

THE THERMAL DECOMPOSITION

OF

METHYL VINYL ETHER

A thesis submitted in partial fulfil-
ment of the requirements for the degree
of Master of Applied Science.

by,

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INTRODUCTION

This work has been done to supplement and continue that of Gordon Henry Turner as reported by him in his thesis "The Thermal Decomposition of Dimethyl Acetal", now on file in the library of the University of British Columbia.

For an outline of previous studies leading to this present work, I refer the reader to the above mentioned thesis. There he will find all the details necessary for the understanding and appreciation of this thesis. For the most part I have referred to Turner's thesis, when explanations of the different phases of this present study are contained therein.

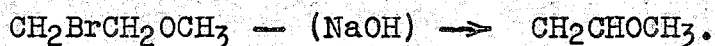
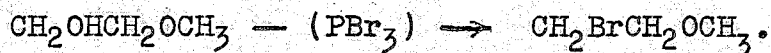
Turner found that dimethyl acetal decomposes to give methyl alcohol and methyl vinyl ether. It was thus considered desirable to study the thermal decomposition of methyl vinyl ether in the hope that it would throw more light on the decomposition mechanism of the acetal.

Although this work has confirmed assumptions made in explaining the decomposition mechanism of dimethyl acetal, it has not been completed to the writer's satisfaction. There are still complicating factors which could bear further investigation. The reader's attention will be drawn to these as they are mentioned in the following pages.

EXPERIMENTAL

Preparation of Methyl Vinyl Ether.

This preparation was carried out after the method of Dr. Wm. Chalmers (1).



An excess of the methyl ether of ethylene glycol (8-10 moles) was mixed with two moles of anhydrous ethyl ether and placed in a three-necked flask provided with a reflux condenser, stirrer and dropping funnel. The flask was cooled in ice and water and two moles of phosphorus tri-bromide were added dropwise with vigorous stirring. The mixture was then warmed on a water bath for several hours and allowed to stand over night. Methyl bromo-ethyl ether was separated from the above by repeated distillation.

The methyl vinyl ether was made by the reaction between the methyl bromo-ethyl ether and sodium hydroxide. This was accomplished in generators attached directly to the apparatus used in studying the thermal decomposition. These generators are shown in figures 1 and 2, and are described in the paragraphs immediately following.

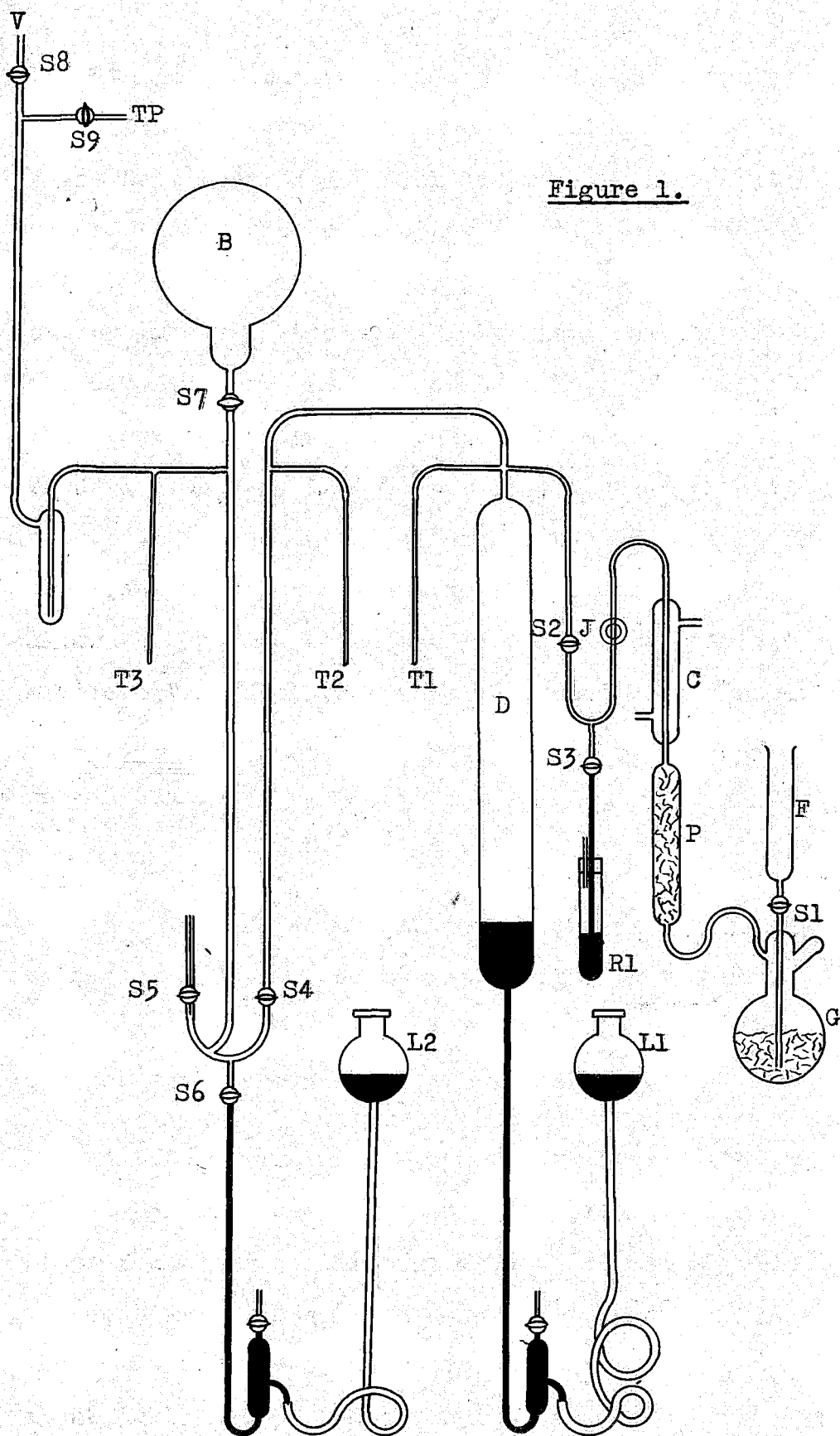
First Generator.

The ether used in making runs 1a, 2a, 3a, 4a, and 5a was made in the generator shown in figure 1.

The generator G and the column P were filled with sodium hydroxide pellets. With stopcocks S1, S3, S5, S6 and S9 closed, and S2, S4, S7 and S8 open, and whole apparatus as seen in this diagram was evacuated through the vacuum line V, which leads through a mercury diffusion pump to a Cenco Hi-vac. Then stopcocks S4, S7 and S8 were closed.

About 30ml. methyl bromo-ethyl ether were introduced into the generator through the funnel F and stopcock S1. On warming the generator on a water bath, methyl vinyl ether distilled off and passed through the column P into a gas holder D (approx. 600ml. capacity). The apparatus was so designed that any of the bromo-ether leaving G would condense in the condenser C and run back into P, where it would be in contact with sodium hydroxide.

After the reaction in G was complete, S3 was opened until mercury from the reservoir R1 had risen above S2. Then both S2 and S3 were closed and the generator, column and condenser were removed by disconnecting the ground glass joint J.

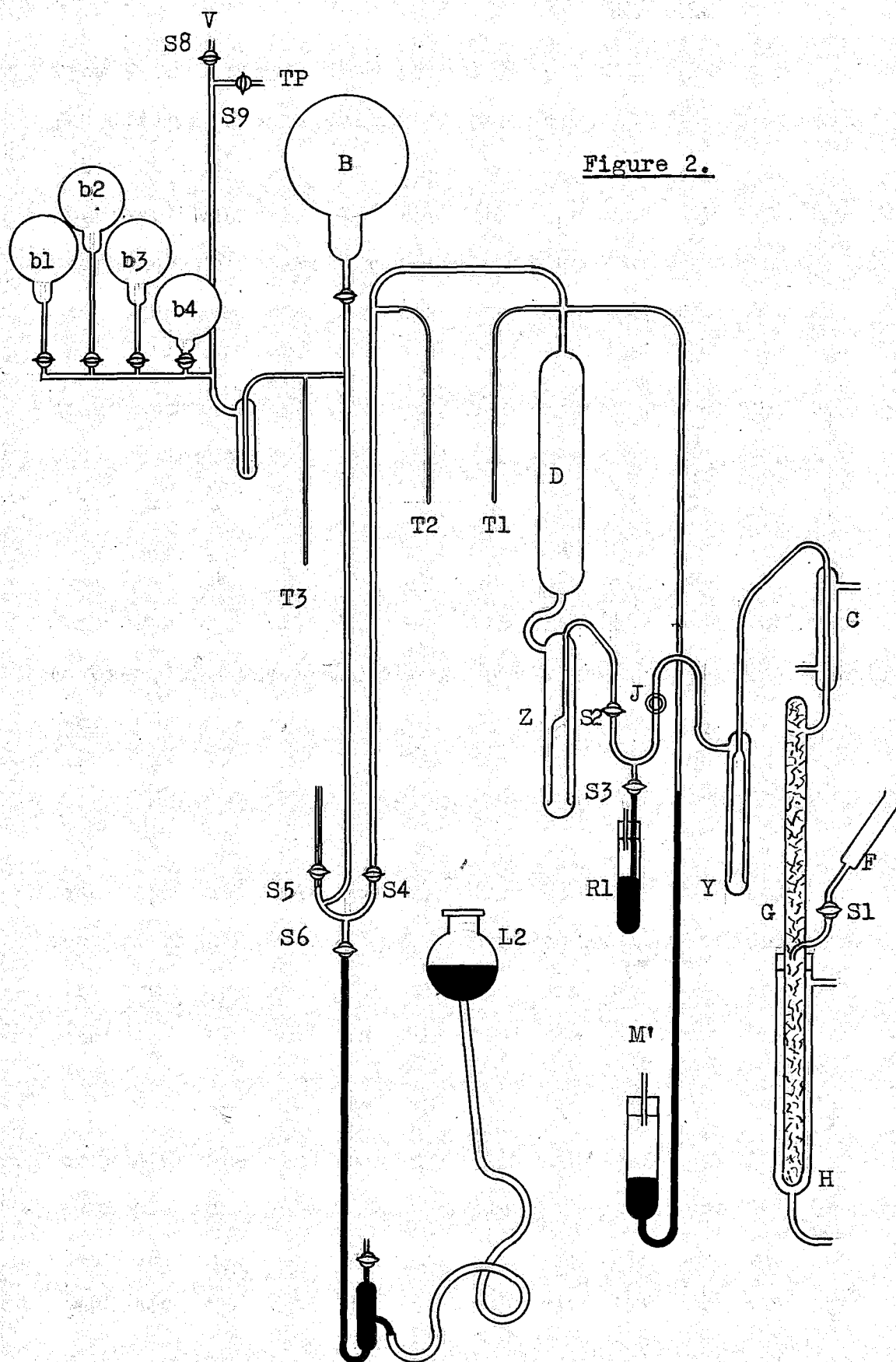


The gas contained in D now consisted of methyl vinyl ether together with any permanent gases (which might have been formed from impurities in the bromo-ether or from the bromo-ether itself) and possibly a trace of the bromo-ether. The Vinyl ether was frozen out by immersing the tube T1 in liquid air and raising the leveling bulb L1 to increase the pressure in D. The permanent gases were pumped off through S4 and S8. Then with only S4 and S7 open, the liquid air was removed. Before all of the ether had evaporated into the storage bulb B, S7 was closed and S8 opened to allow the residue to be pumped off. Thus only the middle fraction of the gases which had been generated in G were stored, and the lighter and heavier fractions were discarded.

Second Generator.

In spite of the precautions taken in the above method of preparation, it was thought that a more efficient type of generator could be devised. Therefore the generator shown in Figure 2 was built.

As before, the whole apparatus was evacuated, and all stopcocks closed with the exception of S2. The traps Y and Z were immersed in dry ice and liquid air respectively. Then, with cold water flowing through the condenser C and hot water through the jacket H, about 30ml. methyl bromo-ethyl ether were introduced



from F into the sodium hydroxide packed generator G. The design of this generator was such that any bromo-ether which evaporated while the pressure in the apparatus was still low would be in contact with sodium hydroxide for a longer period of time before passing into the condenser; and that which condensed in C could run down to the heated part of the generator. What little bromo-ether passed through the condenser was caught in the dry ice trap. Thus only the very low boiling point constituents found their way to the liquid-air trap.

After the reaction was complete, S2 was sealed with mercury and the generator, condenser and dry-ice trap were removed. Then S4 and S8 were opened and the permanent gases pumped off.

On the removal of the liquid air, the first fraction of methyl vinyl ether evaporating was stored in B. The remainder was taken from the trap to T1 by immersing this tube in liquid air. Then, on the removal of the liquid air from T1, part of the ether was allowed to evaporate into D and the rest was sealed off in T1.

The ether stored in D was used in all of the b-runs, and that stored in B was used in the c-runs. When a decomposition run was to be made, the ether was taken to the reaction chamber through S5. After the run had been completed, the products of the decomposition were removed

through S5 and stored in the previously evacuated storage bulbs b1, b2, b3 and b4.

Removal of Gaseous Samples.

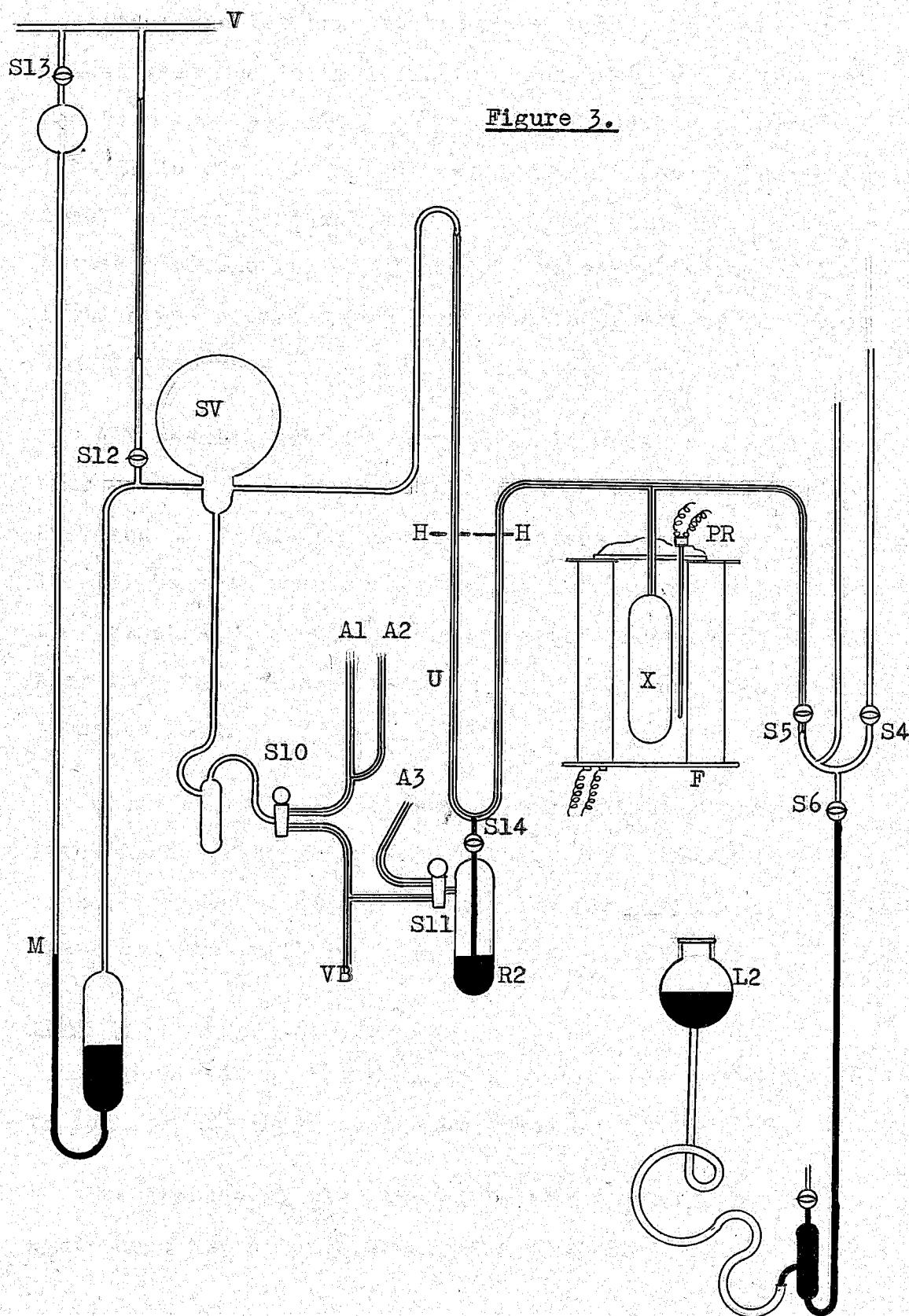
To remove gaseous samples for analysis, the appropriate stopcocks were opened and the gas to be analysed was pumped off through S9 to a burette - a Topley pump being used for this pumping. The samples taken from the burette were stored over mercury and microanalysed (2).

Reaction Chamber And Pressure Measuring Apparatus.

Figure 3 shows the method of accomplishing the thermal decomposition of the methyl vinyl ether at constant volume, and of measuring the pressure at progressive stages throughout the decomposition.

The furnace F, enclosing the decomposition chamber X and the platinum resistance thermometer PR, was brought to the desired temperature, and the whole apparatus as seen in figure 3 was evacuated through S5, S12 and S13. Then all other stopcocks were closed and S14 was opened until mercury from the reservoir R2 had risen into the U-tube U to the level H. It will be seen that manipulation of S10, S11 and S14 leading to the air leaks A1, A2 and A3, and through VB to a vacuum bottle, made it possible to control the mercury level in either or both of the arms of the U-tube.

Figure 3.



Ether was let into X through S5 until the level in U showed that the desired initial pressure for the reaction had been reached. Then S5 was closed and air allowed into SV (a stabilizing volume) through A1 and A2 until the level in U was brought back to H. The time which elapsed between the closing of S5 and the re-establishing of the level H was recorded together with the pressure read from the manometer M.

Air was let into Sv at regular intervals; and, each time the level H was re-established by the pressure building up in X, the time and pressure were recorded. It will be seen that each time the level H was established the pressure in Sv was the same as the pressure in X, and therefore the pressure measured by M was identical with the pressure in X.

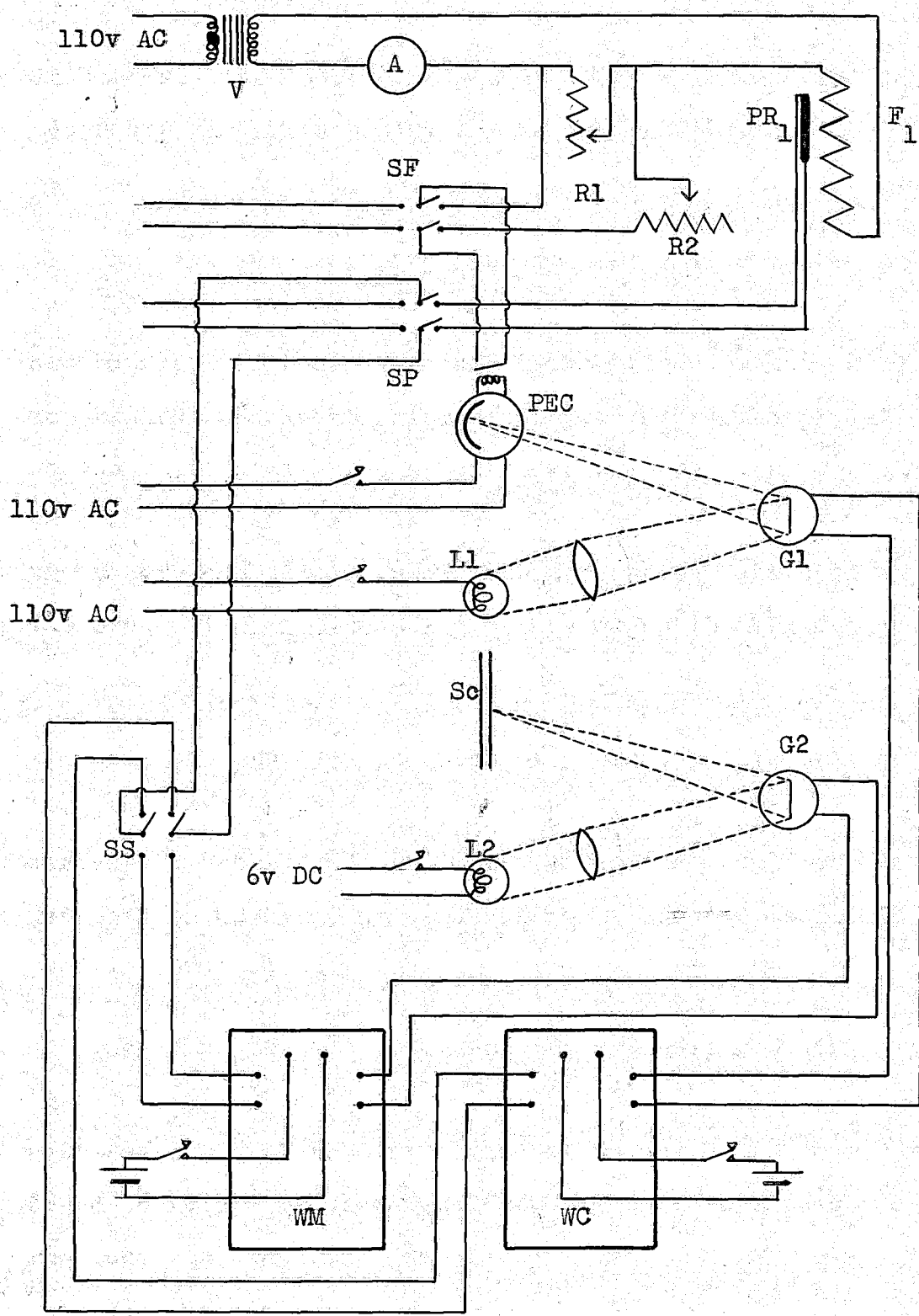
Other parts of the apparatus not explained above are leveling bulbs to manipulate mercury for sealing stop-cocks, capillary tubes to retard the flow of gases, and traps to catch wild mercury, liquid products etc.

Temperature Control.

Figure 4. is a wiring diagram showing the methods used to control and measure the temperature.

The furnace F1 was coupled in series with a variable resistance R1, an ammeter A and a 110V-5amp variac V.

WIRING DIAGRAM.



Across R1 was a secondary circuit consisting of another variable resistance R2 and a photoelectric relay (PEC) in series. The double throw switch SF was placed in the secondary circuit to accomodate another and similar arrangement for another furnace.

The platinum resistance thermometer PR1 was wired across the center poles of the double throw switch SS - another double throw switch SP being placed in this line to accomodate the platinum resistance thermometer used in conjunction with the other furnace. The side of the switch SS led to the wheatstone bridge WC and from there to the galvanometer G1 used with the photoelectric relay. The other side of SS was led to the wheatstone bridge WM and from there to a second galvanometer G2.

With the proper adjustment of R1 and R2 any desired temperature in the furnace could be maintained by the correct setting of WC, and this temperature could be measured on WM by means of the light L2 and the scale Sc used in conjunction with G2.

The above method of controlling and measuring the temperature in the furnace was found to be entirely satisfactory. At no time during a run was the temperature found to vary more than 0.05°C on either side of the recorded temperature of the run.

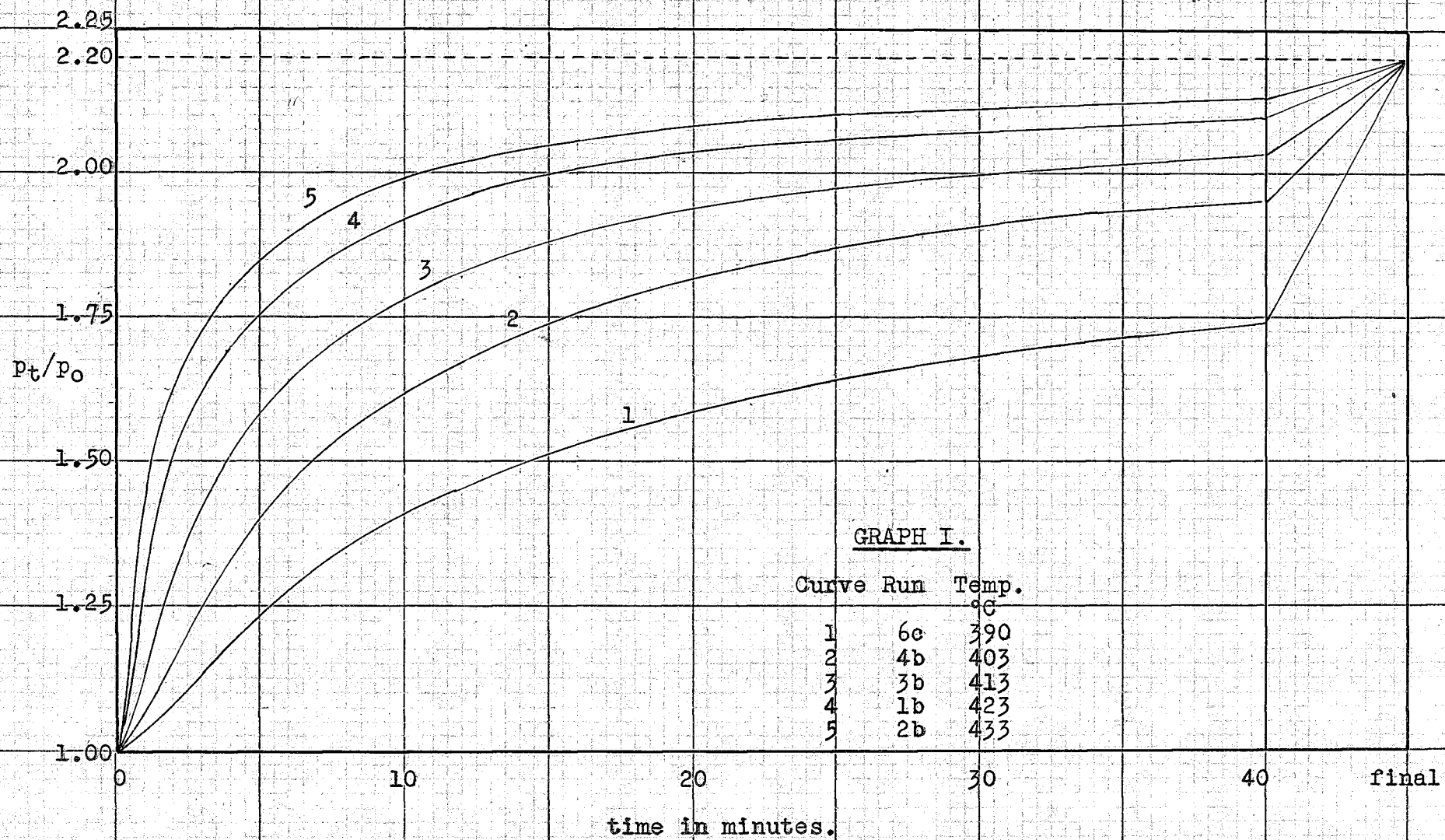
TREATMENT OF THE DATA — PART 1.

Pressure - Time Graphs.

Experimental total pressures were plotted as ordinates against time as abscissae. From the curves so obtained, "smoothed" values of the total pressures corresponding to equal increments of time were tabulated and used in the following calculations.

Graph 1. shows the type of curves obtained when total pressures were divided by corresponding initial pressures and plotted against time. Dividing by the initial pressures facilitates comparisons of fractional increases in pressure from one time to another during a given run, or from one run to another for a given time.

Each curve will be seen to turn upwards at the beginning. The length of time for which this was noted varied from curve to curve and seemed to depend upon the temperature and initial pressure and upon the condition of the reaction chamber. For relatively high temperatures and for high initial pressures the effect was nearly indiscernable because of the more rapid increases in total pressure due to the main reaction. It is difficult, therefore to calculate the dependence of this "induction" period upon temperature and (or) pressure. Experiments with air proved that it was not due to the heating of the



ether from room temperature to the temperature of the run. This takes an immeasurably short time.

Order of the Reaction.

Graph II. shows $\frac{p_o}{p_f - p_t}$ plotted against time, where p_o is the initial pressure, p_f is the final pressure and p_t is the total pressure at time t . The initial pressures were calculated from the final pressures by dividing by 2.2. This value was determined by introducing methyl vinyl ether into the cold reaction chamber, measuring the pressure, heating until the decomposition was complete and then measuring the final pressure. The value 2.2 is an average of several runs made in this manner.

The fact that the curves in Graph II. approach linearity shows the decomposition reaction to approximate an overall second order rate.

If the reaction were second order the ratios $\frac{t_{1/4}}{t_{1/2}}$ and $\frac{t_{3/4}}{t_{1/2}}$ should be $1/3$ and 3 respectively; where $t_{1/4}$, $t_{1/2}$ and $t_{3/4}$ are the times necessary for decomposition of $1/4$, $1/2$ and $3/4$ of the ether respectively. Table 1 shows that the above ratios would indicate an approximately second order reaction. From this we may conclude that the main reaction in the thermal decomposition of methyl vinyl ether is definitely second order.

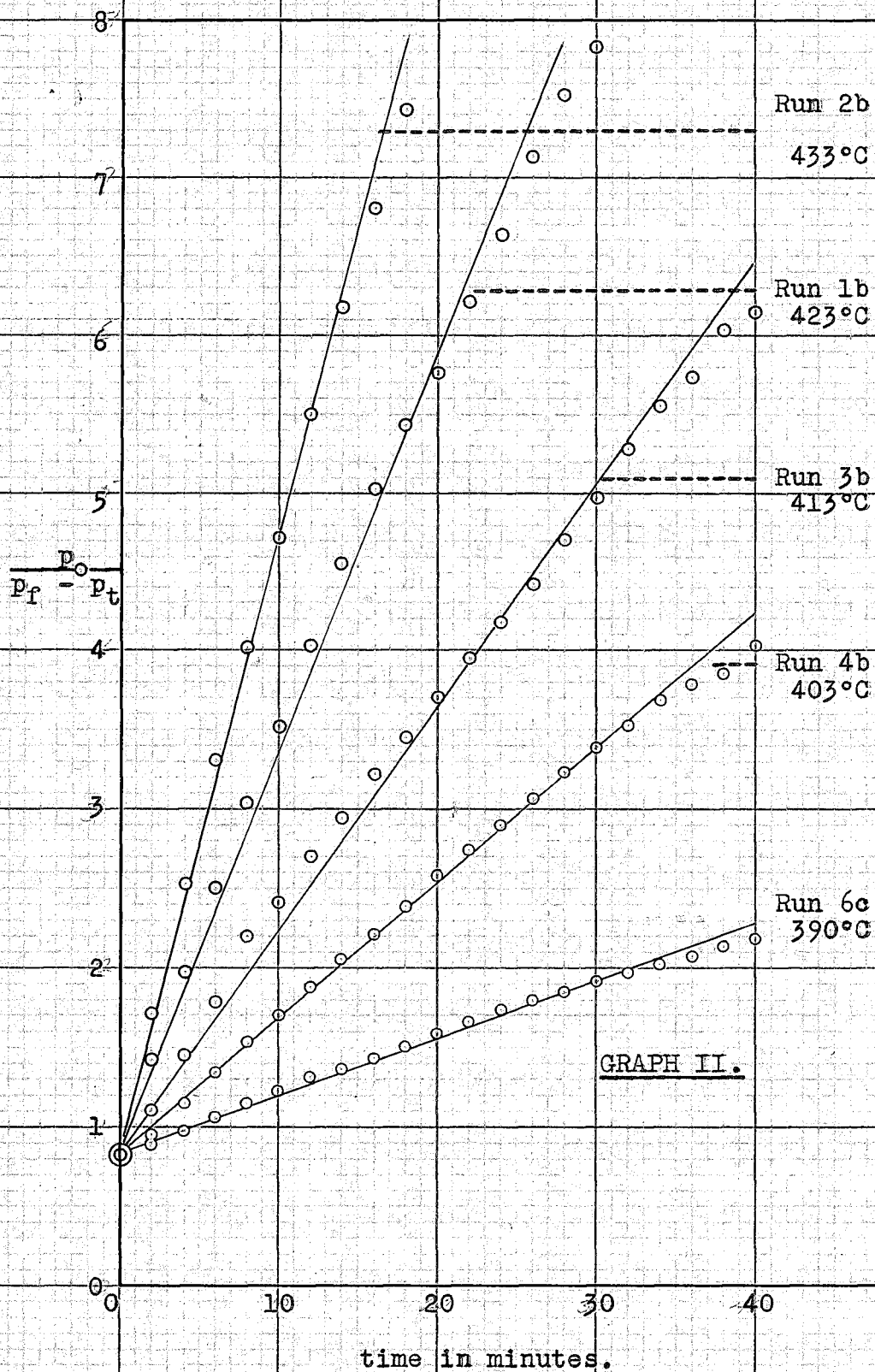


TABLE 1.

Run	T°C	$\frac{t_{1/4}}{t_{1/2}}$	$\frac{t_{3/4}}{t_{1/2}}$
1a	400	----	----
5a	423	.41	2.70
2a	423	.37	3.99
3a	430	.35	2.88
4a	439	.37	3.13
4b	403	.35	3.03
3b	413	.36	3.24
5b	414	.39	2.60
1b	423	.36	3.25
2b	433	.36	3.24
6c	390	.31	----
3c	403	.19	3.14
5c	414	.36	3.53
1c	414	.44	3.53
2c	423	.28	2.99
4c	433	.33	3.13
7c	413	.41	2.95
averages		.35	3.15

Reaction Rate Constant.

Reaction rate constants (k_2) were calculated for each run by use of the formula-

$$k_2 = \frac{S-1}{t} \left(\frac{1}{p_f - p_t} - \frac{1}{p_f - p_o} \right) \text{ ----(appendix (1))}$$

where S is the ratio of final to initial pressures determined as described above.

Values for k_2 calculated in this manner did not show any definite dependence upon temperature. This was assumed to be partially due to what I have, for convenience, termed the "induction" period. As will be seen in the following example (chosen to show this effect), the determination of an exact constant for the rate of the main reaction was almost impossible - at least by this method.

Since values of k_2 so calculated were in most cases constant over considerable periods of time, it was decided that the main decomposition reaction was definitely second order. Since averaging values such as those in table 2 would not give good results, the reaction rate constants used for further calculations were obtained from the formula -

$$k_2 = \frac{2.2}{t_{1/2} p_f} \text{ -----(appendix (2))}$$

The constants obtained in this manner are tabulated in table 3.

These values showed better agreement for runs at the same temperature and showed a temperature relationship

TABLE 2.Run 1c 414°C

t min.	p cm.	k ₂ x10 ³
0	7.00	
2	7.55	5.0
4	8.20	5.0
6	8.85	6.7
8	9.50	7.1
10	10.15	8.5
12	10.70	9.4
14	11.05	9.5
16	11.30	9.4
18	11.50	9.1
20	11.60	8.7
22	11.75	8.4
24	11.90	8.3
26	12.05	8.3
28	12.15	8.2
30	12.30	8.2
32	12.40	8.1
34	12.50	8.1
36	12.60	8.1
38	12.70	8.1
40	12.85	8.2
p _r = 15.40		

effect of
induction
period

TABLE 3.

Run	T°C	p_o cm	$t_{1/2}$ min^{-1}	k_2	Remarks
1a	400	13.30	----	-----	p_o too low.
5a	423	6.32	4.40	.0359	
2a	423	10.95	8.65	.0105	
3a	430	9.40	2.90	.0273	
4a	439	9.40	2.48	.0428	
					proven unreliable by p_o/p_f-p_t vs t .
4b	403	12.90	9.52	.0081	p_o too low.
3b	413	17.20	5.27	.0110	
5b	414	5.85	9.25	.0185	
1b	423	19.60	2.78	.0183	
2b	433	20.10	1.85	.0269	
6c	390	21.10	22.10	.0022	
3c	403	15.05	21.65	.0031	
5c	414	17.40	7.68	.0075	
1c	414	7.00	15.30	.0093	
2c	423	15.80	8.10	.0112	
4c	433	10.50	4.75	.0200	
7c	413	6.07	14.95	.0111	

as seen in Graph III. It will be noticed that the points in this graph congregate in zones, and that the averages of points within each zone show a definite trend from zone to zone.

Energy of Activation.

The energy of activation (E) for a second order reaction is given by the equation -

$$k_2 = AT^{1/2} \cdot e^{-\frac{E}{RT}}$$

from which we may derive:

$$E = 2.303R \frac{d \log_{10} k_2}{d \frac{1}{T}} - \frac{RT}{2} \text{ --(appendix(3))}$$

and since $\frac{RT}{2}$ is relatively small compared with E,

$$E \approx - 2.303R \frac{d \log_{10} k_2}{d \frac{1}{T}} = \text{const.}$$

Thus plotting $\log_{10} k_2$ against $\frac{1}{T}$ should give a straight line.

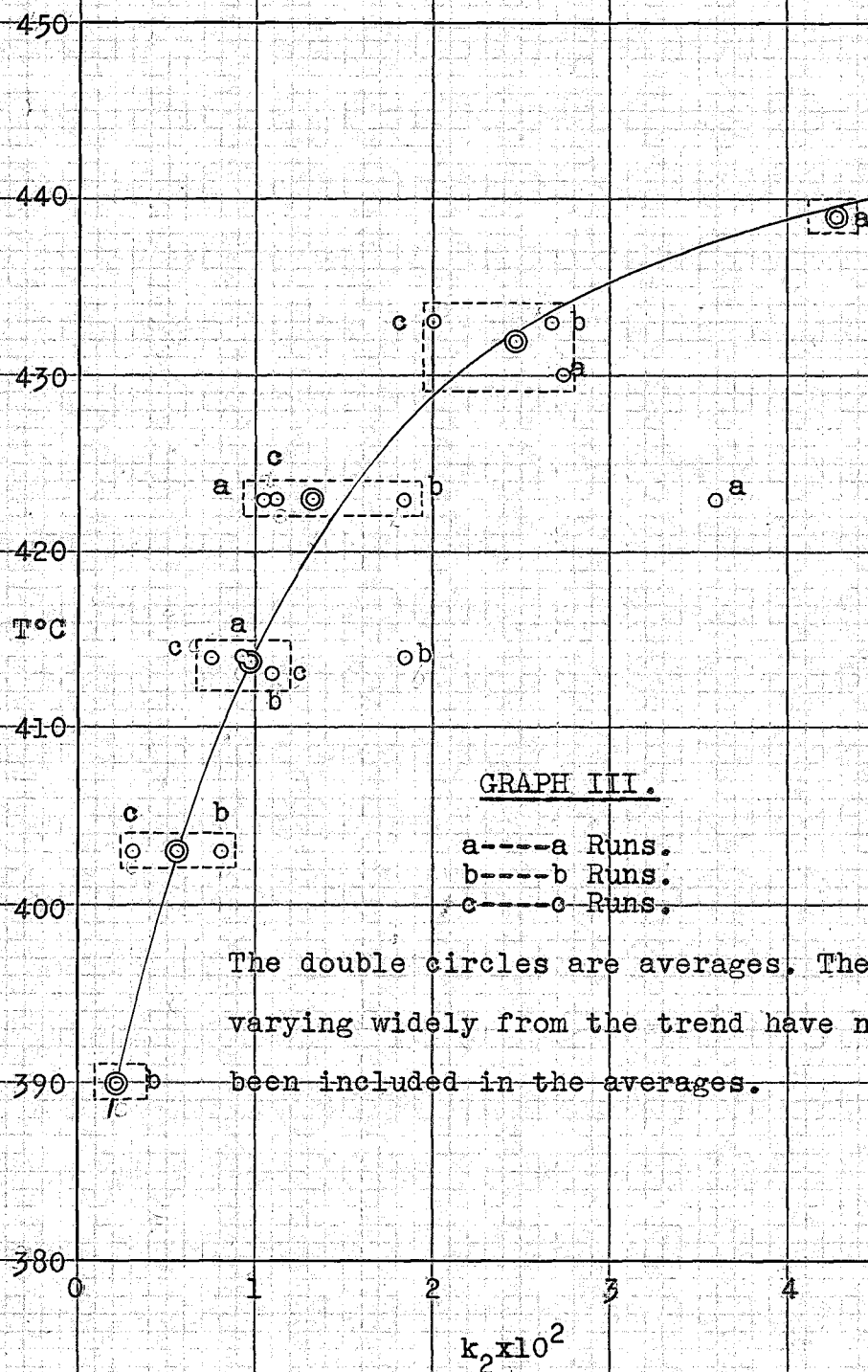
This however was not the case. But on plotting $\log_{10} k_2$ against T the straight line in Graph IV. was obtained - indicating the relationship

$$E = 2.303R \frac{d \log_{10} k_2}{d T} T^2 \text{ --(appendix (4))}$$

$$= 0.1T^2 - 0.992 T$$

$$= 48,300 \text{ cal at } 430^\circ\text{C}$$

$$\text{and } 44,600 \text{ cal at } 400^\circ\text{C.}$$



450

440

430

420

T°C

410

400

390

380

1.50

1.75

2.00

2.25

2.50

2.75

 $-\log_{10} k_2$ GRAPH IV.

○

○

○

○

○

The fact that the overall reaction was proven to approximate a second order rate would indicate that, although this last equation may give values of the activation energy which are of the right order of magnitude, the equation itself could hardly be expected to hold over any reasonably large range of temperatures.

TREATMENT OF THE DATA — PART II.

Effect of the Ratio of Final to Initial Pressures.

The dependence, or apparent dependence of the activation energy upon temperature was thought to be due to the condition of the reaction chamber. It will be remembered that the ratios of final to initial pressures were taken as 2.2 for every run. If, however, the pressure - time curves are extrapolated to zero time, the actual values of this ratio vary and 2.2 is just an average. It is ^{true} time that the difference between these values and the average was never more than five percent, but the following calculations show that their use in place of the average gives a constant value for the activation energy while having little effect upon the other data.

Using the individual values of $\frac{p_f}{p_o}$ and the p_o 's from extrapolation of the pressure - time curves, it was found that the curves in Graphs I and II were not noticeably shifted, and that the approximation of an overall second

order rate was indicated as before.

Table 4. shows the values of $s=p_f/p_o$ and the effect they have on previously calculated data. The blank spaces in table 4 correspond to curves which could not be extrapolated to zero time.

The Reaction Rate Constant.

Table 5. gives the values of k_2 calculated by use of the formula

$$k_2 = 1/p_o t_{1/2}. \quad (\text{appendix (2)})$$

This table includes only runs for which the pressure - time curves could be extrapolated to zero time. With the exception of k_2 for run 4b, the values in columns a and b check quite closely, but it will be seen that those in column b show more regularity than those in column a.

Energy of Activation.

Under this heading in part I it was explained that, for a second order reaction, the energy of activation is given by the equation

$$E = -2.303R \frac{d(\log_{10} k_2)}{d(1/T)} = \text{constant.}$$

and plotting $\log_{10} k_2$ against $1/T$ should give a straight line. Graph V. shows this condition fulfilled for the reaction rate constants in column b, table 5. The slope of the line in Graph V. is -5,000, giving

$$E = 24,900 \text{ calories.}$$

This value would appear to be extremely low and is definitely not in agreement with that previously calculated.

TABLE 4.

NOTE - $s=2.2$ for (a) columns and is variable for (b) columns.

Run	T°C	p_o cm		p_f cm	s		$t_{1/2}$ min		$\frac{t_{1/4}}{t_{1/2}}$		$\frac{t_{3/4}}{t_{1/2}}$	
		(a)	(b)	(a&b)	(A)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
6c	390	21.10	20.95	46.40	2.2	2.22	22.10	21.75	.31	.31	----	----
1a	400	13.30	-----	29.25	2.2	-----	-----	---	---	----	----
4b	403	12.90	12.40	28.40	2.2	2.29	9.52	5.93	.35	.36	3.03	2.57
3c	403	15.05	-----	33.10	2.2	-----	21.65	-----	.19	---	3.14	-----
3b	413	17.20	16.80	37.85	2.2	2.25	5.27	6.58	.36	.28	3.24	2.51
5b	414	5.85	5.90	12.85	2.2	2.18	9.25	12.60	.39	.30	2.60	3.00
1c	414	7.00	-----	15.40	2.2	-----	15.30	-----	.44	---	3.53	-----
5c	414	17.40	17.10	38.30	2.2	2.24	7.68	7.27	.36	.35	3.53	3.72
7c	413	6.07	-----	13.35	2.2	-----	14.90	-----	.41	---	2.95	-----
1b	423	19.60	19.33	43.12	2.2	2.24	2.78	2.79	.36	.34	3.25	3.21
2a	423	10.95	-----	24.10	2.2	-----	8.65	-----	.37	---	3.99	-----
5a	423	6.32	-----	13.90	2.2	-----	4.40	-----	.41	---	2.70	-----
2c	423	15.80	-----	34.75	2.2	-----	8.10	-----	.28	---	2.99	-----
3a	430	9.40	-----	20.70	2.2	-----	2.90	-----	.35	---	2.88	-----
4c	433	10.50	10.40	23.10	2.2	2.22	4.75	4.50	.33	.34	3.13	3.23
2b	433	20.10	19.22	44.22	2.2	2.30	1.85	1.75	.36	.35	3.24	3.28
4a	439	9.40	9.80	20.65	2.2	2.09	2.48	3.20	.37	.33	3.13	3.34
averages									.35	.33	3.15	3.11

TABLE 5.

NOTE - $s=2.2$ for (a) columns and is variable
for (b) columns.

Run	T°C	k_2	
		(a)	(b)
6a	390	.0022	.0022
4b	403	.0081	.0136
3b	413	.0110	.0095
5c	414	.0075	.0081
1b	423	.0183	.0185
4c	433	.0200	.0214
2b	433	.0269	.0298
4a	439	.0428	.0339

.0027

.0026

.0025

.0024

 $\frac{1}{T^{\circ}\text{C}}$

.0023

.0022

.0021

.0020

1.0

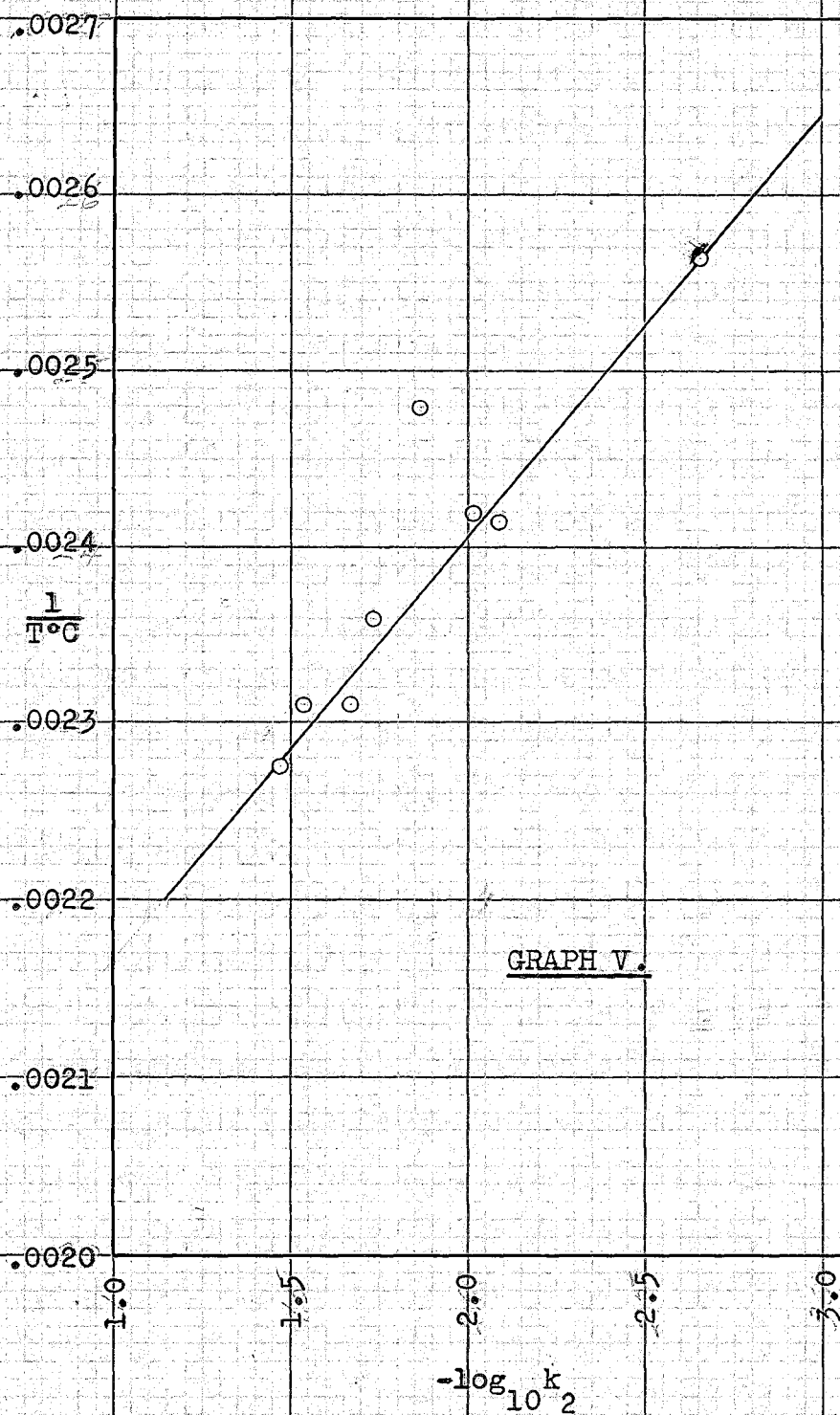
1.5

2.0

2.5

3.0

3.5

 $-\log_{10} k_2$ GRAPH V.

To obtain the best value for the energy of activation it was decided to use all of the individual values for k_2 and solve for the slope $\frac{d(\log_{10} k_2)}{d(\frac{1}{T})}$ by the method of least squares. Thus

$$\sum -\log_{10} k_2 = m \sum \frac{1}{T} + b.$$

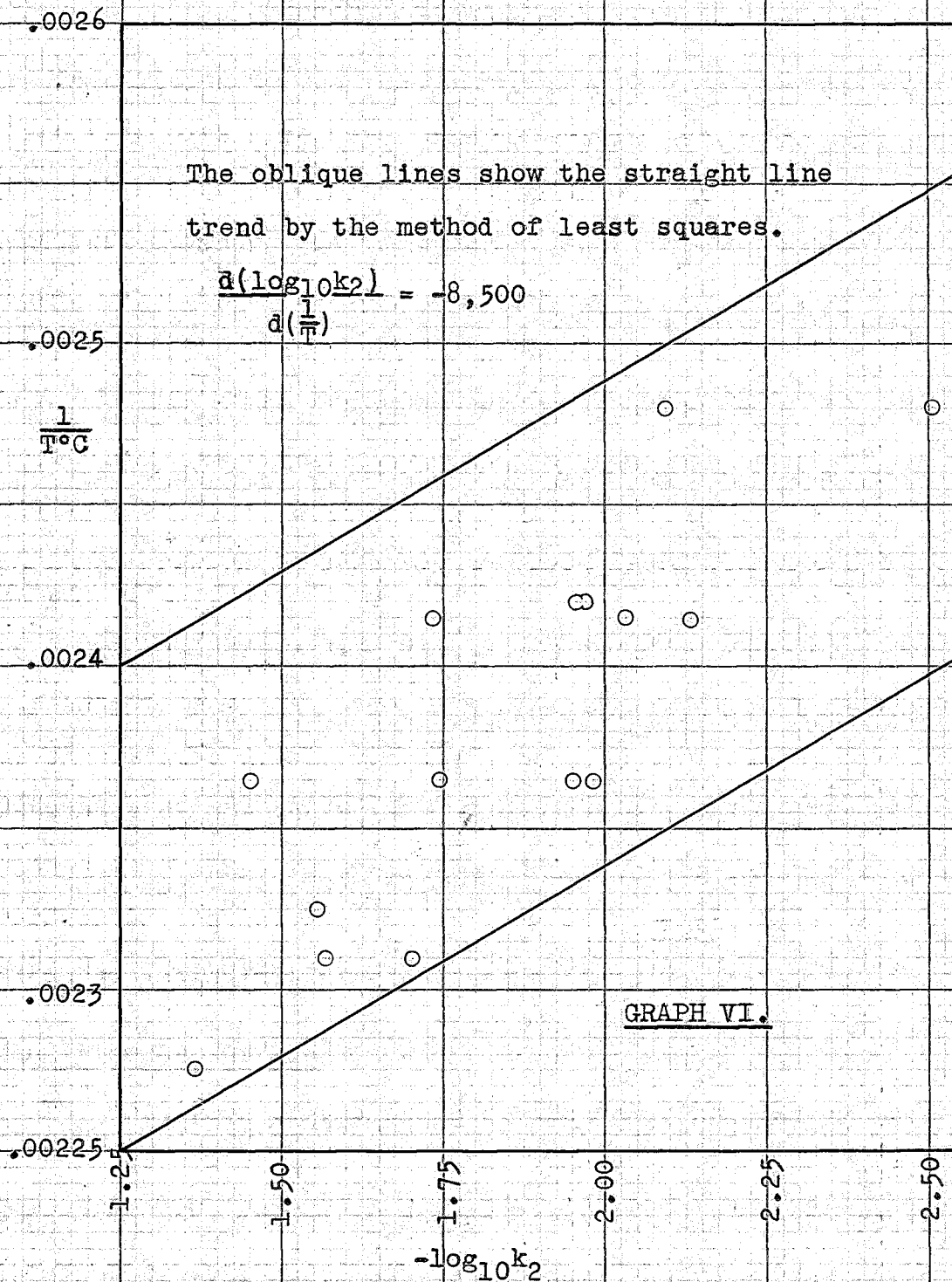
where the slope $m = \frac{d(\log_{10} k_2)}{d(\frac{1}{T})}$

$$\begin{aligned} & n, \sum (-\log_{10} k_2) \\ &= \frac{\sum \frac{1}{T}, \sum (-\frac{\log_{10} k_2}{T})}{n, \sum \frac{1}{T}} \\ & \quad \sum \frac{1}{T}, \sum (\frac{1}{T})^2 \\ &= -8,500 \end{aligned}$$

From this we have:

$$\begin{aligned} E &= -8,500 \times (-2.303)(1.985) \\ &= 38,800 \text{ calories.} \end{aligned}$$

Although plotting the reaction rate constants first calculated against $1/T$ does not show any definite trend (Graph VI.), the activation energy calculated from these by the above method is obviously the best value obtainable from the data in hand. On consideration of the work of Turner and of the reaction rates in this thesis, it will be seen that 38,800 calories is reasonable for the energy of activation in the thermal decomposition of methyl vinyl ether.



COMPLICATING FACTORS.

In addition to the runs previously discussed, four runs were made with a reaction chamber packed with glass tubing to give a surface 6.25 times as great as that of the unpacked chamber. The information gained from these runs threw more light onto factors such as:-

- (i) The effect of extent of surface.
- (ii) The effect of condition of surface.

To study these effects, four runs (2a, 2c, 8c, and 11c) all made at 423°C were considered as follows.

Extent of Surface.

Graph VII. shows that there is a reaction dependent upon the extent of surface which tend to suppress the building up of pressure due to the main reaction. Thus we have the branching of the two sets of lines - the lower branch in each set showing the result of adding to the extent of surface in contact with the decomposing ether. This may be taken as an indication of a free radical mechanism (3).

Condition of Surface.

The condition of the walls of the reaction chamber is by far the most important factor. Reference to Graph VII. shows that the extent of surface does not have much effect upon the general shape of the pressure - time curve, while the number of runs previously made in a chamber (whether

2.25

2.00

1.75

1.50

 p_t/p_o

1.25

1.00

0

10

20

30

40

time in minutes.

- 1 Run 8 c 423°C.
3 Run 2 a 423°C.
2 Run 11 c 423°C.
4 Run 2 c 423°C.

4

2

3

1

GRAPH VII.

packed or not) is of great importance in this respect.

On comparing the values of $t_{1/2}$ (table 6.) we find a good index to the dependence on wall conditioning of what must be the combining of free radicals on the walls.(4).

If we assume a chain mechanism involving free radicals, we may conclude that the combining of these radicals on the chamber walls terminates the chain and slows up the decomposition. As more and more runs are made in a given chamber, the walls become conditioned in such a manner that the free radical combination is slowed up. This leads to a faster overall decomposition rate.

Effect of Wall Reaction on Rate Constant.

The effects of both extent and condition of surface are seen in table 7. Increased surface decreases the rate constant as seen by comparing the constants for 8c and 11c with those for 2c and 2a respectively. Conditioning of the surface also increases the rate constants as seen by comparing k_2 for 8c with that for 11c. The constants for 2c and 2a do not show this effect. This may be due to their not being accurate enough and to the extent of surface of the unpacked chamber not being great compared with the initial pressures.

Little has been said and little can be said about what has been previously termed the "induction period". A study of the pressure - time curves shows that this period at the

TABLE 6.Runs at 423°C.

Run	no. of previous runs	$t_{1/2}$	k_2	Remarks.
8c	0	20.38	.0029	packed with glass tubing.
2c	1	9.10	.0112	
11c	3	8.55	.0069	packed with glass tubing
2a	3	8.65	.0105	
5a	5	4.40	.0359	
1b	6	2.78	.0185	

TABLE 7.Runs at 423°C.

Run	Packing	No. of previous runs	k_2
8c	yes	0	.0029
2c	no	1	.0112
11c	yes	3	.0069
2a	no	3	.0105

beginning of each run varies with initial pressure, condition of surface, temperature and extent of surface. These factors are written in the order of their effect - initial pressure being most important.

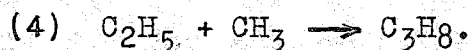
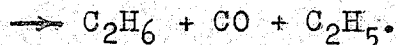
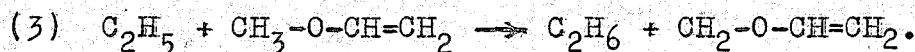
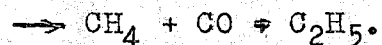
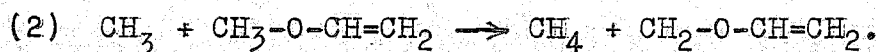
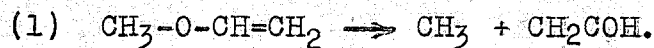
SUMMARY OF RESULTS

The following is a tabulated summary of the results of this work on the thermal decomposition of methyl vinyl ether.

1. The overall rate of decomposition is second order.
2. An increase in surface lowers the rate.
3. "Conditioning" the walls increases the rate.
4. There are three main factors -
 - (a) the main decomposition.
 - (b) the induction period dependent upon -
 - I. initial pressure.
 - II. condition of surface.
 - III. temperature of decomposition.
 - IV. extent of surface.
 - (c) a free radical mechanism dependent upon -
 - I. condition of surface.
 - II. extent of surface.
5. The activation energy is approximately 39,000 calories per mole.

MECHANISM OF DECOMPOSITION

It is difficult to propose a mechanism for the decomposition until analyses of the intermediate and final products have been completed. Following, however, are equations giving what appear to be likely steps in the decomposition -



Equation (4) is presumably the reaction terminating the chain. This would be dependent upon the extent and condition of the surface of the reaction chamber (5)

REFERENCES.

- (1) Preparation of Ethers of Vinyl Alcohol - Wm. Chalmers.
Canadian Journal of Research 7, 464-71 (1932).
- (2) The Thermal Decomposition of Dimethyl Acetal - G. H.
Turner. - a thesis, U.B.C. (1941).
- (3) The Aliphatic Free Radicals. - F.O.Rice and K.Rice.-
book, Johns Hopkins (1935).
- (4) On the Polymerization of Ethylene and Propylene by
Free Alkyl Radicals. - Beech and Rust (Shell Development,
J. Chem. Phys., 9 - 480 (1941).
- (5) Reference (3).

APPENDIX

Symbols used in the following derivations are as listed below -

p_o = initial pressure.

p_f = final pressure.

p_t = total pressure at time t .

p_{t1} = pressure of undecomposed ether at time t .

s = ratio of final to initial pressure.

$t_{1/4}$, $t_{1/2}$ and $t_{3/4}$ = 1/4, 1/2 and 3/4 life respectively.

- (1) To obtain the reaction rate constant from the pressure - time data.

$$-\frac{dp}{dt} = k_2 p^2$$

$$-\frac{dp}{p^2} = k_2 dt.$$

$$k_2 t = \frac{1}{p_{t1}} - \frac{1}{p_o} \dots \dots \dots (1)$$

but $p_f = s p_o$. giving

$$p_t = p_{t1} + s(p_o - p_{t1}).$$

$$p_{t1} = \frac{p_f - p_t}{s-1} \dots \dots \dots (2)$$

and at zero time

$$p_o = \frac{p_f - p_o}{s-1} \dots \dots \dots (3)$$

from equations (1), (2) and (3)

$$k_2 t = \frac{s-1}{p_f - p_t} - \frac{s-1}{p_f - p_o}$$

$$\text{thus } k_2 = \frac{s-1}{t} \left(\frac{1}{p_f - p_t} - \frac{1}{p_f - p_o} \right).$$

(2) To obtain the reaction rate constant from the half life.

From part (1)

$$p_t = \frac{p_f - p_0}{s-1}$$

for $t_{1/2}$

$$p_t = 1/2 p_0 \text{ and } p_t = p_{t_{1/2}}$$

then

$$p_{t_{1/2}} = p_f - (s-1) \frac{1}{2} p_0 = \left(1 - \frac{s-1}{s} \left(\frac{1}{2} \right) \right) p_f$$

simly.

$$p_{t_{1/4}} = \left(1 - \frac{s-1}{s} \left(\frac{3}{4} \right) \right) p_f$$

and

$$p_{t_{3/4}} = \left(1 - \frac{s-1}{s} \left(\frac{1}{4} \right) \right) p_f$$

Thus, from the calculated values for the total pressures at $t_{1/4}$, $t_{1/2}$ and $t_{3/4}$ the values of $t_{1/4}$, $t_{1/2}$ and $t_{3/4}$ can be read from the pressure - time curves.

$$- \frac{dp}{dt} = k_2 p^2$$

To get the reaction rate constant in terms of the half life, we integrate the above equation as p goes from p_0 to $\frac{1}{2}p_0$ and t goes from 0 to $t_{1/2}$.

$$k_2 = \frac{1}{p_0 t_{1/2}}$$

but $p_0 = \frac{p_f}{s}$, therefore

$$k_2 = \frac{s}{p_f t_{1/2}}$$

and for $s=2.2$

$$k_2 = \frac{2.2}{p_f t_{1/2}}$$

(3) The activation energy.

For a second order reaction

$$k_2 = AT^{1/2} e^{-\frac{E}{RT}}$$

$$\ln k_2 = -\frac{E}{RT} + \ln A + \frac{1}{2} \ln T \dots \dots \dots (1)$$

differentiating (1) with respect to $1/T$

$$\frac{d(\ln k_2)}{d(1/T)} = -\frac{E}{R} - \frac{T}{2}$$

$$\begin{aligned} E &= -R \frac{d(\ln k_2)}{d(1/T)} - \frac{RT}{2} \\ &= -R \frac{D(\log_{10} k_2)(2.303)}{d(1/T)} - \frac{RT}{2} \end{aligned}$$

(4) Differentiating (1) in part (3) with respect to T .

$$\begin{aligned} E &= \frac{d(\ln k_2)}{dT} RT^2 - \frac{RT}{2} \\ &= 2.303 R \frac{d(\log_{10} k_2)}{dT} T^2 - \frac{RT}{2} \end{aligned}$$