

The Thermal Decomposition of
Normal Butyraldehyde

by

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A Thesis submitted for the Degree of

MASTER OF ARTS

in the Department

of

Chemistry

The University of British Columbia

April 1937

*Accepted on behalf of
the Department of Chemistry.*

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Introduction

Of the aliphatic aldehydes, formaldehyde, acetaldehyde and propionaldehyde have been the subject of considerable study from the point of view of thermal decomposition. However, the mechanisms of these decompositions is still in a state of flux. Since butyraldehyde has received but little attention and since it was thought that a study of its decomposition might yield information of value in solving the problem of the decomposition mechanisms of this series this research was undertaken.

The decomposition of formaldehyde ⁽¹⁾ is believed to be an homogeneous, bimolecular reaction with the appearance, simultaneously, of condensation products. The pyrolysis of acetaldehyde ⁽²⁾ is anhomogeneous reaction also, but the mechanism is not so well defined. The order of the reaction was, for a time, thought to be approximately 2. ⁽³⁾ Later it was calculated to be 1.5. ⁽⁴⁾ The work of Hinshelwood indicates the process of decomposition to be a series of quasi-unimolecular ⁽⁵⁾ reactions. The general conclusion is that acetaldehyde decomposes in a kinetically complex manner, although the products are almost 100% CH₄ and CO.

The Rice Herzfeld Chain Mechanism theory came into prominence through being able to give a satisfactory mechanism for the decomposition of acetaldehyde and a number of other reactions including formaldehyde and propionaldehyde. But at present the theory is being subjected to severe criticism by

(6) Steacie, Patat and Sachsse.

Propionaldehyde decomposes in a kinetically complex manner as a result of several quasi-molecular reactions according to Hinshelwood.⁽⁸⁾

It is to be expected, therefore, that the decomposition of butyraldehyde will be a complex affair. The results so far obtained bear out this prediction.

Apparatus and Experimental Method:

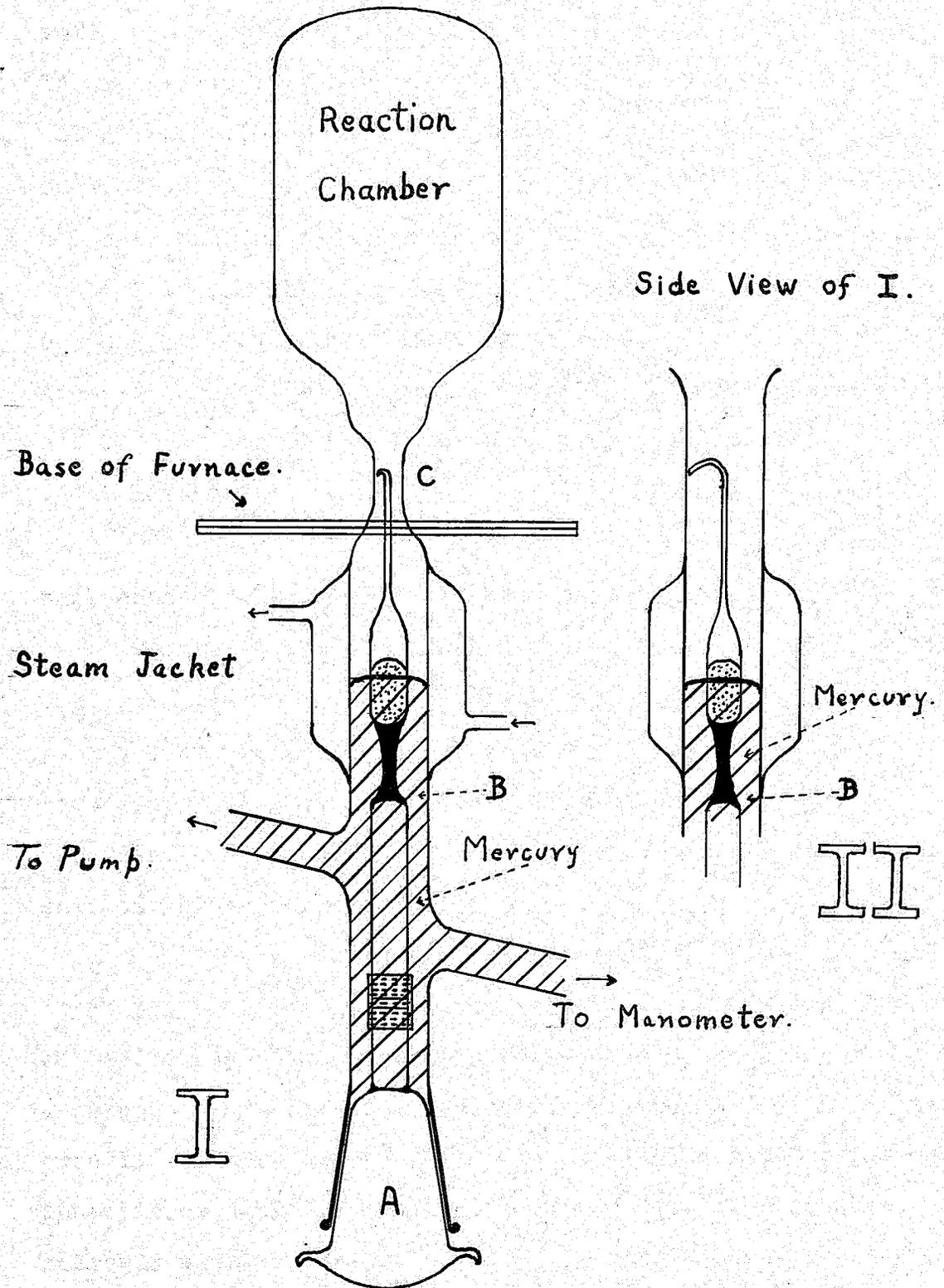
The apparatus used during the earlier part of the research was the same as that used on some previous reaction work at this University. Details of the apparatus and the method of using it are given in a paper on "The Thermal Decomposition of Crotonaldehyde". Trans. of Roy. Soc. of Can. Sec. III, 1936, P.66.

Modified Apparatus

Later on a modification was made in the apparatus which materially improves the ease of operation. A short glass rod was sealed on to the plug A. Another glass rod of length such as to reach the pt. B was fastened to the short piece by means of rubber tubing. This gives a necessary flexibility. The neck of the reaction chamber

See Diagram (Face p.3)

DIAGRAM OF NEW APPARATUS



was flattened at C. Diagram II shows an enlargement of this constriction. The sample bulb was constructed with a solid glass tip, about $\frac{3}{4}$ " long, on one end and a fairly large capillary on the other end. After it was filled with the sample the tip was sealed off and then bent into an hook as shown in III. The capillary must be made of such a length that when everything is in place the hook lies in the constriction. The sample bulb was sealed on to the long glass rod at B. It is important that the sample bulb is not in the furnace, for ^{if} it gets too warm it will explode. At a temperature of 100° however the pressure does not exceed 3 atmos. for butyraldehyde.

When ready to start the plug was turned until the hook snapped off. The butyraldehyde being at a pressure of 2 - 3 atmos. immediately rushed up into furnace providing the capillary was not too fine. Within 15 seconds at the most the aldehyde had reached the temperature of the furnace and the reaction had begun. The stop-cock to the pressure reading apparatus was then opened. From then on the process was the same as in the former method.

The advantages of this method are (1) A more definite initial time can be obtained. (2) There is no danger of losing any of the sample due to spilling in the part of the apparatus below the steam jacket. This was a difficulty frequently met with before. (3) The Hg level can be set at one's convenience, and hence if the expected initial pressure corresponds with the actual initial pressure a more accurate

initial time can be found.

Preparation of the Butyraldehyde.

I. A quantity of butyraldehyde prepared by the British Drug House was fractionated four times, the last fraction had the temperature range of $74.1 - 74.6^{\circ}$. The recorded boiling point of butyraldehyde is 75.7° C. The thermometer correction has been allowed for. The index of refraction, measured by a Pulfrich Refractometer, and in an atmosphere of air gave a value of 1.28483. The recorded value is 1.38433.

This product was used in Runs 4, 5 and 6.

II. Preparation of butyraldehyde by synthesis. This method ~~is~~^{was} adapted for butyraldehyde from a method for preparing Propionic aldehyde. (Reference 8). A mixture of 1000 c.c. of H_2O , 120 c.c. conc. H_2SO_4 and 121 g. of $K_2Cr_2O_7$ was added to 120 g. of butyl alcohol by means of a dropping funnel. About one hour was required to add the mixture. The butyl alcohol was contained in a 2 litre flask and heated in an oil bath at a temperature of about $105^{\circ} - 110^{\circ}$. The reactants must be thoroughly, in fact, violently, stirred. The efficiency of the reaction depends on this to a large extent.

A mixture of BuOH, H_2O , and BuAl vapor pass through a reflux condenser. This was kept at about 80° preferably. If the temperature was higher more butyl alcohol and more water went over into the cold condenser and so into the receiver. The reflux condenser, it was found, must be long - about 3 feet - for best results. The temperature of the oil bath was not

allowed to be much over 110° otherwise the formation of water vapor was so rapid as to carry the butyl alcohol clear through the reflux condenser and into the receiver. The neck and side arm of the reaction flask were insulated.

The layers were separated and the upper one was dried with calcium chloride and then fractionated twice in the presence of calcium chloride and once again without calcium chloride. This fraction had a B.P. range of $75.1 - 76.0^{\circ}$. The index of refraction was measured and found to be 1.38460. The accepted value is 1.38433. It seemed, therefore, that in spite of the wide B.P. range, the product was quite pure.

A more accurate idea of the purity of the butyraldehyde was obtained in the following manner. I assumed a linear relation for the variation of index of refraction with composition; also I assumed that the chief impurity is butyl alcohol. From graph No. 4, I obtained an impurity of 1.6% in the butyraldehyde which had an index of refraction of 1.38460. The accuracy of the assumption is unknown, but nevertheless it is indicated how close to the correct index of the refraction the observed value must be before the compound whose index of refraction is being tested can be considered even fairly pure.

III. Purification by Precipitation. An attempt was ^{made} to purify butyraldehyde by precipitating it as BuAlNH_3 , and then liberating the BuAl . NH_3 (which must be dry) when passed into a solution of BuAl in ether at 0° C. precipitates white crystalline BuAlNH_3 . This compound decomposes readily into BuAl and

NH_3 at room temperatures. This method was abandoned in favor of the synthesis process and the distillation of the commercial product because of the great difficulty that was encountered in obtaining completely dry NH_3 .

Beilstein does not give methods of purifying butyr-aldehyde.

Treatment of Data.

(1). Initial and Final Pressures.

In treating the experimental data the initial pressure was usually the first to receive attention. It was found graphically as follows:

The initial time being known the pressure readings were plotted against the corresponding time readings. Then the curve was extrapolated back until it cut the pressure axis. This intersection gave the initial pressure.

The question arose: What is the initial time? It takes some time for the gas to warm up to the temperature of the furnace. If this time is relatively long decomposition will begin before the temperature has reached its maximum value and consequently the sudden increase in pressure which indicates the initial time will not be observed. On the other hand if the time of warming up is rapid the gas reaches the temperature before an appreciable amount of it has had a chance to decompose. Hence the first upward surge of pressure when decomposition has begun will be more accurately observable.

To determine how long a time is required for the gas to reach the temperature of the furnace samples of ethyl alcohol were introduced into the furnace, which was at a temperature of 426°C . Ethyl alcohol does not ^{de}compose at this temperature hence when the vapour has reached the temperature of 426° the pressure becomes constant. It was found that not more than fifteen seconds is required for the pressure to become constant. Therefore the initial time was observed with an accuracy of a few seconds when the expected initial pressure was fairly close to the actual initial pressure. However, if it was not, a few seconds were lost in adjusting the pressure in the monometer until it was possible to open the stopcock between the reaction bulb and the monometer.

Next came the problem of obtaining the final pressure. Three methods were used. The first was to allow the run to go until the pressure increase became very small and sensibly linear. The idea being that this small steady increase is due to the decomposition of some of the products. It was found, however, that the pressure increases due to the secondary reactions were sometimes so pronounced as to give a final pressure that was much too high. Especially was this so at higher temperatures. This difficulty was circumnavigated in two ways. One was to plot the pressure-time data until the curve began to show definite signs of approaching an asymptote. It was then extrapolated to this asymptote, which was taken as the final pressure. But this method also failed

at higher temperatures, due to the fact that the effect of secondary reactions became apparent earlier in the runs. Consequently a third method of obtaining the final pressure was used on Runs 11, 12 and 13 which were made at 480° C. This method, due to Hinshelwood, is an approximate method of eliminating the effects of the secondary reactions. The pressure-time data was plotted as usual. The last few points generally lie on a nearly straight line. A line was drawn through these points and extended so as to intersect the pressure axis. From the point of intersection another straight line was drawn parallel to the time axis. (See graphs 1, 2, 3). Next, a new curve was located by moving the points down an amount equal to the distance between the two lines mentioned above. On the graphs the points marked "O" represent the data as observed, the points marked "X" are the "corrected" points. The basis of this method is the assumption that the decompositions involved in the secondary reactions give, for the temperature in question, a linear pressure-time relation. This is very nearly the case.

(2) A Note on Construction of Tables.

The tables deal with Runs 1, 3, 4, 5, 6, 9, 10, 11, 12 and 13. Runs 2 and 7 are omitted because they were spoiled by seepage of butyraldehyde into reaction bulb after the start. This material resulted from spilling when tip was broken. Run 8 is discussed but has no table.

In Tables I to VII the method used in obtaining the

final pressure is noted. When it says "p_f obtained by direct observation" the first method was the one used. In the case where it says "p_f obtained by extrapolation" the second method was used.

In Tables VIII, IX and X the method was that of Hinshelwood, or the third method. Furthermore, these three tables are based upon Graphs 1, 2 and 3 respectively, and not upon the observed data as are Tables I to VII. Thus the values for the pressure and time columns are read off the corrected curves.

(3) Order of the Reaction.

(a) First method of approach.

A method of obtaining some idea of the order of the reaction is to calculate the first and second order constants. This was done and the results are given in Tables I to X. In calculating the first order constant the usual equation was used

$$k_1 = \frac{2.303}{t} \log_{10} \frac{p_f - p_i}{p_f - p}$$

where t is the time, p_f is the final pressure, p_i is the initial pressure, p the pressure in the reaction chamber at any time t.

To calculate the second order constants the equation used was

$$k_2 = \frac{1}{t} \frac{\frac{p}{p_i} - 1}{p_f - p}$$

where the symbols have the same significance as in the previous

equation.

Perhaps at this point the construction of the Tables I to VII should be noted. The column headed "Observation No." gives the number of the reading taken on the apparatus for that particular run. The column headed "Time" gives the time taken from the beginning of the reaction for the corresponding reading. The column headed "Pressure" gives the pressure in the reaction chamber.

In the following paragraphs the first and second order constants will be discussed. k_1 of Table I cannot be compared with other values of k_1 since Run #9 is the only run of this group of ten which was made at 388° C. It is noted however, that the reaction appears to be first order from $\frac{1}{2}$ life to $\frac{3}{4}$ life. The second order constant displays a characteristic which was found in several other runs, namely that it drops to a minimum and then rises again. One other fact of interest appears - both constants drop off from a relatively high value at the beginning. This fact was observed in nearly every run. More will be said about it later.

Next Table II and III will be discussed. They are at approximately the same temperature 433° and 429° C. respectively. Although the runs were made at practically the same temperature they do not compare. Thus the k_1 of run #1 is of quite different value to that of run #2 and furthermore increases with time rather than decreases which is the usual process. The second order constants are also of quite

different magnitude. k_2 of run 1, however, has that effect of dropping off to a minimum and then rising. Just precisely the cause of these anomalies is not known but the information is given for what it may be worth that the butyric aldehyde used in Run #1 was some prepared in May 1936 - the run being made in November 1936 - while the material used in Run #10 was made by the synthesis process (as described earlier in this report) eight days previous to its use.

Since Tables IV, V, VI and VII all deal with runs made at the temperature 455° C. they will be discussed as a group. They all run more or less parallel. Thus the first order constants are of the same magnitude and tend to fall off with increasing time in the same manner, with the exception of Run #6 in which there is a pronounced high value in the early part of the run. This seems to be the high first values of the rate constants observed in most of the runs coming into sharper prominence than usual. The second order constants do not agree with one another quite so well, but the "minimum" effect appears in three out of the four runs, namely in Runs #4, #5, and #6. The butyric aldehyde used in Run #3 was prepared in May 1936. The run was made in November 1936. The material used in Runs #4, #5 and #6 was prepared by distillation from the British Drug House butyric aldehyde (see preparation of Butraldehyde in this report.).

The last three of the Tables, VIII, IX and X, will also be discussed as a group since they pertain to runs made at

480° C. The first two are closely parallel but the third is anomalous. It (Run #13) is quite different from any previous run. Thus, for example, the first order constant begins at a minimum, rises and then falls. The second order constant begins at a minimum and then rises continuously. In every other case of the ten given the initial values of both constants are ^{as} high/compared to later values. No explanation can be offered by the writer. The material was the same as that used in Run #12 and in every other respect the conditions were the same as those of Run #11 and Run #12.

Returning to Runs #11 and #12, i.e., Tables VIII and IX, it is seen that the initial values of the constants are high but not as high as is generally the case. The second order constants tend to drop to a minimum and then rise, but the change is small, so small that there is indication that the reaction is second order at 480° C. The first order constants show their usual tendency to diminish with time. Material used in Run #11 was prepared by synthesis (see Preparation of Butyraldehyde). The material of Run #12 was the same as that of Run #11 except that it was distilled just before using.

That polymerization or formation of higher boiling point compounds by some method or other takes place in the stored butyraldehyde is suspected for the following reasons: In distilling the material for Run #12 a considerable residue of a high boiling point was left in the flask. In a number of cases there have been a residue left in the sample bulb,

but in the case of Run #12 where a freshly distilled sample was used no residue remained. In cases where there was no residue the material had left the bulb so quickly as to carry all with it.

It may be noted here that Runs #11, #12 and #13 were made with the modified apparatus described under Experimental Method.

(b) Second Method of Approach.

Certain criteria may be made use of to ascertain the order of a reaction. One is the fact that if a reaction is unimolecular the rate is independent of the initial pressure and as a consequence the half life period for each of several such reactions, at a given temperature, should be the same. The same applies to $\frac{1}{4}$ life and $\frac{3}{4}$ life of course. Table XI has been compiled so as to show up any such relationship if it exists. It will be discussed later.

Another criterion of the order is: if the reaction is unimolecular, i.e., first order, then

$$\frac{t_{\frac{1}{4}}}{t_{\frac{1}{2}}} = .41 \quad \text{and} \quad \frac{t_{\frac{3}{4}}}{t_{\frac{1}{2}}} = 2$$

If it is second order, then

$$\frac{t_{\frac{1}{4}}}{t_{\frac{1}{2}}} = .33 \quad \text{and} \quad \frac{t_{\frac{3}{4}}}{t_{\frac{1}{2}}} = 3$$

The derivation of these relationships is as follows:

For a first order reaction

$$k_1 t = 2.3 \log_{10} \frac{p_f - p_i}{p_f - p}$$

but $p_a = \frac{p_f - p}{N - 1}$

where p_a is the partial pressure of the reactant. $N = \frac{p_f}{p_i}$

$$k_1 t = 2.3 \log_{10} \frac{p_f - p_i}{(N-1)p_a}$$

Now for $\frac{1}{4}$ life $p_a = \frac{3}{4}p_i$

$$\begin{aligned} \therefore k_1 t_{\frac{1}{4}} &= 2.3 \log_{10} \frac{p_f - p_i}{\left(\frac{p_f}{p_i} - 1\right) \frac{3}{4} p_i} \\ &= 2.3 \log_{10} 4/3. \end{aligned}$$

For $\frac{1}{2}$ life:

$$k_1 t_{\frac{1}{2}} = 2.3 \log_{10} 2$$

Division of $k_1 t_{\frac{1}{4}}$ by $k_1 t_{\frac{1}{2}}$ gives the first relationship

$$\frac{t_{\frac{1}{4}}}{t_{\frac{1}{2}}} = .41$$

The other expressions are derived in a similar manner; the ratios giving the condition for second order coming from the

equation $k_2 t = \frac{p/p_i - 1}{p_f - p}$

Table XI gives the ratios of the $\frac{1}{4}$ life to $\frac{1}{2}$ life and the $\frac{3}{4}$ life to the $\frac{1}{2}$ life calculated from the experimental data.

Having set up the criteria for the use of Table XI the following will give an analysis of the table and will compare the conclusions thereof with the previous conclusions regarding the order. Run #9 shows a tendency to be first order; Table I, (Run #9) shows a similar tendency.

Runs #1 & #10 from a consideration of their $\frac{1}{4}$ life and $\frac{1}{2}$ life periods appears to be first order. The same conclusion is arrived at from a consideration of the ratios. But examination of the Tables #II and #III show no such tendency. Runs #3, #4, #5 and #6 from an examination of the ratios of their $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$ lives show a much greater tendency to be second order than first order. Furthermore there is practically no correlation between the four quarter lives, half lives and three-quarter lives. These conclusions agree in a qualitative way with the fact that Tables IV, V, VI and VII show the reaction to be more second order than first. However, from this data it cannot be definitely said that the reaction is second order.

From the facts that the $\frac{1}{4}$ lives, $\frac{1}{2}$ lives and $\frac{3}{4}$ lives of Runs #11 and #12 correspond closely one might conclude that the reaction, for the temperature of 480° , is first order, but the ratios of the lives indicate second order. Furthermore, the Tables VIII and IX indicate the reaction to be second order.

Run #13 is anomalous here as well as in Table X.

The general conclusion from the foregoing discussion

is that at lower temperatures the reaction shows only a tendency to be first order, but as the temperature is raised the reaction approaches the second order. This statement is confined to the temperature range 400 - 500° C. Some unpublished work by Norton Wilson at this University in part substantiates this conclusion. He concluded that "the reaction is quite closely first order at 435° C. but approaches second order as the temperature is raised."

(4) Run #8 - A Peculiar Phenomenon.

It was decided to make some runs at a lower temperature and so the temperature of the furnace was dropped to 394° C. A sample of butyraldehyde prepared by the synthesis method (see page 4) was introduced into the ^{reaction bulb} ~~pressure~~ immediately. The initial pressure was 12¹²⁸8.m.m. Instead of the pressure rising as is usually the case, the pressure fell during the first 43 minutes and only then began to rise. It was two hours from the beginning before the pressure returned to its initial value. Run #9 was made with the hope of duplicating this phenomenon but no success was had. However, Norton Wilson working in this same research, the year before, reports in some unpublished work the same phenomenon and also that he was unable to duplicate it. About the same length of time as in the present case was required for the pressure, in his case, to reach its original value. But, in his case the phenomenon was more pronounced - the pressure dropping 13.1 m.m. from an initial value of 105.3. In the present case

the pressure dropped only 4.5 m.m.

An explanation might be that the glass walls of the reaction bulb happened to be in a state such that they acted catalytically on the butyraldehyde to form a relatively stable polymer which during the first 43 minutes possessed a formation rate greater than the decomposition rate.

(5) An Hypothesis for the High Initial Values of the Rate Constants.

In every Run represented by the Tables I to X with the exception of the Run #13 high initial values of k_1 were found. The equation for the first order constant is:

$$k_1 = \frac{1}{t} \log_2 \frac{p_f - p_i}{p_f - p}$$

If polymerization is assumed to take place the observed pressure results in a larger value of k_1 than would be expected without polymerization. After some time, which is around 300 seconds for the temperature 485° C., the "constant" k_1 approaches its "normal" values. This may be explained on the basis that polymerization has ceased and that the pressures observed are entirely due to decomposition products of butyraldehyde. The rate of polymerization would determine the degree to which the initial values of k_1 would vary from their "normal" values. Run #6 (Table VII) for example has very high initial values of k_1 ; thus, on the basis of the hypothesis, the rate of polymerization for Run #6 would be high.

The assumption of polymerization was suggested by Run #8 with its peculiarity.

The treatment of k_2 is similar:

$$k_2 = \frac{1}{t} \frac{p/p_1 - 1}{p_f - p}$$

If p is smaller than expected then k_2 will be larger than expected, for the denominator of this expression becomes smaller much faster than the numerator as p is diminished. Thus the assumption applies also to the second order "constants" which, experimentally, display the same phenomena as the first order "constants".

Gas Analysis.

Owing to the fact that a new apparatus for gas analysis was being tested during the period of this research, only a few analyses were made. In all but one it was found that the apparatus had leaked, so that only one analysis is available. The analysis given by Norton Wilson in his report (unpublished) will be given here for the purpose of comparison.

	I	II
CO ₂	0.3%	1.9%
CO	38.0%	35.8%
O ₂	0.0%	0.0%
H ₂	2.5%	1.9%
C ₂ H ₄	8.4%	17.3%
C ₃ H ₆	8.0%	1.4%
CH ₄	23.0%	
C ₂ H ₆	13.0%	44%
C ₃ H ₈	8.0%	

Column I gives the figures of Norton Wilson, and they are for a run made at 435° C. Column II gives the figures obtained from the analysis of Run #12 in this research. The temperature of the run was 480° C., the initial pressure 169 mm. In this case the saturated hydrocarbons were determined as a group. The two sets of figures are in fair agreement with the exception of the unsaturated hydrocarbons. This discrepancy is to be expected because propylene decomposes at a relatively rapid rate at 480° ⁽¹⁰⁾.

As yet due to insufficient data no attempt has been made to work out a mechanism of the reactions with the aid of this gas analysis.

Energy of Activation:

The energy of activation calculated from the half lives of Runs #4, #10 and #11 and their corresponding temp-

eratures is 22,700 calories per mole. The value of the energy of the activation calculated by Norton Wilson (unpublished work) from his rate constants at 435 and 455° C. was about 50,000 calories per mole.

Summary.

A new apparatus for introducing butyraldehyde into the reaction chamber has been described.

The reaction, in the temperature range 390 - 480° C., shows a tendency to be first order at the lower temperatures but approaches the second order as the temperature is raised.

The pressure range studied was from 96 m.m. to 310 m.m of Hg.

An hypothesis to explain the high initial values of the rate constants has been suggested.

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Table I.

Run #9	Temperature 388°	N = 2.32	\bar{x} p _f = 236 m.m.	
No. of Reading	Time (mins)	Pressure (m.m)	k ₁ (t in secs)	k ₂ (t in secs)
2	3	103.3	5.36 x 10 ⁻⁵	5.44 x 10 ⁻⁷
3	5	103.7	4.22 x 10 ⁻⁶	
5	8.5	104.6		3.88 x 10 ⁻⁷
6	16	105.6	1.87	2.76
8	69.	109.4		1.47
10	156	115.5		1.21
13	176	116.1	1.05	1.12
17	221	118.1		1.07
22	365	127.0		1.04
24	425	180.0	.96	1.10
29	687	143.4		1.08
33	933	153.6	.87	1.11
37	1099	146.0		1.16
38	1361	169.0	.84	1.21
43	1648	178.9	.86	1.33

* p_f obtained by direct observation.

$\frac{1}{4}$ life period = 525 min.

$\frac{1}{2}$ life period = 1345 min.

$\frac{3}{4}$ life period = 2165 min.

Table II.

Run # 1. Temperature 433^o. *
 $p_f = 546$ m.m. $p_i = 251$ m.m.

$$\frac{p_f}{p_i} = N = 2.18$$

Observ- ation No.	Pressure (m.m.)	Time (secs)	k_1	k_2
1	253.3	210	3.28×10^{-5}	2.86×10^{-7}
2	256.1	455	4.15	1.67
3	260.5	1005	3.23	1.60
5	265.3	1635	2.98	1.35
7	272.8	2325	3.30	1.50
9	288.9	3400	4.04	1.80
11	307.9	4620	4.60	2.10
14	343.5	2010	5.35	2.62
19	408.9	12445	6.20	3.70
21	444.5	16320	6.55	4.65

* p_f obtained by direct observation.

$\frac{1}{2}$ life period 5350

$\frac{1}{2}$ life period 11200

Table III.

Run #10.

Temperature 429°

* $p_f = 283 \text{ mm. } p_i = 117 \text{ mm.}$

$$N = \frac{p_f}{p_i} = 2.42$$

Obs.No.	Time (mins)	Pressure (m.m.)	k_1	k_2
2	1.50	119.3	1.53×10^{-4}	1.36×10^{-6}
4	3.25	121.1	1.30	1.14
6	7.75	124.1	0.89	0.83
7	12.00	127.2	0.86	0.78
9	36.75	137.2	0.72	0.44
11	64.25	156.6	0.70	0.27
13	93.75	175.0	0.69	0.23
15	328.75	229.9	0.58	0.19
20	528.75	254.3	0.55	0.13

* p_f observed directly.

$\frac{1}{4}$ life period = 73 mins.

$\frac{1}{2}$ life period = 190 min.

$\frac{3}{4}$ life period = 400 min.

Table IVI.

Run #3.

Temp. 455°.

*
 $p_f = 722.$

$p_i = 310.$

$N = 2.33$

Obs.No.	Time (secs)	Pressure (m.m.)	k_1	k_2
1	65	327.3	634×10^{-4}	2.14×10^{-6}
2	120	340.3	6.40	2.
3	220	357.5	5.62	1.87
4	330	373.3	5.06	
6	510	395.4	4.53	1.66
8	940	435.8	3.98	
11	1735	486.5	3.22	1.35
13	3130	541.3	2.63	1.33
16	5700	595.8	2.07	1.28
19	8325	629.6	1.79	1.22

*
 p_f obtained by assuming $N = 2.33$ from previous work and calculating from p_i . This had to be done because the reaction was allowed to proceed too far before a final readings were taken, secondary reactions thus set in and as a consequence the pressure became too high.

$\frac{1}{4}$ life = 690 secs.

$\frac{1}{2}$ life = 2,400 secs.

$\frac{3}{4}$ life = 7,500 secs.

Table V.

Run #4. Temp. 455°. *
 $p_f = 406$ m.m. $p_i = 2.1$ m.m.
 $N = 2.1$

Obs.No.	Time (secs)	Pressure (m.m.)	k_1	k_2
1	210	210.0	4.01×10^{-4}	2.10×10^{-6}
2	290	215.7	3.90	2.14
4	600	232.0	3.35	1.93
5	780	238.6		1.82
6	940	244.9		1.76
7	1285	256.4	2.75	1.68
9	2060	278.2		1.66
10	3070	301.1	2.28	1.69
12	4510	321.9	2.06	1.75
15	8000	353.5	1.75	2.00

* p_f obtained by direct observation.

$\frac{1}{4}$ life period = 1000 secs.

$\frac{1}{2}$ life period = 3000 secs.

$\frac{3}{4}$ life period = 8000 secs.

Table VI.

Run #5.

Temp. 455°

*
 $p_f = 310.$ $p_i = 136.$

$N = 2.28$

Obs.No.	Time (secs)	Pressure (m.m.)	k_1	k_3
1	210	152.1	4.60×10^{-4}	3.52×10^{-6}
2	320	158.8	4.38	3.50
3	470	166.4	4.07	3.34
4	700	172.5	3.42	2.85
5	855	179.1	3.28	2.81
7	1420	193.1	2.79	2.52
9	2325	210.1		2.35
11	3435	225.0		2.24
13	5080	243.1	1.87	2.31
15	7190	258.4		2.40
17	9240	270.1	1.59	2.67
18	10500	275.0	1.	2.78

*
 p_f obtained by direct observation.

$\frac{1}{4}$ life period = 870 secs. $\frac{1}{2}$ life period = 3,200 secs.

$\frac{3}{4}$ life period = 8,520 secs.

Table VII.

Run # 6.

Temp. 455°

$$* P_f = 244 \text{ m.m.} \quad P_i = 96 \text{ m.m.}$$

$$N = \frac{P_f}{P_i} = 2.54$$

Obs.No.	Time (secs)	Pressure (m.m.)	k_1	k_2
1	10	99.4	22000×10^{-4}	2.10×10^{-5}
2	120	112.8	10.1	1.34
3	155	118.9	10.9	1.23
4	230	125.7	9.8	1.15
5	330	132.8	8.7	1.06
8	945	152.6	5.1	0.69
10	1720	166.9	3.3	0.56
12	2690	180.9	3.1	0.52
14	3810	193.6	2.9	0.54
16	5040	203.9	2.7	0.56
18	6480	212.6	2.4	0.61
20	8280	220.8	2.3	0.69

* p_f obtained by extrapolation of the p - t curve to infinite time.

$\frac{1}{4}$ life-period = 330 secs.

$\frac{1}{2}$ life-period = 1900 secs.

$\frac{3}{4}$ life-period = 5,600 secs.

Table VIII.

Based on Corrected Curve.

Run #11.

Temp. 480°

$p_f = 455$ m.m. $p_i = 190$

$$N = \frac{p_f}{p_i} = 2.40$$

Time (Secs)	Pressure (m.m.)	k_1	k_2
85	225.6	1.70×10^{-3}	$.94 \times 10^{-5}$
150	242.0	1.46	.86
200	255.0	1.44	.82
400	290.0	1.18	.795
660	322.0	1.04	.79
750	334.0		.84
900	349.0	1.02	.88
1200	369.0		.91
1570	387.0	.88	1.06

$\frac{1}{4}$ life period = 200 secs.

$\frac{1}{2}$ life period = 660 secs

$\frac{3}{4}$ life period = 1570 secs.

Table IX.

Based on Corrected Curve.

Run #12.

Temp. 480°

$p_f = 360$ m.m. $p_i = 169$ m.m.

$$\frac{p_f}{p_i} = N = 2.13$$

Time(secs)	Pressure (m.m.)	k_1	k_2
100	200	1.75×10^{-3}	1.16×10^{-5}
190	217	1.52	1.05
300	230		0.92
500	252	1.14	1.06
650	265	1.01	0.92
900	282		0.96
1200	297	0.93	1.00
1600	312	0.87	1.13

$\frac{1}{4}$ life period = 190 secs.

$\frac{1}{2}$ life period = 650 secs.

$\frac{3}{4}$ life period = 1600 secs.

Table X.

Based on Corrected Curve.

Run #13.

Temp. 480°

$p_f = 543$ m.m. $p_i = 245$ m.m.

$$N = \frac{p_f}{p_i} = 2.22$$

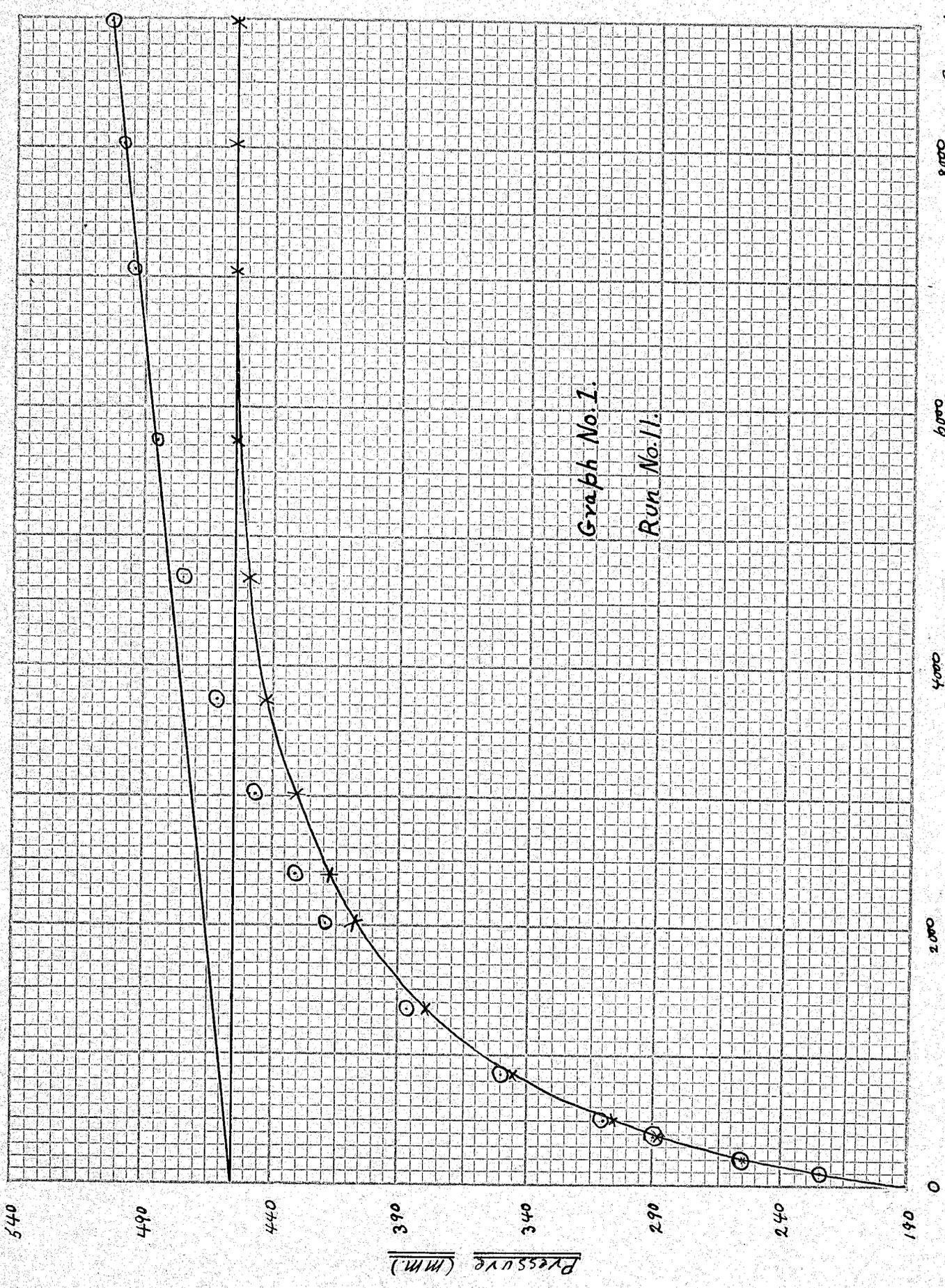
Time (secs)	Pressure(m.m)	k_1	k_2
30	251.4	$.75 \times 10^{-3}$	$.30 \times 10^{-5}$
105	269.8	.82	.35
225	296.1	.83	.38
340 $t_{\frac{1}{4}}$	319.0	.84	.39
500	347.0	.84	.43
700	373.0	.80	.44
870 $t_{\frac{1}{2}}$	394.0	.79	.47
1200	424.0		.51
1865 $t_{\frac{3}{4}}$	468.0	.74	.67
2500	494.0		.83

$\frac{1}{4}$ life period = 340 secs. $\frac{1}{2}$ life period = 870 secs.

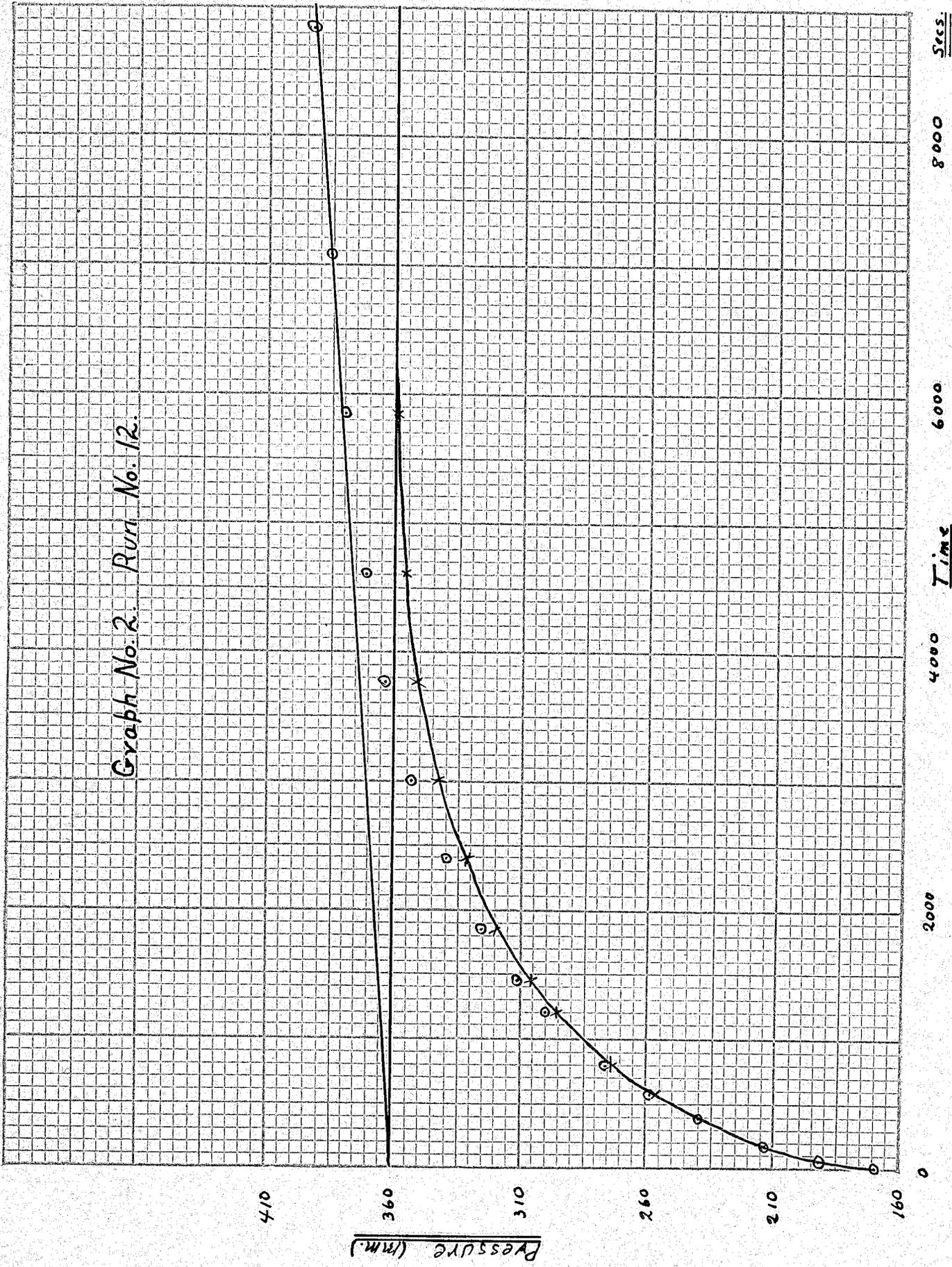
$\frac{3}{4}$ life period = 1865 secs.

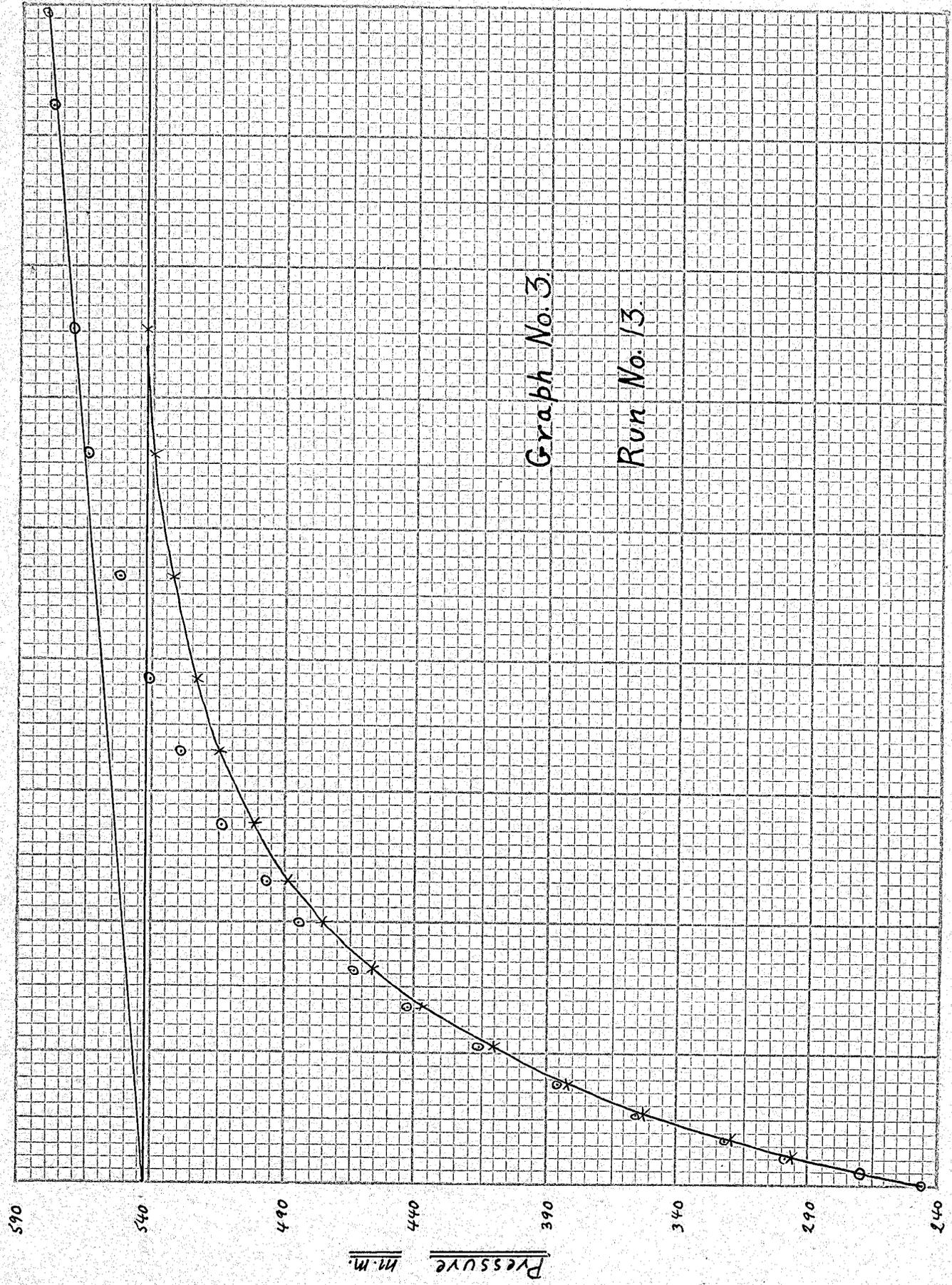
Table XI.

Run.	Temp.	Init'l Pressure.	$\frac{1}{4}$ life	$\frac{1}{2}$ life	$\frac{3}{4}$ life	$t_{\frac{1}{4}}/t_{\frac{1}{2}}$	$t_{\frac{3}{4}}/t_{\frac{1}{2}}$
9	388°C.	102 m.m.	525 min.	1345 min.	2165 min.	.39	1.61
10	429°	117 "	4380sec.	11400sec.	24000sec.	.38	2.14
1	433°	251 "	5350 "	11200 "	--	.48	--
3	455°	310 "	690 "	2400 "	7500 "	.29	3.12
4	455°	193 "	1000,"	3000 "	8000 "	.30	2.67
5	455°	136 "	870 "	3200 "	8520 "	.27	2.67
6	455°	96 "	330 "	1900 "	5600 "	.17	2.95
k1	480°	190 "	200 "	660 "	1570 "	.30	2.38
12	480°	169 "	190 "	650 "	1600 "	.29	2.46
13	480°	245 "	340 "	870 "	1865 "	.26	2.14



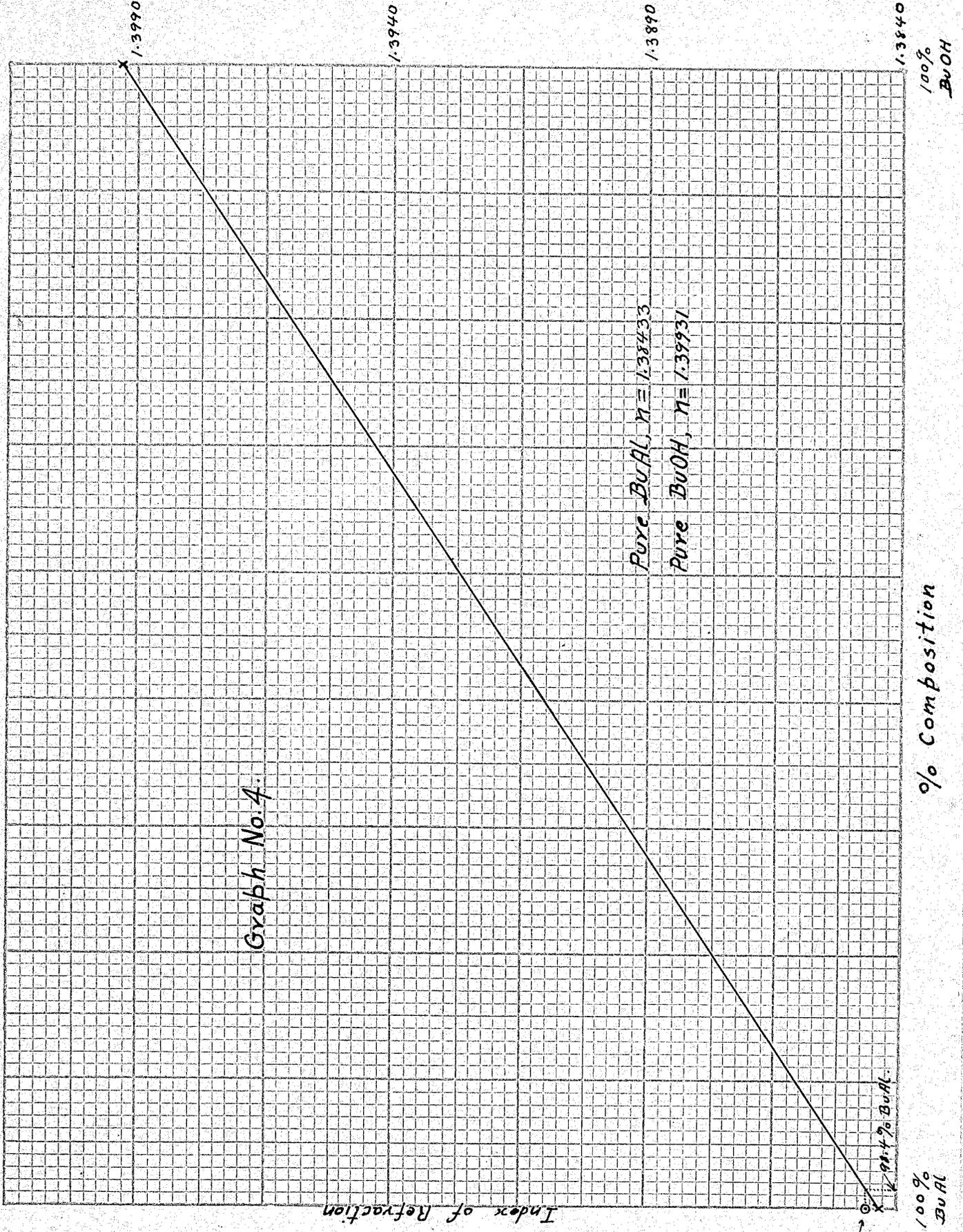
Graph No. 2. Run No. 12.





Graph No. 3.

Run No. 13.



1.3990

1.3940

1.3890

1.3840

100% BuAl

100% BuOH

% Composition

100% BuOH