium perchlorate, it was desired to have it very pure, so Kahlbaum's "K" Analyzed Potassium Chloride was recrystallized three times, dried at 110°C and pulverized. It was initially found to be free from potassium Chlorate.

Ferric Oxide. A solution of Mohr's salt was oxidized by boiling with nitric acid until no test for ferrous iron was obtained with ferricyanide. It was precipitated with ammonium hydroxide, filtered, dissolved in hydrochloric acid and reprecipitated with ammonium hydroxide. The precipitate

was washed free from chlorides and sulphates, dried and then ignited at red heat in a platinum dish with frequent stirring during the heating. It was then ground in an agate mortar and upon sifting a sample, it was found that the size of the particles was as follows:

Larger than 60 mesh	0.09%
Between 60 and 80 mesh	0.76%
Smaller than 80 mesh	99.15%

Microscopic examination revealed that the particles had an average size of 0.011 mm. Analysis of the sample according to the method of Zimmernann and Reinhart⁽³³⁾ showed that it was practically pure ferric oxide. The results were 99.94% and 100.09% Fe_2O_3 .

Analytical Methods.

Determinations of chloride were made by the method of Fr. Mohr⁽³⁴⁾. Chlorates were determined by boiling with an excess of acidified standard ferrous sulphate solution and titrating the excess iron with permanganates.⁽³⁵⁾ A qualitative test for chlorates in the presence of perchlorates was adapted from the quantitative method by Treadwell-Hall.⁽³⁶⁾ To a cold water solution of the portion to be tested, 1 cc. of 15% potassium iodide solution and 1 cc. of starch emulsion was added. Acidifying with dilute hydrochloric acid caused an immediate development of a perceptible blue color when only 1 mg. of potassium chlorate was present and a very distinct coloration when 5 mg. were used. A saturated solution of potassium perchlorate would not give this test, which is based

upon the fact that chloric acid readily oxidizes hydriodic acid while perchloric acid does not. When carbon disulphide was used as indicator instead of starch the test was not as delicate.

Preliminary Experiments

In several preliminary experiments a Liebig absorption bulb containing potassium iodide solution was inserted between the reaction test tube and the gas burette shown in the apparatus diagram. No free iodine was discovered after the gas evolved from potassium chlorate or perchlorate had passed through and its use was discontinued in the remaining part of the investigation. These observations confirm Wagner's statement that no chlorine is evolved from pure potassium chlorate.

A portion of potassium perchlorate was heated in an open test tube until fused and oxygen was being evolved freely. After sudden cooling, it was free from chlorates by the above test. Another portion of pure potassium perchlorate and one containing 10% potassium chloride were heated for three weeks at an average temperature of 357°C and likewise were found free from chlorate. These experiments were taken to prove that potassium chlorate is not formed in heating potassium perchlorate either strongly or moderately.

Preparation of Mixtures of Potassium Perchlorate and Ferric Oxide in Molecular Ratios.

Portions of potassium perchlorate and ferric oxide were weighed in such amounts that the proportion between them was in approximately simple molecular ratios. They were intimately mixed and kept in glass stoppered bottles in a dessicator to prevent adsorption of moisture.

Table 6 shows in the first column the approximate molecular ratio, the second and third the amounts of potassium perchlorate and ferric oxide weighed out, in the fourth the actual molecular ratio and in the fifth the percent of potassium perchlorate in the mixture.

TABLE 6

Preparation of Mixtures of KClO_4 and Fe_2O_3

Nominal-Molecular Ratio	Wt. KClO_4	Wt. Fe_2O_3	Actual-Molecular Ratio	% KClO_4 in mixture
$6\text{KClO}_4\text{-}1\text{ Fe}_2\text{O}_3$	2.0436	0.3923	$6\text{KClO}_4\text{-}0.9995\text{Fe}_2\text{O}_3$	83.896
$3\text{ KClO}_4\text{-}2\text{Fe}_2\text{O}_3$	2.4660	1.8944	$3\text{KClO}_4\text{-}1.9998\text{Fe}_2\text{O}_3$	44.932
$3\text{KClO}_4\text{-}4\text{ Fe}_2\text{O}_3$	2.0460	3.1440	$3\text{KClO}_4\text{-}4.0002\text{Fe}_2\text{O}_3$	39.422
$1\text{KClO}_4\text{-}2\text{ Fe}_2\text{O}_3$	2.5274	5.8253	$1\text{KClO}_4\text{-}2.0000\text{Fe}_2\text{O}_3$	30.258
$1\text{KClO}_4\text{-}4\text{ Fe}_2\text{O}_3$	2.0519	9.4589	$1\text{KClO}_4\text{-}4.0011\text{Fe}_2\text{O}_3$	17.826

Decomposition of Potassium Perchlorate

The reaction test tubes specially made of Pyrex glass were cleaned thoroughly in a sulphuric acid dichromate bath,

washed with distilled water, dried in an oven at 125 - 150°C and kept in a dessicator over calcium chloride until needed for use. Approximately the desired amount of material, either pure potassium perchlorate, pure potassium chlorate or a mixture of these with catalyst was put in the weighed tube. A second weighing after removing the very slight amount of material which stuck to the inner walls and lip of the tube gave the weight of the material added. The tubes were then fitted with rubber stoppers and connected with the gas burettes. The joints were shellaced and after drying were tested with 10 cm. of mercury pressure. When the furnace had attained equilibrium at or slightly above the desired temperature, the tubes were suddenly plunged into the Wood's metal bath. The interval between simultaneous readings of the gas burettes, furnace temperature, room temperature and barometric pressure depended upon the speed of decomposition.

After a final reading had been taken the tube was removed from the furnace and cooled to room temperature. The contraction in gas volume on cooling was equal to the expansion of the air sealed in the apparatus, when raised from room temperature to that of the furnace. Hence this volume was subtracted from the burette readings to obtain the actual volume of the oxygen evolved. It was assumed that the gas in passing through the capillary tube to the measuring burette became cooled to room temperature. All these data are incorporated in the tables to be given later.

Calculations based on the Data obtained by
Decomposing Potassium Perchlorate

Tables 7 to 58 inclusive with the exceptions of Tables 14, 15, 22, 29, 36 and 44 give the experimental observations on the decomposition of potassium perchlorate. The heading of each shows the ratio mixture of potassium perchlorate and ferric oxide used, the weight of sample, this multiplied by the percent of perchlorate in the mixture giving the weight of potassium perchlorate used, the room temperature and the barometric pressure corrected to 0°C. Below these are tabulated: the time of the observation in minutes beginning when the reaction tube was thrust into the furnace; the Centigrade temperatures of the furnace as shown by the thermocouple readings; the volume of gas (O_2) evolved under the temperature and pressure conditions mentioned, the values being the burette readings minus the contraction when the tube was withdrawn from the furnace; the amount of potassium perchlorate (x) which if completely decomposed would generate this volume of oxygen expressed in fractions of the original amount present and ($a - x$), the fraction of potassium perchlorate which remained undecomposed. The value x is calculated by the equation,

$$x = \frac{(\text{vol of } O_2)(273)(\text{Bar. Press.})(\text{wt. } KClO_4 \approx 1 \text{ cc } O_2 \text{ under S.T.P.})}{(\text{Room Temp})(760)(\text{wt. of } KClO_4 \text{ in sample})}$$

Since at the start the fraction of potassium perchlorate undecomposed is unity, the values of ($a - x$) or concentration of

reacting substance is found by subtracting x from 1.

This way of obtaining the concentration during the experiment would not give comparable results when different amounts of foreign material are present if the reaction was bi- or poly-molecular. But, since it was found that when pure potassium perchlorate was heated the observations gave a most constant value for the velocity coefficient when calculated according to the equation for a first order reaction, the velocity coefficients in the presence of ferric oxide could be calculated in the same way, taking for convenience the initial concentration of potassium perchlorate as one.

The lower part of each table shows the 'times' and values of ' $a - x$ ' used to calculate K by the equation

$$K = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$$

where $a - x_1$ is the value of $a - x$ at the time t_1 and $a - x_2$ at the time t_2 . Thus, values of K of equal weight were obtained and averaged. The average deviation of the values of K and its percentage of the average value of K have been computed in each case to show the uniformity of the observations. In cases where the material was unfused, when taken from the furnace, it is so noted in the table.

In the tables excepted above, and table 59, the velocity coefficients and the average temperature of the individual experiments have been assembled for each mixture of potassium perchlorate and ferric oxide. Due to the complexity of catalysis in two solid phases, the velocity coefficients of the unfused but catalyzed experiments have been omitted from further calculations.

The constants A and B in Arrhenius' equation have been evaluated by the method of least squares for each set of data. The experimental values of K and the equation derived therefrom are plotted on the graph following each table. In order to obtain comparable velocity coefficients for the various mixtures of catalyst, K's were calculated from the latter for various Centigrade temperatures. Since these should be most accurate within the range of experimental temperatures, the calculated values of K at constant temperatures (500°, 525°, 550°, 575°) were compared with the molecular concentration of the catalyst present. It was found (see Table 60 and Graph 11) that the increase in the velocity coefficient was proportional to the concentration of catalyst. That is,

$$K_c - K_0 \propto C$$

where K_c is the velocity coefficient of the catalyzed reaction, K_0 the velocity coefficient of the uncatalyzed reaction at the same temperature and C is the molecular concentration of the catalyst. Or, at constant temperature the expression $\frac{K_c - K_0}{C}$ is a constant.

Desiring to know the relation between these latter constants and the temperature, the values obtained were applied to an equation similar to Arrhenius'

$$(1) \quad \log \frac{K_c - K_0}{C} = A/T + B,$$

and a straight line relation as shown on Graph 12 resulted.

Hence the constants A and B were evaluated (Table 61).

Equation (1) may be transformed as follows:

$$\text{taking the antilog} \quad \frac{K_c - K_0}{C} = e^{A/T + B}$$

solving for K_c
$$K_c = C e^{\frac{A}{T+B}} K_0$$

But since K_0 is also a function of the temperature by the relation,

$$\log K_0 = A_0/T + B \quad \text{or} \quad K_0 = e^{A_0/T + B_0},$$

$$K_c = C e^{A/T + B} \cdot e^{A_0/T + B_0}$$

Since in all calculations Briggs' logs have been used instead of natural logs and since K_c in the last equation applies for all concentrations of catalyst (zero included) the subscript c may be dropped and the equation written

$$K = C \cdot 10^{A/T + B} \cdot 10^{A_0/T + B_0}$$

where K, C and T have the significance defined above and the constants have the following numerical values:

$$A = -10,587$$

$$B = 11,5679$$

$$A_0 = -13,246$$

$$B_0 = 14.0348$$

Velocity coefficients have been calculated by this equation for a few of the experimental conditions and in Table 62 are compared with those directly calculated from the data.

TABLE 7.

Catalyst Ratio = No catalyst
 Wt. of sample = .2607
 Room Temp. = 27°C
 Barometer = 738.2

Time min.	Temp. °C	ϕ_2	x	a - x
0	455.1			
110	477.7	.15	.00173	.99827
150	480.	.40	420	.99580
155	481.6	.42	441	.99559
160	481.8	.46	483	.99517
165	481.8	.52	545	.99455
170	481.4	.56	587	.99413
260	468.9	.86	902	.99098
350	452.8	1.20	1259	.98741
355	450.0	1.23	1291	.98709
360	449.3	1.26	1322	.98678
365	448.0	1.27	.01333	.98667

Av. 466.6

Material Unfused

Time t=200	a - x ₁	a - x ₂	K
150-350	.99580	.98741	1.84 x 10 ⁻⁵
155-355	.99559	.98709	1.81
160-360	.99517	.98678	1.84
165-365	.99455	.98667	1.72

Av. 1.80 x 10⁻⁵

Av. Dev. $\pm 0.04 \times 10^{-5}$ (2.2%)

TABLE 8.

Catalyst Ratio = No catalyst
 Wt. of Sample = .2464
 Room Temp. = 25°C
 Barometer = 742.5

Time min.	Temp.	O ₂	x	a - x
0	541.0			
2	539.0	.24	.0027	.9973
4	539.9	.59	.0066	.9934
6	540.3	.99	.0111	.9889
8	541.0	1.42	.0160	.9840
10	541.5	1.81	.0210	.9790
12	541.5	2.42	.0272	.9728
14	541.7	2.97	.0334	.9666
16	542.5	3.76	.0423	.9577
18	543.0	4.55	.0512	.9488
20	543.2	5.35	.0601	.9399
22	543.2	6.15	.0691	.9309
24	543.6	6.85	.0770	.9230
26	543.6	7.60	.0854	.9146
28	543.6	8.25	.0928	.9072
30	543.8	9.00	.1012	.8988

Av. 543°

Material Unfused

Time t=10	a - x ₁	a - x ₂	K
10-20	.9790	.9399	1.770 x 10 ⁻³
12-22	.9728	.9309	1.912
14-24	.9666	.9230	2.005
16-26	.9577	.9146	2.000
18-28	.9488	.9072	1.947
20-30	.9399	.8988	1.942

Av. 1.929 x 10⁻³

± 0.059 x 10⁻³ (3.1%)

TABLE 9.

Catalyst Ratio = No catalyst
 Wt. of Sample = .2216
 Room Temp. = 25°C
 Barometer = 735.0

Time min.	Temp.	O ₂	x	a - x
0	560.0			
4	557.3	1.27	.0157	.9843
8	560.8	3.34	.0413	.9587
12	562.8	5.92	.0733	.9267
16	564.2	8.10	.1002	.8998
17	564.0	8.70	.1077	.8923
18	564.2	9.50	.1176	.8824
19	564.2	10.15	.1256	.8744
20	564.4	11.00	.1361	.8639
21	564.8	11.70	.1448	.8552
22	564.4	12.30	.1522	.8478
23	564.6	12.90	.1596	.8404
24	564.6	13.55	.1677	.8323
25	564.6	14.35	.1776	.8224
26	564.6	15.10	.1868	.8132
27	564.6	15.85	.1961	.8039
28	564.4	16.55	.2048	.7952
29	564.4	17.30	.2141	.7859
30	<u>564.4</u>	18.10	.2240	.7760

Av. 564.5

Material Unfused

Time t=10	a - x ₁	a - x ₂	K
16-26	.8998	.8132	4.395 x 10 ⁻³
17-27	.8923	.8039	4.531
18-28	.8824	.7952	4.519
19-29	.8744	.7859	4.634
20-30	.8639	.7760	<u>4.660</u>

Av. 4.548 x 10⁻³

± 0.078 x 10⁻³ (1.7%)

TABLE 10.

Catalyst Ratio = No catalyst
 Wt. of Sample = .1504
 Room Temp. = 26°C
 Barometer = 744.3

Time (min.)	Temp.	O ₂	x	a - x
0	539.3			
30	539.8	3.27	.0600	.9400
35	540.8	4.03	.0739	.9261
40	540.6	4.80	.0880	.9120
45	540.6	5.70	.1045	.8955
50	540.6	6.63	.1216	.8784
Av.	541.			
90	537.9	17.35	.3214	.6786
95	537.5	19.00	.3520	.6480
100	536.2	20.70	.3835	.6165
105	537.7	22.47	.4162	.5838
110	537.5	24.30	.4502	.5498
135	535.5	31.55	.5806	.4194
140	535.0	32.80	.6035	.3965
145	534.6	33.83	.6225	.3775
150	534.4	34.88	.6418	.3582
155	534.8	35.80	.6588	.3412
160	535.2	36.90	.6790	.3210
165	535.5	37.90	.6974	.3026
170	535.9	38.80	.7140	.2860
175	536.4	39.80	.7324	.2676
Av.	536			

Material Unfused

Time	a - x	K
0-30	.9400	0.896 x 10 ⁻³
0-35	.9261	0.953
0-40	.9120	1.000
0-45	.8955	1.072
0-50	.8784	1.126
Av.	1.010 x 10 ⁻³	± 0.072 x 10 ⁻³ (7.1%)

Material fused

Time	a - x ₁	a - x ₂	K
t=60			
90-150	.6786	.3582	4.625 x 10 ⁻³
95-155	.6480	.3412	4.643
100-160	.6165	.3210	4.724
105-165	.5838	.3026	4.756
110-170	.5498	.2860	4.730
Av.			4.696 x 10 ⁻³
			± 0.049 x 10 ⁻³ (1.0%)

TABLE 11.

Catalyst Ratio = No catalyst
 Wt. of Sample = .1893
 Room Temp. = 27°C
 Barometer = 737.6

Time min.	Temp.	O ₂	x	a - x
0	---			
60	535.0	1.60	.0231	.9769
120	548.2	4.36	.0634	.9366
150	550.0	12.03	.1749	.8251
155	549.3	14.43	.2098	.7902
160	549.3	17.33	.2519	.7481
165	549.5	20.43	.2970	.7030
170	549.5	23.88	.3471	.6529
180	551.3	31.13	.4525	.5475
185	552.1	34.85	.5066	.4934
190	552.0	38.25	.5560	.4440
195	552.2	41.58	.6044	.3956
200	552.3	44.45	.6461	.3539
205	552.6	47.25	.6868	.3132
210	553.0	49.78	.7286	.2764
215	<u>553.3</u>	52.23	.7592	.2408

Av. 551.

Time t=35	a - x ₁	a - x ₂	K
150-185	.8251	.4934	6.380 x 10 ⁻³
155-190	.7902	.4440	7.153
160-195	.7481	.3956	7.906
165-200	.7030	.3539	8.514
170-205	.6529	.3132	9.115
180-215	.5475	.2408	<u>7.335</u>

Av. 7.734 x 10⁻³± 0.961 x 10⁻³ (12.4%)

TABLE 12.

Catalyst Ratio = No catalyst
 Wt. of sample = .2627
 Room Temp. = 25°C
 Barometer = 735.9

Time.(min.)	Temp.	O ₂	x	a - x
0	580.			
2	574.2	1.5	.0157	.9843
3	574.6	2.9	.0303	.9697
4	575.4	4.3	.0449	.9551
5	575.7	5.55	.0580	.9420
6	576.0	6.6	.0690	.9310
7	576.0	7.7	.0805	.9195
8	576.6	8.6	.0899	.9101
	Av. 575			
12	577.2	14.4	.1505	.8495
16	577.4	23.3	.2435	.7565
17	577.4	25.6	.2675	.7325
18	577.4	28.5	.2978	.7022
19	577.4	31.25	.3266	.6734
20	577.6	34.7	.3626	.6374
23	577.6	44.0	.4598	.5402
26	577.2	53.8	.5623	.4377
27	577.2	56.6	.5915	.4085
28	577.2	59.4	.6208	.3792
29	577.2	61.8	.6459	.3541
30	577.2	64.4	.6730	.3270

Time	Material Unfused a - x ₂	K
2-3	.9697	6.49 x 10 ⁻³
2-4	.9551	6.54
2-5	.9420	6.36
2-6	.9310	6.05
2-7	.9195	5.92
2-8	.9101	5.67
	Av. 6.175 x 10 ⁻³	± 0.29 x 10 ⁻³ (4.7%)

Time t=10	Material fused a - x ₁	a - x ₂	K
16-26	.7565	.4377	2.376 x 10 ⁻²
17-27	.7325	.4085	2.637
18-28	.7022	.3792	2.676
19-29	.6734	.3541	2.791
20-30	.6374	.3270	2.899
		Av. 2.676 x 10 ⁻²	
			± 0.135 x 10 ⁻² (5.0%)

TABLE 13.

Catalyst Ratio = No catalyst
 Wt. of Sample = .1028
 Room Temp. = 25°C
 Barometer = 734.8

Time min.	Temp.	ϕ_2	x	a - x
0	621.5			
1	617.6	1.2	.0320	.9680
1 1/2	617.2	3.2	.0853	.9147
2	617.4	4.8	.1280	.8720
2 1/3	617.2	6.4	.1707	.8293
2 2/3	617.2	8.1	.2160	.7840
3	617.2	10.1	.2693	.7307
3 1/3	617.0	12.3	.3280	.6720
3 2/3	617.2	14.5	.3867	.6133
4	617.2	17.1	.4560	.5440
4 1/3	617.2	19.4	.5173	.4827
4 2/3	617.2	21.7	.5787	.4213
5	617.0	24.2	.6453	.3547
5 1/3	616.8	26.4	.7040	.2960
5 2/3	617.0	27.9	.7439	.2561
6	<u>617.0</u>	29.4	.7840	.2160

Av. 617

Time t=2	a - x ₁	a - x ₂	K
2 2/3-4 2/3	.7840	.4213	0.1349
3 -5	.7307	.3547	0.1569
3 1/3-5 1/3	.6720	.2960	0.1780
3 2/3-5 2/3	.6133	.2561	0.1896
4 -6	.5440	.2160	<u>0.2006</u>

Av. 0.1720

± 0.209

(12.2%)

TABLE 14.

KClO ₄ (not fused)						
Table No.	t°C	1/T Abs.	1/T ²	K	log K	1/T log K
7	467	.001351	.0 ₅ 1825200	.0 ₄ 180	-4.74473	-.006410129
10	541	.001228	1507984	.001010	-2.99568	-.00367895
8	543	.001226	1503076	.001929	-2.71467	-.003328185
9	564	.001195	1428025	.004548	-2.34218	-.002798905
12	575	<u>.001178</u>	<u>1387684</u>	<u>.00617</u>	<u>-2.20971</u>	<u>-.002603038</u>
		.006178	.0 ₅ 7651969		-15.00697	-.018818952

$$.000007651969A + .006178B = .018818952$$

$$.006178A + 5B = 15.00697$$

$$.001238583A + B = 3.0461237$$

$$.0012356A + B = 3.0013940$$

$$.000002983A = .0447297$$

$$A = 14994.87$$

$$B = -15.52627$$

$$14995 \frac{1}{T} + \log K = 15.52627$$

<u>log K</u>	<u>:</u>	<u>1/T</u>
0	:	.0010354
-1	:	11021
-2	:	11688
-3	:	12355

TABLE 15.

KClO ₄ (fused)						
Table No.	t°C	1/T Abs.	1/T ²	K	log K	1/T log K
10	536	.001236	.0 ₅ 1527696	.004696	-2.32827	-.0 ₂ 2871123
11	551	.001214	. 1473796	.007734	-2.11160	-. 2563483
12	577	.001176	1382976	.02676	-1.57251	- 1849272
13	617	<u>.001124</u>	<u>1263376</u>	<u>.1720</u>	<u>- .76447</u>	<u>-.0₂0859264</u>
		.004750	.0 ₅ 5647844		-6.77685	-.0 ₂ 8143142

$$.000005647844A + .004750B = .008143142$$

$$.004750A + 4B = 6.77685$$

$$.00118902A + B = 1.7143457$$

$$.00118750A + B = 1.6942125$$

$$.00000152A = .0201332$$

$$A = 13245.5$$

$$B = -14.0348$$

$$13245.5 \frac{1}{T} + \log K = 14.0348$$

<u>log K</u>	<u>:</u>	<u>1/T</u>	<u>t°</u>	<u>:</u>	<u>T</u>	<u>:</u>	<u>K</u>
0	:	.010596	400	:	673	:	.0 ₅ 2257
-1	:	.011351	450	:	723	:	.0 ₄ 5183
-2	:	.012106	500	:	773	:	.0 ₃ 7936
-3	:	.012861	525	:	798	:	.002654
-3.8	:	.013465	550	:	823	:	.008702
			575	:	848	:	.02601
			600	:	873	:	.07284
			620	:	893	:	.1593
			640	:	913	:	.3366

GRAPH 5

 KClO_4 - No catalyst

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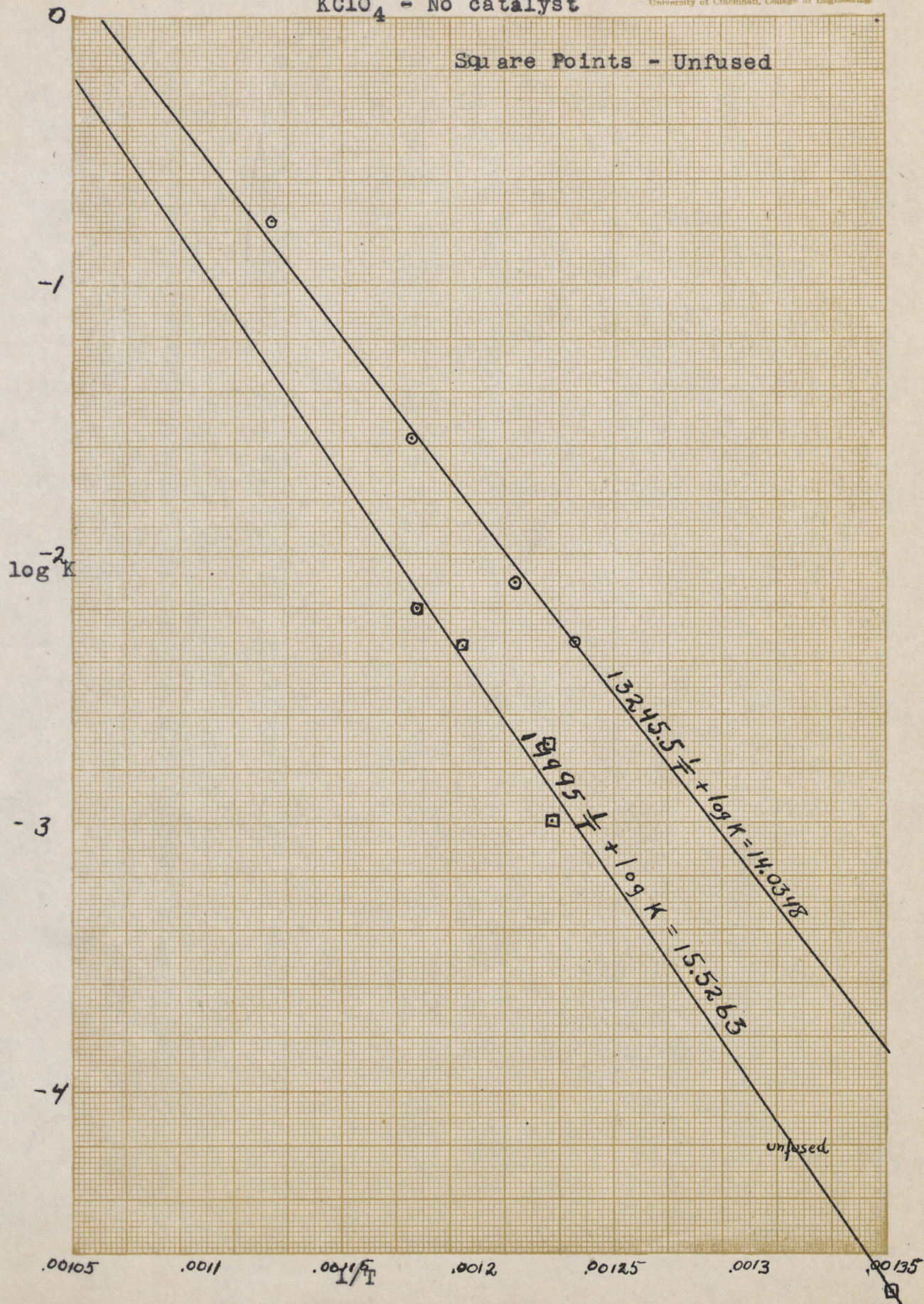


TABLE 16.

Catalyst Ratio=6 KClO_4 - 1 Fe_2O_3
 Wt. of Sample = .2042x.83896=.1713
 Room Temp. = 25°C
 Barometer = 741.7

Time min.	Temp. 0°C	O_2	x	$a - x$
0	540.3			
4	536.4	1.23	.0199	.9801
8	541.5	3.23	.0522	.9478
10	542.0	4.37	.0706	.9294
12	542.5	5.27	.0851	.9149
14	542.7	6.07	.0980	.9020
16	543.0	6.96	.1124	.8876
18	543.0	7.76	.1253	.8747
20	543.4	8.61	.1391	.8609
22	543.6	9.36	.1512	.8488
24	543.8	10.26	.1657	.8343
26	543.8	11.16	.1803	.8197
28	543.8	12.11	.1956	.8044
30	544.0	13.25	.2140	.7860

Av. 543.

Material Unfused

Time t=10	$a - x_1$	$a - x_2$	K
10-20	.9294	.8609	3.325×10^{-3}
12-22	.9149	.8488	3.256
14-24	.9020	.8343	3.389
16-26	.8876	.8197	3.457
18-28	.8747	.8044	3.639
20-30	.8609	.7860	3.953

Av. 3.503×10^{-3} $\pm 0.195 \times 10^{-3}$ (5.6%)

TABLE 17.

Catalyst Ratio = $6\text{KClO}_4 - 1\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.2962 \times .83884 = .2485$
 Room Temp. = 22°C
 Barometer = 745.4

Time min.	Temp.	O_2	x	$a - x$
0	465.0			
25	485.0	.97	.01097	.98903
125	518.0	23.51	.2658	.7342
130	519.2	26.00	.2939	.7061
135	518.2	28.73	.3248	.6752
140	518.7	31.50	.3561	.6439
145	518.4	34.31	.3879	.6121
150	518.4	37.06	.4190	.5810
155	517.7	39.51	.4467	.5533
160	517.5	41.98	.4746	.5254
165	518.2	44.31	.5010	.4990
170	518.7	46.50	.5257	.4743
175	519.6	48.69	.5505	.4495
180	520.0	51.04	.5771	.4229
185	519.2	53.20	.6015	.3985
190	518.7	55.30	.6252	.3748
195	517.5	57.21	.6468	.3532
200	516.8	58.86	.6732	.3268
205	516.5	60.27	.6814	.3186
210	516.1	61.34	.6935	.3065
215	515.5	62.72	.7091	.2909
220	515.1	63.71	.7203	.2797
225	<u>514.7</u>	65.20	.7372	.2628

Av. 518

Time t=60	$a - x_1$	$a - x_2$	K
125-185	.7342	.3985	4.423×10^{-3}
130-190	.7061	.3748	4.584
135-195	.6752	.3532	4.690
140-200	.6439	.3268	4.909
145-205	.6121	.3186	4.726
150-210	.5810	.3065	4.629
155-215	.5533	.2909	4.654
160-220	.5254	.2797	4.563
165-225	.4990	.2628	<u>4.641</u>

Note: A different mixture was used in this run. Hence % of KClO_4 (83.884) is slightly different.

Av. 4.647×10^{-3} $+0.087 \times 10^{-3}$ (1.9%)

TABLE 18.

Catalyst Ratio = $6\text{KCl}_4 - 1\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.2243 \times .83896 = .1882$
 Room Temp. = 23°C
 Barometer = 745.4

Time min.	Temp.	O_2	x	a - x
0	545.5			
25	543.9	17.44	.2594	.7406
30	545.1	21.83	.3247	.6753
35	545.1	26.71	.3973	.6027
40	545.5	31.44	.4677	.5323
45	545.8	36.43	.5419	.4581
50	545.8	40.98	.6096	.3904
55	546.5	45.02	.6697	.3303
60	546.9	48.21	.7172	.2828
65	<u>547.7</u>	51.80	.7706	.2294

Av. 546

Time t=20	a - x_1	a - x_2	K
25-45	.7406	.4581	1.043×10^{-2}
30-50	.6753	.3904	1.190
35-55	.6027	.3303	1.306
40-60	.5323	.2828	1.373
45-65	.4581	.2294	<u>1.502</u>

Av. 1.283×10^{-2}
 $\pm 0.133 \times 10^{-2}$ (10.4%)

TABLE 19

Catalyst Ratio = $6\text{KClO}_4 - 1\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.1593 \times .83896 = .1338$
 Room Temp. = 23°C
 Barometer = 735.0

Time min.	Temp.	O_2	$\bar{x}$	$a - \bar{x}$
0	559.2			
4	554.8	2.85	.0588	.9412
8	555.6	6.25	.1290	.8710
12	556.0	9.4	.1939	.8061
16	556.0	12.8	.2641	.7359
17	.0	13.7	.2827	.7173
18	.0	14.65	.3023	.6977
19	.0	15.6	.3219	.6781
20	555.8	16.55	.3415	.6585
22	.8	18.4	.3796	.6204
24	556.0	20.4	.4209	.5791
26	.0	22.4	.4622	.5378
27	.2	23.2	.4787	.5213
28	.2	24.3	.5014	.4986
29	.2	25.3	.5220	.4780
30	.2	26.2	.5406	.4594

Av. 556

Time $t=10$	$a - x_1$	$a - x_2$	$\cdot K$
16-26	.7359	.5378	1.362×10^{-2}
17-27	.7173	.5213	1.386
18-28	.6977	.4986	1.459
19-29	.6781	.4780	1.519
20-30	.6585	.4594	1.564

Av. 1.458×10^{-2} $\pm 0.067 \times 10^{-2}$ (4.6%)

TABLE 20.

Catalyst Ratio = $6\text{KClO}_4 - 1\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.2430 \times .83896 = .2039$
 Room Temp. = 25°C
 Barometer = 735.6

Time	Temp.	O_2	x	$a - x$
0	582.5			
3	580.4	6.85	.0942	.9058
6	582.5	15.3	.2104	.7896
7	583.2	18.8	.2585	.7415
8	583.8	22.3	.3067	.6933
9	584.3	27.2	.3741	.6259
10	585.0	32.5	.4469	.5531
11	585.3	37.1	.5102	.4898
12	585.5	42.5	.5845	.4155
13	585.9	47.0	.6463	.3537
14	586.5	51.5	.7082	.2918
15	<u>587.0</u>	55.4	.7618	.2382

Av. 585

Time $t=5$	$a - x_1$	$a - x_2$	K
6-11	.7896	.4898	4.148×10^{-2}
7-12	.7415	.4155	5.031
8-13	.6933	.3537	5.846
9-14	.6259	.2918	6.628
10-15	.5531	.2382	<u>7.317</u>

Av. 5.794×10^{-2}

$\pm 0.964 \times 10^{-2}$ (16.6%)

TABLE 21.

Catalyst Ratio = $6\text{KClO}_4 - 1\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.2201 \times .83896 = .1847$
 Room Temp. = 25°C
 Barometer = 734.7

Time min.	Temp.	O_2	x	$a - x$
0	612			
1	605	3.3	.0490	.9510
2	604.6	10.4	.1543	.8457
2 1/3	604.6	13.3	.1974	.8026
2 2/3	604.6	15.8	.2345	.7655
3	604.6	19.0	.2820	.7180
3 1/3	604.6	22.4	.3324	.6676
3 2/3	604.6	25.7	.3814	.6186
4	604.6	29.4	.4363	.5637
4 1/3	604.6	33.9	.5031	.4969
4 2/3	604.6	37.5	.5565	.4435
5	604.6	40.6	.6025	.3975
5 1/3	604.6	42.8	.6351	.3649
5 2/3	604.6	45.0	.6678	.3322
6	604.6	48.2	.7153	.2847
6 1/3	<u>604.6</u>	50.1	.7435	.2565

Av. 605

Time t=2	$a - x_1$	$a - x_2$	K
2 2/3-4 2/3	.7655	.4435	0.1185
3 -5	.7180	.3975	0.1284
3 1/3-5 1/3	.6676	.3649	0.1312
3 2/3-5 2/3	.6186	.3322	0.1350
4 -6	.5637	.2847	0.1484
4 1/3-6 1/3	.4969	.2565	<u>0.1431</u>

Av. 0.1341

± .0081 (6.0%)

TABLE 22.



Table No.	t°C	1/T Abs.	1/T ²	K	log K	1/T log K
16	543	.001225		.003503	-2.45556	
17	518	.001265	.051600225	.004647	-2.33283	-.002951030
18	546	.001222	1493284	.01283	-1.89177	-.002311743
19	556	.001206	1454436	.01458	-1.83624	-.002214505
20	585	.001165	1357225	.05794	-1.23702	-.001441128
21	605	.001139	1297321	.1341	-.87257	-.000993857

$$.005997 \cdot .057202491 = -8.17043 \quad -.009912263$$

$$.000007202491A + .005997B = .009912263$$

$$.005997A + 5B = -8.17043$$

$$.00120102A + B = 1.652870$$

$$.00119940A + B = 1.634086$$

$$.00000162A = .018784$$

$$A = 11,595.$$

$$B = -12.27303$$

$$11,595 \frac{1}{T} + \log K = 12.27303$$

log K	1/T	t°	T	K
0	: .0010585	400	: 673	: .041107
-1	: .0011447	450	: 723	: .031720
-2	: .0012310	500	: 773	: .021875
-3	: .0013172	525	: 798	: .025532
		550	: 823	: .01528
		575	: 848	: .03978
		600	: 873	: .09799
		620	: 893	: .1944
		640	: 913	: .3742

GRAPH 6

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Square point - unfused

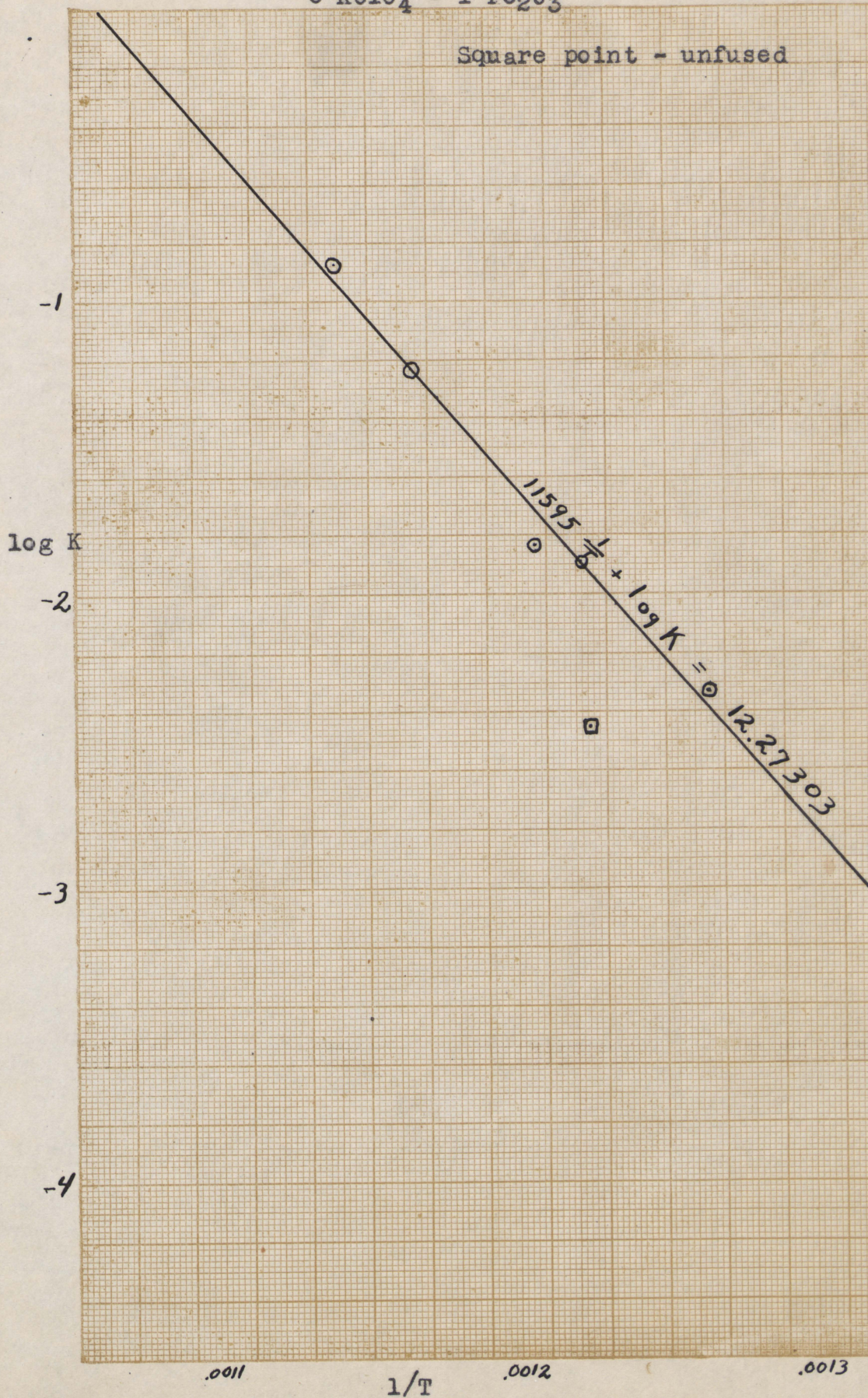


TABLE 23.

Catalyst Ratio = $3\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.4029 \times .44932 = .1811$
 Room Temp. = 28°C
 Barometer = 743.9

Time	Temp.	O_2	x	$a - x$
0	474			
4	471.8	.23	.0035	.9965
8	473.4	.38	.0058	.9942
10	474.4	.44	.0067	.9933
12	474.8	.51	.0077	.9923
14	475.2	.56	.0085	.9915
16	475.4	.63	.0095	.9905
18	475.6	.65	.0099	.9901
20	476.0	.74	.0113	.9887
22	476.0	.78	.0118	.9882
24	476.2	.85	.0129	.9871
26	476.4	.92	.0140	.9860
28	476.4	1.00	.0152	.9848
30	<u>476.4</u>	1.05	.0159	.9841

Av. 475

Material Unfused

Time t=10	$a - x_1$	$a - x_2$	K
10-20	.9933	.9887	2.02×10^{-4}
12-22	.9923	.9882	1.80
14-24	.9915	.9871	1.93
16-26	.9905	.9860	1.97
18-28	.9901	.9848	2.33
20-30	.9887	.9841	<u>2.02</u>
Av.			2.00×10^{-4}
			$\pm 0.11 \times 10^{-4}$ (5.5%)

TABLE 24.

Catalyst Ratio = $3\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.3847 \times .44932 = .1728$
 Room Temp. = 27°C
 Barometer = 742.3

Time	Temp.	O_2	x	a - x
0	485.2			
75	501.6	8.10	.1289	.8711
135	507.0	20.12	.3203	.6797
140	507.3	22.27	.3545	.6455
145	507.8	24.37	.3879	.6121
150	507.9	26.12	.4158	.5842
155	508.0	28.17	.4484	.5516
175	508.5	35.72	.5686	.4314
180	508.5	37.34	.5944	.4056
185	508.3	38.75	.6154	.3846
190	508.0	40.47	.6442	.3558
195	507.7	42.34	.6740	.3260
200	507.3	43.82	.6975	.3025
205	507.2	45.07	.7174	.2826
210	<u>507.0</u>	46.42	.7389	.2611

Av. 508

Time t=50	a - x_1	a - x_2	K
135-185	.6797	.3846	4.946×10^{-3}
140-190	.6455	.3558	5.174
145-195	.6121	.3260	5.499
150-200	.5842	.3025	5.717
155-205	.5516	.2826	<u>5.809</u>

Av. 5.429×10^{-3} $\pm 0.295 \times 10^{-3}$ (5.4%)

TABLE 25.

Catalyst Ratio = $3\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.3503 \times .44932 = .1574$
 Room Temp. = 25°C
 Barometer = 741.9

Time	Temp.	O ₂	x	a - x
0	545.6			
4	539.7	2.4	.0422	.9578
8	540.6	8.8	.1548	.8452
10	540.8	11.4	.2005	.7995
12	541.0	14.0	.2462	.7538
14	541.2	16.55	.2911	.7089
16	541.2	18.95	.3333	.6667
18	541.4	21.3	.3746	.6254
20	541.4	23.9	.4204	.5796
22	541.4	26.5	.4661	.5339
24	541.4	29.2	.5129	.4871
26	541.4	31.8	.5593	.4407
28	541.5	34.2	.6015	.3985
30	541.5	36.7	.6455	.3545

Av. 541

Time t=10	a - x ₁	a - x ₂	K
10-20	.7995	.5796	1.397×10^{-2}
12-22	.7538	.5339	1.498
14-24	.7089	.4871	1.630
16-26	.6667	.4407	1.798
18-28	.6254	.3985	1.957
20-30	.5796	.3545	2.135

Av. 1.736×10^{-2}
 $\pm 0.224 \times 10^{-2}$ (12.9%)

TABLE 26.

Catalyst Ratio = $3\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.4303 \times .44932 = .1933$
 Room Temp. = 25°C
 Barometer = 735.6

Time	Temp.	O_2	x	$a - x$
0	562			
3	557.5	9.0	.1278	.8722
6	558.4	19.2	.2726	.7274
6 1/2	558.4	20.6	.2925	.7075
7	558.6	22.0	.3123	.6877
7 1/2	558.7	23.6	.3351	.6649
8	558.7	25.3	.3592	.6408
8 1/2	558.8	26.9	.3819	.6181
9	558.8	28.4	.4032	.5968
9 1/2	559.0	30.2	.4288	.5712
10	559.0	31.5	.4472	.5528
10 1/2	559.0	33.1	.4699	.5301
11	559.0	35.1	.4983	.5017
11 1/2	559.0	36.4	.5168	.4832
12	559.2	38.6	.5480	.4520
12 1/2	559.2	40.2	.5707	.4293
13	559.2	42.1	.5978	.4022
13 1/2	559.4	43.9	.6232	.3768
14	559.4	45.6	.6474	.3526
14 1/2	559.4	47.4	.6729	.3271
15	559.4	48.8	.6928	.3072

Av. 559

Time	$a - x_1$	$a - x_2$	K
$t=5$			
6 -11	.7274	.5017	3.227×10^{-2}
6 1/2-11 1/2	.7075	.4832	3.312
7 -12	.6877	.4520	3.645
7 1/2-12 1/2	.6649	.4293	3.800
8 -13	.6408	.4022	4.046
8 1/2-13 1/2	.6181	.3768	4.299
9 -14	.5968	.3526	4.571
9 1/2-14 1/2	.5712	.3271	4.842
10 -15	.5528	.3072	5.103

Av. 4.094×10^{-2} $\pm 0.542 \times 10^{-2}$ (13.2%)

TABLE 27.

Catalyst Ratio = $3\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.3795 \times .44932 = .1705$
 Room Temp. = 24°C
 Barometer = 741.2

Time	Temp.	O ₂	x	a - x
0	586.5			
2	584.6	12.8	.2083	.7917
2 1/3	585.1	15.4	.2506	.7494
2 2/3	585.2	17.6	.2864	.7136
3	585.6	19.9	.3239	.6761
3 1/3	586.1	22.6	.3678	.6322
3 2/3	586.5	25.1	.4085	.5915
4	586.8	27.6	.4492	.5508
4 1/3	587.2	31.1	.5062	.4938
4 2/3	587.8	33.9	.5517	.4483
5	588.2	36.9	.6006	.3994
5 1/3	588.4	40.1	.6526	.3474
5 2/3	588.6	43.5	.7080	.2920
6	589.0	46.3	.7535	.2465

Av. 587

Time t=2	a - x ₁	a - x ₂	K
2 1/3-4 1/3	.7494	.4933	0.908×10^{-1}
2 2/3-4 2/3	.7136	.4483	1.009
3 -5	.6761	.3994	1.143
3 1/3-5 1/3	.6322	.3474	1.300
3 2/3-5 2/3	.5915	.2920	1.533
4 -6	.5508	.2465	1.746

Av. 1.273×10^{-1} $\pm 0.253 \times 10^{-1}$ (19.9%)

TABLE 28.

Catalyst Ratio = $3\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.3796 \times .44932 = .1705$
 Room Temp. = 25°C
 Barometer = 734.7

Time	Temp.	O ₂	x	a - x
0	606.0			
1	601.0	7.3	.1174	.8826
1 1/2	600.8	14.8	.2379	.7621
1 3/4	600.8	18.4	.2958	.7042
2	600.8	21.9	.3522	.6478
2 1/4	600.8	25.8	.4148	.5852
2 1/2	600.8	29.7	.4775	.5225
2 3/4	600.8	32.3	.5193	.4807
3	600.8	35.3	.5675	.4325
3 1/4	601.0	39.4	.6334	.3666
3 1/2	601.0	43.3	.6961	.3039
3 3/4	<u>601.0</u>	46.9	.7540	.2460

Av. 601

Time t=1 1/4	a - x ₁	a - x ₂	K
1 1/2-2 3/4	.7621	.4807	1.601×10^{-1}
1 3/4-3	.7042	.4325	1.694
2 -3 1/4	.6478	.3666	1.978
2 1/4-3 1/2	.5852	.3039	2.277
2 1/2-3 3/4	.5225	.2460	<u>2.617</u>

Av. 2.034×10^{-1} $\pm 0.331 \times 10^{-1}$ (16.3%)

TABLE 29.



Table No.	T°C	1/T abs.	1/T ²	K	log K	1/TlogK	Residuals
23	475°	.001337		.00020	-3.69897		
24	508°	.001280	.051638400	.005429	-2.26528	-.002899559	+.0570
25	541°	.001229	1510441	.01736	-1.76045	-.002163593	-.0538
26	559°	.001202	1444804	.04094	-1.38785	-.001668196	-.0071
27	587°	.001163	1352569	.1273	-.89483	-.001040687	-.0151
28	601°	<u>.001144</u>	<u>1308736</u>	<u>.2034</u>	<u>-.69165</u>	<u>-.000791248</u>	<u>-.0111</u>

$$.006018 \text{ } .057254950 \quad -7.00004 \quad -.008563283$$

$$.000007254950A + .006018B = .008563283$$

$$.006018A + 5B = 7.00004$$

$$.0012055A + B = 1.422945$$

$$.0012036A + B = 1.400008$$

$$.0000019A = .022937$$

$$A = 12072.1$$

$$B = -13.12997$$

$$12072.1 \frac{1}{T} + \log K = 13.12997$$

log K :	1/T	t°	:	T	:	K
0	: .010876	400	:	673	:	.041557
-1	: .011705	450	:	723	:	.032709
-2	: .012533	500	:	773	:	.023257
-3	: .013361	525	:	798	:	.01005
		550	:	823	:	.02894
		575	:	848	:	.07835
		600	:	873	:	.20030
		625	:	898	:	.48601
		640	:	913	:	.80820

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Square point unfused

log K

-3

-4

.0011

1/T

.0012

.0013

$$12072.1 \frac{1}{T} + \log K = 13.12997$$



TABLE 30.

Catalyst Ratio = $3\text{KClO}_4 - 4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.5205 \times .39422 = .2052$
 Room Temp. = 25°C
 Barometer = 742.2

Time	Temp.	O_2	x	a - x
0	461.5			
4	457.2	.25	.00337	.99663
8	457.0	.30	.00405	.99595
10	457.4	.39	.00526	.99474
12	457.6	.39	.00526	.99474
14	458.1	.43	.00580	.99420
16	458.3	.48	.00648	.99352
18	458.5	.48	.00648	.99352
20	458.5	.51	.00688	.99312
22	458.5	.58	.00783	.99217
24	458.5	.63	.00850	.99150
26	458.5	.66	.00891	.99109
28	458.5	.68	.00918	.99082
30	458.5	.70	.00945	.99055

Av. 458

Material Unfused

Time	a - x_1	a - x_2	K
10-20	.99474	.99312	0.7079×10^{-5}
12-22	.99474	.99217	1.124
14-24	.99420	.99150	1.181
16-26	.99352	.99109	1.044
18-28	.99352	.99082	1.182
20-30	.99312	.99055	1.125

Av. 1.061×10^{-5} $\pm 0.106 \times 10^{-5}$ (10.0%)

TABLE 31.

Catalyst Ratio = $3\text{KClO}_4 - 4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.50094 \times .39422 = .1975$
 Room Temp. = 25°C
 Barometer = 735.1

Time	Temp.	O_2	x	a - x
0	508.0			
15	503.3	3.85	.0535	.9465
70	501.9	23.70	.3291	.6709
75	501.9	26.95	.3656	.6344
80	506.3	29.85	.4145	.5855
85	506.3	32.70	.4541	.5459
90	506.3	35.20	.4888	.5112
135	507.3	52.77	.7328	.2672
140	507.1	54.33	.7544	.2456
145	507.1	55.90	.7762	.2238
150	506.7	57.52	.7987	.2013
155	<u>506.7</u>	58.40	.8109	.1891

Av. 507

Time	a = x_1	a - x_2	K
t=65			
70-135	.6709	.2672	6.151×10^{-3}
75-140	.6344	.2456	6.340
80-145	.5855	.2238	6.425
85-150	.5459	.2013	6.665
90-155	.5112	.1891	<u>6.644</u>

Av. 6.445×10^{-3} $\pm 0.168 \times 10^{-3}$ (2.6%)

TABLE 32

Catalyst Ratio = $3\text{KClO}_4-4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.4906 \times .39422 = .1934$
 Room Temp. = 30°C
 Barometer = $.738.7$

Time	Temp.	O_2	x	$a - x$
0	510.4			
4	508.4	1.35	.0189	.9811
8	510.7	3.8	.0532	.9468
12	512.6	8.4	.1177	.8823
16	515.3	14.05	.1969	.8031
17	515.7	15.4	.2158	.7842
18	516.0	16.7	.2340	.7660
19	516.2	17.75	.2488	.7512
20	516.4	18.9	.2649	.7351
26	516.6	26.4	.3700	.6300
27	516.6	27.6	.3868	.6132
28	516.8	29.0	.4064	.5936
29	516.8	30.15	.4225	.5775
30	<u>516.8</u>	31.4	.4400	.5600

Av. 516

Time	$a - x_1$	$a - x_2$	K
$t=10$			
16-26	.8031	.6300	1.054×10^{-2}
17-27	.7842	.6132	1.068
18-28	.7660	.5936	1.107
19-29	.7512	.5775	1.142
20-30	.7351	.5600	<u>1.182</u>

Av. 1.110×10^{-2} $\pm 0.041 \times 10^{-2}$ (3.7%)

TABLE 33.

Catalyst Ratio = $3\text{KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.3654 \times .39422 = .1440$
 Room Temp. = 25°C
 Barometer = 738.9

Time	Temp.	O_2	x	$a - x$
0	534.5			
4	532.4	3.1	.0593	.9407
8	534.9	9.78	.1875	.8125
10	535.9	12.45	.2383	.7617
12	536.5	15.2	.2909	.7091
14	537.0	17.85	.3416	.6584
16	537.3	20.9	.4000	.6000
18	537.9	23.8	.4555	.5445
20	538.2	26.6	.5090	.4910
22	538.4	29.2	.5588	.4412
24	538.8	31.6	.6047	.3953
26	539.0	34.0	.6507	.3493
28	539.2	36.25	.6937	.3063
30	<u>539.4</u>	38.4	.7348	.2652

Av. 538

Time $t=10$	$a - x_1$	$a - x_2$	K
10-20	.7617	.4910	1.907×10^{-2}
12-22	.7091	.4412	2.061
14-24	.6584	.3953	2.216
16-26	.6000	.3493	2.350
18-28	.5445	.3063	2.498
20-30	.4910	.2652	<u>2.675</u>

Av. 2.284×10^{-2} $\pm 0.223 \times 10^{-2}$ (9.8%)

TABLE 34.

Catalyst Ratio = $3\text{KClO}_4 - 4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.3574 \times .39422 = .1409$
 Room Temp. = 25°C
 Barometer = 735.6

Time	Temp.	O_2	x	$a - x$
0	563.8			
2	559.5	2.8	.0545	.9455
4	560.4	9.4	.1831	.8169
5	560.9	12.1	.2357	.7643
5 1/2	560.9	13.8	.2688	.7312
6	561.2	15.4	.3000	.7000
6 1/2	561.4	17.2	.3350	.6650
7	561.7	18.6	.3623	.6377
7 1/2	561.7	20.3	.3954	.6046
8	562.0	21.9	.4266	.5734
9	562.2	25.4	.4947	.5053
10	562.3	28.8	.5610	.4490
10 1/2	562.5	30.15	.5941	.4059
11	562.7	32.1	.6252	.3748
11 1/2	562.9	33.7	.6564	.3436
12	563.1	34.9	.6797	.3203
12 1/2	563.1	36.5	.7109	.2891
13	<u>563.1</u>	37.7	.7343	.2657

Av. 562

Time $t=5$	$a - x_1$	$a - x_2$	K
5 -10	.7643	.4490	4.620×10^{-2}
5 1/2 -10 1/2	.7312	.4059	5.072
6 -11	.7000	.3748	5.426
6 1/2 -11 1/2	.6650	.3436	5.735
7 -12	.6377	.3203	5.981
7 1/2 -12 1/2	.6046	.2891	6.408
8 -13	.5734	.2657	<u>6.681</u>

Av. 5.703×10^{-2} $\pm 0.569 \times 10^{-2}$ (10.0%)

TABLE 35.

Catalyst Ratio = $3\text{KClO}_4 - 4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.5407 \times .39422 = .2131$
 Room Temp. = 26°C
 Barometer = 741.2

Time	Temp.	O_2	x	a - x
0	611.8			
1	606.5	11.4	.1474	.8526
1 1/3	606.7	16.0	.2069	.7931
1 2/3	606.5	22.0	.2844	.7156
2	606.5	29.0	.3750	.6250
2 1/3	606.7	39.2	.5068	.4932
2 2/3	606.5	48.3	.6245	.3755
3	606.7	57.8	.7473	.2527
3 1/3	606.7	63.3	.8184	.1816
3 2/3	<u>606.7</u>	67.8	.8766	.1234

Av. 607

Time t=1	a - x ₁	a - x ₂	K
1 1/3-2 1/3	.7931	.4932	0.2063
1 2/3-2 2/3	.7156	.3755	0.2801
2 -3	.6250	.2527	<u>0.3932</u>

Av. 0.2932

± 0.0666 (22.7%)

TABLE 36.



Table No.	t°C	1/T abs.	1/T ²	K	log K	1/T logK
30	458°	.0013680	.0 ₅ 1871422	.0001060	-3.97428	-.005436940
31	507°	.0012821	.0 ₅ 1643780	.006445	-2.19078	-.002808799
32	516°	.0012674	.0 ₅ 1606303	.01110	-1.95468	-.002477356
33	538°	.0012330	.0 ₅ 1520289	.02284	-1.64130	-.002023723
34	562°	.0011976	.0 ₅ 1434246	.05703	-1.24390	-.001489695
35	607°	.0011364	.0 ₅ 1291405	.2932	- .53284	-.000605519
		.00611655	.0 ₅ 7496023		-7.56350	-.009405092

$$.000007496023A + .0061165B = .009405092$$

$$.0061165A + 5B = 7.56350$$

$$.00122554A + B = 1.53766$$

$$.00122330A + B = 1.51270$$

$$.00000224A = .02496$$

$$A = 11,142.9$$

$$B = -12.11836$$

$$11,142.9 \frac{1}{T} + \log K = 12.11836$$

Log K	: 1/T
0	: .0010875
-1	: .0011773
-2	: .0012676
-2.8	: .0013388

t°	:	T	:	K
400	:	673	:	.043642
450	:	723	:	.053209
500	:	773	:	.005050
525	:	798	:	.01429
550	:	823	:	.03793
575	:	848	:	.094966
600	:	873	:	.2262
620	:	893	:	.4369
640	:	913	:	.8198

GRAPH 8



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Square point - Unfused

 $\log \frac{K}{-2}$

-3

-4

.0011

 $1/T$

.0012

.0013

$$1,142.9 \frac{1}{T} + \log K = 12.11836$$

TABLE 37.

Catalyst Ratio = $\text{1KClO}_4\text{-2Fe}_2\text{O}_3$
 Wt. of Sample = $.7681 \times .30258 = .2324$
 Room Temp. = 25°C
 Barometer = 742.2

Time	Temp.	O_2	x	$a - x$
0	463			
4	459.8	.53	.00393	.99607
8	462.2	.58	.00691	.99309
10	463.0	.59	.00703	.99297
12	464.0	.71	.00846	.99154
14	464.9	.78	.00929	.99071
16	465.3	.87	.01036	.98964
18	466.2	.96	.01144	.98856
20	466.5	1.16	.01382	.98618
22	467.0	1.20	.01430	.98570
24	467.5	1.35	.01608	.98392
26	467.7	1.38	.01644	.98356
28	468.4	1.40	.01668	.98332
30	<u>468.2</u>	1.55	.01847	.98153

Av. 466

Material Unfused

Time $t = 10$	$a - x_1$	$a - x_2$	K
10-20	.99308	.98678	3.032×10^{-4}
12-22	.99154	.98570	2.565
14-24	.99071	.98392	2.987
16-26	.98964	.98356	2.681
18-28	.98856	.98332	2.308
20-30	.98678	.98153	<u>2.053</u>

Av. 2.604×10^{-4} $\pm 0.296 \times 10^{-4}$ (11.4%)

TABLE 38.

Catalyst Ratio = $\text{1KClO}_4\text{-2Fe}_2\text{O}_3$
 Wt. of Sample = $.8017 \times .30258 = .2426$
 Room Temp. = 24°C
 Barometer = 734.2

Time min.	Temp.	O_2	x	$a - x$
0	469.4			
120	479.4	8.55	.0969	.9031
185	481.2	14.25	.1614	.8386
240	481.0	18.87	.2138	.7862
310	477.0	23.85	.2702	.7298
315	476.8	24.10	.2730	.7270
320	476.6	24.48	.2773	.7227
325	480.0	24.75	.2804	.7196
330	479.7	25.00	.2832	.7168
388	479.0	27.80	.3162	.6838
460	487.3	32.90	.3733	.6267
540	485.4	39.02	.4437	.5563
610	488.5	43.00	.4890	.5110
615	490.1	43.23	.4917	.5083
620	490.3	43.58	.4956	.5044
625	491.0	43.80	.4981	.5018
630	<u>491.4</u>	44.10	.5016	.4984

Av. 481

Material Unfused

Time t=300	$a - x_1$	$a - x_2$	K
310-610	.7298	.5110	5.159×10^{-4}
315-615	.7270	.5083	5.180
320-620	.7227	.5044	5.206
325-625	.7196	.5019	5.216
330-630	.7168	.4984	<u>5.261</u>

Av. 5.204×10^{-4}
 $\pm 0.028 \times 10^{-4}$ (.05%)

TABLE 39.

Catalyst Ratio = $\text{1KClO}_4\text{-2Fe}_2\text{O}_3$
 Wt. of Sample = $.7707 \times .50258 = .2332$
 Room Temp. = 30°C
 Barometer = 73818

Time	Temp.	O_2	x	$a - x$
0	514.5			
4	511.8	1.60	.0186	.9814
8	513.6	5.75	.0668	.9332
12	515.0	14.25	.1656	.8344
16	515.8	22.05	.2563	.7437
17	516.0	23.75	.2761	.7239
18	516.2	25.35	.2947	.7053
19	516.2	26.95	.3133	.6867
20	516.4	28.45	.3307	.6693
23	516.6	32.75	.3807	.6193
26	516.8	37.20	.4324	.5676
27	516.8	38.35	.4458	.5542
28	516.8	39.70	.4615	.5385
29	516.8	41.00	.4766	.5234
30	516.8	42.40	.4929	.5071

Av. 516

Time $t=10$	$a - x_1$	$a - x_2$	K
16-26	.7437	.5676	1.174×10^{-2}
17-27	.7239	.5542	1.160
18-28	.7053	.5385	1.172
19-29	.6867	.5234	1.179
20-30	.6693	.5071	1.205

Av. 1.178×10^{-2} $\pm 0.011 \times 10^{-2}$ (0.9%)

TABLE 40.

Catalyst Ratio = $\text{1KClO}_4\text{-2Fe}_2\text{O}_3$
 Wt. of Sample = $.5869 \times .30258 = .1776$
 Room Temp. = 26°C
 Barometer = 736.8

Time	Temp.	O ₂	x	a - x
0	536.2			
3	532.5	2.7	.0417	.9583
6	533.6	12.1	.1867	.8133
7 1/2	533.6	16.1	.2484	.7516
8	533.8	16.9	.2607	.7393
8 1/2	533.8	18.1	.2792	.7208
9	533.8	19.2	.2962	.7038
9 1/2	533.8	20.15	.3108	.6892
10	534.0	21.1	.3255	.6745
11	534.0	23.3	.3594	.6406
12	534.0	25.2	.3888	.6112
12 1/2	534.0	26.3	.4057	.5943
13	534.0	27.1	.4181	.5819
13 1/2	533.8	28.1	.4335	.5665
14	533.8	29.05	.4482	.5518
14 1/2	533.8	30.0	.4628	.5372
15	533.6	30.85	.4759	.5241

Av. 534

Time t=5	a - x ₁	a - x ₂	K
7 1/2-12 1/2	.7516	.5943	2.040×10^{-2}
8 -13	.7393	.5819	2.079
8 1/2-13 1/2	.7208	.5663	2.095
9 -14	.7038	.5518	2.113
9 1/2-14 1/2	.6892	.5372	2.144
10 -15	.6745	.5241	2.191

Av. 2.110×10^{-2} $\pm 0.039 \times 10^{-2}$ (1.8%)

TABLE 41.

Catalyst Ratio = $1\text{KClO}_4 - 2\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.6234 \times .30258 = .1886$
 Room Temp. = 25°C
 Barometer = 735.6

Time	Temp.	O ₂	x	a - x
0	558.8			
2552	552.2	3.2	.0466	.9534
4	553.6	13.9	.2022	.7978
4 1/2	553.8	16.6	.2415	.7585
5	553.8	18.3	.2662	.7338
5 1/2	553.8	20.5	.2982	.7018
6	554.2	22.6	.3288	.6712
6 1/2	554.2	25.0	.3637	.6368
7	554.4	26.9	.3913	.6087
7 1/2	554.6	29.1	.4234	.5766
8	554.6	31.0	.4510	.5490
8 1/2	554.8	33.5	.4874	.5126
9	554.8	35.6	.5179	.4821
9 1/2	555.0	37.8	.5499	.4501
10	555.0	40.0	.5819	.4181
10 1/2	555.2	42.5	.6183	.3817
11	555.0	43.9	.6397	.3603
11 1/2	555.2	46.1	.6707	.3293
12	555.2	48.0	.6983	.3017
12 1/2	555.2	50.0	.7274	.2726
13	555.2	51.5	.7492	.2508

Av. 555

Time	a - x ₁	a - x ₂	K
t=5			
4 -9	.7978	.4821	4.375×10^{-2}
4 1/2 -9 1/2	.7585	.4501	4.533
5 -10	.7338	.4181	4.886
5 1/2 -10 1/2	.7018	.3817	5.290
6 -11	.6712	.3603	5.404
6 1/2 -11 1/2	.6368	.3293	5.728
7 -12	.6087	.3017	6.096
7 1/2 -12 1/2	.5766	.2726	6.507
8 -13	.5490	.2508	6.805

Av. 5.514×10^{-2} $\pm 0.685 \times 10^{-2}$ (12.4%)

TABLE 42.

Catalyst Ratio = $\text{1KClO}_4\text{-2Fe}_2\text{O}_3$
 Wt. of Sample = $.6284 \times .30258 = .1901$
 Room Temp. = 25°C
 Barometer = 736.8

Time	Temp.	O_2	x	$a - x$
0	559.0			
2	555.4	5.2	.0752	.9248
4	557.2	17.3	.2501	.7489
4 1/2	557.6	19.9	.2877	.7123
5	557.8	22.3	.3224	.6776
5 1/2	558.2	25.1	.3628	.6372
6	558.4	27.7	.4004	.5996
7 1/2	559.2	36.7	.5305	.4605
9	560.0	44.6	.6447	.3553
9 1/2	560.2	47.5	.6867	.3133
10	560.6	49.7	.7185	.2815
10 1/2	560.8	52.2	.7546	.2454
11	<u>560.8</u>	53.9	.7792	.2208

Av. 559

Time	$a - x_1$	$a - x_2$	K
$t=5$			
4 - 9	.7499	.3553	6.488×10^{-2}
4 1/2 - 9 1/2	.7123	.3133	7.134
5 - 10	.6776	.2815	7.630
5 1/2 - 10 1/2	.6372	.2454	8.288
6 - 11	.5996	.2208	<u>8.677</u>

Av. 7.643×10^{-2} $\pm 0.671 \times 10^{-2}$ (8.8%)

TABLE 43.

Catalyst Ratio = $\text{1KClO}_4\text{-2Fe}_2\text{O}_3$
 Wt. of Sample = $.7847 \times .30258 = .2374$
 Room Temp. = 26°C
 Barometer = 741.2

Time	Temp.	O_2	x	$a - x$
0	581.8			
1	578.5	3.7	.0429	.9571
2	579.2	16.1	.1869	.8131
2 1/3	579.6	19.8	.2298	.7702
2 2/3	579.8	24.0	.2786	.7214
3	580.2	27.6	.3204	.6796
3 1/3	580.7	32.0	.3627	.6373
3 2/3	581.0	36.9	.4283	.5717
4	581.3	40.7	.4724	.5276
4 1/3	582.0	45.7	.5305	.4695
4 2/3	582.2	50.1	.5818	.4182
5	582.5	55.3	.6419	.3581
5 1/3	583.0	63.3	.7347	.2653
5 2/3	583.2	64.9	.7533	.2467
6	584.0	68.9	.7997	.2003

Av. 582

Time $t = 2$	$a - x_1$	$a - x_2$	K
2 1/3-4 1/3	.7702	.4695	1.075×10^{-1}
2 2/3-4 2/3	.7214	.4182	1.184
3 -5	.6796	.3581	1.391
3 1/3-5 1/3	.6373	.2653	1.903
3 2/3-5 2/3	.5717	.2467	1.825
4 -6	.5276	.2008	2.098

Av. 1.594×10^{-1} $\pm 0.363 \times 10^{-1}$ (22.8%)

Table 44.



Table No.	t°C	1/T abs.	1/T ²	K	log K	1/TlogK
37	466°	.0013532	.0 ₅ 1831096	.0 ₃ 2604	-3.58436	-.0 ₂ 4850286
38	481°	.0013263	.0 ₅ 1758966	.0 ₃ 5204	-3.28366	-.0 ₂ 4354987
39	516°	.0012674	.0 ₅ 1606371	.01178	-1.92885	-.0 ₂ 2444676
40	534°	.0012392	.0 ₅ 1535511	.02110	-1.67572	-.0 ₂ 2076481
41	555°	.0012077	.0 ₅ 1458611	.05514	-1.25853	-.0 ₂ 1519964
42	559°	.0012019	.0 ₅ 1444619	.07643	-1.11674	-.0 ₂ 1342236
43	582°	.0011696	.0 ₅ 1367942	.1594	-.79751	-.0 ₂ 932760

$$.0060858 \quad .0_5 7413054 \quad -6.77735 \quad -.0_2 8316117$$

$$.000007413054A + .0060858B = .008316117$$

$$.0060858A + 5B = 6.77735$$

$$.001218090A + B = 1.36648$$

$$.001217160A + B = 1.35547$$

$$.000000930A = .01101$$

$$A = 11838.7$$

$$B = -13.05413$$

$$11838.7 \frac{1}{T} + \log K = 13.05413$$

log K	:	1/T
0	:	.0011027
-1	:	.0011871
-2	:	.0012716
-3	:	.0013561

t°	:	T	:	K
400	:	673	:	.0 ₄ 2905
450	:	723	:	.0 ₃ 4783
500	:	773	:	.0 ₂ 5481
525	:	798	:	.01654
550	:	823	:	.04670
575	:	848	:	.1240
600	:	873	:	.3113
620	:	893	:	.6265
640	:	913	:	1.2228

GRAPH 9.



University of Cincinnati, College of Engineering

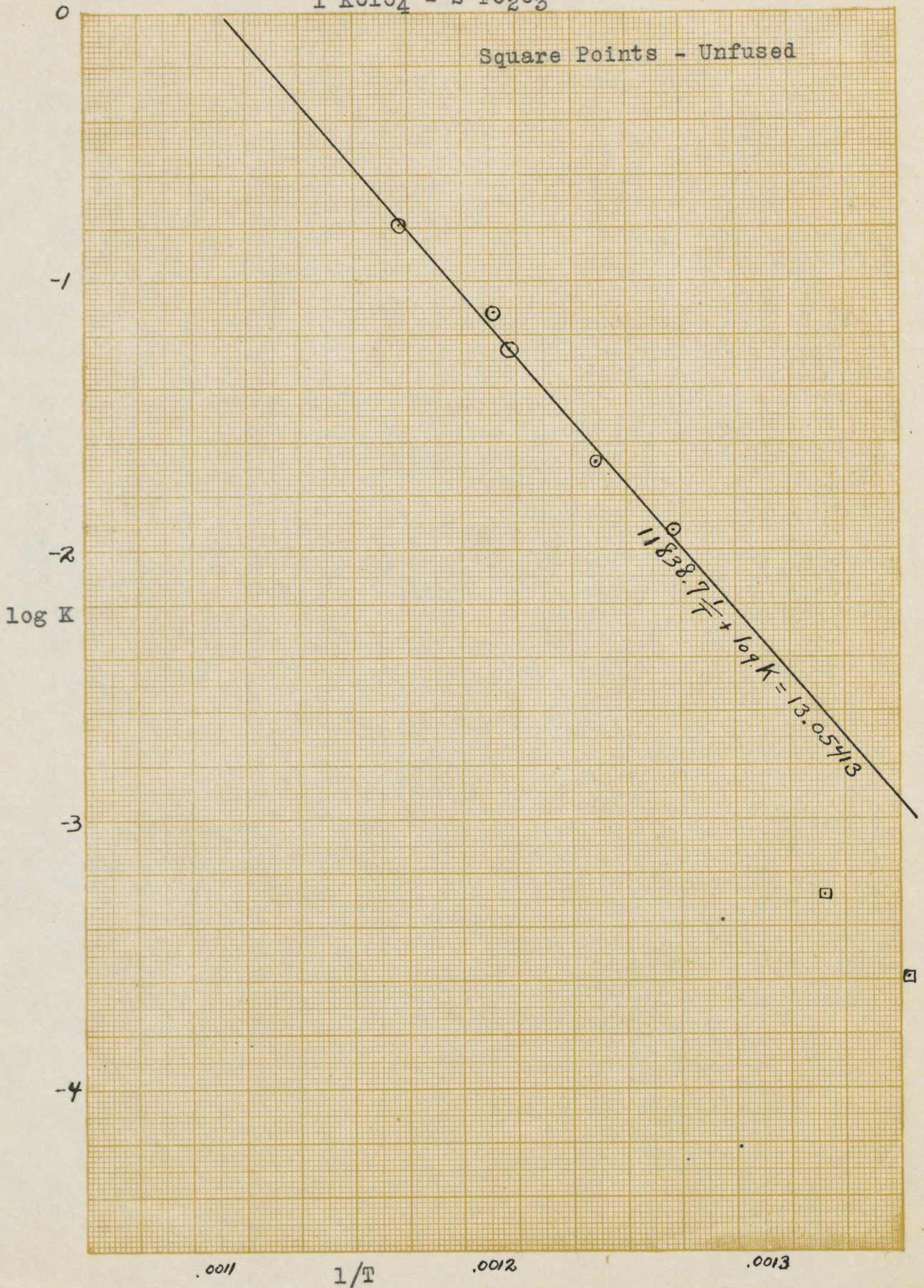


TABLE 45.

Catalyst Ratio = $\text{1KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.8306 \times .17826 = .1481$
 Room Temp. = 25°C
 Barometer = 742.1

Time	Temp.	O_2	x	$a - x$
0	471.5			
4	467	.25	.00468	.99532
8	467.8	.55	.01028	.98972
10	468.3	.67	.01253	.98747
12	468.8	.79	.01477	.98523
14	469.2	.93	.01739	.98261
16	469.4	1.08	.02019	.97981
18	469.2	1.18	.02206	.97794
20	469.4	1.33	.02487	.97513
22	469.8	1.48	.02767	.97233
24	469.2	1.60	.02992	.97008
26	469.2	1.73	.03235	.96765
28	469.2	1.83	.03422	.96578
30	<u>469.4</u>	1.98	.03702	.96298

Av. 469

Material Unfused

Time	$a - x_1$	$a - x_2$	K
$t=10$			
10-20	.98747	.97513	5.461×10^{-4}
12-22	.98523	.97233	5.724
14-24	.98261	.97008	5.574
16-26	.97981	.96765	5.424
18-28	.97794	.96578	5.434
20-30	.97513	.96298	<u>5.445</u>

Av. 5.510×10^{-4} $\pm 0.092 \times 10^{-4}$ (1.7%)

TABLE 46.

Catalyst Ratio = $\text{KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.9222 \times .17826 = .1644$
 Room Temp. = 26°C
 Barometer = 737.7

Time	Temp.	O_2	x	a - x
0	474.2			
95	482.0	10.79	.1800	.8200
100	482.0	11.40	.1902	.8098
105	482.2	11.92	.1989	.8011
110	482.4	12.50	.2086	.7914
115	482.2	13.09	.2184	.7816
175	475.2	17.34	.2893	.7107
270	483.2	26.54	.4428	.5572
345	483.5	32.06	.5349	.4651
350	483.7	32.46	.5416	.4584
355	483.5	32.88	.5486	.4514
360	484.4	33.25	.5548	.4452
365	<u>484.4</u>	33.50	.5590	.4410

Av. 481

Material Unfused

Time t=250	a - x_1	a - x_2	K
95-345	.8200	.4651	9.850×10^{-4}
100-350	.8098	.4584	9.886
105-355	.8011	.4514	9.965
110-360	.7914	.4452	9.994
115-365	.7816	.4410	<u>9.942</u>

Av. 9.927×10^{-4} $\pm 0.048 \times 10^{-4}$ (0.5%)

TABLE 47.

Catalyst Ratio = $\text{1KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $1.1223 \times 1.7826 = .2001$
 Room Temp. = 30°C
 Barometer = 738.8

Time	Temp.	O ₂	x	a - x
0	514.5			
5	509.6	3.3	.0447	.9553
10	511.0	10.85	.1470	.8530
15	512.0	19.5	.2642	.7358
16	512.0	21.15	.2866	.7134
17	512.0	22.8	.3089	.6911
18	512.0	24.25	.3286	.6714
19	512.0	25.9	.3509	.6491
20	512.0	27.3	.3699	.6301
25	511.8	33.7	.4566	.5434
26	511.8	34.9	.4729	.5271
27	511.8	36.1	.4892	.5108
28	511.8	37.1	.5027	.4973
29	511.8	38.2	.5176	.4824
30	511.8	39.25	.5318	.4682

Av. 512

Time t=10	a - x ₁	a - x ₂	K
15-25	.7358	.5434	1.316×10^{-2}
16-26	.7134	.5271	1.314
17-27	.6911	.5108	1.313
18-28	.6714	.4973	1.304
19-29	.6491	.4824	1.289
20-30	.6301	.4682	1.290

Av. 1.304×10^{-2} $\pm 0.010 \times 10^{-2}$ (0.8%)

TABLE 48.

Catalyst Ratio = $\text{1KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.6547 \times .17826 = .1167$
 Room Temp. = 22°C
 Barometer = 735.7

Time	Temp.	O_2	x	$a - x$
0	534.3			
4	531.1	2.40	.0570	.9430
8	532.6	9.90	.2352	.7648
9	532.8	11.80	.2803	.7197
10	533.2	13.50	.3207	.6793
11	533.2	15.55	.3694	.6306
12	533.2	16.80	.3991	.6009
13	533.4	18.10	.4300	.5700
14	533.6	19.50	.4633	.5367
15	533.6	20.95	.4977	.5023
16	533.6	22.40	.5322	.4678
17	533.6	23.65	.5619	.4381
18	533.6	24.70	.5868	.4132
19	533.8	25.70	.6106	.3894
20	534.0	26.80	.6367	.3633
21	534.2	27.85	.6616	.3384
22	534.2	28.75	.6830	.3170
23	534.2	29.70	.7056	.2944
24	534.2	30.60	.7270	.2730
25	<u>534.2</u>	31.50	.7484	.2516

Av. 533.5

Time $t=10$	$a - x_1$	$a - x_2$	K
8-18	.7648	.4132	2.674×10^{-2}
9-19	.7197	.3894	2.668
10-20	.6793	.3633	2.718
11-21	.6306	.3384	2.703
12-22	.6009	.3170	2.777
13-23	.5700	.2944	2.893
14-24	.5367	.2730	2.938
15-25	.5023	.2516	<u>3.002</u>

Av.. 2.797×10^{-2} $\pm 0.111 \times 10^{-2}$ (4.0%)

TABLE 49.

Catalyst Ratio = $\text{LKClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = .9926 x .17826 = .1769
 Room Temp. = 23°C
 Barometer = 735.6

Time	Temp.	O ₂	x	a - x
0	545.2			
3	540.0	3.89	.0607	.9393
6	541.0	15.68	.2448	.7552
6 1/2	541.3	17.38	.2714	.7286
7	541.3	19.58	.3057	.6943
7 1/2	541.5	21.38	.3338	.6662
8	541.7	22.97	.3587	.6413
8 1/2	542.0	24.57	.3837	.6163
9	542.2	25.87	.4040	.5960
9 1/2	542.2	27.37	.4274	.5726
10	542.4	28.77	.4492	.5508
13	543.2	36.11	.5638	.4362
16	543.8	42.11	.6590	.3410
16 1/2	543.8	43.06	.6724	.3276
17	543.8	43.86	.6849	.3151
17 1/2	544.2	44.55	.6956	.3044
18	544.2	45.25	.7066	.2934
18 1/2	544.4	46.10	.7198	.2802
19	544.4	46.75	.7300	.2700
19 1/2	544.6	47.60	.7433	.2567
20	544.6	48.05	.7503	.2497

Av..543

Time t=10	a - x ₁	a - x ₂	K
6 -16	.7552	.3410	3.463 x 10 ⁻²
6 1/2-16 1/2	.7286	.3276	3.472
7 -17	.6943	.3151	3.431
7 1/2-17 1/2	.6662	.3044	3.402
8 -18	.6413	.2934	3.396
8 1/2-18 1/2	.6163	.2802	3.425
9 -19	.5960	.2700	3.439
9 1/2-19 1/2	.5726	.2567	3.484
10 -20	.5508	.2497	3.436

Av. 3.439 x 10⁻² $\pm 0.023 \times 10^{-2}$ (0.7%)

TABLE 50.

Catalyst Ratio = $\text{1KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.6179 \times .17826 = .1101$
 Room Temp. = 22°C
 Barometer = 738.5

Time	Temp.	O_2	x	$a - x$
0	553.2			
4	549.8	8.74	.2208	.7792
5	550.2	11.93	.3014	.6986
6	551.0	13.73	.3469	.6531
7	551.7	16.52	.4174	.5826
8	552.2	18.72	.4730	.5270
9	552.5	20.31	.5132	.4868
10	552.7	22.31	.5637	.4363
11	553.0	24.31	.6143	.3857
12	553.4	25.91	.6547	.3453
13	553.9	27.70	.6999	.3001
14	554.1	28.95	.7315	.2685
15	<u>554.3</u>	30.20	.7631	.2369

Av. 552.6

Time $t=6$	$a - x_1$	$a - x_2$	K
4-10	.7792	.4363	4.198×10^{-2}
5-11	.6986	.3857	4.300
6-12	.6531	.3453	4.613
7-13	.5826	.3001	4.802
8-14	.5270	.2685	4.881
9-15	.4868	.2369	<u>5.213</u>

Av. 4.668×10^{-2}

$\pm 0.298 \times 10^{-2}$ (6.4%)

TABLE 51.

Catalyst Ratio=1KClO₄-4Fe₂O₃
 Wt. of Sample = .8481x.17826=.1512
 Room Temp. = 23°C
 Barometer = 735.7

Time	Temp.	O ₂	x	a - x
0	556.7			
2	552.5	2.90	.0530	.9470
4	555.6	13.49	.2464	.7536
4 1/2	555.8	16.24	.2967	.7033
5	556.3	18.43	.3367	.6633
5 1/2	556.7	20.33	.3714	.6286
6	557.4	22.33	.4079	.5921
6 1/2	557.6	24.13	.4408	.5592
7	558.0	25.93	.4737	.5263
7 1/2	558.4	27.82	.5082	.4918
8	558.9	29.52	.5393	.4607
8 1/2	559.1	31.22	.5704	.4796
9	559.3	32.62	.5959	.4041
9 1/2	559.8	33.91	.6195	.3805
10	560.0	35.21	.6432	.3568
10 1/2	560.2	36.61	.6688	.3312
11	560.5	37.81	.6908	.3092
11 1/2	560.7	38.91	.7108	.2892
12	561.0	40.01	.7309	.2691
12 1/2	561.0	40.91	.7474	.2526
13	561.2	41.80	.7636	.2364

Av. 558.8

Time t=5	a - x ₁	a - x ₂	K
4 - 9	.7536	.4041	5.413 x 10 ⁻²
4 1/2 - 9 1/2	.7033	.3805	5.336
5 - 10	.6633	.3568	5.386
5 1/2 - 10 1/2	.6286	.3312	5.566
6 - 11	.5921	.3092	5.643
6 1/2 - 11 1/2	.5592	.2892	5.727
7 - 12	.5263	.2691	5.826
7 1/2 - 12 1/2	.4918	.2526	5.787
8 - 13	.4607	.2364	5.795

Av. 5.609 x 10⁻²± 0.16 x 10⁻² (2.9%)

TABLE 52.

Catalyst Ratio = $\text{1KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.5855 \times .17826 = .1044$
 Room Temp. = 24°C
 Barometer = 741.1

Time	Temp.	O_2	x	a - x
0	568.8			
1	562.2	1.2	.0319	.9681
2	562.0	3.9	.1037	.8963
3	562.2	8.6	.2286	.7714
3 1/2	562.2	10.6	.2805	.7195
4	562.2	12.4	.3296	.6704
4 1/2	562.4	14.3	.3774	.6226
5	562.4	15.8	.4200	.5800
5 1/2	562.4	17.3	.4598	.5402
6	562.6	18.7	.4970	.5030
7	562.6	21.0	.5582	.4418
8	562.6	23.3	.6193	.3807
8 1/2	562.6	24.2	.6432	.3568
9	562.6	25.1	.6671	.3329
9 1/2	562.8	25.9	.6884	.3116
10	562.8	26.7	.7097	.2903
10 1/2	562.8	27.55	.7327	.2673
11	<u>562.8</u>	28.3	.7522	.2478

Av. 562.5

Time t=5	a - x_1	a - x_2	K
3 - 8	.7714	.3807	6.134×10^{-2}
3 1/2 - 8 1/2	.7195	.3568	6.092
4 - 9	.6704	.3329	6.080
4 1/2 - 9 1/2	.6226	.3116	6.010
5 - 10	.5800	.2903	6.012
5 1/2 - 10 1/2	.5402	.2673	6.111
6 - 11	.5030	.2478	<u>6.149</u>

Av. 6.085×10^{-2} $\pm 0.043 \times 10^{-2}$ (0.7%)

TABLE 53.

Catalyst Ratio=1KClO₄-4Fe₂O₃
 Wt. of Sample = .9875 x .17826 = .1760
 Room Temp. = 25°C
 Barometer = 737.0

Time	Temp.	O ₂	x	a - x
0	563.0			
1	557.8	1.7	.0266	.9734
2	557.8	9.1	.1422	.8578
3	558.2	19.2	.3001	.6999
3 1/2	558.4	23.0	.3595	.6405
4	558.4	26.5	.4142	.5858
4 1/2	558.6	29.8	.4658	.5342
5	558.8	33.0	.5158	.4842
5 1/2	559.0	35.2	.5502	.4498
6	559.0	36.9	.5768	.4232
6 1/2	559.2	39.8	.6221	.3779
7	559.2	41.5	.6487	.3513
7 1/2	<u>559.4</u>	43.5	.6799	.3201

Av. 559

Time	A - x ₁	a - x ₂	K
t=2 1/2			
3 -5 1/2	.6999	.4498	7.681 x 10 ⁻²
3 1/2-6	.6405	.4232	7.199
4 -6 1/2	.5858	.3779	7.615
4 1/2-7	.5342	.3513	7.281
5 -7 1/2	.4842	.3201	<u>7.189</u>
Av.			7.393 x 10 ⁻²
			<u>± 0.204 x 10⁻²</u> (2.8%)

TABLE 54.

Catalyst Ratio= $\text{KClO}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.5080 \times .17826 = .0906$
 Room Temp. = 25°C
 Barometer = 735.6

Time	Temp.	O_2	x	a - x
0	577.7			
1	571.6	5.0	.0318	.9682
2	572.0	12.4	.2561	.7439
2 1/2	572.2	15.4	.3470	.6530
3	572.2	18.3	.4349	.5651
3 1/2	572.6	21.0	.5167	.4833
4	573.0	23.3	.5864	.4136
4 1/2	573.2	25.7	.6591	.3409
5	573.2	27.8	.7228	.2772
5 1/2	<u>573.6</u>	29.4	.7713	.2287

Av. 573

Time t=2	a - x_1	a - x_2	K
2 -4	.7439	.4136	0.1275
2 1/2-4 1/2	.6530	.3409	0.1411
3 -5	.5651	.2772	0.1547
3 1/2-5 1/2	.4833	.2287	<u>0.1625</u>

Av. 0.1465

± 0.0122 (8.3%)

TABLE 55.

Catalyst Ratio=1KClO₄-4Fe₂O₃
 Wt. of Sample =.8682x.17826=.1548
 Room Temp. = 26°C
 Barometer = 735.0

Time	Temp.	O ₂	x	a - x
0	580.2			
2	576.5	10.3	.1819	.8181
3	577.3	20.1	.3549	.6451
3 1/3	577.5	22.3	.3938	.6062
3 2/3	577.5	24.9	.4397	.5603
4	578.1	27.5	.4856	.5144
4 1/3	578.1	29.9	.5280	.4720
4 2/3	578.1	31.8	.5615	.4385
5	578.5	34.0	.6004	.3996
5 1/3	578.5	36.0	.6357	.3643
5 2/3	579.0	37.5	.6622	.3378
6	579.0	39.1	.6889	.3111
6 1/3	579.2	40.7	.7187	.2813
6 2/3	<u>579.4</u>	42.0	.7416	.2584

Av. 578.4

Time t=2	a - x ₁	a - x ₂	K
3 1/3-5 1/3	.6062	.3643	0.1102
3 2/3-5 2/3-	.5603	.3378	0.1099
4 -6	.5144	.3111	0.1092
4 1/3-6 1/3	.4720	.2813	0.1119
4 2/3-6 2/3	.4385	.2584	<u>0.1148</u>

Av. 0.1112

± 0.0017 (1.5%)

TABLE 56.

Catalyst Ratio= $\text{1KC10}_4\text{-4Fe}_2\text{O}_3$
 Wt. of Sample = $.7787 \times .17826 = .1388$
 Room Temp. = 26°C
 Barometer = 735.0

Time	Temp.	O_2	x	a - x
0	599.5			
2	590.4	13.95	.2746	.7254
2 1/3	590.4	17.75	.3495-	.6505
2 2/3	589.8	21.75	.4282	.5718
3	589.8	25.15	.4952	.5048
3 1/3	589.8	28.35	.5582	.4418
3 2/3	589.6	31.55	.6212	.3788
4	589.2	33.85	.6664	.3336
4 1/3	589.2	36.35	.7156	.2844
4 2/3	589.2	38.35	.7550	.2450
5	589.2	40.35	.7944	.2056
5 1/3	589.2	41.55	.8180	.1820
5 2/3	589.2	42.75	.8417	.1583
6	<u>589.2</u>	43.85	.8633	.1367

Av. 589.3

Time t=2	a - x_1	a - x_2	K
2 1/3-4 1/2	.6505	.2844	0.1797
2 2/3-4 2/3	.5718	.2450	0.1840
3 -5	.5048	.2056	0.1950
3 1/3-5 1/3	.4418	.1820	0.1926
3 2/3-5 2/3-	.3788	.1583	0.1895
4 -6	.3336	.1367	<u>0.1937</u>

Av. 0.1891

 ± 0.0048 (2.5%)

TABLE 57.

Catalyst Ratio = $1\text{KClO}_4 - 4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $.7327 \times .17826 = .1306$
 Room Temp. = 26°C
 Barometer = 738.6

Time	Temp.	O_2	x	$a - x$
0	612.3			
1-	606.1	1.8	.0378	.9622
2	606.0	14.2	.2986	.7014
2 $1/3$	606.0	19.4	.4079	.5921
2 $2/3$	606.0	23.6	.4962	.5038
3	606.5	28.4	.5972	.4028
3 $1/3$	606.5	32.7	.6876	.3124
3 $2/3$	<u>606.7</u>	35.6	.7482	.2518

Av. 606.3

Time	$a - x_1$	$a - x_2$	K
t=1			
2 -3	.7014	.4028	0.2409
2 $1/3$ -3 $1/3$	.5921	.3124	0.2777
2 $2/3$ -3 $2/3$	.5038	.2518	<u>0.3012</u>

Av.. 0.2733

± 0.0216 (7.9%)

TABLE 58.

Catalyst Ratio = $1\text{KClO}_4\text{-}4\text{Fe}_2\text{O}_3$
 Wt. of Sample = $1.3220 \times 1.7826 = .2303$
 Room Temp. = 25°C
 Barometer = 736.7

Time	Temp.	O_2	x	$a - x$
0	616.2			
1	608.2	4.6	.0549	.9451
2	608.2	28.0	.3342	.6658
2 $\frac{1}{3}$	608.4	37.2	.4440	.5560
2 $\frac{2}{3}$	608.6	45.2	.5394	.4606
3	609.0	54.0	.6444	.3556
3 $\frac{1}{3}$	<u>609.4</u>	61.8	.7375	.2625

Av. 608.7

Time	$a - x_1$	$a - x_2$	K
$t=1$			
2 -3	.6658	.3556	0.2724
2 $\frac{1}{3}$ -3 $\frac{1}{3}$	.5560	.2625	<u>0.3259</u>

Av. 0.2992

± 0.0267 (9.0%)

TABLE 59.



Table t°C No.	1/Tabs.	1/T ²	K	log K	1/T logK
45 469	.001348		.0005510	-3.25885	-.002131173
46 481	.001326		.0009927	-3.00318	

47 512	.001274	.0 ₅ 1623076	.01304	-1.88472	-.002401133
48 533.5	.001240	.0 ₅ 1537600	.02797	-1.55331	-.001926104
49 543.0	.001225	.0 ₅ 1500625	.03439	-1.46357	-.001792873
50 552.6	.001211	.0 ₅ 1466521	.04668	-1.33087	-.001611684
51 558.8	.001202	.0 ₅ 1444804	.05609	-1.25111	-.001503834
52 562.5	.001197	.0 ₅ 1432809	.06085	-1.21574	-.001455241
53 559	.001202	.0 ₅ 1444804	.07393	-1.13118	-.001359678
54 573	.001182	.0 ₅ 1397124	.1465	-.83416	985977
55 578.4	.001175	.0 ₅ 1380625	.1112	-.95390	1120832
56 589.3	.001160	.0 ₅ 1345600	.1891	-.72331	839040
57 606.3	.001137	.0 ₅ 1292769	.2733	-.56336	640540
58 608.7	.001134	.0 ₅ 1285956	.2992	-.52410	594329
	.014339	.0 ₄ 17152313		-13.42933	.016231265

$$.0₄17152313A + .014339B = .016231265$$

$$.014339A + 12B = 13.42933$$

$$.001196200A + B = 1.1319660$$

$$.001194917A + B = 1.1191108$$

$$.000001283A = .0128552$$

$$A = 10,020$$

$$B = -10.85396$$

$$10,020 \frac{1}{T} + \log K = 10.85395$$

log K : 1/T
0 : .001083
-1 : .001183
-2 : .001283

t	:	T	:	K
400	:	673	:	.0 ₄ 9234
450	:	723	:	.0 ₃ 9886
500	:	773	:	.0 ₂ 7789
525	:	798	:	0.01984
550	:	823	:	0.04775
575	:	848	:	0.1091
600	:	873	:	0.2378
620	:	893	:	0.4299
640	:	913	:	0.7571

GRAPH 10.

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Square Points - Unfused

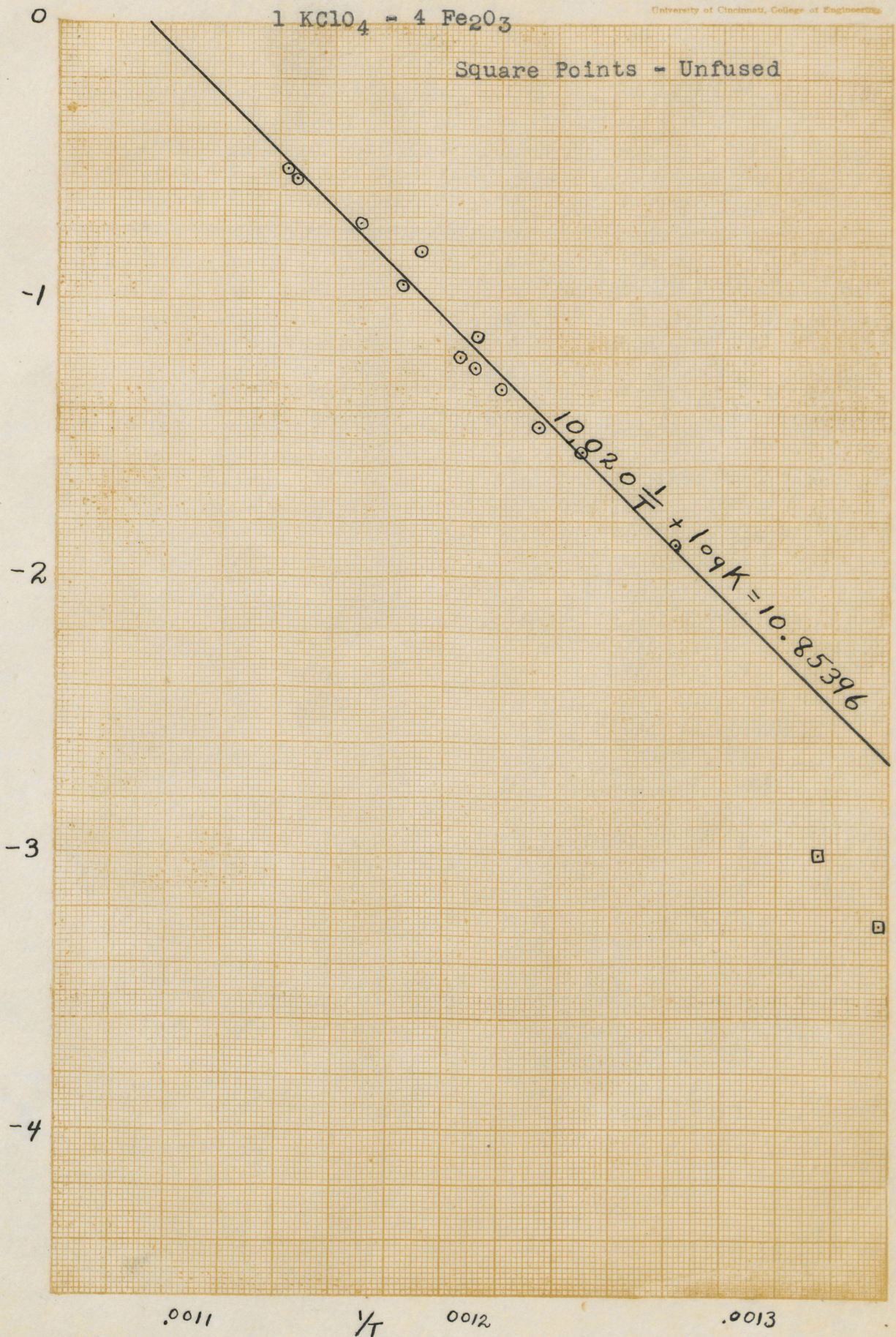
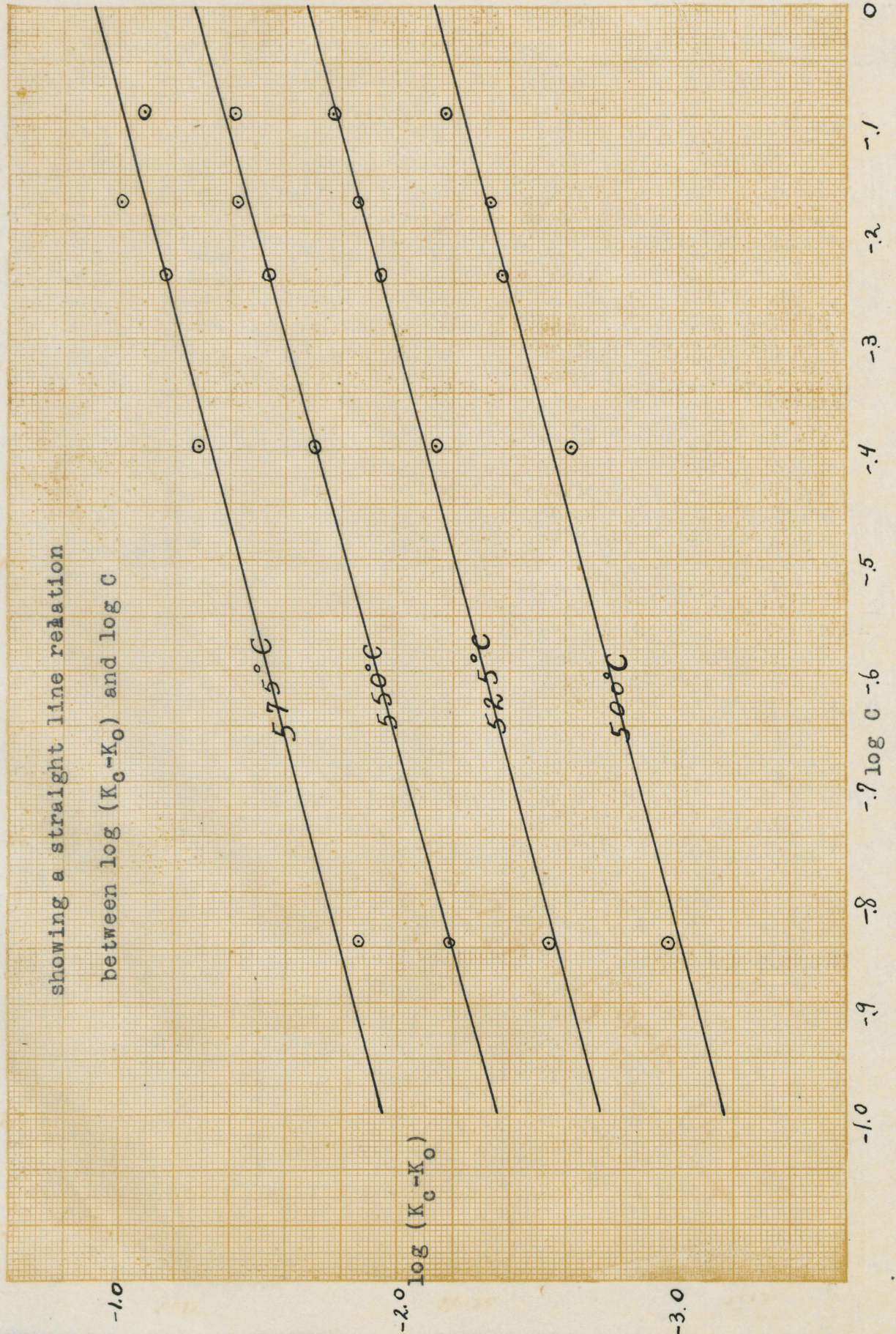
 $\log K$ 

TABLE 60.

Temp.	KClO ₄	6KClO ₄ 1Fe ₂ O ₃	3KClO ₄ 2Fe ₂ O ₃	3KClO ₄ 4Fe ₂ O ₃	1KClO ₄ 2Fe ₂ O ₃	1KClO ₄ 4Fe ₂ O ₃	conc. cata- lyst (C)
0		.14286	.40000	.57142	.66667	.80000	
		-.84510	-.39794	-.24304	-.17609	-.09691	log C
500	.037936	.021875	.023257	.025050	.025481	.027789	K _c
525	.022654	.025532	.01005	.01429	.01654	.01984	
550	.028702	.01528	.02894	.03793	.04670	.04775	
575	.02601	.03978	.07835	.09496	.1240	.1091	
500	-3.10040	-2.72700	-2.48718	-2.29671	-2.26114	-2.10852	log K _c
525	-2.57610	-2.25712	-1.99783	-1.84497	-1.78146	-1.70243	
550	-2.06038	-1.81588	-1.53850	-1.42102	-1.33068	-1.32103	
575	-1.58486	-1.40034	-1.10596	-1.02246	-0.90658	-0.96208	
500		.021081	.022463	.024256	.024687	.026995	K _c -K _o
525		.022878	.027396	.01164	.01389	.01719	
550		.026578	.02024	.02923	.03800	.03905	
575		.01377	.05234	.06895	.09799	.0831	
500		-2.96617	-2.60854	-2.37100	-2.32911	-2.15521	log(K _c -K _o)
525		-2.54091	-2.13100	-1.93405	-1.84730	-1.76472	
550		-2.18191	-1.69379	-1.53417	-1.42022	-1.40838	
575		-1.86107	-1.28117	-1.16147	-1.00882	-1.08040	
500		.027567	.026157	.027448	.027030	.028744	$\frac{K_c - K_o}{C}$
525		.02015	.01849	.02037	.02132	.02149	
550		.04605	.05060	.05115	.05700	.04881	
575		.09639	.1308	.1207	.1470	.1039	

Temp.	Av.	$\frac{K_c - K_o}{C}$
500	0.007389	+ 8.6%
525	0.02036	+ 4.1%
550	0.05072	+ 5.3%
575	0.1198	+ 11.4%

GRAPH 11.
log Vel. Const vs. log Conc. Catalyst



GRAPH 12.

$$\log \frac{K_c - K_o}{C} \quad \text{vs} \quad \frac{1}{T}$$

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showing that the expression $\frac{K_c - K_o}{C}$
varies with the temperature
according to an expression
similar to Arrhenius'.

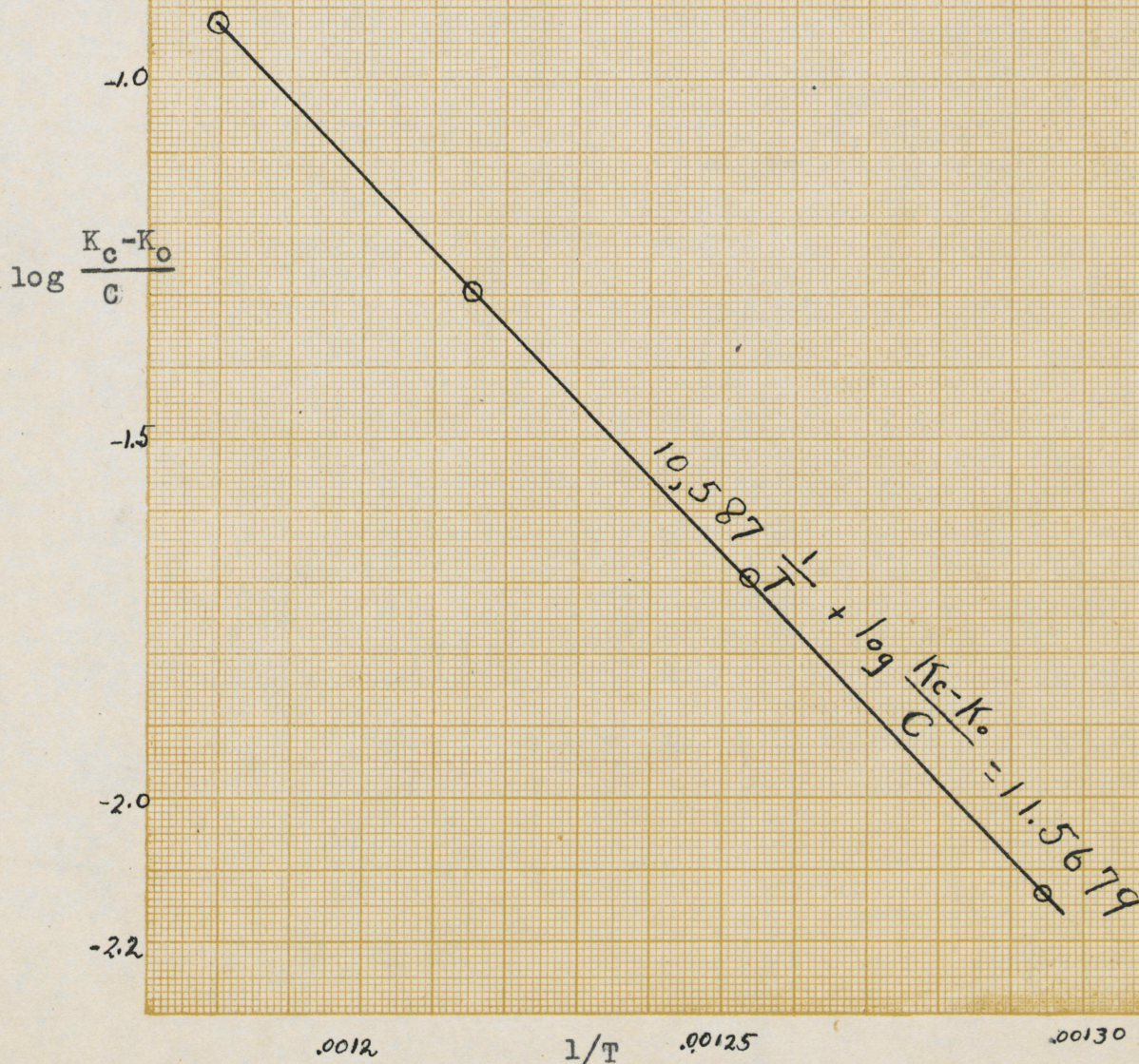


TABLE 61.

Evaluation of constants A + B in the Equation

$$\log \frac{K_c - K_o}{C} + \frac{A}{T} + B = 0$$

$1/T$	$1/T^2$	$\frac{K_c - K_o}{C}$	$\log \frac{K_c - K_o}{C}$	$\frac{1}{T} \log \frac{K_c - K_o}{C}$
.0012937	.051673660	.007389	-2.13141	-.002757405
.0012531	.051570259	.02036	-1.69122	-.002119268
.0012150	.051476225	.05072	-1.29482	-.001573207
<u>.0011792</u>	<u>.051390513</u>	<u>.1198</u>	<u>-0.92154</u>	<u>-.001086680</u>
.0049410	.056110657		-6.03899	-.007536560

$$.000006110657A + .0049410B = .007536560$$

$$.0049410A + 4B = 6.03899$$

$$.00123672A + B = 1.5253106$$

$$.00123525A + B = 1.5097475$$

$$.00000147\hat{A} = .0155631$$

$$A = 10,587$$

$$B = -11.5679$$

$$10,587 \frac{1}{T} + \log \frac{K_c - K_o}{C} = 11.5679$$

$$\log \frac{K_c - K_o}{C} : \frac{1}{T}$$

-1.0	:	.0011872
-1.5	:	.0012343
-2.0	:	.0012816

TABLE 62.

Comparison of Values of K calculated from general
equation (K) and directly from data. ($K_{\text{Obs.}}$)

Conc. of Catalyst	Temp. Abs.	K	$K_{\text{Obs.}}$
0	809	.004587	.004696
0	850	.02827	.02676
.14286	791	.004125	.004647
.14286	858	.006369	.05794
.40000	781	.005301	.005429
.40000	832	.04087	.04094
.57142	780	.006776	.006445
.57142	835	.05909	.05703
.66667	789	.01121	.01178
.66667	828	.05148	.05514
.80000	785	.01110	.01304
.80000	851	.1367	.1112

Decomposition of Potassium Chlorate

Portions of potassium chlorate were weighed in the same manner as the perchlorate. Additions of potassium chloride as catalyst, however, were made to the individual samples instead of weighing out portions of a mixture made up once for all, since it was not desired to make mixtures in simple molecular ratios.

Potassium chlorate decomposes on heating according to two reactions and thus it was necessary to determine both the oxygen evolved and the perchlorate formed at various stages of the reaction. This was done by subtracting from the amount of potassium chlorate originally present both the amount decomposed to oxygen and the amount remaining at any particular time. Seven samples were weighed and heated respectively for intervals of time in arithmetic sequence. Obviously, the difference between these intervals was smaller, the higher the temperature. Four of these samples were placed in the furnace at the beginning of the experiment and one was heated throughout the experiment. When the other three tubes had been heated for the second, third and sixth intervals, these were removed and replaced respectively by the remaining three which by the end of the seventh interval had been heated for the fifth, fourth and first intervals. Thus, the four holes of the furnace were continuously occupied and there could be determined the chlorate remaining after heating for the seven different intervals. Observations of the potassium chlorate decomposing to oxygen were made only on the samples heated

for the sixth and seventh intervals, but, since they merely involved the reading of the gas burettes, were taken more often.

The entire reaction residue was dissolved in water, the solution divided into aliquot portions and the chlorate content in each was determined by the procedure mentioned under Analytical Methods.

Calculations based on the Data obtained by Decomposing Potassium Chlorate

Tables 63, 67, 71 and 75 (taken at four temperatures) show the experimental observations from which were determined the fractions of potassium chlorate equivalent to the oxygen evolved. Tables 64, 68, 72 and 76 show the results of the analyses of the reaction residues, and below, the correction (w), calculated as previously noted, for the perchlorate which has decomposed. The last two columns give respectively the amount of potassium chlorate transformed to perchlorate and the amount of potassium chlorate decomposed to potassium chloride and oxygen. (See also graphs 13, 19, 25 and 32 which have been used in the calculations.)

In graphs 14, 20, 26 and 33 the correction (w) is plotted against time in order to interpolate it for the correction of the oxygen evolved. In graphs 15, 21, 27 and 34 the amount (z) of potassium chlorate decomposing to oxygen is plotted against time in order to determine the tangent $\Delta z / \Delta t$ at various points during the decomposition. Graphs 28 and

35 show the amount ($\bar{y}$) of potassium chlorate transformed by the other reaction into perchlorate. From these the tangent $\Delta y / \Delta t$ was read to determine k_1 by the differential equation because the value k_2 requisite for calculating k_1 by the integrated equation was obviously incorrect, since the k_2, t curve contained a maximum.

Tables 65, 69, 73 and 77 embody the following data: first column, the time of the observations in minutes or hours; second column, the potassium chlorate decomposed directly to potassium chloride and oxygen (z); third column, that transformed to potassium perchlorate (y); fourth column, the potassium chlorate remaining ($a - x$); fifth column, the slope of the z, t curve at the time given in the first column; which divided by ($a - x$) gives k_2 in the sixth column; seventh column, the value of k_1 calculated by either the differential or integrated equations; and the last column, the concentration of the potassium chloride produced in equivalents of potassium chlorate. This is obtained by adding one fourth of y to z .

Since k_1 rapidly increased as the reaction proceeded, it was desired to ascertain whether this was paralleled either by the concentration of potassium chloride or of perchlorate. Initial additions of potassium chloride to the chlorate, which will be more fully explained later, was found to give in a certain time an increased yield of potassium perchlorate without materially affecting the decomposition yielding oxygen. The curves on graphs 16, 22, 29 and 36, on which $\log C_{KCl}$ is

plotted against $\log k_1$, show, however, that k_1 is not proportional to any power of the concentration of potassium chloride. But, by extrapolating a k_1, t curve to $t=0$, (graphs 17, 23, 30 and 37) a value for k_1 (k_0) was obtained when the concentration of the potassium chloride was zero. It was discovered by the graphical method that the value $k_1 - k_0$ was proportional to the cube of the concentration of the potassium chloride as shown on graphs 18, 24, 31 and 38. Hence, the values

$\frac{k_1 - k_0}{C_{KCl}^3}$ were computed. These values (p) are tabulated in the last columns of tables 66, 70, 74 and 78.

The values of k_2 , $\frac{k_1 - k_0}{C_{KCl}^3}$, and T were assembled

in tables 79 and 80 and the logs of the constants were plotted against the reciprocal of the absolute temperature in graphs 39 and 40. On account of the meagerness of the data, the constants of Arrhenius' equation were not calculated for these relations, as was done for the potassium perchlorate decompositions.

In table 81, as previously mentioned, are tabulated the results of experiments on the heating of potassium chlorate to which initial additions of potassium chloride had been made. All of the tubes were placed in, and taken out of the furnace at the same time. They were then analyzed for chlorate and it was noticed (column 6) that more chlorate had suffered change in the tubes containing the greater amount of potassium chloride. In the first group, determinations

of the fraction of chlorate, decomposing to oxygen directly, were made for each sample and, subtracted from the total fraction changed, gave the fraction transformed to potassium perchlorate. Since the fraction yielding oxygen varied slightly while the potassium chloride increased from 0 to 12%, determination of the amount of chlorate participating in this side reaction was made in the later groups only with the initially pure potassium chlorate. This decision was unfortunate, since in the last experiment, due to the lower temperature and the additions of potassium chloride, the mixtures were unfused at the end of, and probably throughout the experiment. However, even when solid the disappearance of potassium chlorate paralleled the concentration of potassium chloride. Thus it is evident that the transformation of potassium chlorate to potassium perchlorate is catalyzed by potassium chloride. It would be interesting to find out if a greater yield of potassium perchlorate from the chlorate, than that reported by Blau and Weingand⁽¹⁷⁾, could be effected by this means. For commercial operation, the inefficiency of the higher fusion point of the melt and the lower percentage of potassium perchlorate in the residue might, however, counterbalance the efficiency of the increased yield.

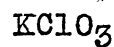
TABLE 63.

KClO₃ Sample Wt.
 A = .5374
 B = .6025

Time hrs.	Furnace Temp.	Room Temp.	Barometer	Oxygen		Fraction KClO ₃ O ₂ evolved		Av.
				A	B	A	B	
0	419.0	20°	740.3	0.88	1.1			
1	404.5			0.88	1.10	.0054	.0060	.0057
2	410.1	21°	739.0	1.73	1.73	.0106	.0095	.0100
3	410.5	22°	738.2	2.42	2.45	.0148	.0133	.0140
4	405.6	22°	738.1	3.11	2.93	.0190	.0160	.0175
5	406.9	22°	738.2	3.62	3.34	.0221	.0182	.0196
6	413.8	22°	738.2	4.35	3.86	.0264	.0210	.0237
7	404.3	23°	739.0	5.03	4.35	.0306	.0236	.0271
8	414.5	23°	739.9	5.75	4.80	.0351	.0261	.0306
9	415.8	23°	740.8	6.42	5.27	.0392	.0287	.0340
10	408.7		741.2	7.02	5.68	.0429	.0310	.0370
11	403.3	22°	741.3	7.62	5.97	.0467	.0326	.0396
12	405.2	22°	742.1	8.09	6.29	.0497	.0344	.0420
13	413.4	21°	742.4	8.71	6.64	.0537	.0365	.0453
14	417.1	22°	742.7	9.31	7.26	.0572	.0398	.0485
15	412.7	22°	743.1	9.96	7.70	.0612	.0425	.0518
16	406.8	22°	743.4	10.51	8.06	.0646	.0442	.0544
17	404.1	22°	743.9	10.93	8.37	.0672	.0459	.0566
18	408.0	22°	744.1	11.43	8.72	.0703	.0479	.0591
19								
20	407.8	22°	744.3	12.34	9.36	.0742	.0514	.0628
21	407.0	22°	744.3	12.83	9.67	.0790	.0531	.0660
22	406.0	24°	744.7	13.26	10.01	.0811	.0546	.0678
23	405.6	24°	744.7	13.64	10.28	.0834	.0561	.0698
24	404.7	24°	744.7	14.15	10.58	.0866	.0577	.0722
25	415.8	23°	744.4	14.28				
26	416.6	23°	744.4	14.82				
27	405.6	23°	743.4	15.11				
28	410.3	23°	743.2	15.56		.0954		(.0810)

Av. 408.9

TABLE 64.



Analysis of Residues
Calculation of W
T = 408.9

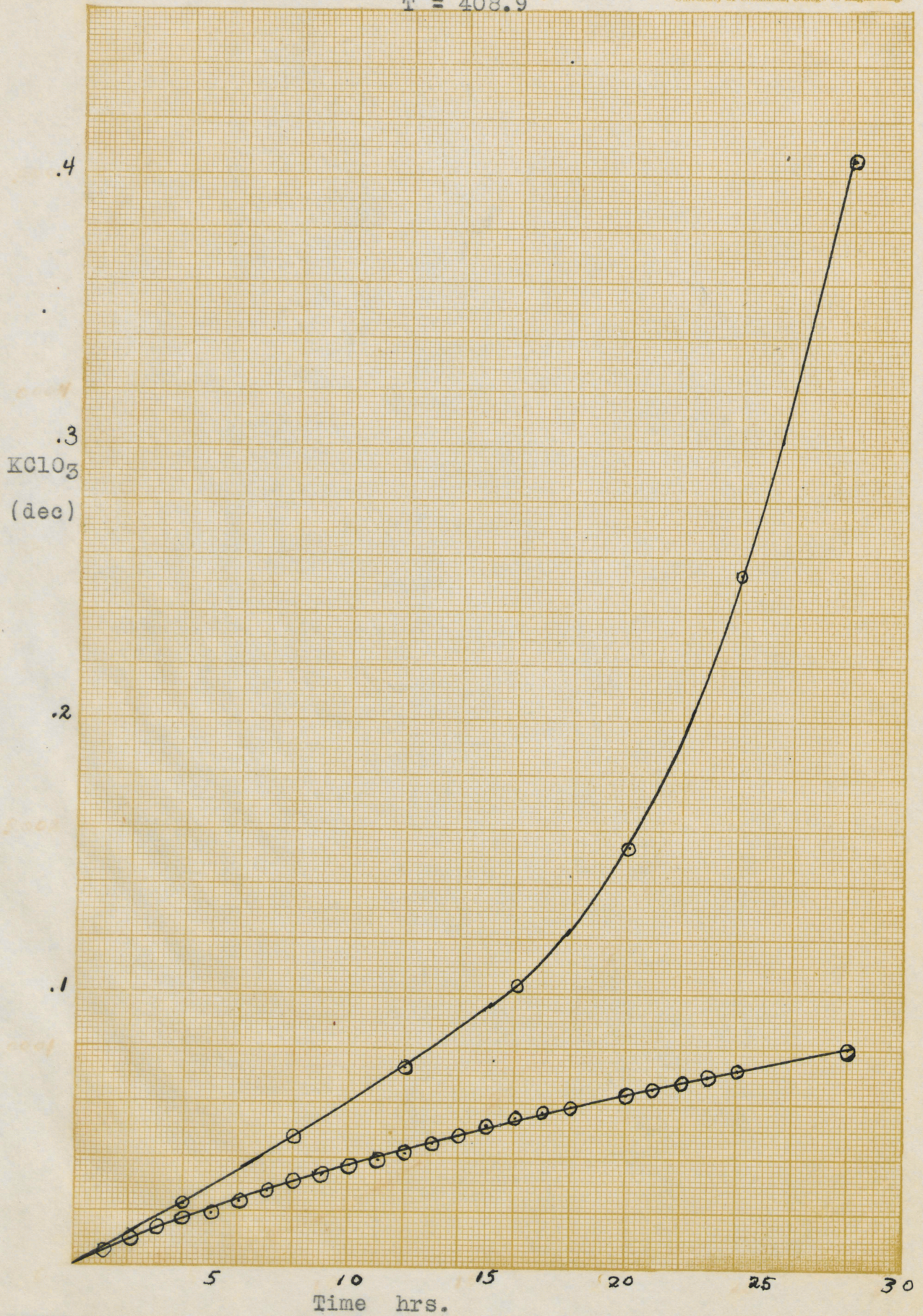
Wt. of Sample	Time heated hrs.	Wt. KClO_3 in Residue	Fraction KClO_3 untransformed	Fraction KClO_3 transformed
.6721	4	.6565	.9768	.0232
.5488	8	.5232	.9533	.0467
.7714	12	.7152	.9271	.0729
.6449	16	.5787	.8974	.1026
.7646	20	.6468	.8460	.1540
.6025	24	.4497	.7464	.2536
.5374	28	.3193	.5941	.4059

Time hrs.	Total Fraction KClO_3 trans.	Fraction KClO_3 giving O_2	Fraction KClO_3 giving KClO_4	W	KClO_3 forming KClO_4 once corrected	KClO_3 forming O_2 directly
4	.0232	.0175	.0057	.00000	.0057	.0175
8	.0467	.0306	.0161	.00001	.0161	.0306
12	.0729	.0420	.0309	.00002	.0309	.0420
16	.1026	.0544	.0482	.00003	.0483	.0543
20	.1540	.0628	.0912	.00006	.0913	.0627
24	.2536	.0722	.1814	.00011	.1816	.0720
28	.4059	(.0810)	.3249	.00021	.3254	.0805

GRAPH 13.

Decomposition Curves for KClO_3 $T = 408.9$

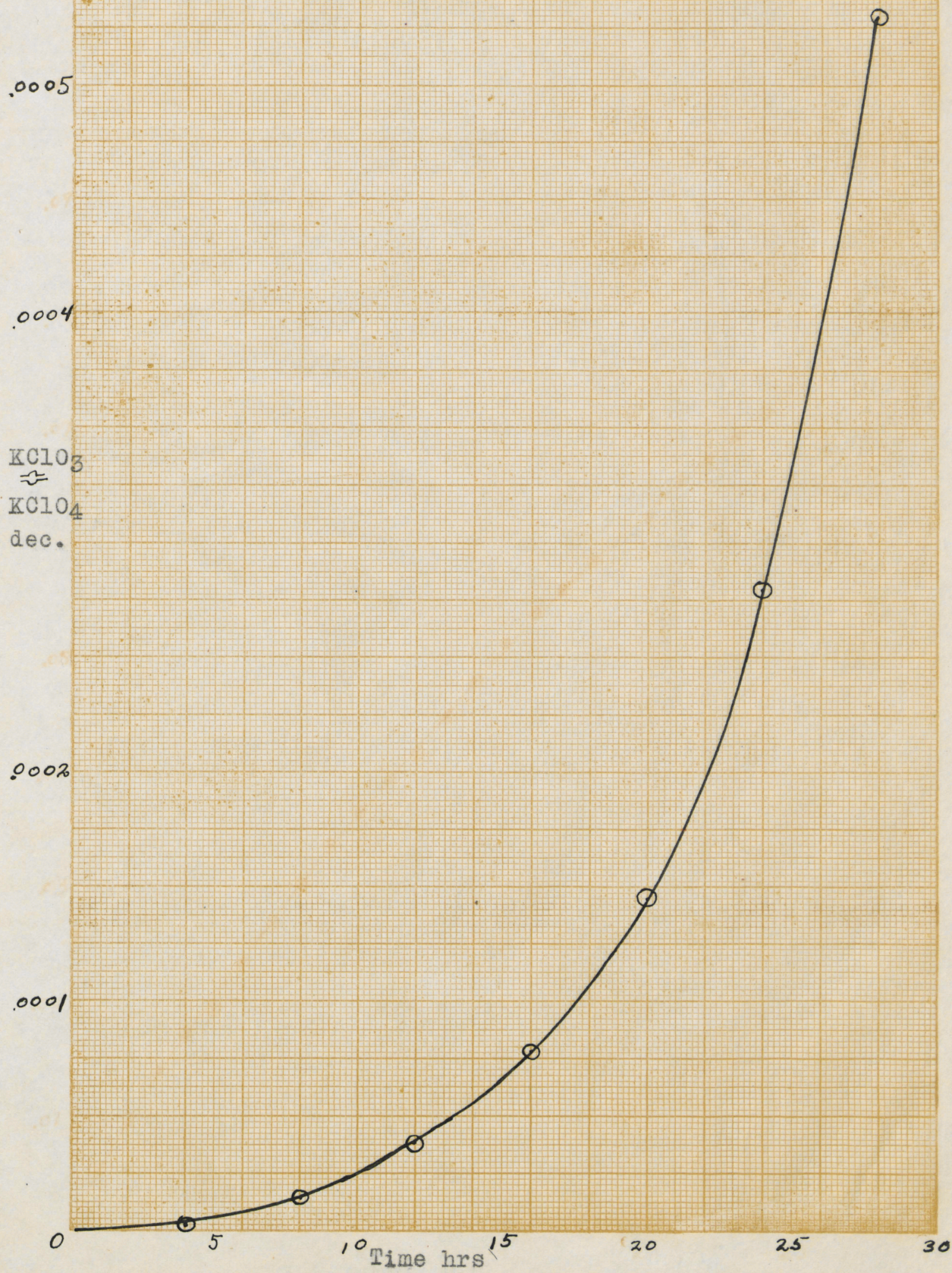
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GRAPH 14.

Correction for $\text{KClO}_4 \rightarrow \text{O}_2$ $T = 408.9$

University of Cincinnati, College of Engineering

for interpolation of w 

GRAPH 15.

z vs. t

T = 408.9

University of Cincinnati, College of Engineering

for obtaining tangents

z/ t

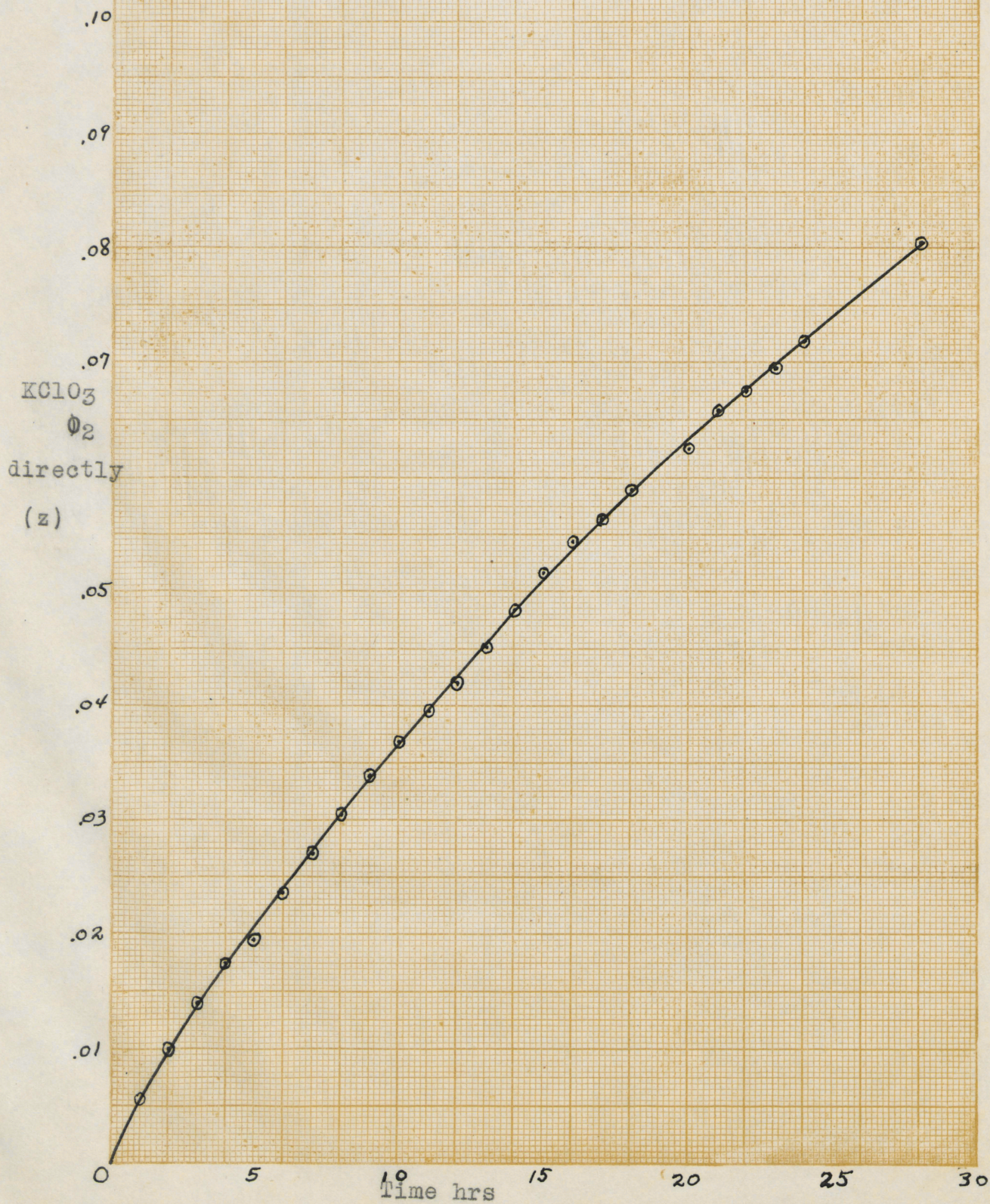


TABLE 65.

Calculation of k_2 and k_1 $T = 408.9$

Time hrs.	$\text{KClO}_3 \rightarrow \text{O}_2$ z	$\text{KClO}_3 \rightarrow \text{KClO}_4$ y	Conc. KClO_3 a - x	$\Delta z / \Delta t$	$\frac{\Delta z / \Delta t}{a - x}$ k_2	k_1	Conc. KClO_3 $\rightarrow \text{KCl}$ formed C_{KCl}
1	.0057		.9936	.00448	.004509		
2	.0100		.9880	.00397	.004015		
3	.0140		.9823	.00375	.003818		
4	.0175	.0057	.9768	.00355	.003634	.0029071	.0189
5	.0196		.9705	.00338	.003483		
6	.0237		.9644	.00331	.003432		
7	.0271		.9584	.003195	.003334		
8	.0306	.0161	.9533	.003085	.003236	.0031331	.0346
9	.0340		.9465	.003005	.003175		
10	.0370		.9401	.002958	.003146		
11	.0396		.9335	.002905	.003112		
12	.0420	.0309	.9271	.002875	.003101	.0036369	.0487
13	.0453		.9200	.002845	.003092		
14	.0484		.9132	.002785	.003050		
15	.0516		.9054	.002738	.003024		
16	.0543	.0483	.8974	.002655	.002958	.0043590	.0664
17	.0565		.8872	.002515	.002770		
18	.0591		.8753	.002400	.002742		
19	.		.8615	.002330	.002705		
20	.0627	.0913	.8460	.002275	.002689	.0068306	.0855
21	.0658		.8270	.002205	.002666		
22	.0676		.8050	.002160	.002683		
23	.0696		.7780	.002135	.002744		
24	.0719	.1816	.7464	.002115	.002834	.0143790	.1173
25							
26							
27							
28	.0805	.3254	.5941			.036286	.1619

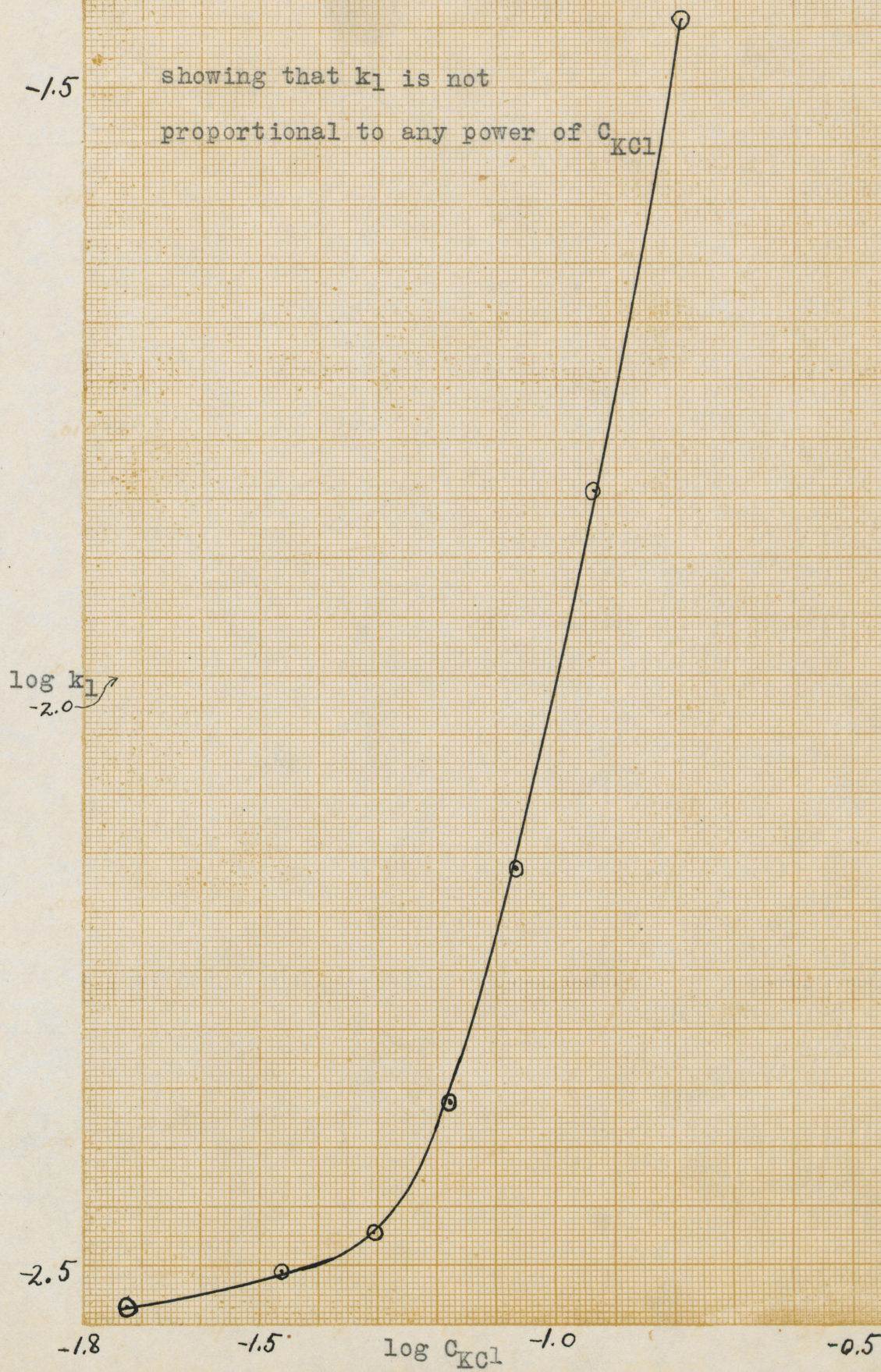
Av. .003062

 $\pm .000259$ (8.5%)

GRAPH 16.

 $\log k_1$ vs. $\log C_{KCl}$ $T = 408.9$

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GRAPH 17.

 k_1 vs. t $T = 408.9$

University of Cincinnati, College of Engineering



GRAPH 18.

 $\log k_1 - k_0$ vs. $\log C_{KCl}$
 $T = 408.9$

University of Cincinnati, College of Engineering

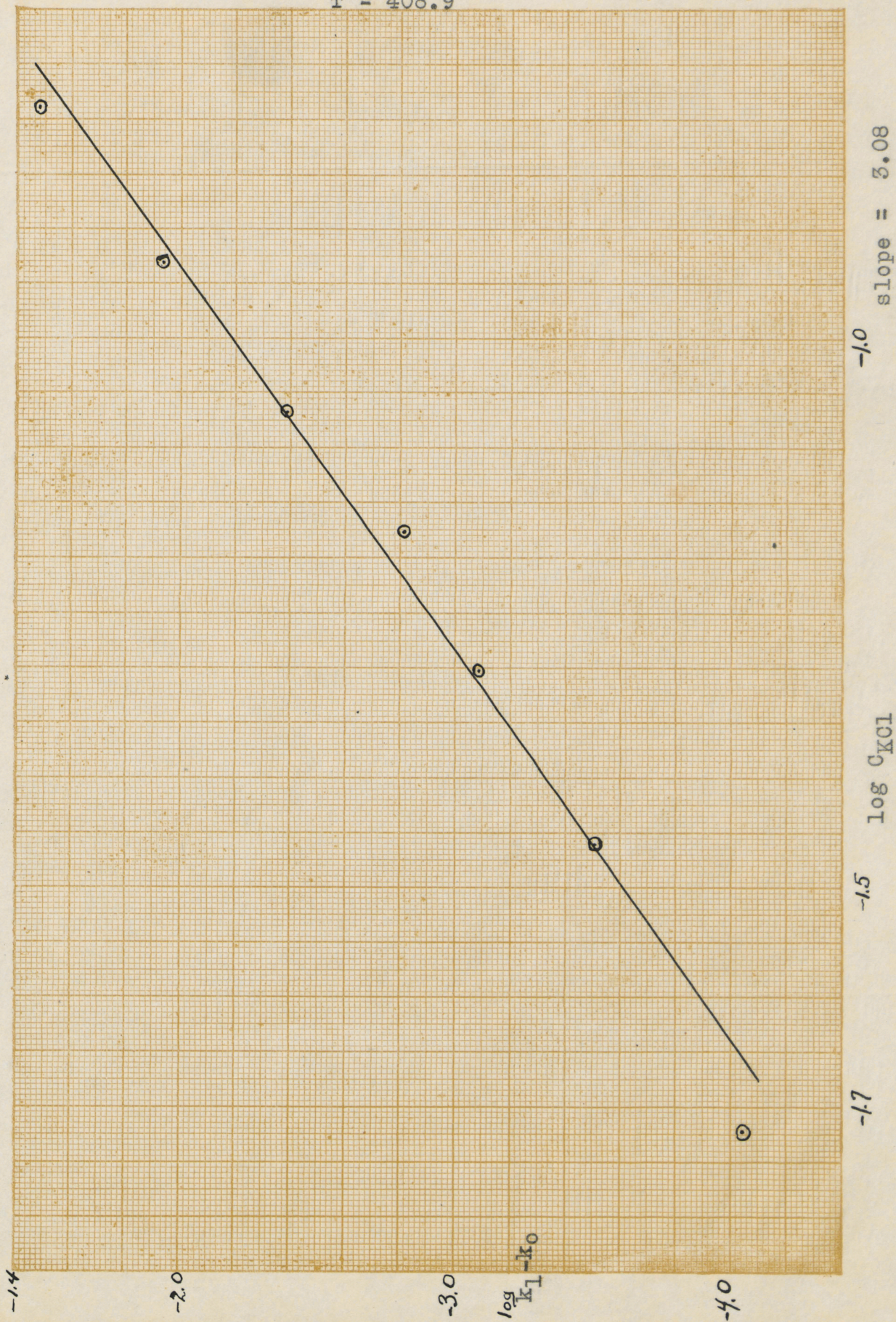


TABLE 66. Calculation of $\frac{k_1 - k_0}{C_{KCl}^3}$

T = 408.9

Time hrs	Conc. $KClO_3 \rightarrow KCl$ formed C_{KCl}	$k_1 - k_0$ $k_0 = .00282$	$(k_1 - k_0) / C_{KCl}^3$ p
4	.0189	.00009	13.331
8	.0346	.00031	7.484
12	.0497	.00082	6.679
16	.0664	.00154	5.260
20	.0855	.00401	6.416
24	.1173	.01156	7.162
28	.1619	.03347	7.887

Av. 7.746 $\pm$ 1.636 (21.1%)

If t is in minutes 0.1291

TABLE 67.

$KClO_3$ Wt. of Sample = .4970
 Room Temp. = 23°C
 Barometer = 740.3

Time min.	Temp.	O ₂	Fraction $KClO_3 \rightarrow O_2$ evolved.
0	473.4		
15	456.2		
30	460.9	1.62	.0107
45	457.9	2.19	.0145
60	458.6	2.79	.0184
75	458.5	3.29	.0217
90	460.3	3.69	.0244
105	461.3	4.29	.0283
120	461.9	4.78	.0315
135	458.3	5.09	.0336
150	458.3	5.59	.0369
165	459.2	5.99	.0395
180	459.9	6.40	.0422
195	459.2	6.82	.0450
210	460.7	7.34	.0484
225	459.9	7.92	.0523
240	458.1	8.41	.0555
255	467.0	8.91	.0588
270	465.1	9.41	.0621
285	459.9	9.89	.0653
300	459.2	10.19	.0672
315	460.9	10.51	.0694
330	460.1	10.95	.0723
345	458.6	11.39	.0752
360	458.5	11.75	.0775

Av. 460.1

Note: Other tube from which O₂ was to be collected was broken

TABLE 68.

 KClO_3

Analysis of Residues
Calculation of W
 $T = 460.1$

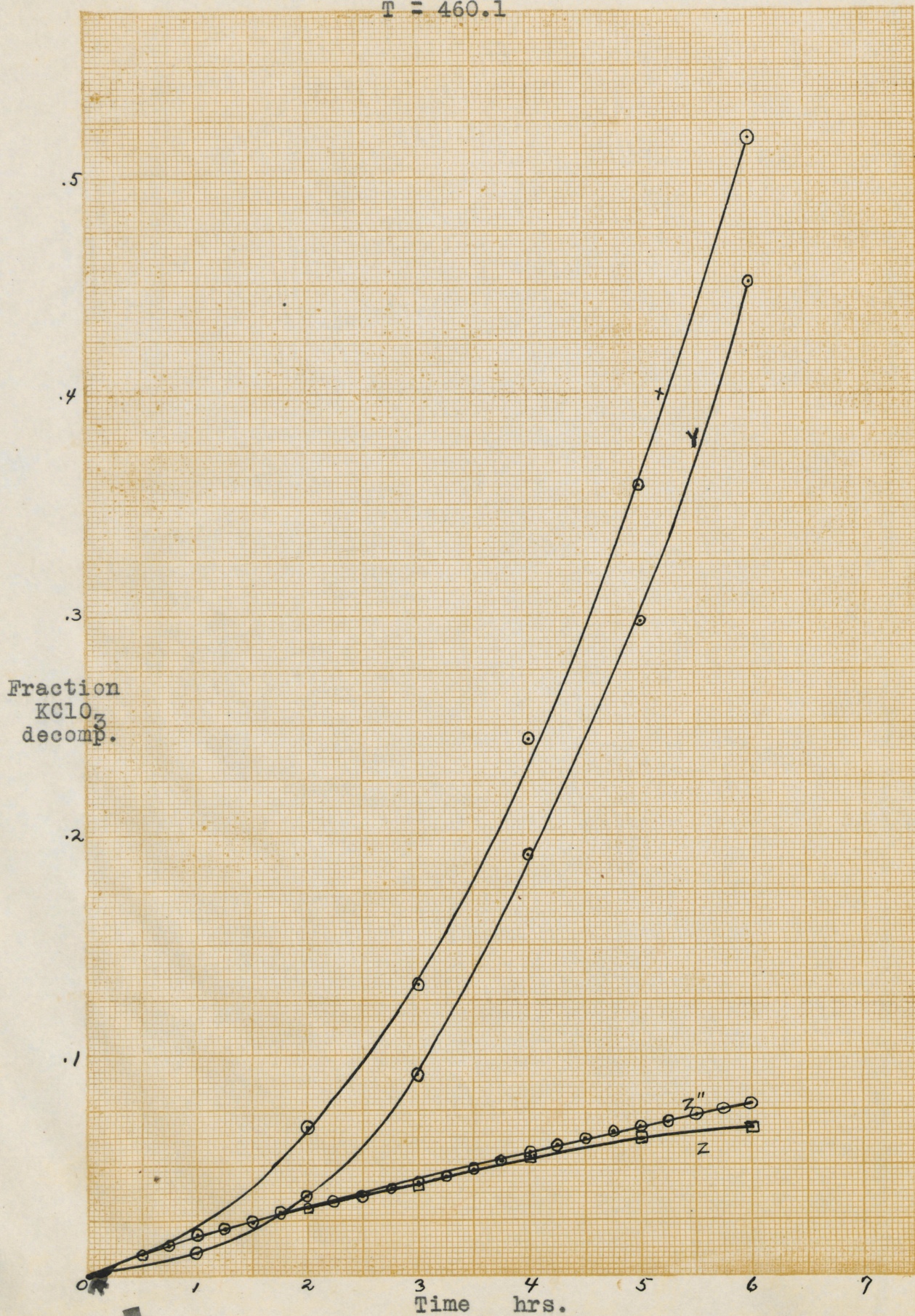
Wt. of Sample	Time heated min,	Wt. KClO_3 in Residue	Fraction KClO_3 untransformed	Fraction KClO_3 transformed
.5357	60	.5260	.9819	.0181
.5153	120	.4806	.9326	.0674
.5765	180	.5003	.8678	.1322
.4696	240	.3552	.7563	.2437
.5249	300	.3363	.6407	.3593
.4970	360	.2396	.4820	.5180

Time	Total Fraction KClO_3 trans.	Fraction giving O_2	Fraction giving KClO_4	W_1	KClO_4 formed once corrected	W_2	KClO_3 forming KClO_4 twice corrected	KClO_3 forming O_2 directly
60	.0181	.0184						
120	.0674	.0315	.0359	.00019	.0306	.00019	.0361	.0313
180	.1322	.0422	.0900	.00067	.0772	.00068	.0910	.0412
240	.2437	.0555	.1882	.00149	.1620	.00151	.1911	.0526
300	.3593	.0672	.2921	.00257	.2526	.00262	.2980	.0613
360	.5180	.0775	.4405	.00392	.3824	.00401	.4511	.0669

GRAPH 19.

Decomposition Curves for KClO_3

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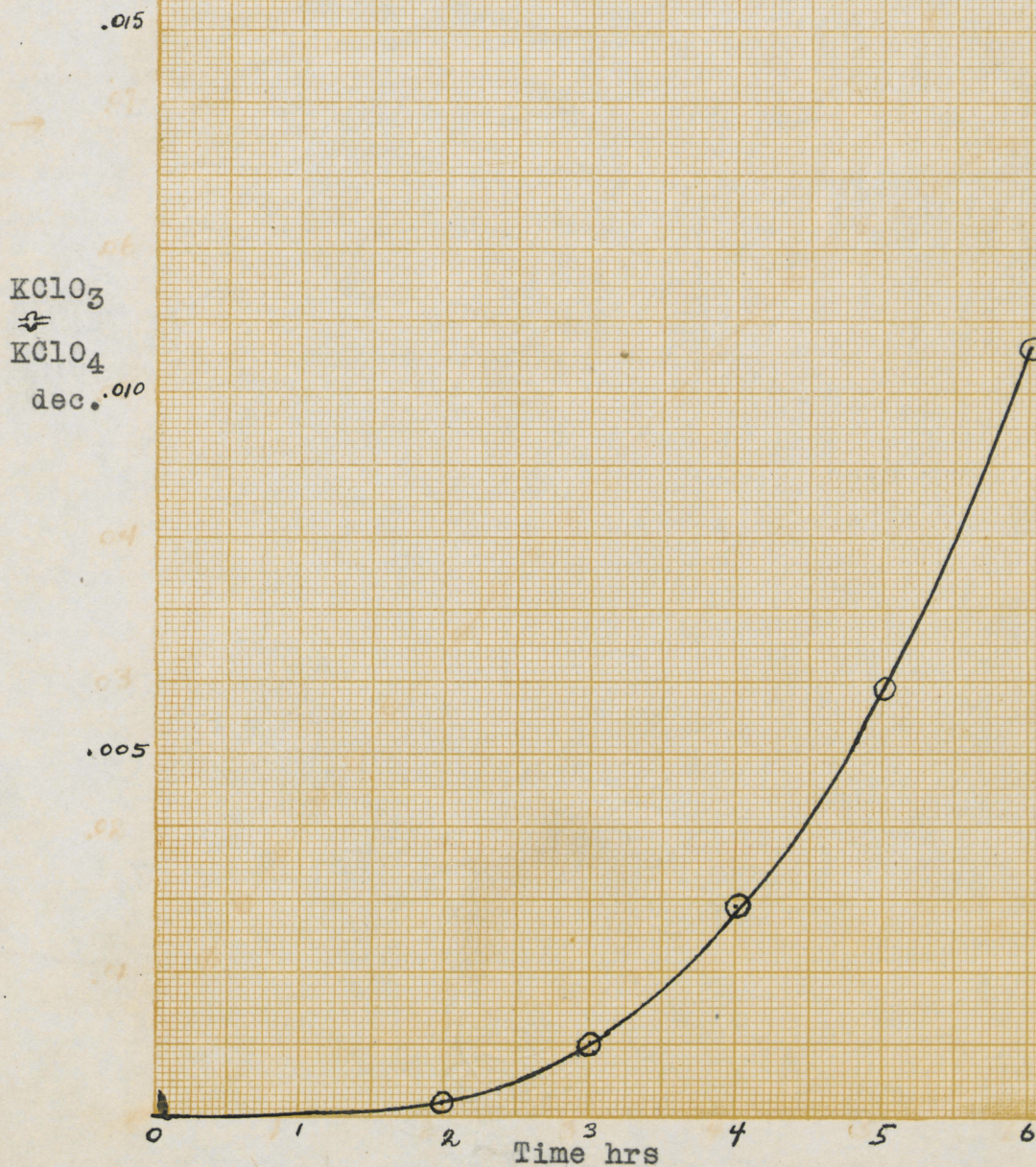
 $T = 460.1$ 

GRAPH 20.

Correction for $\text{KClO}_4 \rightarrow \text{O}_2$ $T = 460.1$

University of Cincinnati, College of Engineering

for interpolation of w



GRAPH 21.

z vs. t

T = 460.1

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for obtaining tangents $\Delta z / \Delta t$

KClO₃
→ O₂
directly
(z)

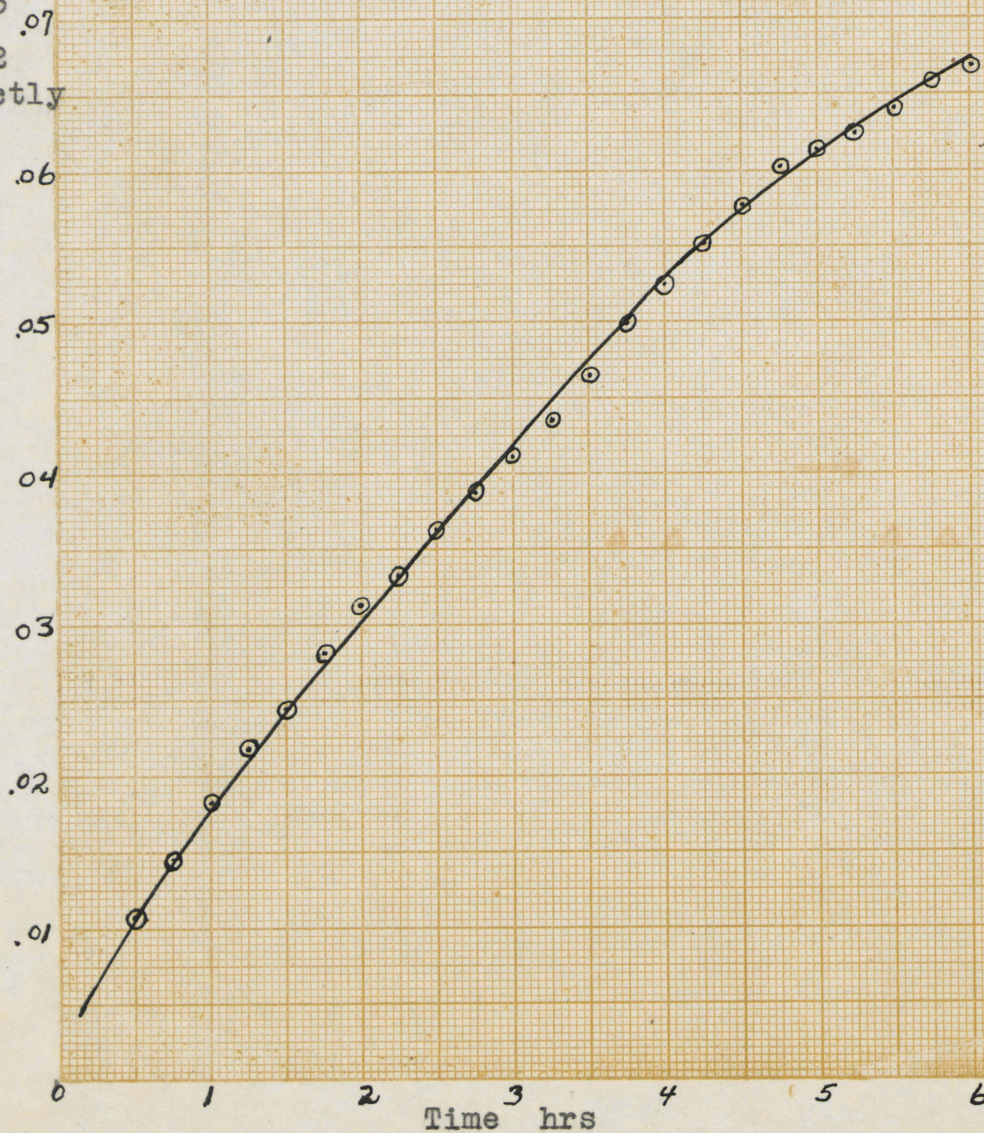


TABLE 69.

Calculations of k_2 and k_1 $T = 460.1$

Time min.	$\text{KClO}_3 \rightarrow \text{O}_2$ z	$\text{KClO}_3 \rightarrow \text{KClO}_4$ y	Conc. KClO_3 $a - x$	$\Delta z / \Delta t$	$\frac{\Delta z / \Delta t}{a - x}$ k_2	k_1	Conc. $\text{KClO}_3 \rightarrow \text{KCl}$ formed. C_{KCl}
30	.0107		.9910				
45	.0145		.9855				
60	.0184		.9819	.0002267	.0002308		
75	.0217		.9708	.0002133	.0002197		
90	.0243		.9606	.0002053	.0002138		
105	.0282		.9485	.0002020	.0002130		
120	.0313	.0361	.9326	.0001990	.0002133	.0004122	.0403
135	.0333		.9197	.0001960	.0002132		
150	.0364		.9035	.0001937	.0002143		
165	.0388		.8855	.0001926	.0002172		
180	.0412	.0910	.8678	.0001900	.0002190	.0007167	.0634
195	.0436		.8445	.0001863	.0002207		
210	.0466		.8213	.0001823	.0002220		
225	.0500		.7960	.0001733	.0002178		
240	.0526	.1911	.7563	.0001687	.0002230	.0014770	.1004
255	.0553		.7395	.0001590	.0002150		
270	.0579		.7075	.0001410	.0001993		
285	.0603		.6750	.0001273	.0001887		
300	.0613	.2980	.6407	.0001190	.0001858	.0026180	.1358
315	.0625		.6035	.0001113	.0001842		
330	.0641		.5640	.0001043	.0001850		
345	.0660		.5238				
360	.0669	.4511	.4820			.0063303	.1797

Av. .0002103 $\pm$.0000118 (5.25%)Solving for 'n' for reaction $\text{KClO}_3 \rightarrow \text{O}_2$

Time	$n = \frac{\log(\Delta z / \Delta t)_1 - \log(\Delta z / \Delta t)_2}{\log(a - x)_1 - \log(a - x)_2}$
60-240	1.13
75-255	1.08
90-270	1.23
105-285	1.36
120-300	1.37
135-315	1.34
150-330	1.31

GRAPH 22.

 $\log k_1$ vs. $\log C_{KCl}$ $T = 460.1$

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-0.5 showing that k_1 is not proportional
to any power of C_{KCl}

 $\log k_1$
-1.0

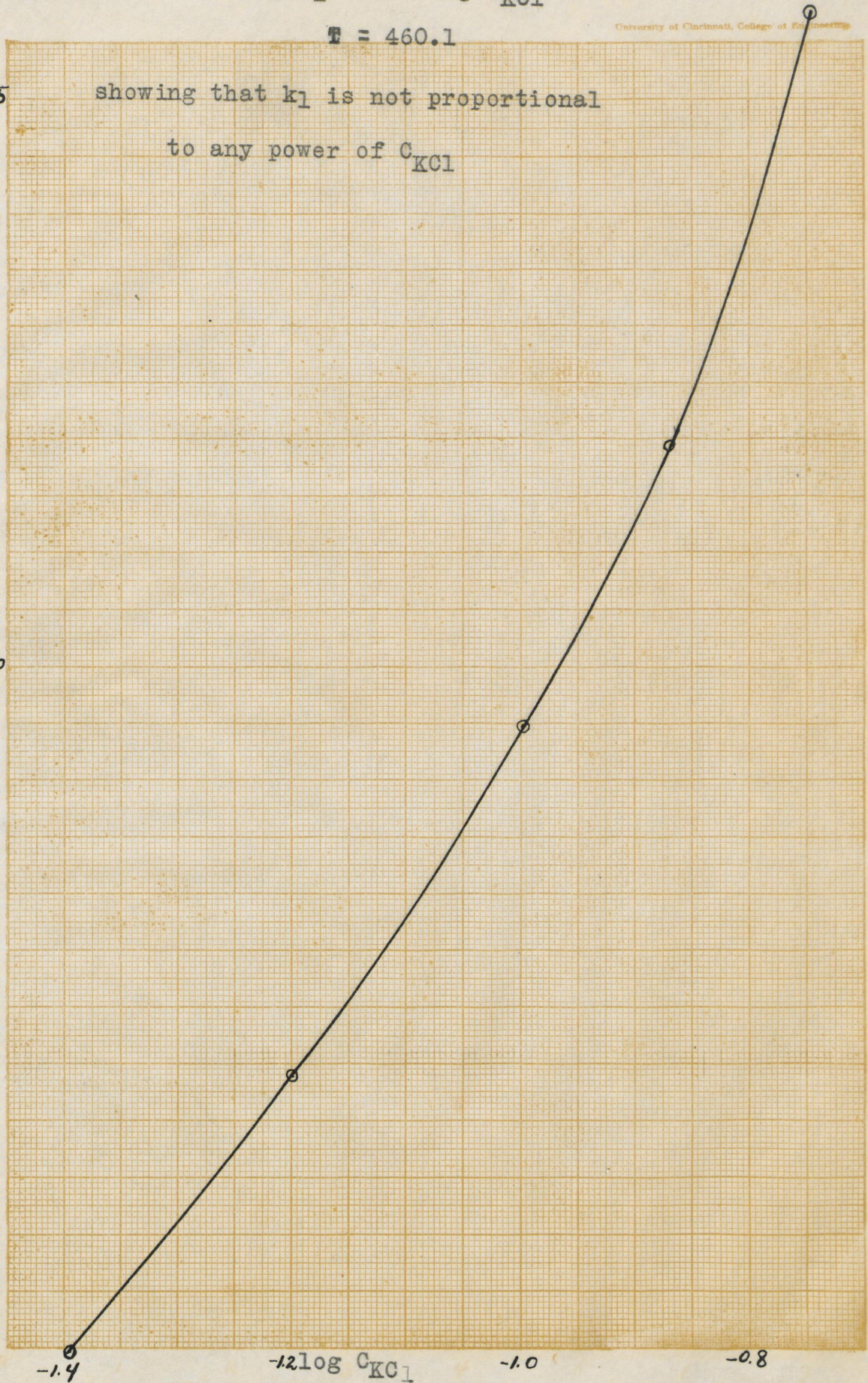
-1.5

-1.4

 $-1.2 \log C_{KCl}$

-1.0

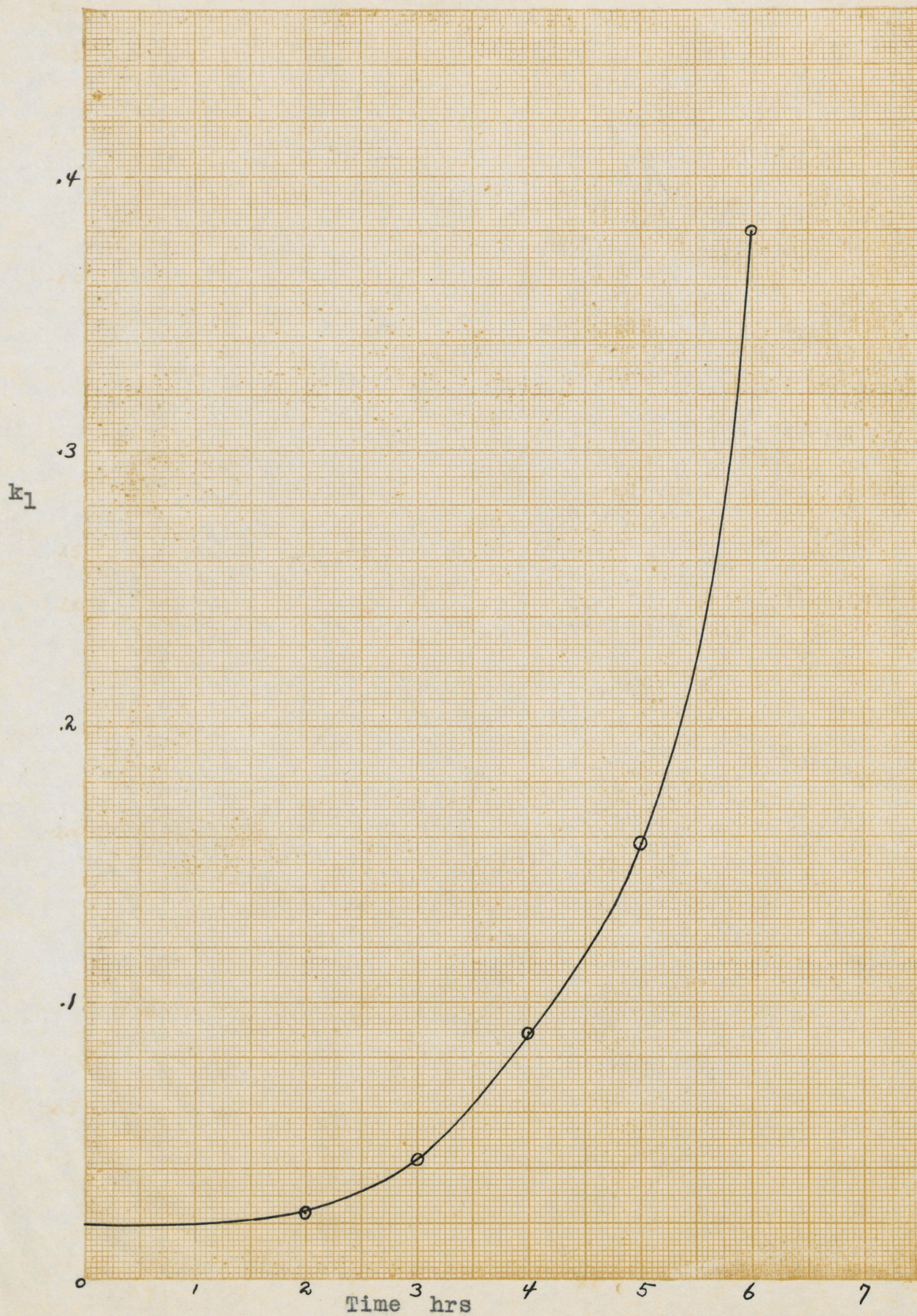
-0.8



GRAPH 23.

 k_1 vs. t $T = 460.1$

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GRAPH 24.

 $\log k_1 - k_0$ vs. $\log C_{KCl}$ $T = 460.1$

University of Cincinnati, Ohio slope = 2.80

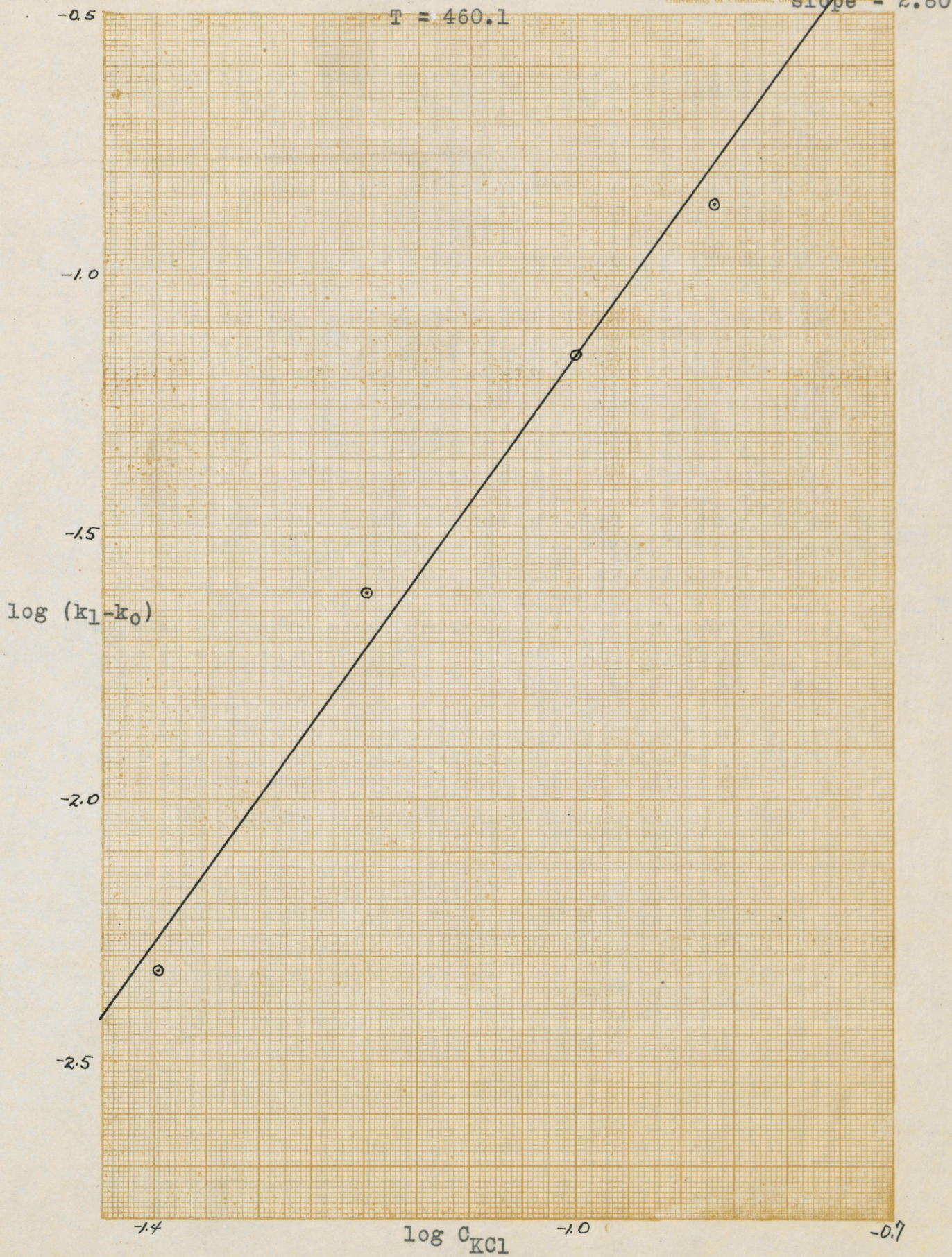


TABLE 70.

Calculation of $\frac{k_1 - k_0}{C_{KCl}^3}$

$T = 460.1$

Time min.	Conc. $KClO_3$ KCl formed C_{KCl}	$k_1 - k_0$ $k_0 = .000333$	$(k_1 - k_0)/C_{KCl}^3$ p
120	.0403	.000078	1.197
180	.0634	.000383	1.612
240	.1004	.001143	1.129
300	.1358	.002285	0.912
360	.1979	.005997	<u>1.033</u>

Av. 1.177

± 0.182 (15.4%)

TABLE 71.

KClO₃

Sample Wt.

A = 0.6412

B = 0.6118

Room Temp. = 20°

Barometer = 744.2

Time min.	Temp.	Oxygen		Fraction KClO ₃ O ₂ evolved		Av.
		A	B	A	B	
0	504.					
3	491.2	.72	1.07	.0037	.0059	.0048
6	494.5	1.72	2.08	.0089	.0113	.0101
9	498.2	2.62	2.88	.0136	.0156	.0146
12	498.6	3.52	3.73	.0182	.0202	.0192
15	497.1	4.22	4.45	.0219	.0242	.0230
18	494.5	4.99	5.20	.0258	.0282	.0270
21	489.1	5.52	5.65	.0286	.0307	.0296
24	487.4	6.04	6.25	.0313	.0339	.0326
27	487.2	6.52	6.65	.0338	.0361	.0350
30	487.2	7.12	7.17	.0369	.0389	.0379
33	485.5	7.43	7.57	.0385	.0411	.0398
36	488.0	7.92	8.02	.0410	.0435	.0422
39	491.5	8.52	8.60	.0441	.0467	.0454
42	495.3	9.10	9.17	.0471	.0498	.0485
45	494.5	9.84	9.90	.0510	.0537	.0534
48	496.4	10.43	10.45	.0540	.0567	.0554
51	497.3	11.12	11.16	.0576	.0606	.0591
54	497.5	11.73	11.75	.0608	.0638	.0623
57	496.4	12.32	12.35	.0638	.0670	.0654
60	494.5	12.92	12.90	.0669	.0700	.0685
63	491.3	13.42	13.35	.0695	.0725	.0710
66	489.3	13.82	13.77	.0716	.0747	.0732
69	489.1	14.15	14.20	.0733	.0771	.0752
72	490.2	14.57	14.55	.0755	.0790	.0772
75	491.5	15.02	15.05	.0778	.0817	.0798
78	493.5	15.44	15.55	.0800	.0844	.0822
81	494.1	16.02	16.05	.0830	.0871	.0850
84	494.7	16.46	16.55	.0854	.0898	.0874
87	494.3	16.92	17.14	.0876	.0930	.0899
90	493.8	17.57	17.35	.0910	.0942	.0926
93	488.8	17.82		.0923		(.0941)
96	488.8	18.22		.0944		(.0961)
99	490.8	18.57		.0962		(.0980)
102	491.0	18.92		.0980		(.0998)
105	490.6	19.30		.1000		(.1015)

Av..492.4

Note: Bracketed numbers in last column by extrapolation from curve.

TABLE 72.

 KClO_3

Analysis of Residues

Calculation of W

$$T = 492.4$$

Wt. of Sample	Time Heated min.	Wt. KClO_3 in Residue	Fraction KClO_3 untransformed	Fraction KClO_3 transformed
.5682	15	.5183	.9121	.0879
.5831	30	.4519	.7750	.2250
.5449	45	.3696	.6783	.3217
.5641	60	.2938	.5208	.4792
.7578	75	.3514	.4637	.5363
.6412	105	.1568	.2446	.7554

Time min.	Total Fraction KClO_3 transformed	Fraction KClO_3 giving O_2	Fraction giving KClO_4	W ₁	KClO_4 formed once corrected	W ₂	KClO_3 forming KClO_4 twice corrected	KClO_3 forming O_2 directly
15	.0879	.0230	.0649	.0005	.0555	.0005	.0655	.0224
30	.2250	.0379	.1871	.0020	.1611	.0020	.1900	.0350
45	.3217	.0534	.2683	.0035	.2335	.0036	.2755	.0462
60	.4792	.0685	.4107	.0053	.3595	.0054	.4242	.0550
75	.5363	.0798	.4565	.0068	.4052	.0070	.4784	.0579
90		.0926						
105	.7554	.1015	.6539	.0171	.5896	.0181	.6970	.0584

GRAPH 25.

Decomposition Curves for KClO_3 $T = 492.4$

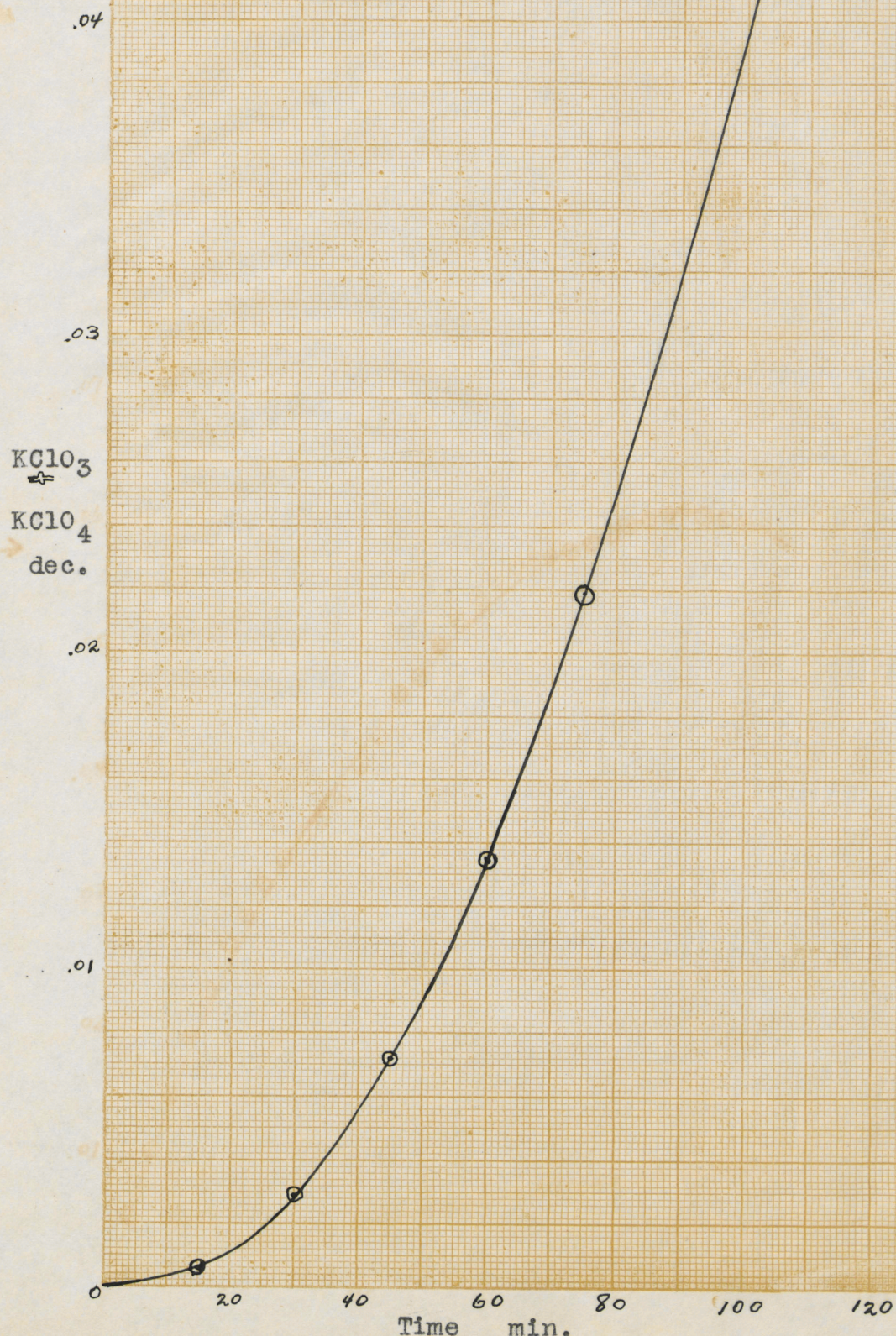
University of Cincinnati, College of Engineering



GRAPH 26.

Correction for $\text{KClO}_4 \rightarrow \text{O}_2$ $T = 492.4$

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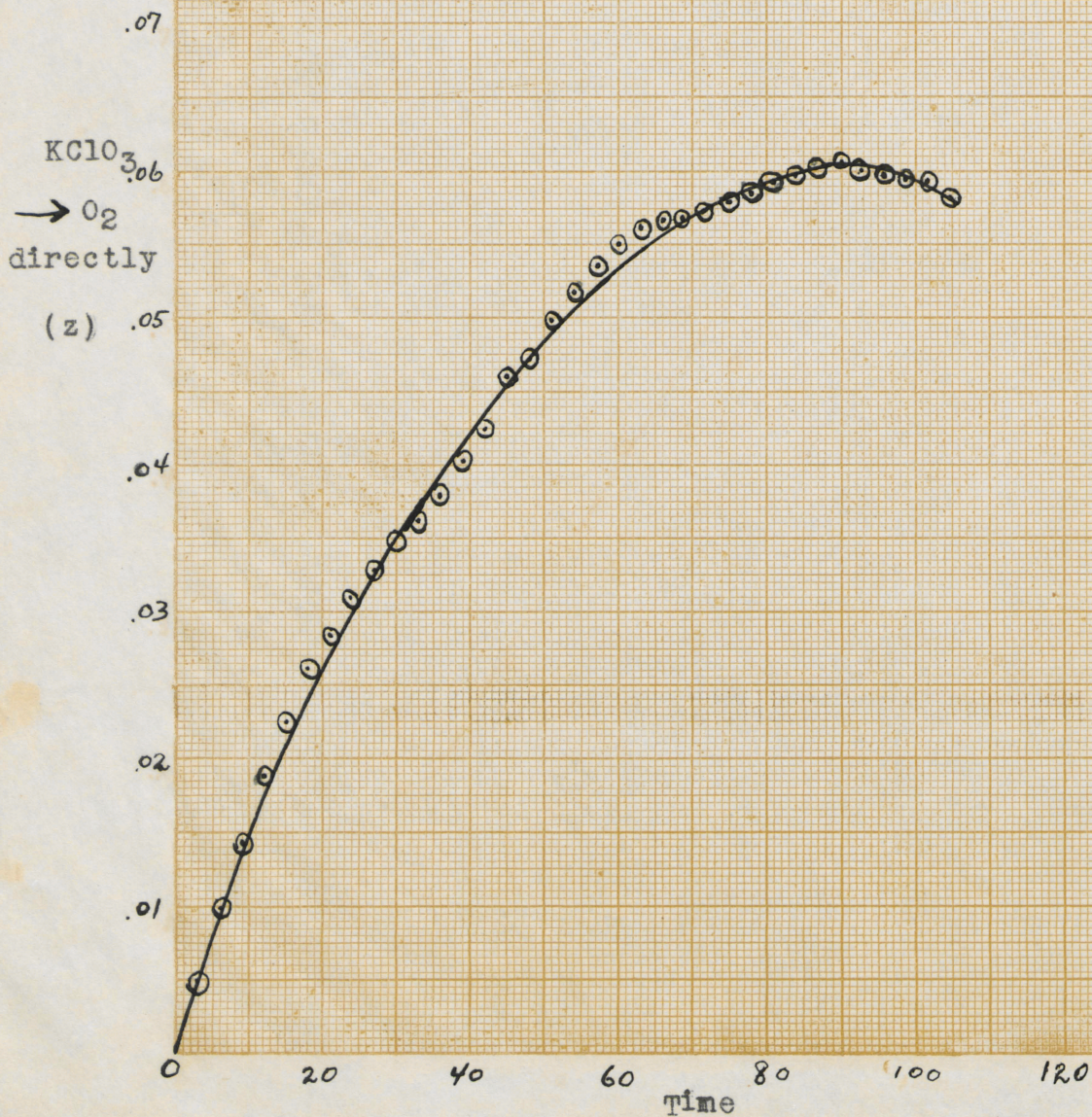
for interpolation of w 

GRAPH 27.

z vs. t

T = 492.4

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for obtaining tangents $\Delta z / \Delta t$ 

GRAPH 28.

 $T = 492.4$

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for obtaining tangents $\Delta y / \Delta t$

KClO₃
KClO_{4.6}
(corrected)

.7

.5

.4

.3

.2

0

50

100

Time min

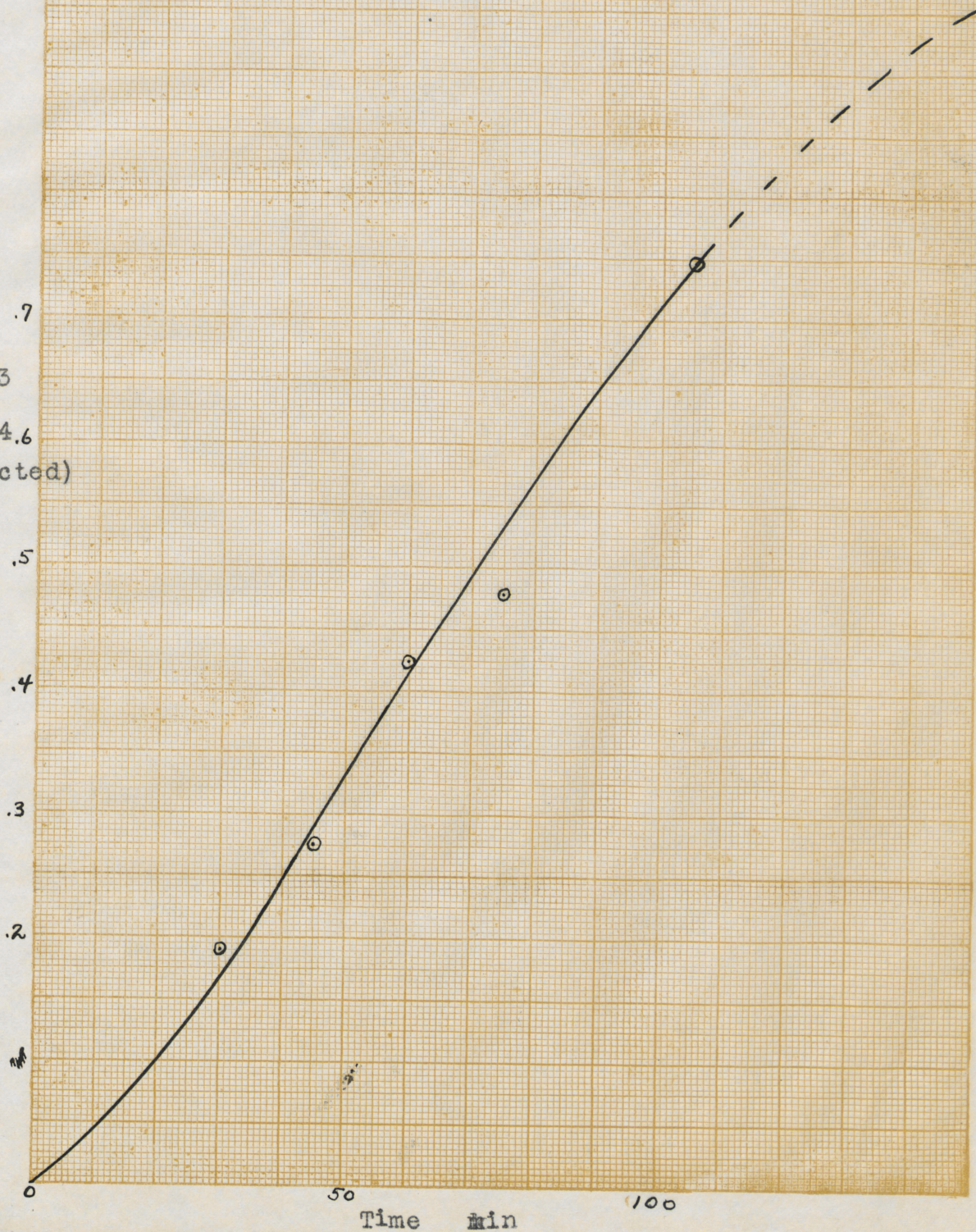


TABLE 73.

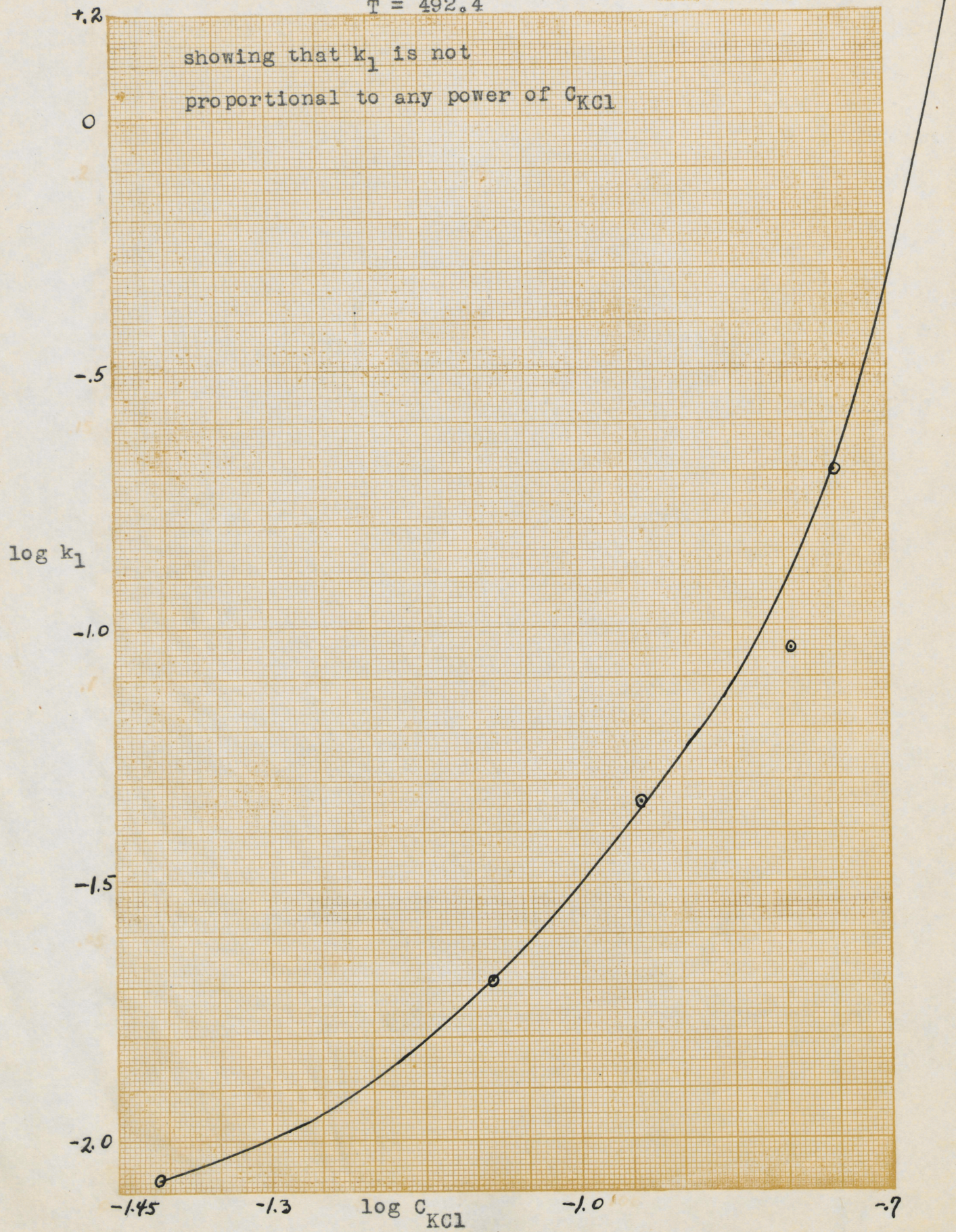
Calculation of k_2 and k_1 $T = 492.4$

Time min.	$\text{KClO}_3 \rightarrow \text{O}_2$	$\text{KClO}_3 \rightarrow \text{KClO}_4$	Conc. KClO_3 $a - x$ (from curve)	$\Delta z / \Delta t$	$\frac{\Delta z / \Delta t}{a - x}$	$\Delta y / \Delta t$	$\frac{\Delta y / \Delta t}{(a - x)^4}$	Conc. KClO_3 $\frac{y}{a}$ KCl formed. C_{KCl}
	z	y			k_2		k_1	
3	.0048		.988	.001568	.001587			
6	.0100		.973	.001488	.001529			
9	.0144		.955	.001290	.001351			
12	.0188		.936	.001188	.001269			
15	.0224	.0655	.912	.001110	.001217	.00567	.008193	.0388
18	.0262		.887	.001030	.001161			
21	.0284		.860	.000964	.001121			
24	.0310		.830	.000868	.001046			
27	.0328		.803	.000820	.001021			
30	.0350	.1900	.778	.000784	.001019	.00737	.02043	.0825
33	.0362		.753	.000748	.000993			
36	.0378		.728	.000718	.000986			
39	.0402		.703	.000670	.000953			
42	.0424		.681	.000657	.000965			
45	.0462	.2755	.658	.000640	.000973	.00854	.04569	.1151
Av. of first 15 values of k_2					.001153	$\pm$.000167	(14.4%)	
48	.0472		.635	.000605	.000953			
51	.0498		.613	.000556	.000907			
54	.0517		.591	.000527	.000892			
57	.0535		.569	.000472	.000830			
60	.0550	.4242	.548	.000429	.000783	.00814	.09059	.1610
63	.0561		.527	.000389	.000738			
66	.0567		.506	.000346	.000684			
69	.0569		.485	.000315	.000649			
72	.0571		.464	.000269	.000580			
75	.0579	.4784	.443	.000242	.000546	.00769	.19968	.1775
78	.0584		.422	.000205	.000486			
81	.0593		.402	.000181	.000450			
84	.0597		.378	.000152	.000402			
87	.0602		.363	.000111	.000306			
90	.0606		.344			.00710	.50408	
93	.0600							
96	.0598							
99	.0595							
102	.0594							
105	.0584	.6970	.245			.00618	1.7264	.2326

GRAPH 29.

 $\log k_1$ vs. $\log C_{KCl}$ $T = 492.4$

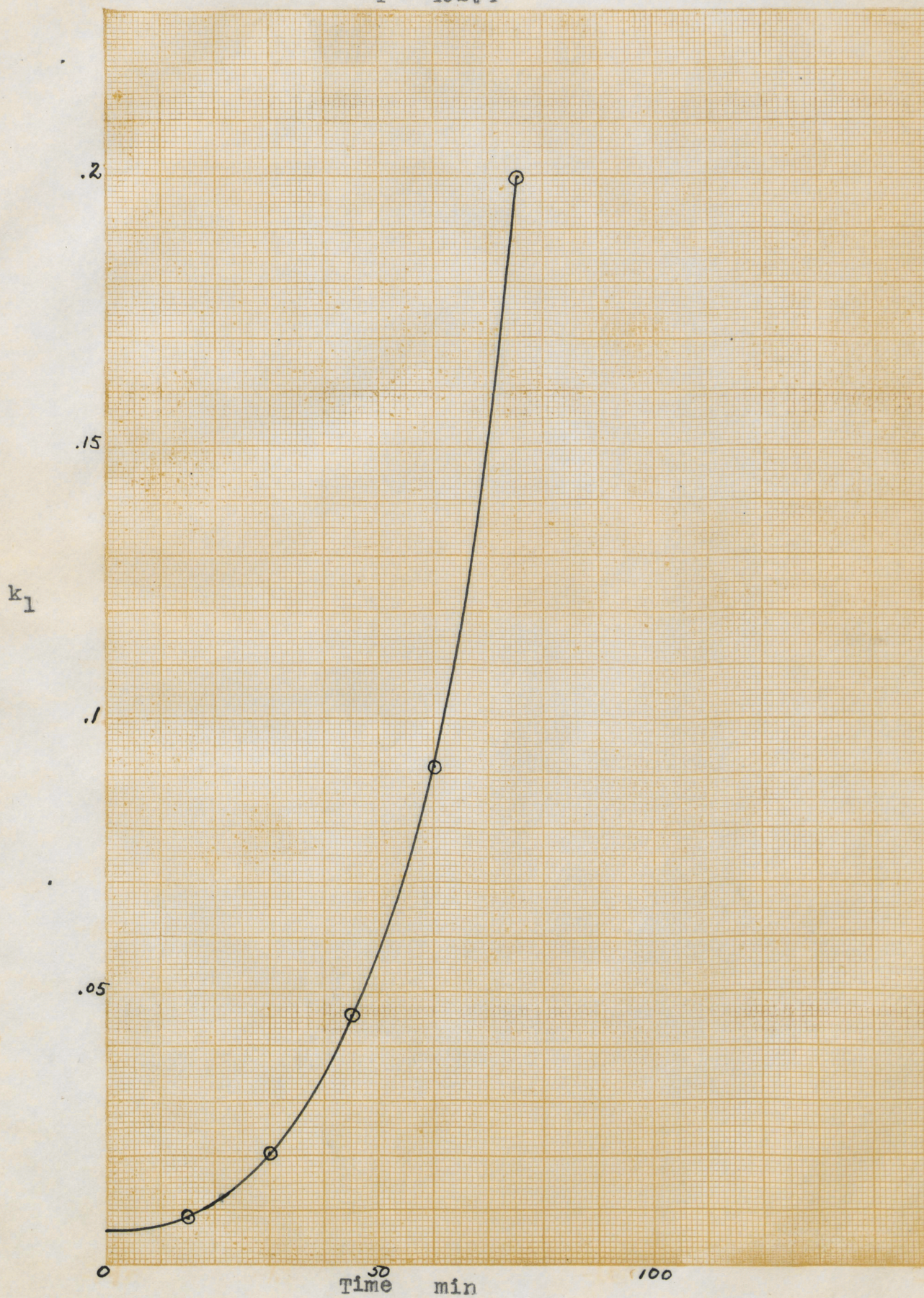
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GRAPH 30.

 k_1 vs. t $T = 492.4$

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GRAPH 31.

 $\log k_1 - k_0$ vs. $\log C_{KCl}$ $T = 492.4$

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 $\log (k_1 - k_0)$ slope =
2.92-3
-1.45

-1.3

 $\log C_{KCl}$

-1.0

-0.7

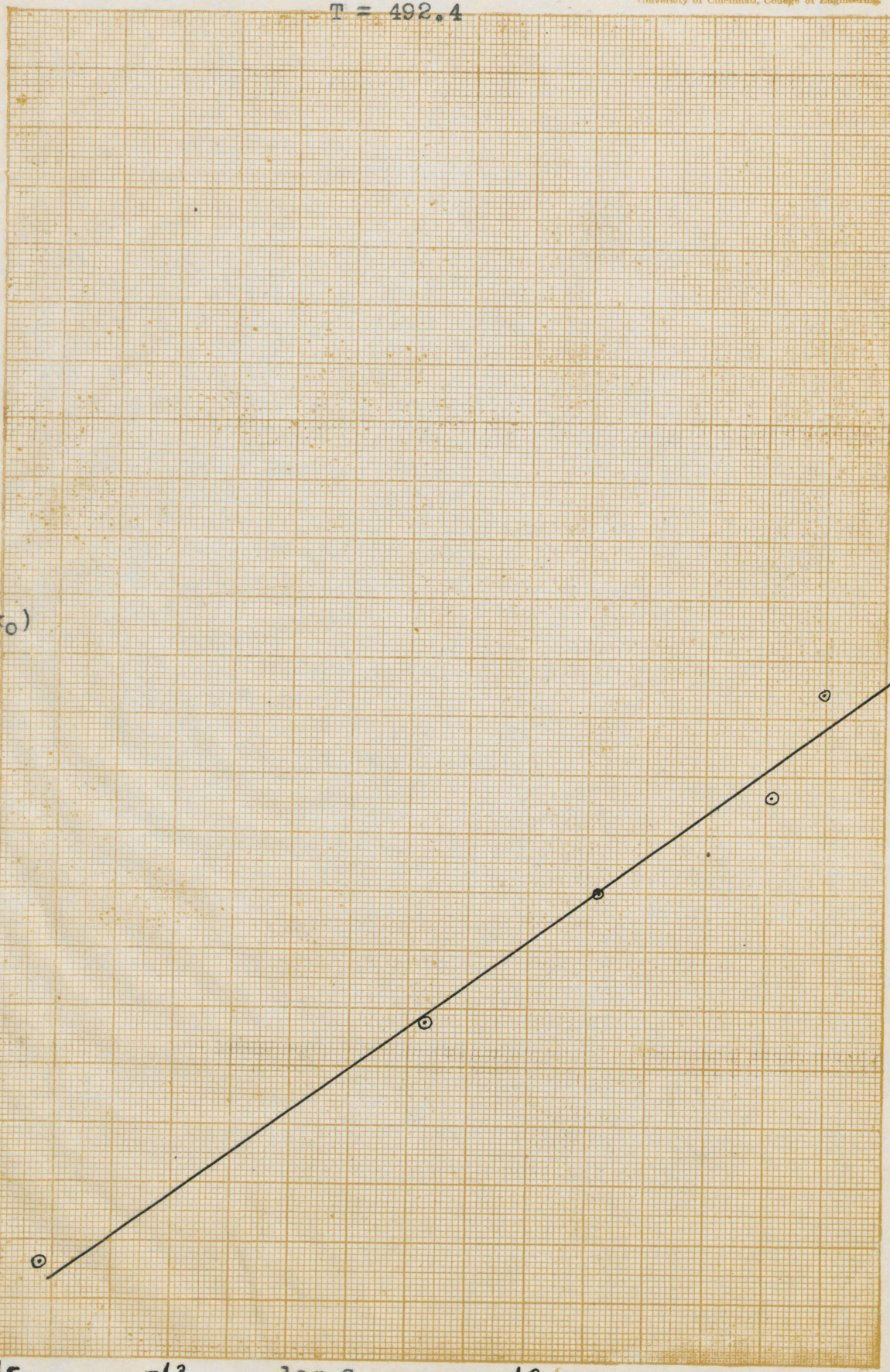


TABLE 74.

Calculation of $\frac{k_1 - k_0}{c_{\text{KCl}}^3}$

$$T = 492.4$$

Time min.	Conc. KClO_3 KCl formed c_{KCl}	$k_1 - k_0$ $k_0 = .0061$	$k_1 - k_0 / c_{\text{KCl}}^3$ p
15	.0388	.0021	35.95
30	.0825	.0143	25.47
45	.1151	.0396	25.97
60	.1610	.0845	20.25
75	.1775	.1936	<u>34.62</u>
Av. 28.45			± 5.27 (18.5%)

TABLE 75.

 KClO_3

Sample Wt.
 A = .6901
 B = .6626
 Room Temp. = 22°
 Barometer = 731.2

Time min.	Temp.	Oxygen		Fraction KClO_3 → O_2 evolved		Av.
		A	B	A	B	
0	504.8					
3	488.7	.98	.85	.0046	.0042	.0044
6	493.3	1.90	1.82	.0089	.0089	.0089
9	496.8	2.88	2.70	.0136	.0132	.0134
12	499.3	3.68	3.55	.0173	.0174	.0174
15	500.6	4.61	4.55	.0217	.0223	.0220
18	503.9	5.63	5.54	.0265	.0272	.0268
21	506.4	6.60	6.60	.0311	.0324	.0318
24	507.9	7.59	7.55	.0357	.0370	.0364
27	509.5	8.66	8.65	.0408	.0424	.0416
30	510.0	9.78	9.78	.0461	.0480	.0470
33	505.9	11.68	10.55	.0550	.0517	.0534
36	506.4	12.78	11.40	.0607	.0559	.0583
39	507.3	13.86	12.23	.0653	.0600	.0626
42	508.1	14.93	13.12	.0703	.0643	.0673
45	508.5	16.08	13.95	.0757	.0684	.0720
48	502.2	16.83	14.55	.0793	.0714	.0754
51	504.3	17.68	15.25	.0833	.0748	.0790
54	505.1	18.40	15.84	.0866	.0777	.0822
57	505.5	19.18	16.50	.0903	.0809	.0856
60	505.9	19.93	17.10	.0939	.0839	.0889
63	505.7	20.68	17.75	.0974	.0871	.0922
66	506.1	21.38	18.40	.1007	.0902	.0954
69	506.2	22.03	18.95	.1037	.0929	.0983
72	506.2	22.73	19.53	.1070	.0958	.1014
75	506.6	23.43	20.33	.1103	.0997	.1050
78	506.7	24.18	20.95	.1139	.1028	.1084
81	507.3	24.90	21.57	.1173	.1058	.1110
84	507.3	25.63	22.33	.1207	.1095	.1151
87	507.3	26.38	22.95	.1242	.1126	.1184
90	507.5	27.13	23.60	.1278	.1157	.1218
93	502.0	27.78		.1308		
96	503.3	28.48		.1341		
99	504.7	29.18		.1374		
102	505.9	29.78		.1402		
105	506.6	30.48		.1435		

Av. 505.7

TABLE 76.

 KClO_3

Analysis of Residues

Calculation of w

T = 505.7

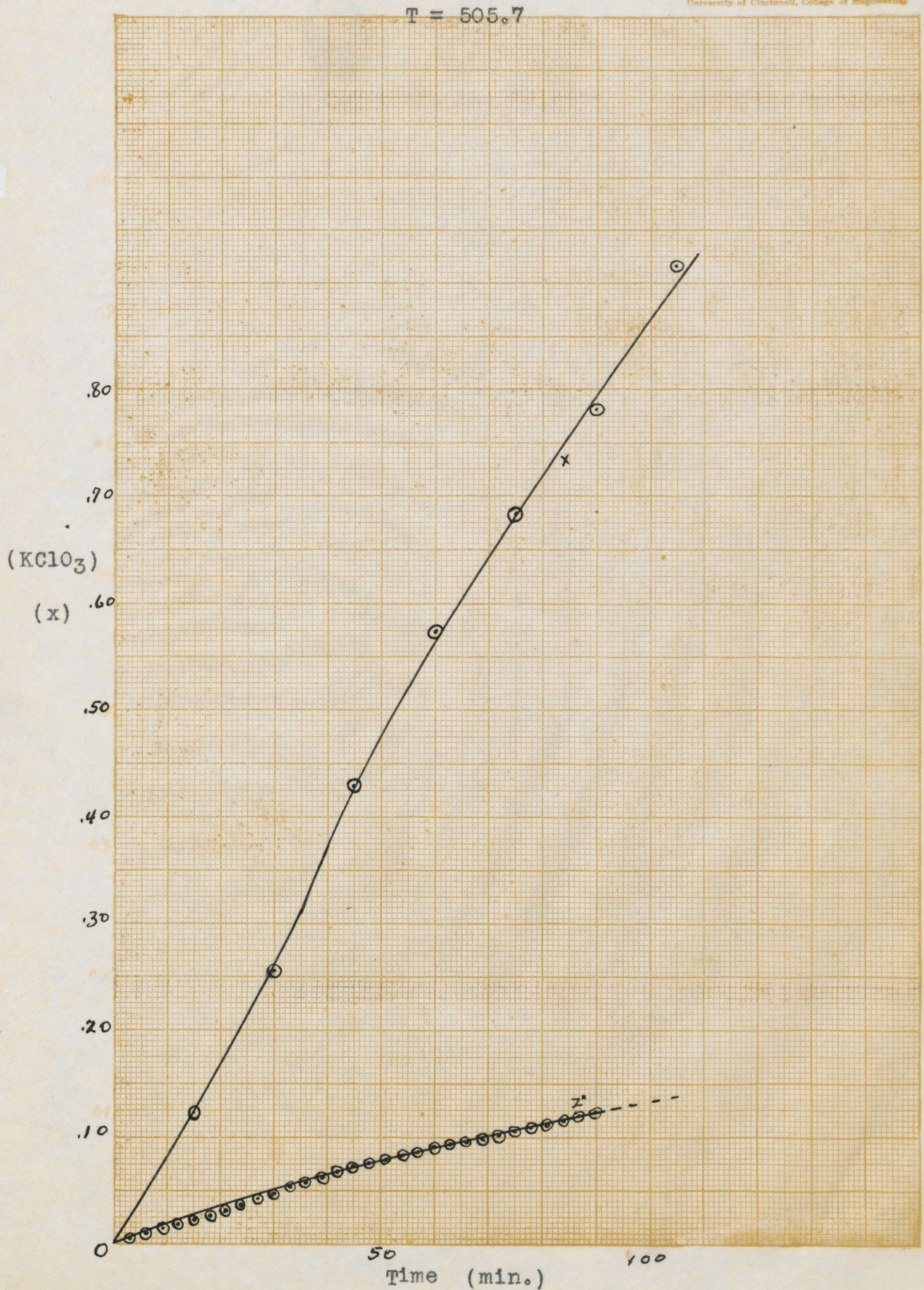
Wt. of Sample	Time Heated min	Wt. KClO_3 in Residue	Fraction KClO_3 untransformed	Fraction KClO_3 Transformed
.7730	15	.6796	.8791	.1209
.7301	30	.5438	.7448	.2552
.6957	45	.3968	.5704	.4296
.8000	60	.3415	.4268	.5732
.6648	75	.2120	.3188	.6812
.6626	90	.1454	.2195	.7805
.6901	105	.0585	.0847	.9153

Time min	Total Fraction KClO_3 giving O_2	Fraction KClO_3 giving KClO_4	w ₁	w ₂	w ₃	KClO_3 forming KClO_4 twice corrected	KClO_3 forming O_2 directly
15	.1209	.0223	.0984	.0014	.0014	.1000	.0207
30	.2552	.0480	.2072	.0044	.0046	.2143	.0409
45	.4296	.0684	.3612	.0082	.0086	.3782	.0514
60	.5732	.0839	.4893	.0123	.0130	.5220	.0512
75	.6812	.0997	.5815	.0155	.0167	.6340	.0472
90	.7805	.1157	.6648	.0181	.0198	.7408	.0397

GRAPH 32.

Decomposition Curves for KClO_3

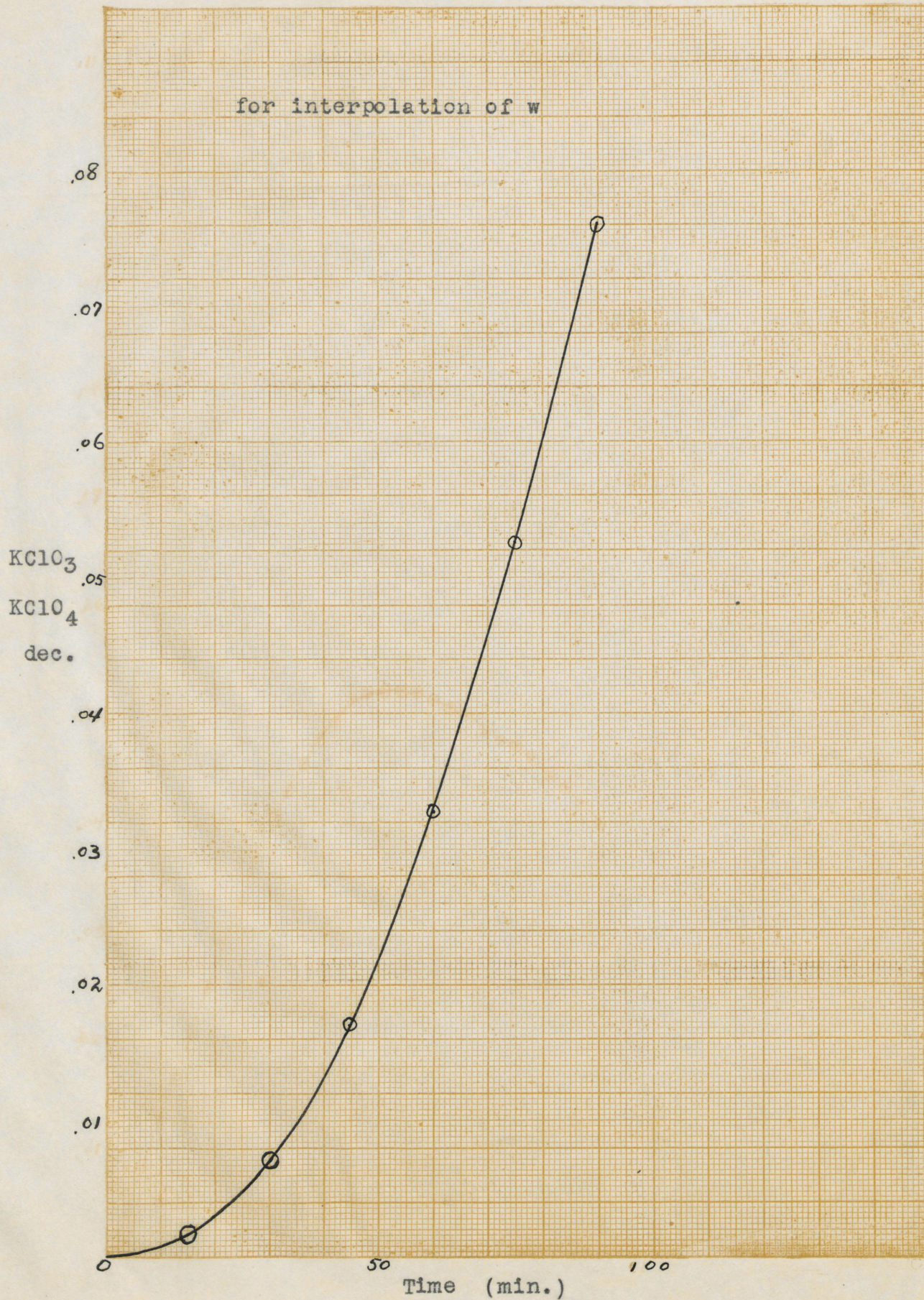
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GRAPH 33.

Correction for $\text{KClO}_4 \rightarrow \text{O}_2$ $T = 505.7$

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GRAPH 34.

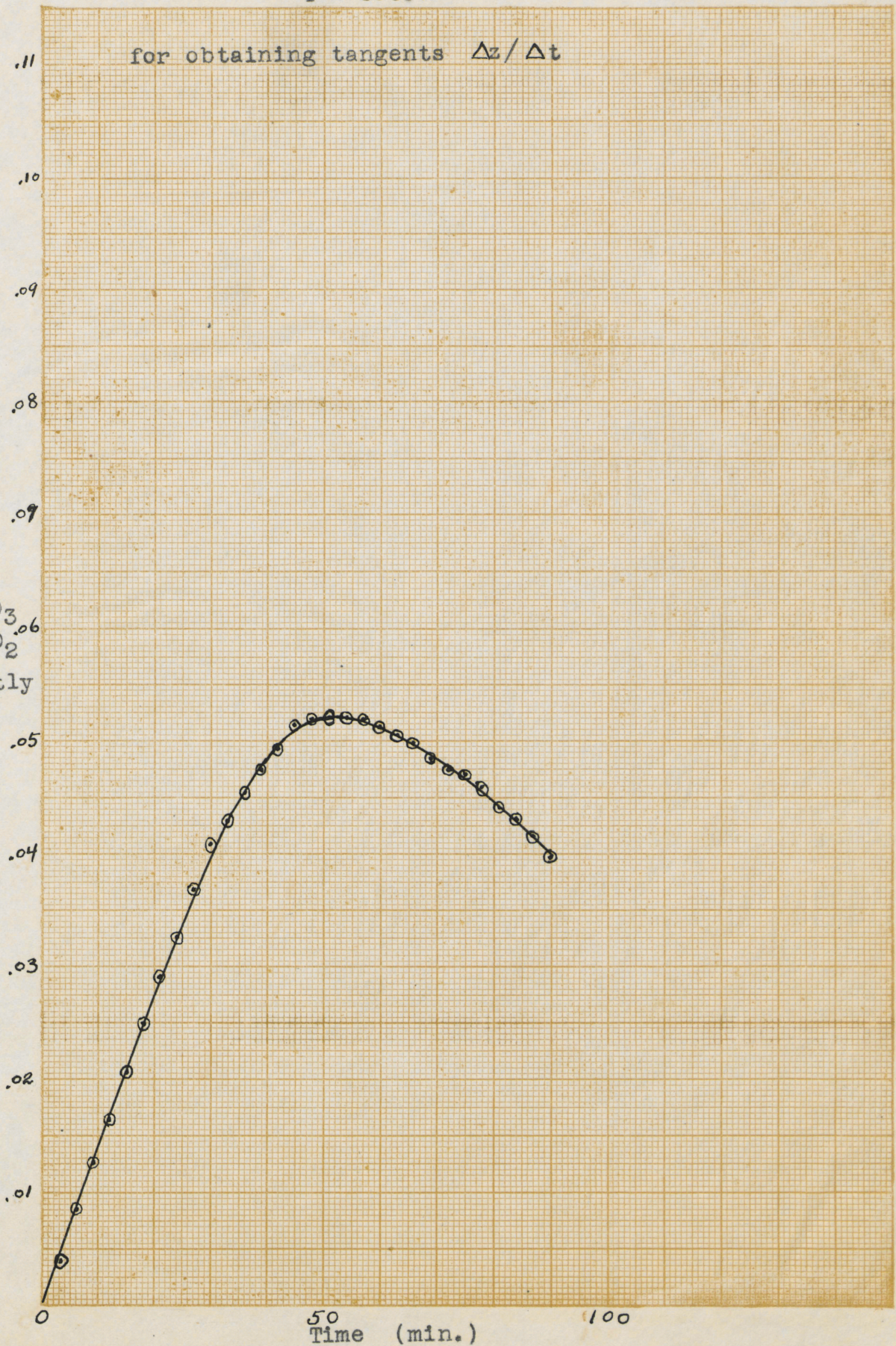
z vs. t

T = 505.7

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for obtaining tangents $\Delta z / \Delta t$

KClO₃ 0.06
 0.02
 directly
 (z)



GRAPH 35.

y vs. t

 $T = 505.7$

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for obtaining tangents $\Delta y / \Delta t$

KClO₃
KClO₄
(corrected)
y

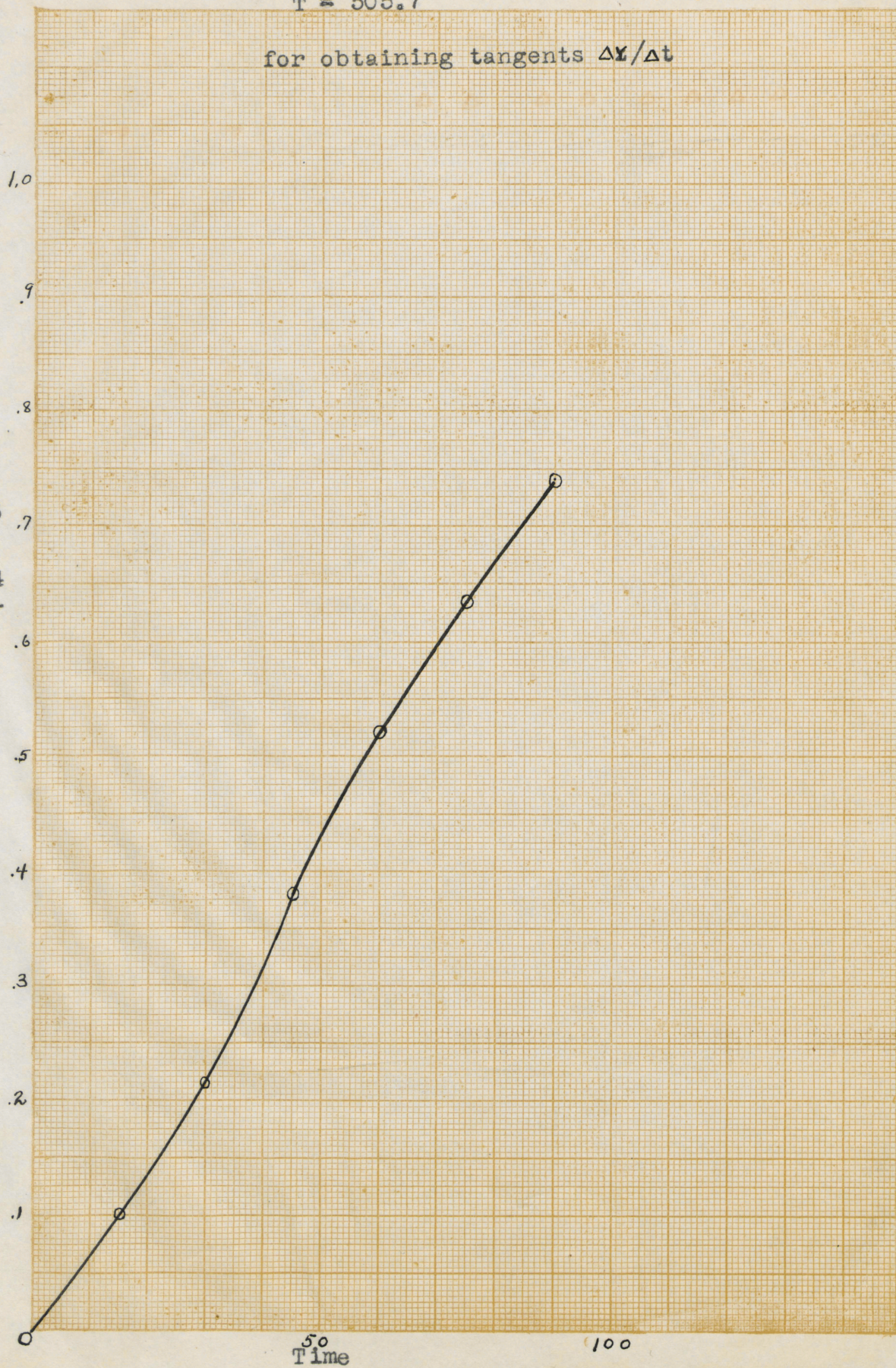


TABLE 77.

Calculation of k_2 and k_1

T = 505.7

Time min.	KClO ₃ → O ₂	KClO ₃ → KClO ₄	Conc. KClO ₃	$\Delta z/\Delta t$	$\frac{\Delta z/\Delta t}{C_{\text{KClO}_3}}$	$\Delta y/\Delta t$	$\frac{\Delta y/\Delta t}{(a\theta x)^4}$	Conc. KClO ₃ → KCl formed C _{KCl}
	z	y	a-x		k ₂		k ₁	
3	.0040		.975	.001418	.001455			
6	.0086		.951	1400	1472			
9	.0126		.926	1388	1495			
12	.0164		.903	1350	1519			
15	.0207	.1000	.879	1335	1523	.00707	.01184	.0457
18	.0249		.854	1300	1538			
21	.0292		.828	1274	1560			
24	.0326		.801	1250	1563			
27	.0368		.773	1208	1443			
30	.0409	.2143	.745	1074	1315	.00894	.02905	.0945
33	.0430		.712	936	1183			
36	.0454		.678	802	1083			
39	.0474		.638	692				
42	.0495		.604					
45	.0514	.3782	.571			.01190	.1124	.1460
48	.0518		.542					
51	.0522		.514					
54	.0520		.488					
57	.0518		.462					
60	.0512	.5220	.436			.00803	.2420	.1817
63	.0505		.411					
66	.0498		.388					
69	.0485		.365					
72	.0474		.342					
75	.0472	.6340	.319			.00734	.7106	.2057
78	.0458		.298					
81	.0441		.274					
84	.0432		.252					
87	.0416		.230					
90	.0397	.7408	.207			.00686	2.956	.2249

Av. .001434

± .000111 (7.7%)

GRAPH 36.

 $\log k_1$ vs. $\log C_{KCl}$ $T = 505.7$

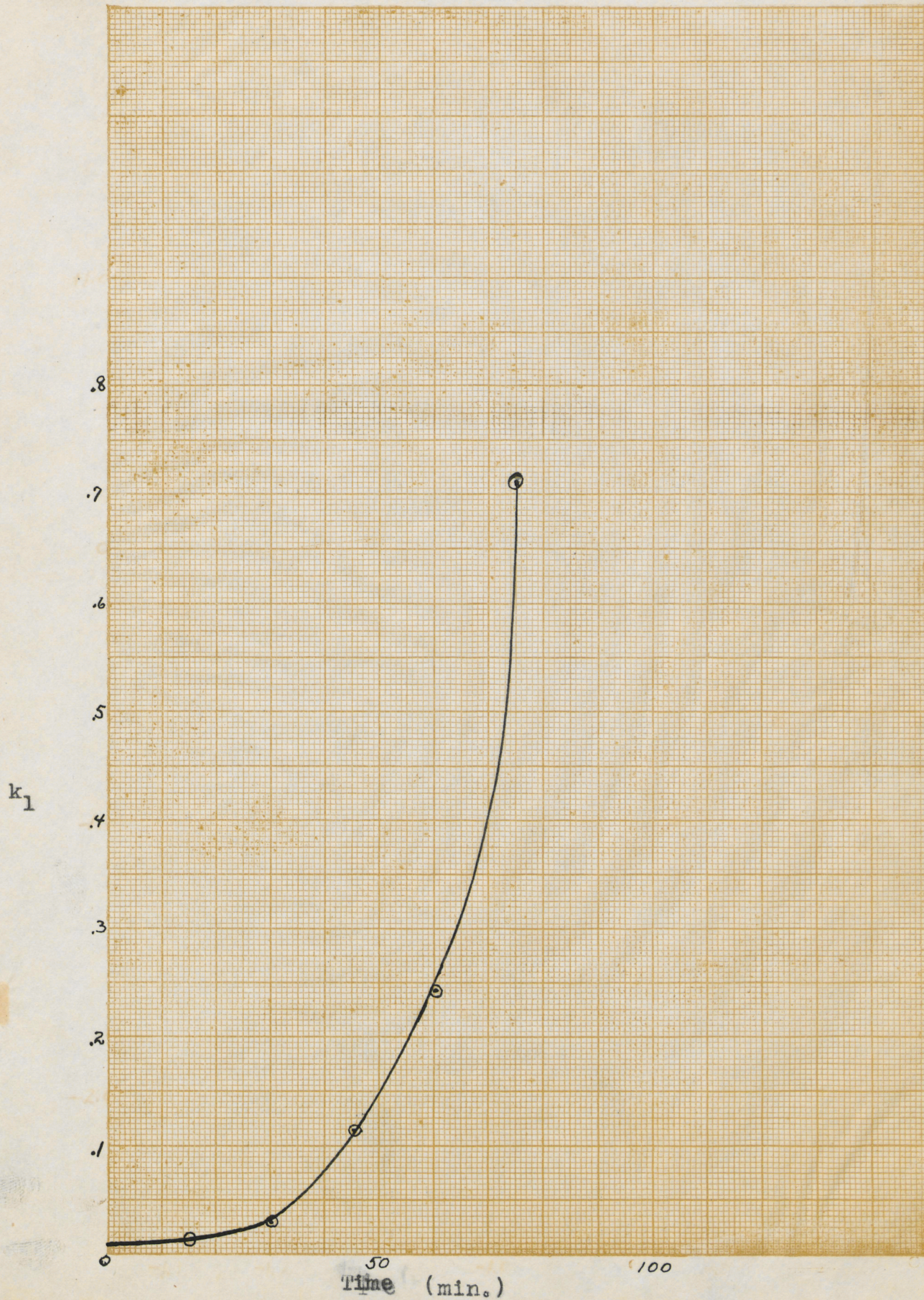
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GRAPH 37.

 k_1 vs. t $T = 505.7$

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GRAPH 38.

 $\log k_1 - k_0$ vs. $\log C_{KCl}$ $T = 505.7$

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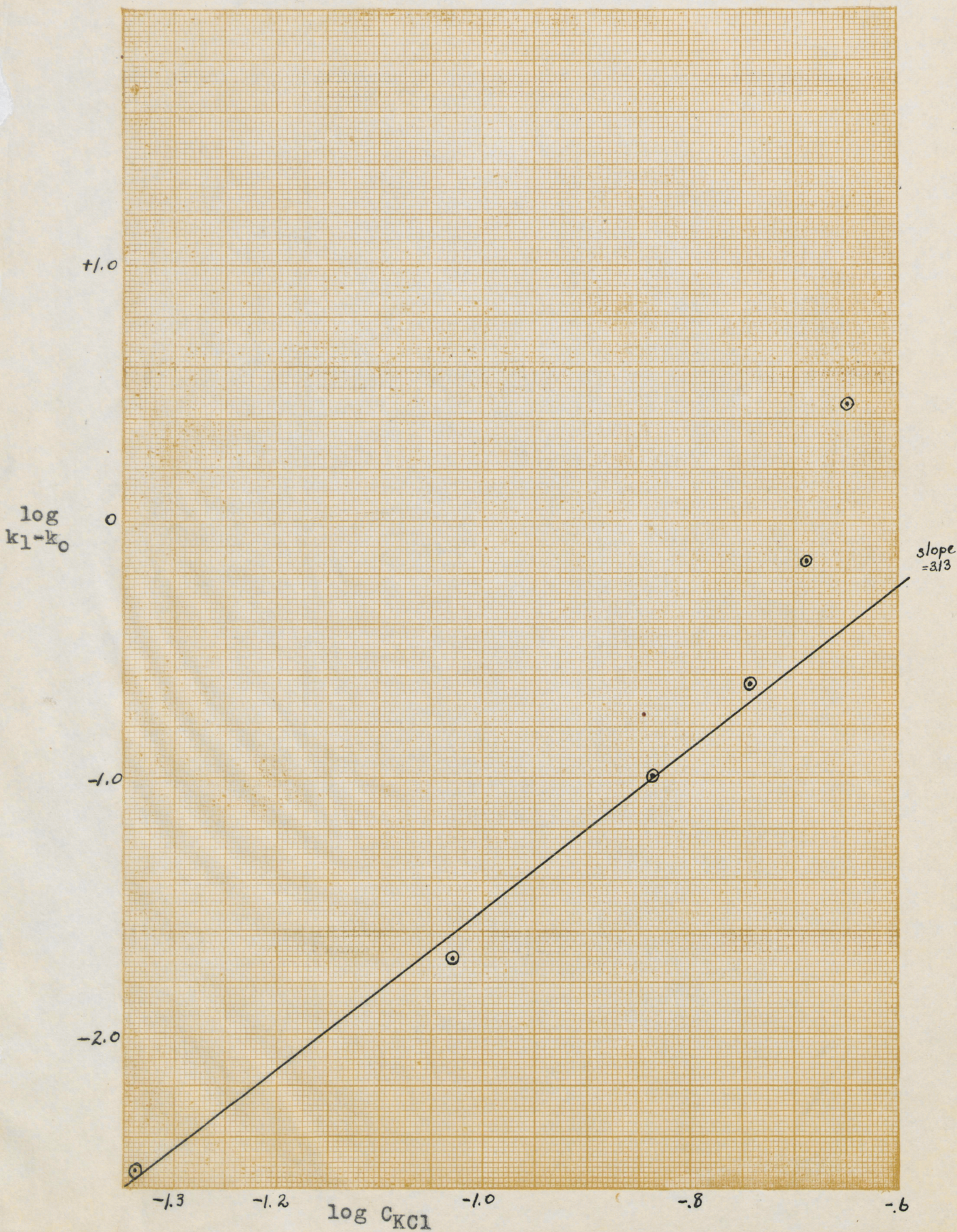


TABLE 78.

Calculation of $\frac{k_1 - k_0}{C_{\text{KCl}}^3}$

T = 505.7

Time	Conc. KClO_3 $\rightleftharpoons$ KCl formed C_{KCl}	$k_1 - k_0$ $k_0 = .009$	$(k_1 - k_0) / C_{\text{KCl}}^3$ p
15	.0457	.003	31.43
30	.0945	.020	23.70
45	.1460	.103	32.34
60	.1817	.233	<u>38.84</u>
	Av. of first 4 values		31.58 $\pm$ 3.99 (12.6%)
75	.2057	.701	80.54
90	.2249	2.947	259.24

TABLE 79.

Relation between k_2 and T

k_2	T_{Abs}	$\log_{10} k_2$	$1/T_{\text{Abs}}$
.00005103	681.9	-4.29217	.0014665
.0002103	733.1	-3.67716	.0013641
.001153	765.4	-2.93817	.0013065
.001434	777.7	-2.84345	.0012858

TABLE 80.

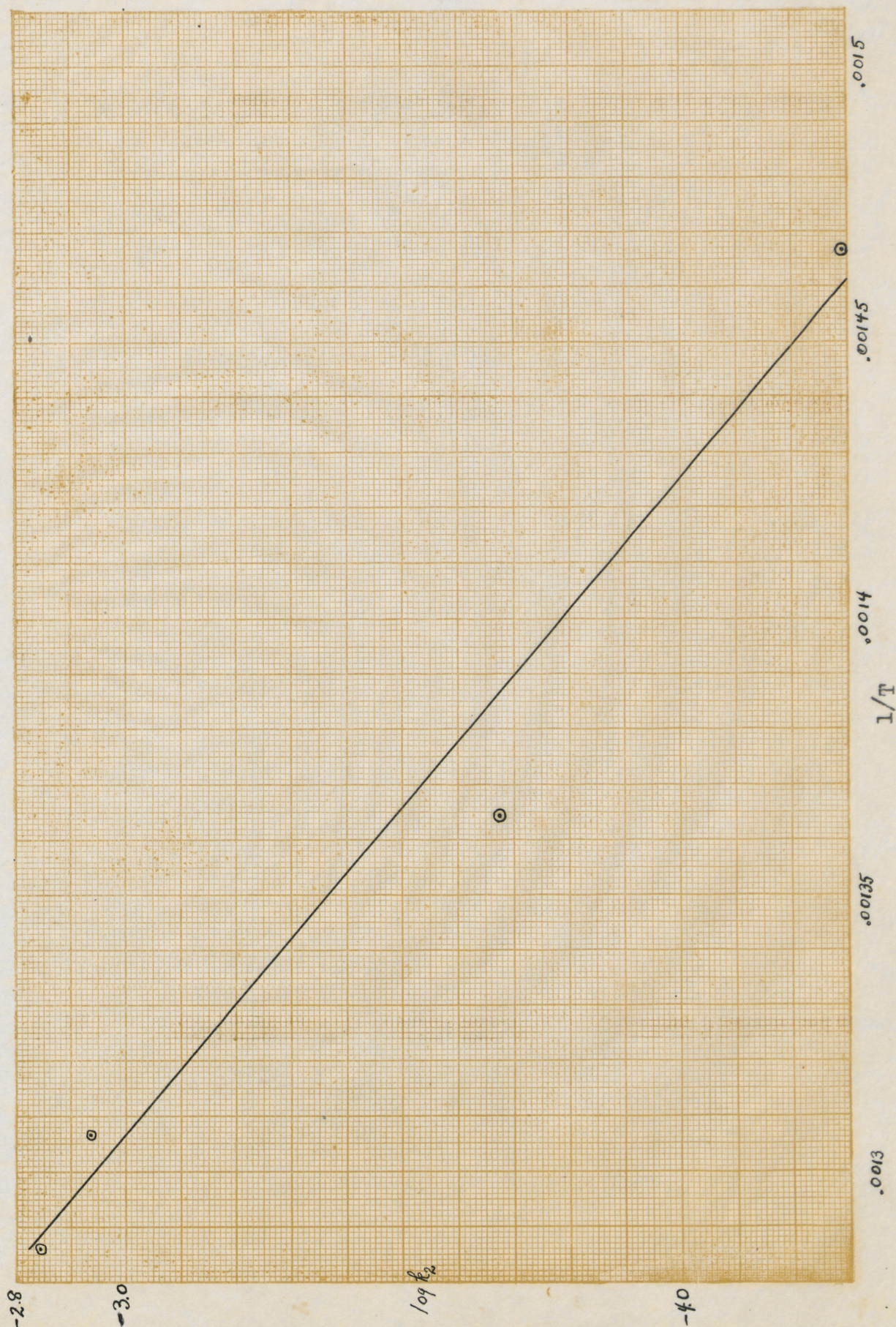
Relation between $\frac{k_1 - k_0}{C_{\text{KCl}}^3}$ and T

$\frac{k_1 - k_0}{C_{\text{KCl}}^3}$	$T_{\text{Abs.}}$	$\log \frac{k_1 - k_0}{C_{\text{KCl}}^3}$	$1/T_{\text{Abs.}}$
(p)			
.1291	681.9	-0.88907	.0014665
1.177	733.1	+0.07065	.0013641
28.45	765.4	+1.46909	.0013065
31.58	777.7	+1.49941	.0012858

GRAPH 39.

 $\log k_2$ vs. $\frac{1}{T}$

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GRAPH 40.

$$\log \frac{k_1 - k_0}{C_{KCl}^3} \quad \text{vs.} \quad \frac{1}{T}$$

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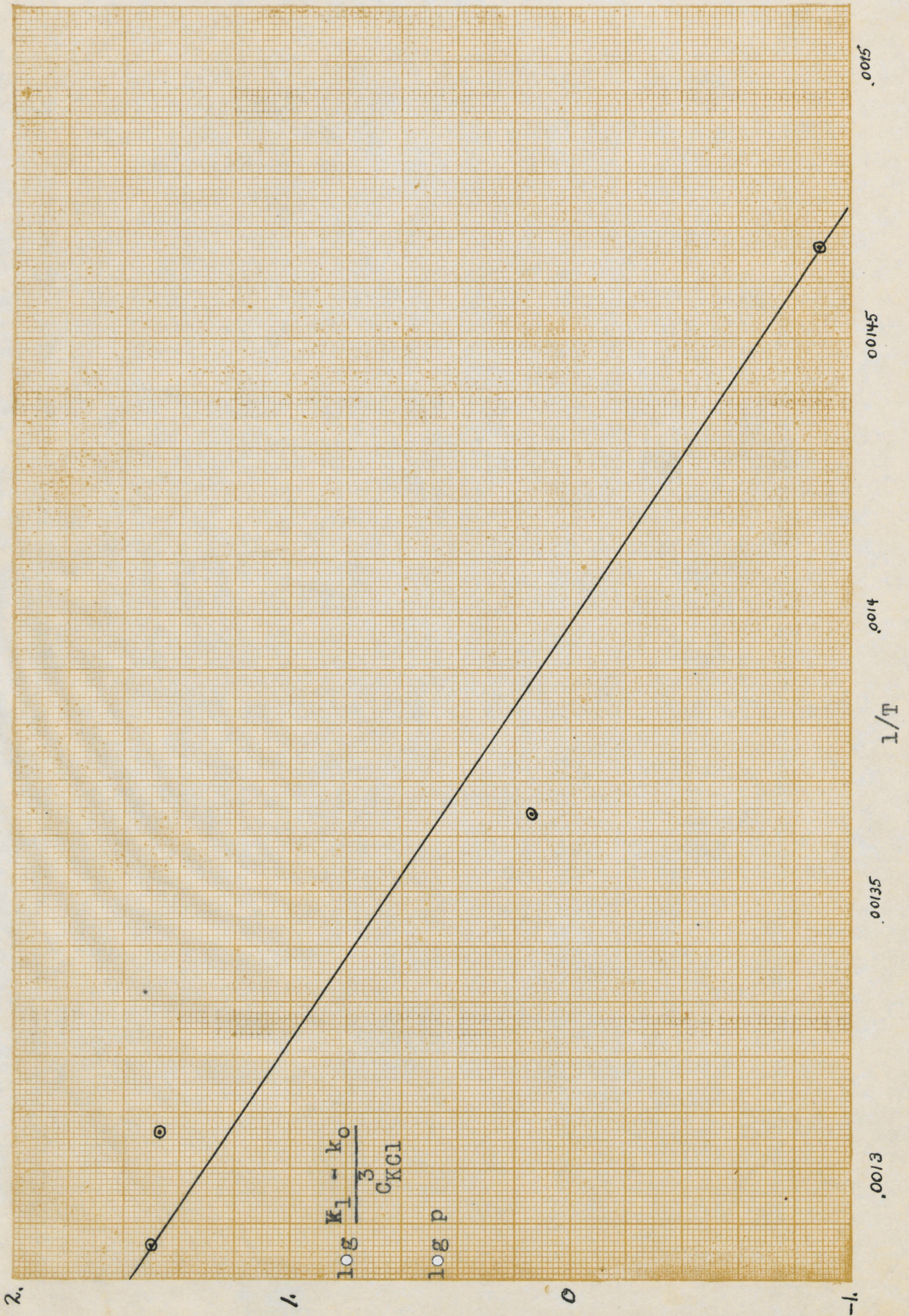


TABLE 81.

Wt. of KClO ₃ taken	Wt. of KCl taken	Initial Conc. of KCl	Wt. of KClO ₃ in Re- sidue	Fraction KClO ₃ untrans.	Frac- tion KClO ₃ Trans.	Frac- tion KClO ₃ giv- ing O ₂	Frac- tion KClO ₃ giv- ing KClO ₄	Remarks
Time = 1 hr. Temp = 463°C								
.4795	. 0	0.00%	.4701	.9804	.0196	.0304	---	Fused
.5035	.0262	4.95%	.4238	.8417	.1583	.0300	.1283	"
.5850	.0473	7.48%	.4492	.7678	.2322	.0299	.2023	"
.5619	.0783	12.23%	.3864	.6876	.3124	.0295	.2829	"
Time = 15 min. Temp = 487°C								
.5682	0	0.00%	.5183	.9121	.0879	.0230	.0649	Fused
.7071	.0185	2.55%	.6531	.9237	.0763		.0533	"
.7456	.0303	3.90%	.6742	.9042	.0958		.0728	"
.6137	.0632	9.34%	.5075	.8268	.1731		.1501	"
.6385	.1037	13.97%	.5003	.7836	.2164		.1934	"
Time = 4 hrs. Temp = 408°C								
.6721	0	0.00%	.6565	.9768	.0232	.0175	.0057	Fused
.6836	.0279	3.92%	.6813	.9967	.0033			Unfused
.7257	.0461	5.97%	.7206	.9929	.0071			"
.7474	.0753	9.15%	.7324	.9800	.0200			"
.7008	.0923	11.64%	.6804	.9710	.0290			"

Summary and Results

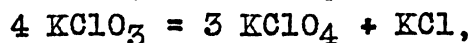
In the preliminary experiments it was found that no chlorine was evolved with the oxygen in the decomposition of potassium chlorate and that potassium perchlorate on heating was not converted into potassium chlorate.

Velocity coefficients of various mixtures of potassium perchlorate and ferric oxide at different temperatures have been determined, and from these, by Arrhenius' formula, isothermal values have been calculated in order to ascertain the relation between the concentration of catalyst and the velocity coefficient at constant temperature.

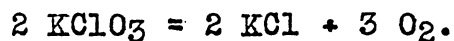
It was found that at a given temperature the increase in the velocity coefficient was proportional to the concentration of ferric oxide.

Also, the particles of ferric oxide during catalysis were changed from an average size of 0.011 mm. to 0.055 mm. It would be interesting to investigate the activity of the catalyst on repeated use and to determine if growth of particles is associated with catalysis.

When potassium chlorate was heated, autocatalysis was evident, since the velocity of the transformation of potassium chlorate into potassium perchlorate at constant temperature increased as the reaction proceeded. This was confirmed by adding various amounts of potassium chloride to the potassium chlorate before heating. These initial additions of potassium chloride as catalyst to the potassium chlorate accelerated the reaction



but did not accelerate the reaction



The velocity coefficient at constant temperature of the reaction, $4 \text{ KClO}_3 = 3 \text{ KClO}_4 + \text{KCl}$, conforms to the expression,

$$k_1 = k_0 + p c_{\text{KCl}}^3 \text{ since } \frac{k_1 - k_0}{c_{\text{KCl}}^3} = (\text{const}) = p,$$

where the symbols have the significance already assigned. Since the calculation of the constant p depends to a great extent upon the judgment used in extrapolating the k_1, t curve, it is tentatively suggested, but not maintained, that the increase in the velocity coefficient ($k_1 - k_0$) varies with the cube of the concentration of potassium chloride.

The logs of the velocity coefficient k_2 and of the expression $\frac{k_1 - k_0}{c_{\text{KCl}}^3}$ (p) have been plotted against the reciprocals of the absolute temperatures and these points lie approximately on straight lines.

Conclusions

In a final summary the following facts developed in this research are preeminent:

- (1) The velocity coefficient of the decomposition of potassium perchlorate is in conformity with Arrhenius' law within the temperature range studied.
- (2) The increase in the velocity coefficient at constant temperature is proportional to the amount

of ferric oxide added.

(3) The expression $\frac{K_c - K_o}{C}$ varies with the temperature

according to the law of Arrhenius.

(4) The decomposition of potassium chlorate to oxygen is not materially affected by the presence of potassium chloride, but its transformation to potassium perchlorate is tremendously accelerated.

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			<u>59</u>	63	(1889)

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