

USE OF CHLOROSULPHONIC ACID TO DIFFERENTIATE
HYDROCARBON TYPES

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USE OF CHLOROSULFONIC ACID TO DIFFERENTIATE
HYDROCARBON TYPES

THESIS

Presented to the Graduate Council of the North
Texas State Teachers College in Partial
Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

By

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Jacksboro, Texas

June, 1941

90532

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CHAPTER I

DEVELOPMENT OF THE METHOD

The use of chlorosulphonic acid in separation and purification of hydrocarbons has been investigated to some extent, mainly by those interested in the separation of hydrocarbons from petroleum.

Ossian Aschan¹ was among the first investigators of the reactions between chlorosulphonic acid and hydrocarbons. Although he studied rates of reaction, he was primarily interested in the reactions themselves and the products obtained. He worked with the hydrocarbons 2, 3-dimethylbutane and 2-methylbutane. He first concluded that the products of the reactions were hydrogen chloride gas and alkyl sulphonic acids. He later revised these conclusions on the grounds that the products reduced potassium permanganate and the odor was not that of hydrogen chloride. His experiments were done at room temperatures and apparently in open vessels. At a lower temperature and in dry air, the reactions gave no indications but that hydrogen chloride was formed.

¹"Nachweis von Diisopropyl im Petroleumather aus Baker," Berichte der Deutschen Chemischen Gesellschaft Annalen der Chemie, XXXI (1898), 1801.

Shepard and Henne² investigated the possibilities of using chlorosulphonic acid in purifying hydrocarbons obtained from petroleum. They took samples previously fractionated and treated them with the acid. They reported a much more vigorous reaction with branched-chain hydrocarbons than with straight-chain hydrocarbons.

Bruun and Hicks-Bruun³ obtained fractions of Oklahoma crude oil by several distillations and treated samples of the fractions with chlorosulphonic acid. They reported that branched-chain compounds and cyclic compounds were attacked vigorously and were destroyed while normal hydrocarbons were affected only slowly.

Shepard, Henne, and Midgley⁴ treated hydrocarbon fractions with chlorosulphonic acid and then further purified them by fractionation in order to obtain samples pure enough for physical constants to be observed.

Leslie and Schicktanz⁵ treated 200 ml. of previously

²Alvin F. Shepard and Albert T. Henne, "Purification of Normal Paraffin Hydrocarbons by Chlorosulfonic Acid Treatment," Industrial Engineering Chemistry, XXII (1930), 356.

³J. H. Bruun and M. W. Hicks-Bruun, "Isolation of Normal Hexane from a Sample of Oklahoma Crude Oil," Bureau of Standards Journal of Research, VI (1931), 369.

⁴A. F. Shepard, A. L. Henne, and T. Midgley, Jr., "Physical Properties of the Normal Paraffin Hydrocarbons, Pentane to Decane," Journal of American Chemical Society, LIII (1931), 1948.

⁵R. T. Leslie and S. T. Schicktanz, "Separation of Normal Octane from Petroleum by Distillation and Crystallization," Bur. Standards J. Research, VI (1931), 377.

purified normal octane from petroleum with 300 ml. of the acid and stirred the mixture constantly for seven days in order to obtain pure normal octane. They based this process on the former work done by Shepard and Henne.

Stubblefield⁶ studied the reactions of chlorosulphonic acid with saturated hydrocarbons with the purpose of determining the rates of reaction. An attempt was then made to correlate these rates with the molecular structure of the compounds.

The work of Stubblefield was done at 0°C. Shepherd⁷ followed this work with a similar investigation at 30°C. In general, his results indicate that a temperature of 30°C. is too high to be used in the determination of rates of reaction between chlorosulphonic acid and hydrocarbons, since at this temperature the reaction takes place too rapidly for accurate observation, and the odor of SO₂ in the "off gas" indicated oxidation of the hydrocarbons.

This study was begun as a follow-up of the work done by Stubblefield and Shepherd. Since 30°C. was found to be too high for experimental work, the temperature of 10°C. was selected.

⁶H. L. Stubblefield, "Chlorosulphonic Acid Reactions with Saturated Hydrocarbons" (Unpublished Master's thesis, Dept. of Chemistry, North Texas State Teachers College, 1939), p. 1.

⁷George Shepherd, "Reactions of Thionyl Chloride, Sulfuryl Chloride, and Chlorosulfonic Acid with Various Types of Hydrocarbons" (Unpublished Master's thesis, Dept. of Chemistry, North Texas State Teachers College, 1940), p. 19.

It was hoped that the rate of reaction of various types of hydrocarbons with chlorosulphonic acid at this temperature would give enough indications of the molecular structure of the compound to serve as a means of analysis for branched-chain hydrocarbons in a mixture of saturated hydrocarbons.

CHAPTER II

EQUIPMENT AND PROCEDURE

This study was made to compare rates of reaction between chlorosulphonic acid and various types of hydrocarbons. The rate of evolution of gas from each reaction was observed volumetrically and considered a measure of reaction rate. All gas volumes were converted to standard conditions.

To measure the gas the special apparatus shown in Figures 1 and 2 was constructed. This apparatus was made entirely of Pyrex except for a gas burette made of soft glass and a rubber tube about 1.5 cm. long connecting the gas burette with the rest of the set-up. The ends of the glass tubes thus connected were "buted" to minimize contact of gas and rubber. All other connections not sealed were ground glass joints. The reaction vessel was a tube about 2.5 cm. in diameter and 6 cm. high. To it was connected a small burette, made from a 10 ml. graduated cylinder, for admitting the chlorosulphonic acid; an opening with a ground cap served as entrance for the hydrocarbon. A stirring rod connected through a mercury seal to an electric motor kept the substances mixed. The entire reaction vessel was surrounded by water at 10°C. in a refrigerating unit which was controlled by a thermo-regulator, the bath variation being $\pm 0.5^{\circ}\text{C}$.

From the reaction vessel, the gas passed into a compensating tube of about 200 ml. capacity which was connected to a 100 ml. gas burette filled with mercury. The compensating tube protected the mercury by causing the evolved hydrogen chloride to displace air into the burette instead of the hydrogen chloride entering it. The mercury level was adjusted by means of a leveling bulb connected by a rubber tube to the burette. The compensating tube and the burette were enclosed in a larger tube through which water from the tap was constantly flowing. A thermometer inside the water jacket provided a means of measuring the temperature of the gas in the burette. That the gas was kept at atmospheric pressure was shown by the use of a small mercury manometer connected to the burette.

The three-way stopcocks were arranged so that more than 100 ml. of gas could be measured in the burette by shutting it off and expelling the gas. A washing tower filled with glass beads and a measured volume of silver nitrate of known concentration was connected with the exit tube so that the discharged gas would be forced through the silver nitrate solution. This washing tower was connected to an auxiliary washing tower containing a known volume of the silver nitrate solution so that any hydrogen chloride which might pass through the first tower would be caught in the second.

The silver nitrate was standardized as follows: a

solution of silver nitrate of approximately 0.15 normality was made, and a solution of potassium thiocyanate of approximately the same concentration was made. A solution of exactly 0.1 normal hydrochloric acid was made by means of a fixanal. Twenty milliliters of the silver nitrate were then titrated with the potassium thiocyanate, using ferric nitrate as an indicator. In this way the strengths of the potassium thiocyanate and the silver nitrate were obtained in terms of the standard hydrochloric acid as is shown below.

24.4 ml. of KCNS required to titrate 20 ml. of AgNO_3 sol.
13.9 ml. required to titrate 20 ml. of AgNO_3 sol.
 after the addition of 10 ml. of 0.1N HCl
 10.5 ml. of KCNS is equivalent to 10 ml. of 0.1N HCl

Therefore the KCNS was 0.0953N and the AgNO_3 was 0.1160N.

Chemicals for this study were obtained from the Research Division of Eastman Kodak Company, Rochester, New York. The hydrocarbons studied were 2-methylbutane, 2, 2, 4-trimethylpentane, 2, 7-dimethyloctane, normal heptane, normal octane, normal decane, normal tetradecane, cyclohexane, methyl cyclohexane, cyclohexene, benzene, and toluene.

In making runs the apparatus was thoroughly cleaned and dried. Before using the apparatus, dry air was drawn through both the reaction vessel and the compensating tubes and burette. The air was passed through a drying tower containing anhydrous calcium chloride before being admitted to the apparatus. The small burette was filled with

chlorosulphonic acid, and then 5 ml. of the acid were allowed to pass into the reaction vessel. A small quantity of the hydrocarbon contained in a stoppered test tube was immersed in the water of the cooling unit at 10°C. until it had reached a constant temperature. One milliliter of the hydrocarbon at 10°C. was admitted from a pipette and the electric stirrer turned on. The system was then closed and the timing begun. The water in the cooling unit was agitated by an electric stirrer in order that the temperature might be kept more nearly constant. The column of mercury was lowered as gas was given off in order to keep the pressure inside the apparatus the same as atmospheric pressure, and frequent readings of the volume of the gas in the burette were taken. The runs were made of as long a period of time as was required for the termination of gas evolution.

CHAPTER III

DATA AND RESULTS

Data from the reactions between chlorosulphonic acid and hydrocarbons are shown in Tables 3 through 16 in the Appendix.

For the last column in each table showing the course of the reaction between chlorosulphonic acid and the hydrocarbon the volume of the gas was corrected to standard conditions by the equation

$$V = V_0 \times \frac{P_0}{760} \times \frac{273}{T_0}$$

in which V_0 = observed volume, P_0 = observed pressure in millimeters of mercury, and T_0 = observed centigrade temperature + 273.

In studying each reaction it was desirable to know what percentage of the evolved gas was hydrogen chloride. A sample calculation is given below. The hydrocarbon which evolved the gas used in the example was normal heptane. The equivalents of hydrogen chloride equals the equivalents of silver nitrate in the absorption unit less the equivalents of potassium thiocyanate required to titrate the excess silver nitrate after the hydrogen chloride absorption.

$$\text{Equivalents of AgNO}_3 \text{ in unit} = \frac{50 \times .116}{1000} = .0058$$

$$\begin{aligned} \text{Equivalents of KCNS to titrate} \\ \text{excess AgNO}_3 = \frac{26.2 \times .116}{1000} = .0025 \end{aligned}$$

$$\text{Equivalents of hydrogen chloride absorbed} = .0033$$

$$\text{Volume of hydrogen chloride} = 22,400 \times .0033 = 74.2 \text{ ml.}$$

$$\text{Per cent hydrogen chloride in evolved gas} =$$

$$\frac{\text{ml. HCl gas}}{\text{ml. of total gas}} \times 100 = \frac{74.2}{643.8} \times 100 = 51.6 \text{ per cent}$$

Similar data for all hydrocarbons are given in Table 2.

There was no odor of SO_2 in the "off gas".

Cyclohexene, benzene, and toluene were tested but the reaction with chlorosulphonic acid proceeded too rapidly to be measurable.

A study of the results indicates in general that branched-chain hydrocarbons react much more rapidly with chlorosulphonic acid than normal hydrocarbons.

Differentiation among the branch-chain hydrocarbons or among the straight-chain hydrocarbons by this method is difficult. From the results obtained with normal heptane and normal octane, two hydrocarbons with chains of very nearly the same length, it appears that with normal hydrocarbons with approximately the same length chains the rate of evolution of gas is greater with the hydrocarbon having an even number of carbon atoms than with the hydrocarbon having an odd number.

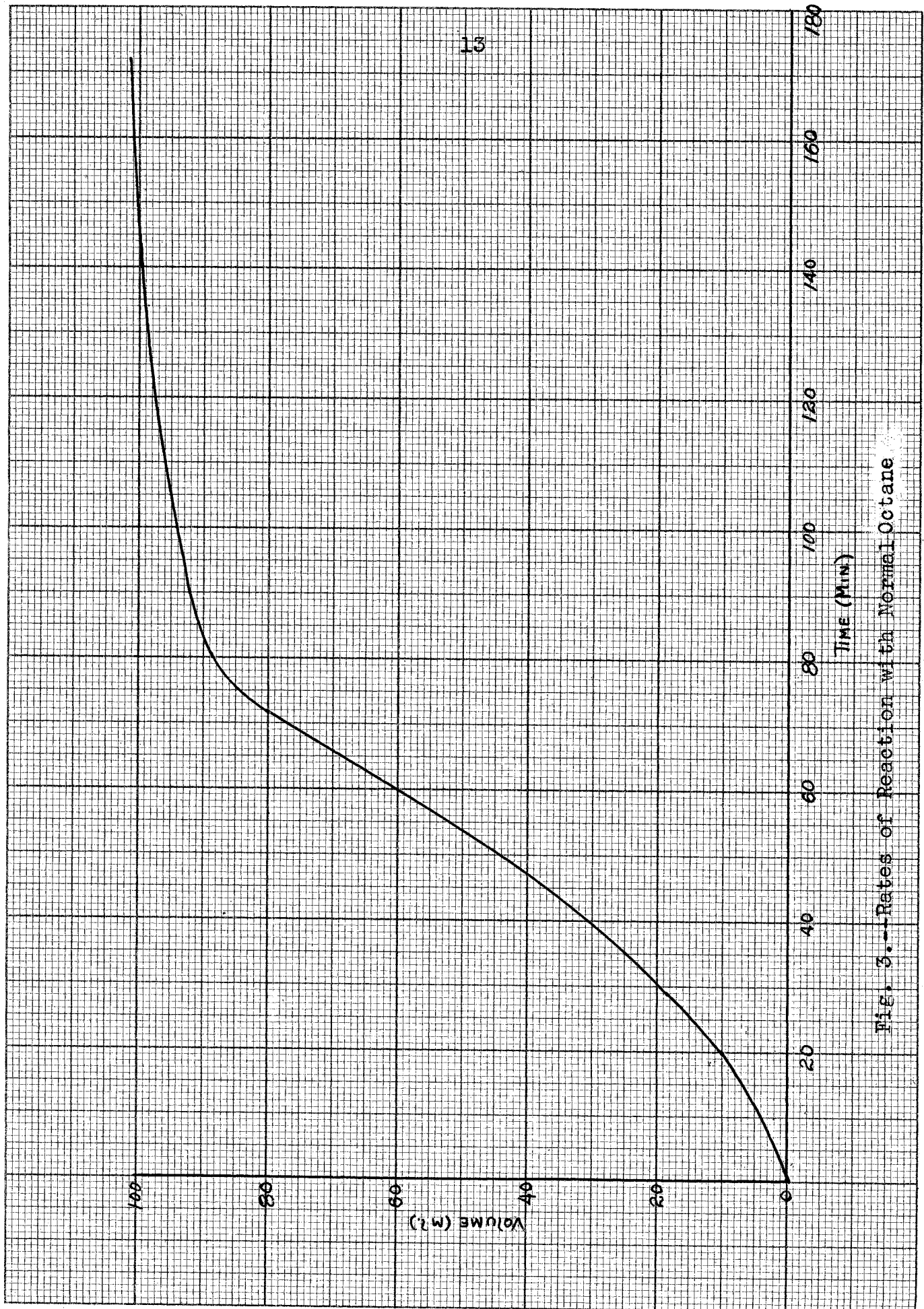


Fig. 3.---Rates of Reaction with Normal Octane

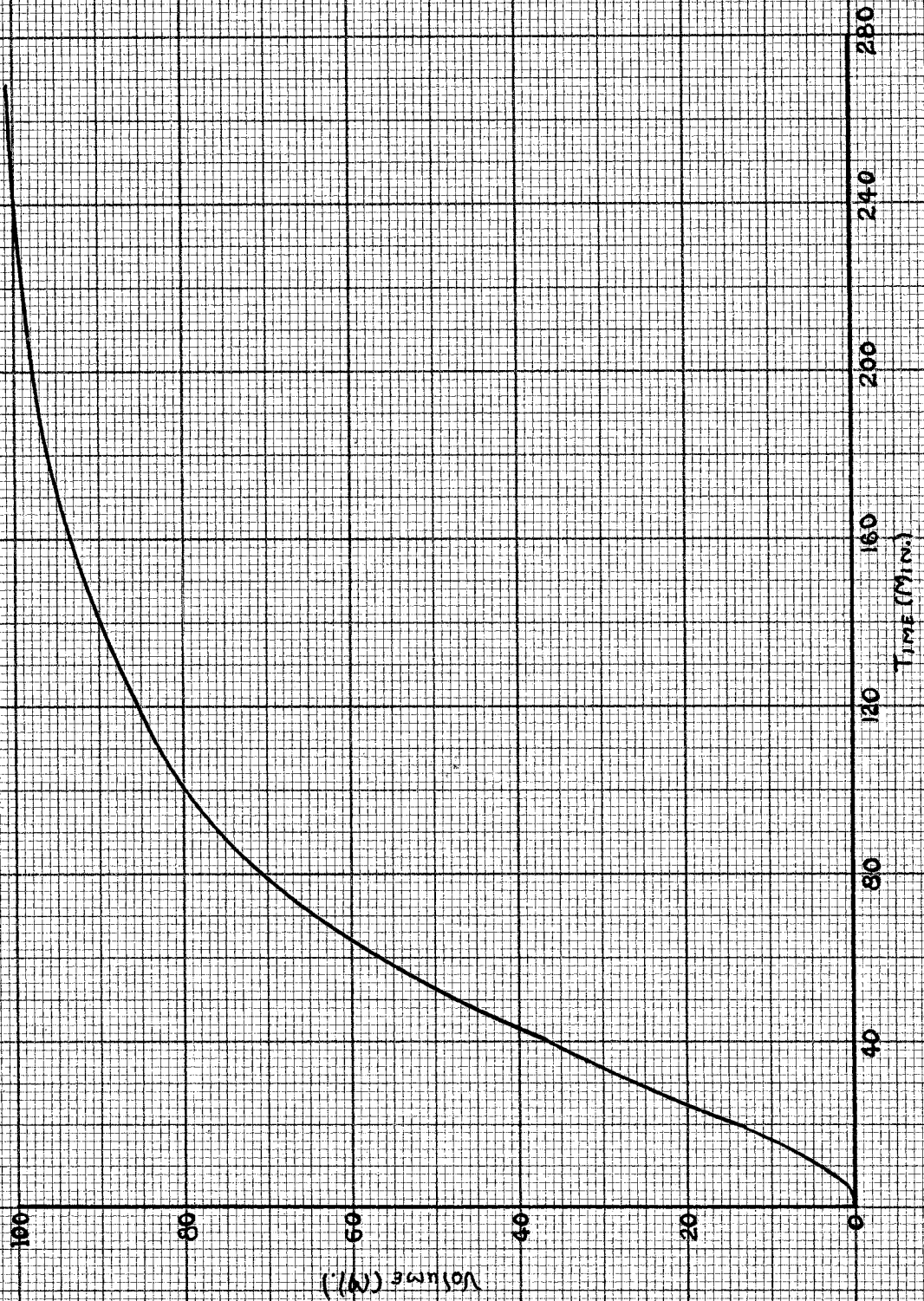


Fig. 4.--Rates of Reaction with Normal Heptane

The results obtained with normal octane and normal tetradecane indicate that an increase in the length of the carbon chain decreases the rate of gas evolution. It should be pointed out, however, that normal decane evolved gas at a slightly more rapid rate than normal octane. This is quite puzzling in view of the fact that Stubblefield¹ found a consistent decrease in rate with an increase in the length of the chain in normal hydrocarbons having an even number of carbon atoms.

The effect of branching in the chain on the rate of reaction may be observed in the results obtained with 2, 2, 4-trimethylpentane and normal octane. Although these hydrocarbons have the same number of carbon atoms in the molecule, an examination of Table 1 will show that the branched-chain hydrocarbon evolved gas over seven times as fast as the normal hydrocarbon. The branched-chain hydrocarbon, 2, 7-dimethyloctane, evolved gas almost twice as fast as the normal hydrocarbon having the same number of carbon atoms, but slower than 2, 2, 4-trimethylpentane.

Branching in cyclic hydrocarbons increases the rate of reaction greatly. Methylcyclohexane evolved gas approximately six times as fast as cyclohexane. Double bonds in cyclic compounds increase the rate of reaction tremendously.

The mixtures of 2, 2, 4-trimethylpentane and normal

¹Stubblefield, op. cit., p. 10.

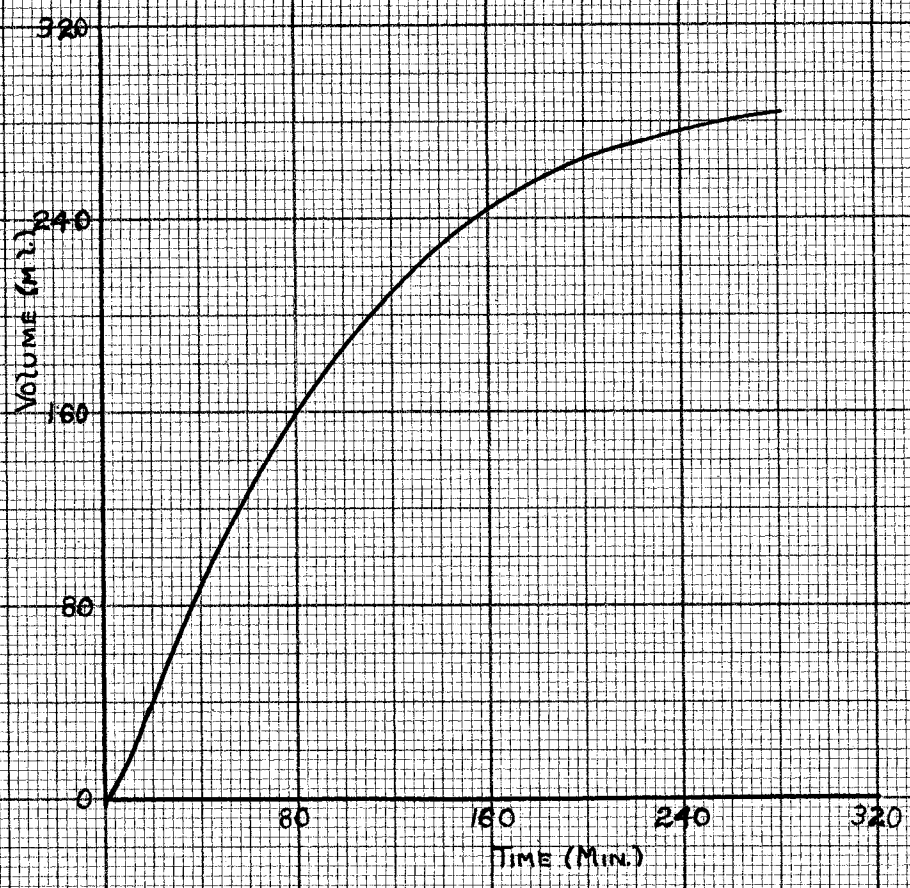


Fig. 5.--Rates of Reaction with Normal Decane.

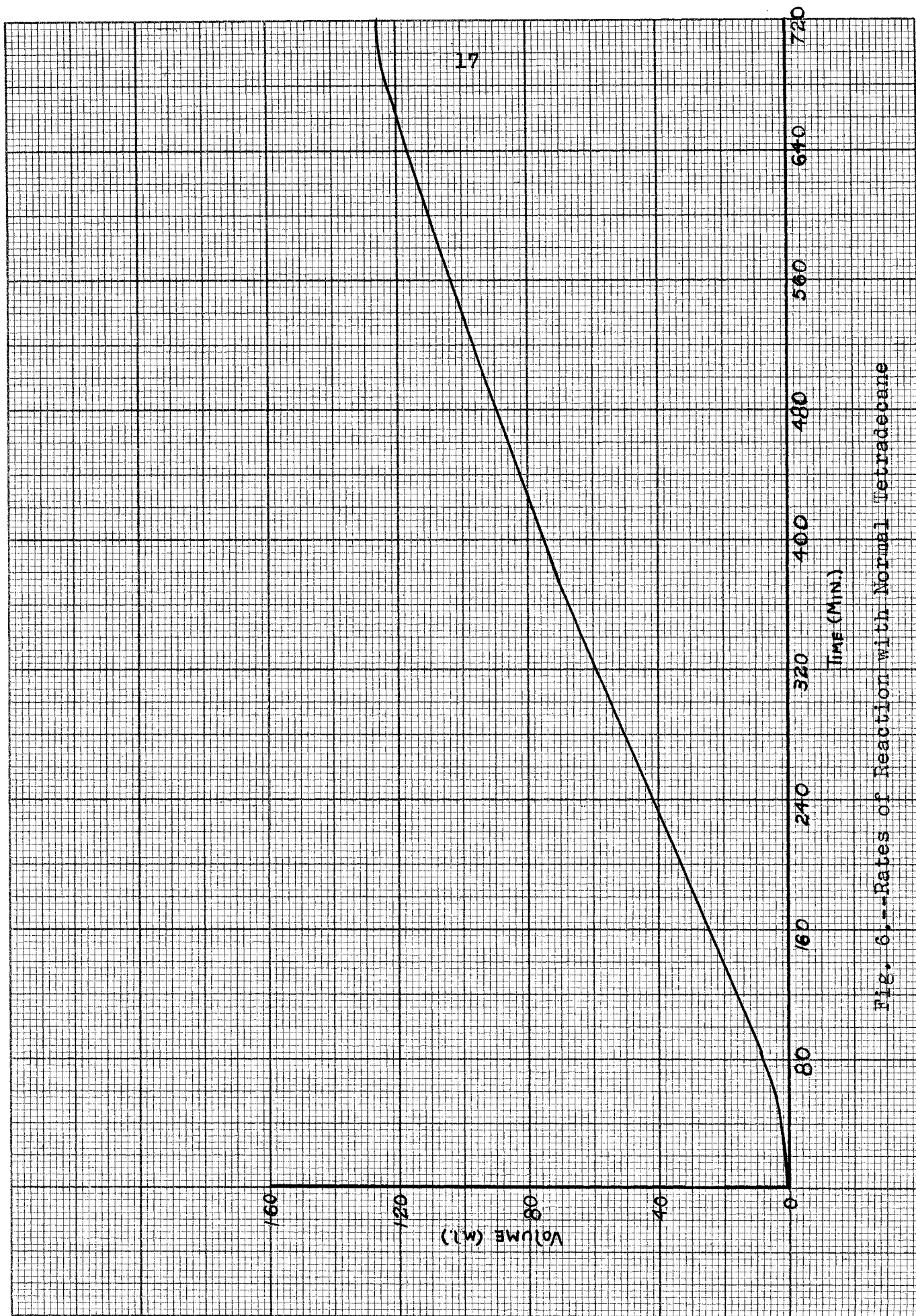


Fig. 6. ---Rates of Reaction with Normal Tetradecane

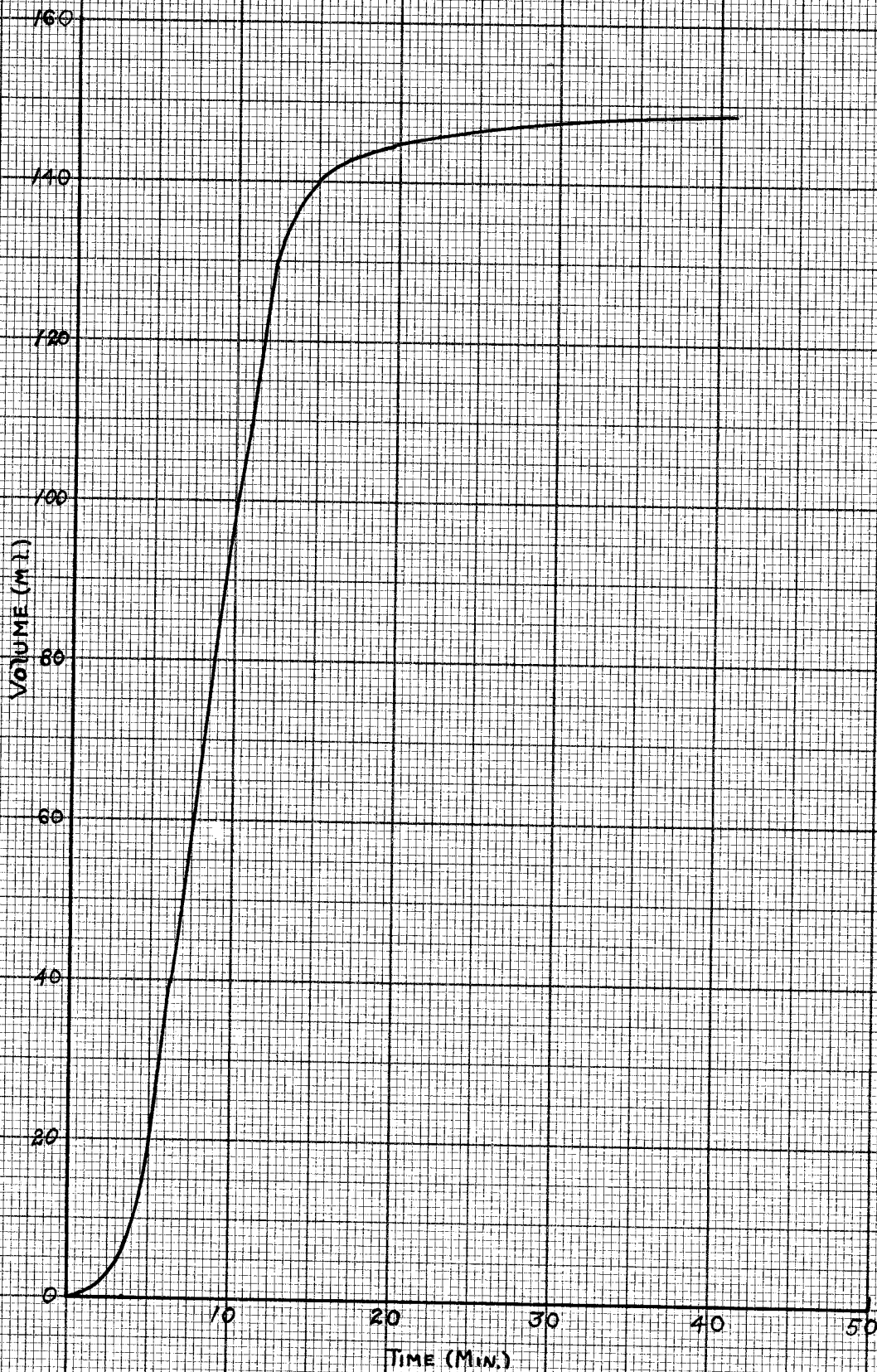


Fig. 7.--Rates of Reaction with 2, 2, 4-Trimethylpentane.

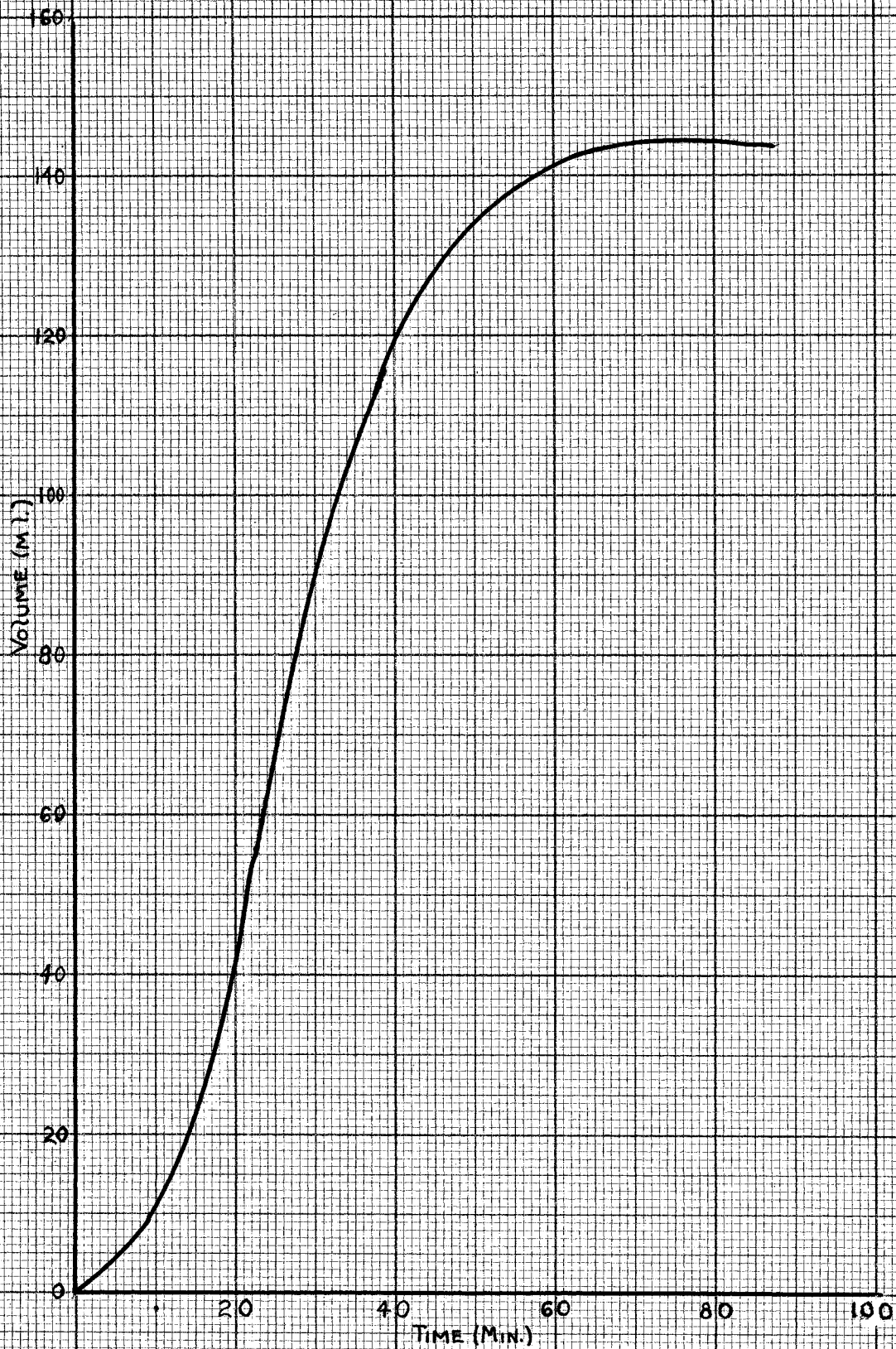


Fig. 8.--Rates of Reaction with 2, 7-Di-methyloctane.

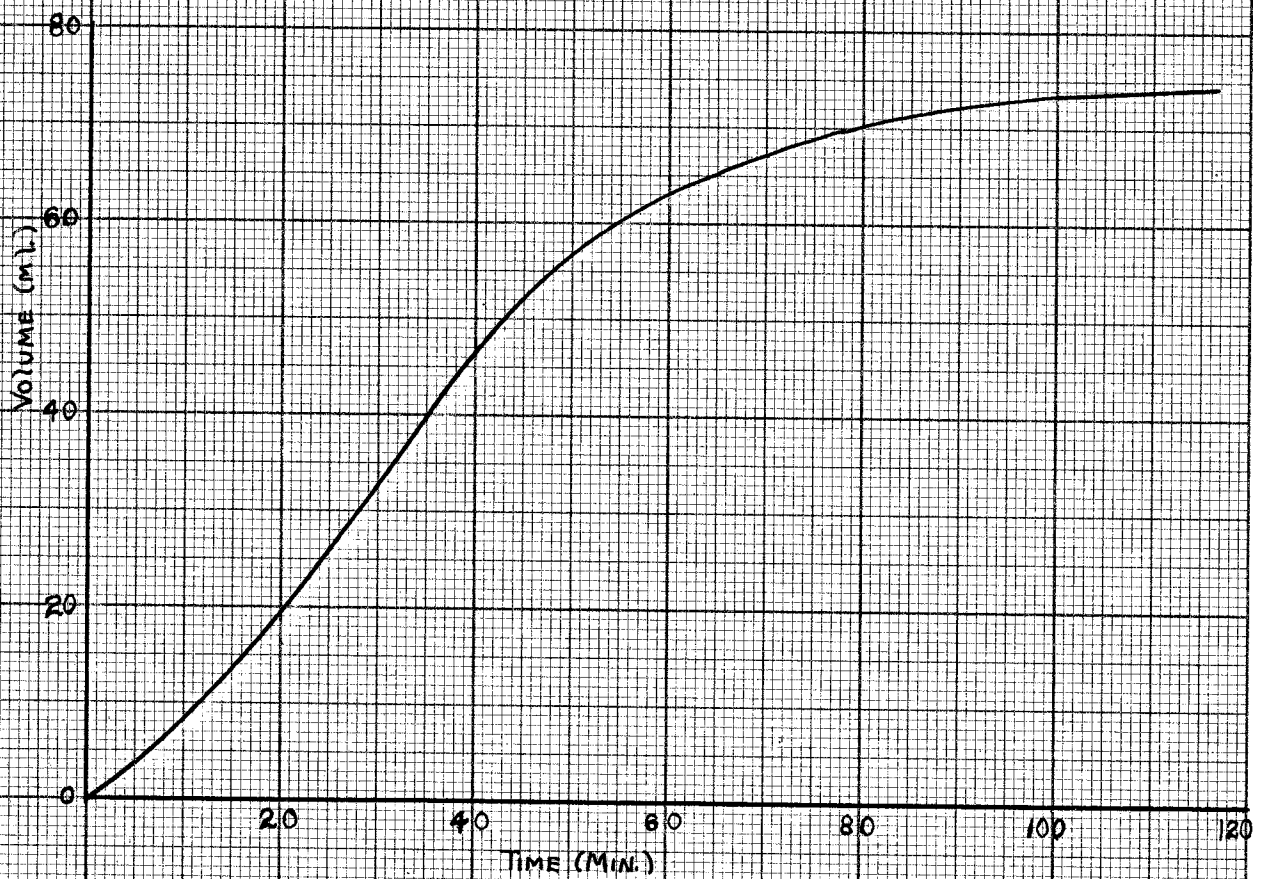


Fig. 9.--Rates of Reaction with Cyclohexane

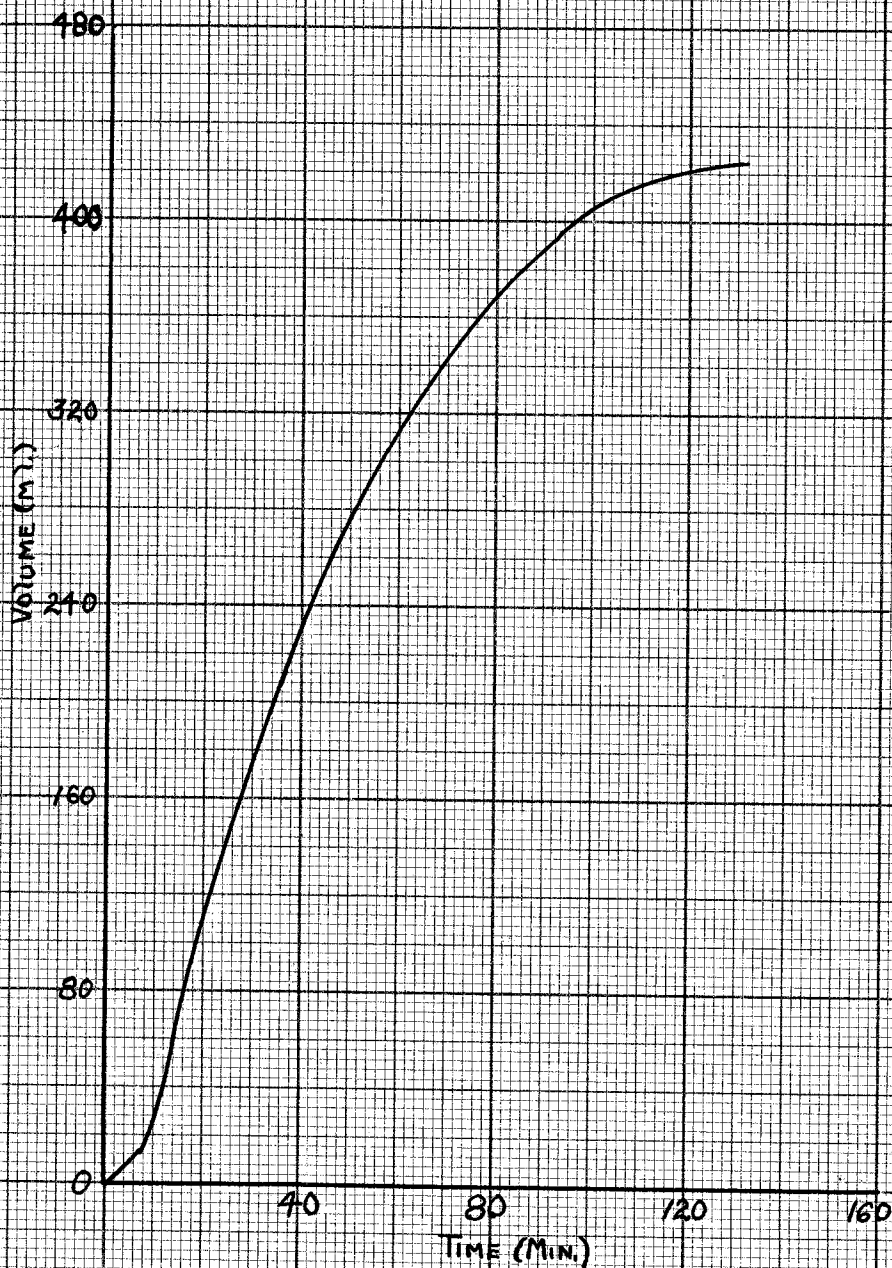


Fig. 10.--Rates of Reaction with Methylcyclohexane.

TABLE 1
RATES OF EVOLUTION OF GAS

Hydrocarbon	Total Volume of Gas (S.T.P.)	Milliliters of Gas per Minute
Normal heptane	100.5	0.94
Normal octane	102.0	1.14
Normal decane	232.0	1.50
Normal tetradecane	126.0	0.18
2-Methylbutane	240.0	9.00
2, 2, 4-Trimethylpentane	148.5	8.58
2, 7-Dimethyloctane	144.0	2.70
Cyclohexane	78.0	0.93
Methylcyclohexane	422.0	6.00
5:1 Mixture of 2, 2, 4-trimethylpentane and normal octane	304.0	5.00
2:1 Mixture of 2, 2, 4-trimethylpentane and normal octane	306.0	5.00
1:1 Mixture of 2, 2, 4-trimethylpentane and normal octane	318.0	5.00
1:2 Mixture of 2, 2, 4-trimethylpentane and normal octane	310.0	4.50
1:5 Mixture of 2, 2, 4-trimethylpentane and normal octane	309.0	4.00

octane evolved gas at rates which decreased with an increase in the percentage of normal octane in the mixture. However, there seems to be no constant relationship between the rates of evolution of gas and the percentage composition of the mixture as shown by Table 1. The rates in this table, expressed as milliliters of gas evolved per minute, were calculated by assuming the rate to be constant during the first portion of the run, which is approximately valid.

The analysis of the evolved gas for percentage of hydrogen chloride shows no consistent results. Normal octane gives a higher percentage of hydrogen chloride than 2, 2, 4-trimethylpentane; yet with one exception in mixtures of the two the percentage of hydrogen chloride decreases with an increase in the percentage of normal octane, as shown in Table 2.

TABLE 2
PERCENTAGE OF HYDROGEN CHLORIDE IN EVOLVED GASES

Hydrocarbon	Ml. 0.1160 AgNO ₃ in Gas Absorber	Ml. 0.0952 KCNS	Ml. HCl Gas Found	Ml. Evolved Gas	Per Cent HCl in Evolved Gas
Normal heptane	50	26.2	74.14	100.5	74.10
Normal octane	50	19.5	88.40	101.5	87.60
Normal decane	50	0.5	129.02	264.0	45.40
Normal tetradecane	50	23.7	100.80	126.9	79.40
2-Methylbutane	50	24.8	77.30	238.0	32.50

TABLE 2--Continued

Hydrocarbon	Ml. 0.1160 AgNO ₃ in Gas Absorber	Ml. 0.0952 KCNS	Ml. HCl Gas Found	Ml. Evolved Gas	Per Cent HCl in Evolved Gas
2, 2, 4-Trimethyl- pentane	100	84.6	81.98	148.2	55.30
2, 7-Dimethyloctane	50	31.4	63.10	143.8	43.90
Cyclohexane	50	41.0	42.50	75.3	56.40
Methylcyclohexane	70	7.1	167.10	422.0	39.60
1:5 Mixture of 2, 2, 4- trimethylpentane and normal octane	50	2.0	125.90	303.8	41.40
2:1 Mixture of 2, 2, 4- trimethylpentane and normal octane	50	1.0	125.90	306.5	41.07
1:1 Mixture of 2, 2, 4- trimethylpentane and normal octane	50	11.8	104.83	317.0	33.10
1:2 Mixture of 2, 2, 4- trimethylpentane and normal octane	50	20.4	86.70	309.0	27.90
1:5 Mixture of 2, 2, 4- trimethylpentane and normal octane	70	31.0	114.90	312.0	36.80

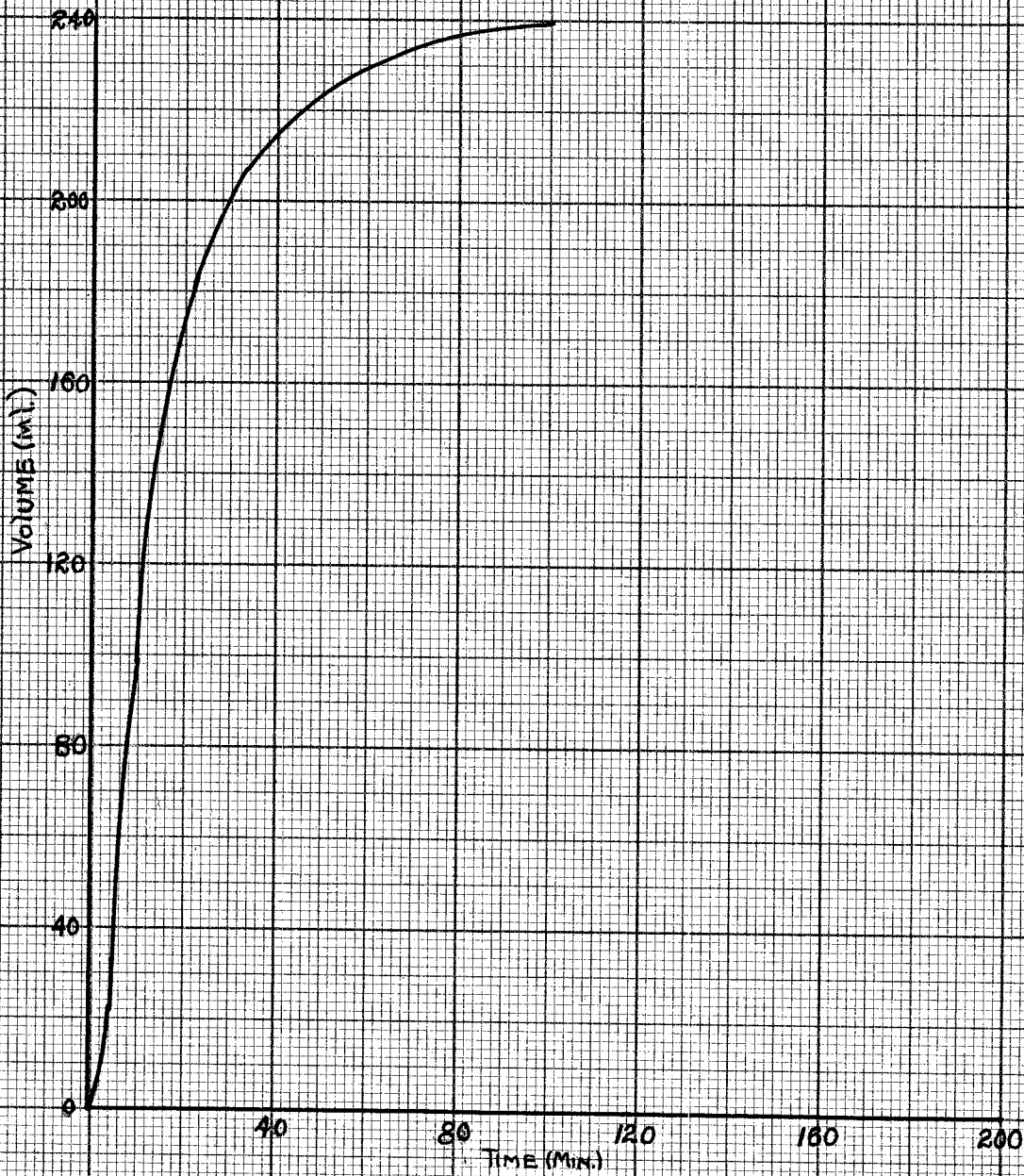


Fig. 11.--Rates of Reaction with 2-Methylbutane



Fig. 12.--Rates of Reaction with a 5:1 Mixture of 2, 2, 4-Trimethylpentane and Normal Octane.

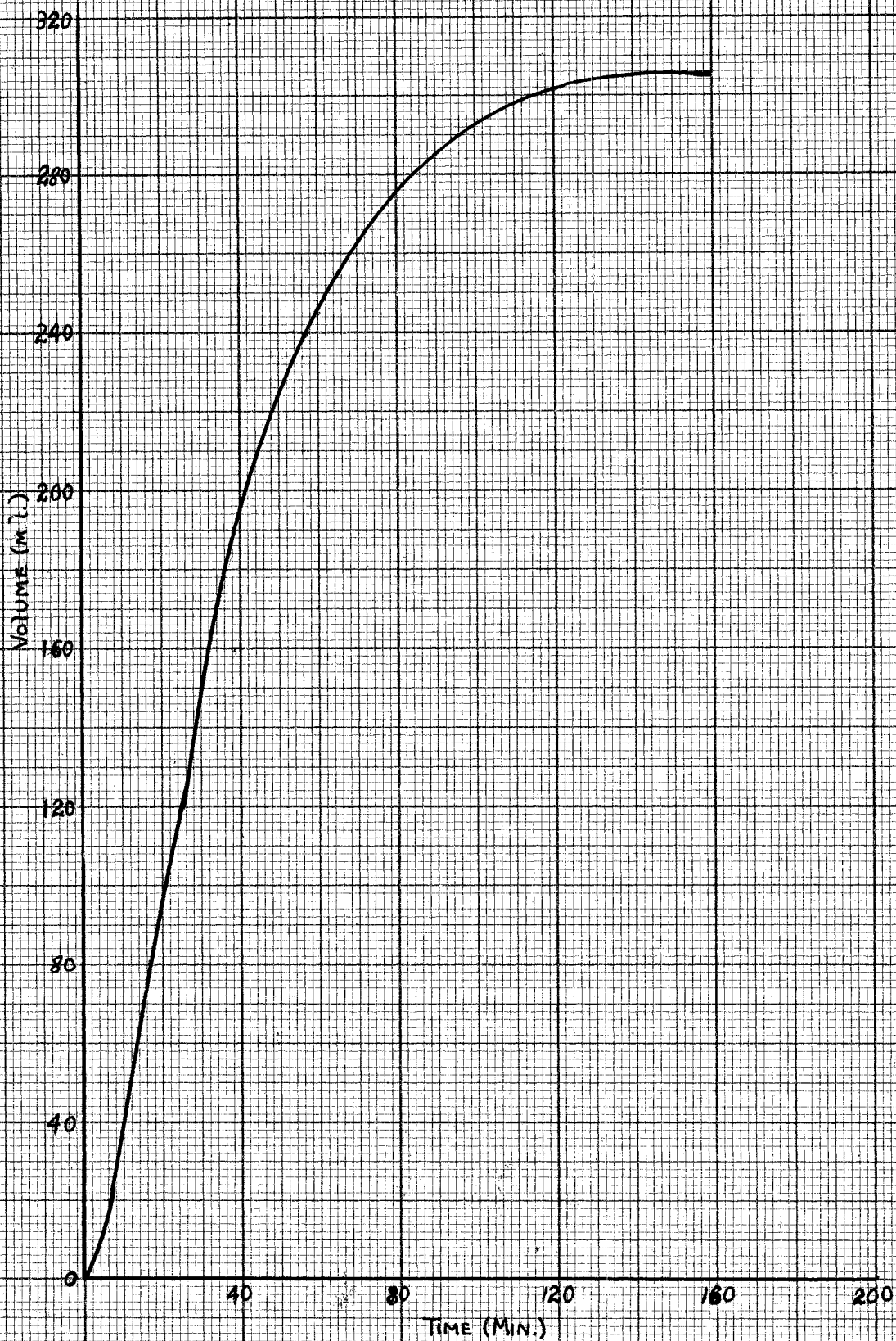


Fig. 13.--Rates of Reaction with a 2:1 Mixture of 2, 2, 4-Trimethylpentane and Normal Octane.

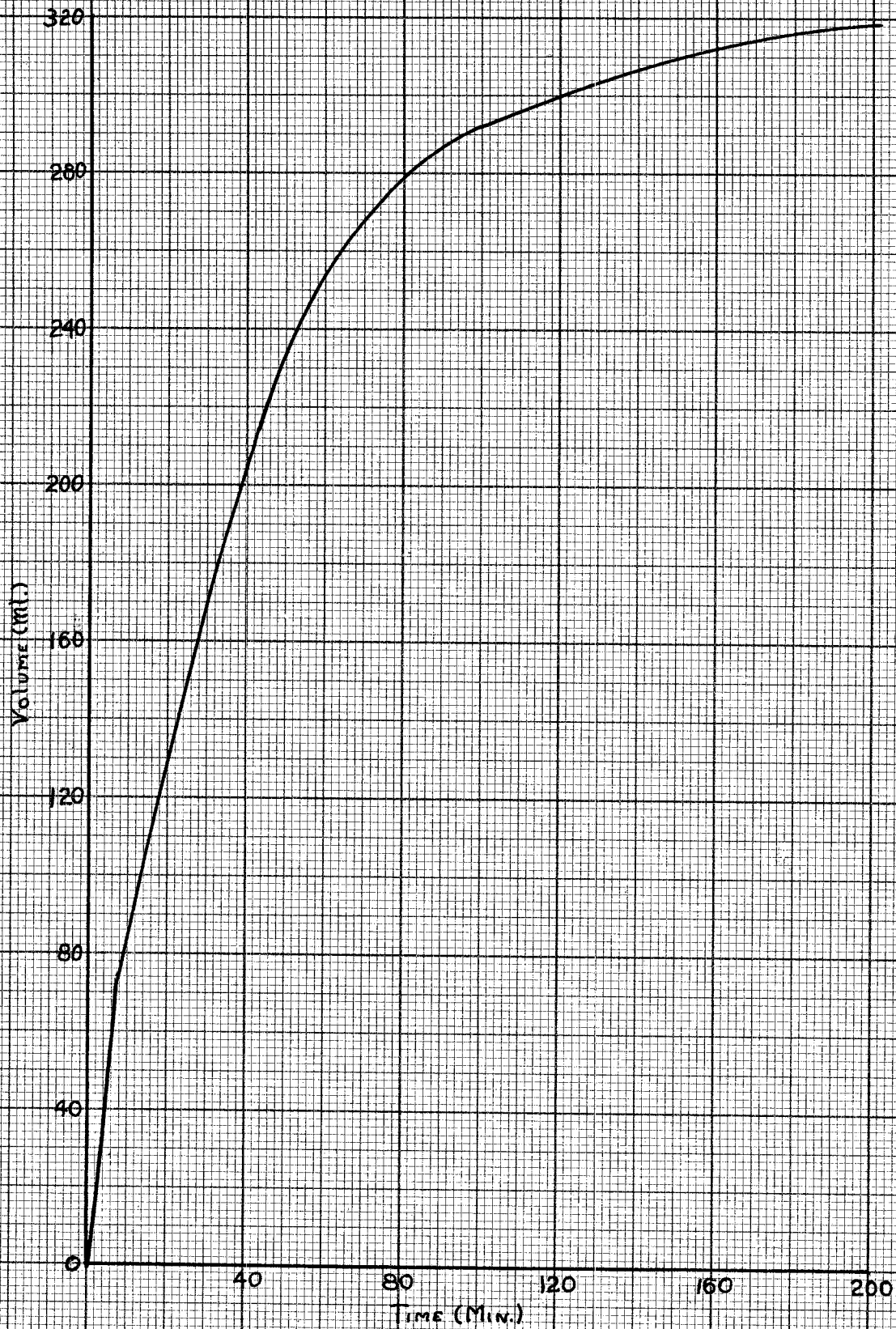


Fig. 14.--Rates of Reaction with a 1:1 Mixture of 2, 2, 4-Trimethylpentane and Normal Octane.

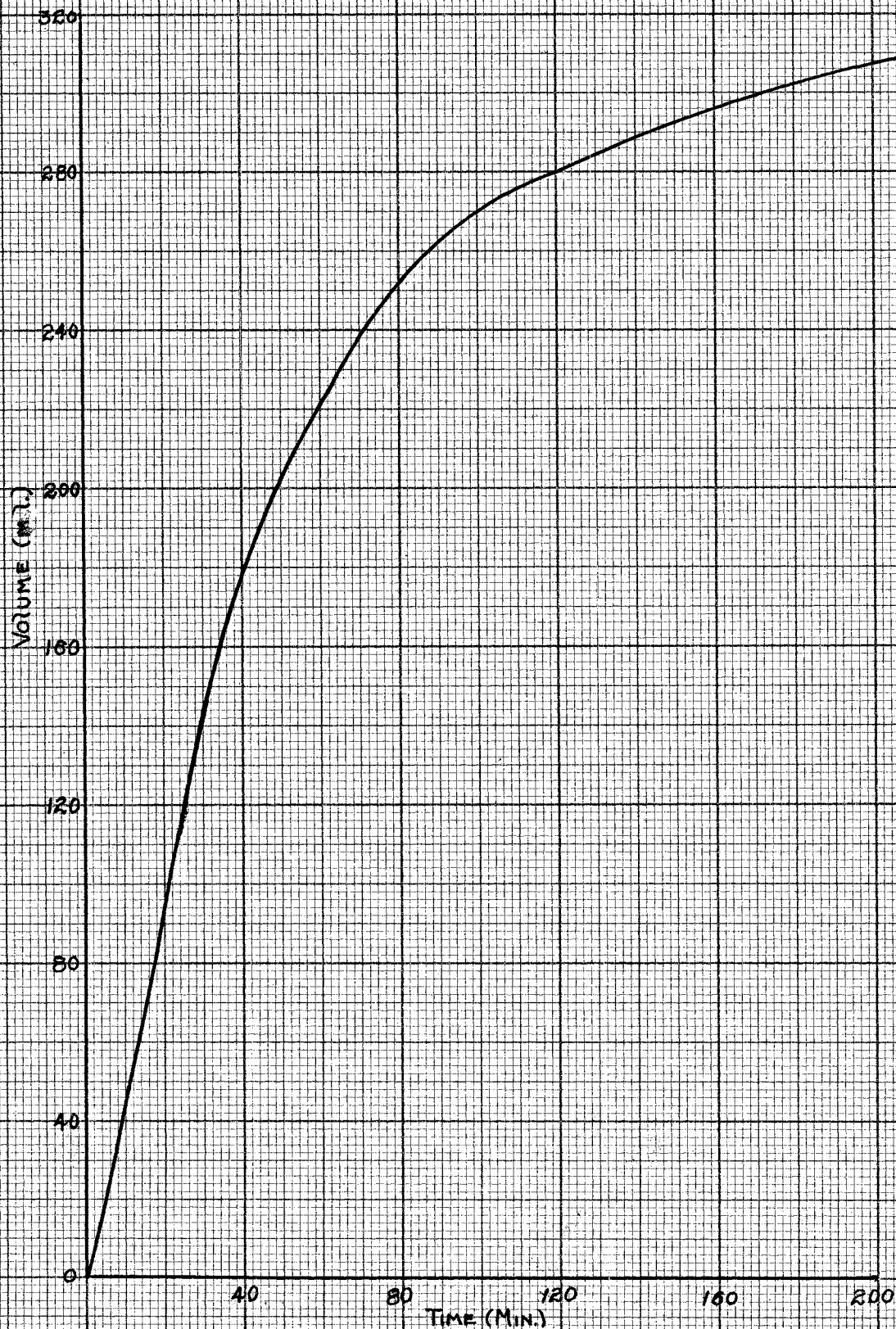


Fig. 15.--Rates of Reaction with a 1:2 Mixture of 2, 2, 4-Trimethylpentane and Normal Octane.

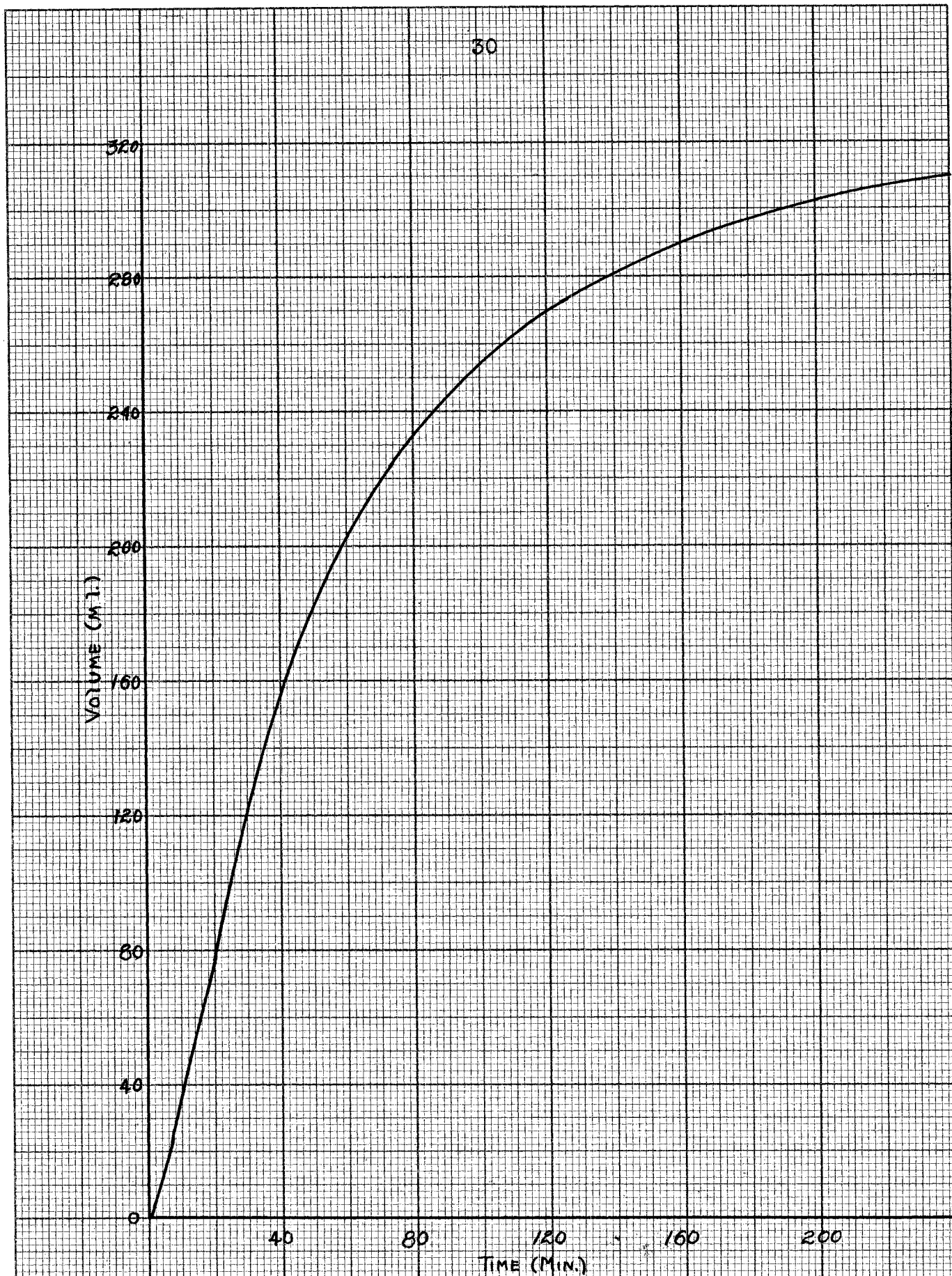


Fig. 16.--Rates of Reaction with a 1:5 Mixture of 2, 2, 4-Trimethylpentane and Normal Octane.

CHAPTER IV

SUMMARY

Reaction rates between chlorosulphonic acid and various hydrocarbons were studied by measuring volumetrically under known conditions of temperature and pressure the evolved gas.

Part of the gas was shown to be hydrogen chloride, and the percentage of hydrogen chloride present in the gas evolved from each hydrocarbon was calculated.

The results seem to indicate in general a wide variation in percentage of hydrogen chloride. The straight-chain hydrocarbons as a rule seem to yield a greater percentage than the branched-chain. Normal octane yielded a much higher percentage than 2, 2, 4-trimethylpentane, yet in mixtures of these two hydrocarbons the percentage of hydrogen chloride found with one exception decreased as the percentage of normal octane increased.

The branched-chain compounds evolved gas much more rapidly than the straight-chains. 2, 2, 4-trimethylpentane evolved gas very rapidly as was to be expected since it contains a tertiary hydrogen atom, yet 2, 7-dimethyloctane with two tertiary hydrogens did not evolve gas as fast as 2, 2, 4-trimethylpentane.

Among the straight-chain hydrocarbons an increase in

length of the carbon chain seems to decrease the rate of reaction.

Cyclohexane reacts slowly, but with methylcyclohexane the rate of reaction increases tremendously, while the presence of a double bond, as in cyclohexene, causes the reaction to proceed almost instantaneously. Cyclic compounds of the benzene type also proceed at a very rapid rate.

More work should be done with a large number of straight-chain hydrocarbons and a large number of branched-chain hydrocarbons in order to gain more generalized facts concerning these two types of hydrocarbons. It would also be well to attempt a more complete analysis of the "off gas" to see what gases besides hydrogen chloride are found.

A complete analysis of the products in the reaction vessel should also be made to test Ashcan's statement that alkyl sulfonic acids were produced by the reaction.

APPENDIX

TABLE 3

COURSE OF THE REACTION WITH NORMAL HEPTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.0	0.0	0.00
3.5	0.5	0.45
4.5	0.7	0.63
6.0	2.2	1.81
10.5	4.6	4.15
13.5	7.6	6.85
17.0	11.4	10.40
20.0	16.1	14.58
22.0	19.7	17.80
24.0	23.5	21.20
27.0	27.4	24.80
29.0	30.8	27.88
37.5	37.3	33.20
42.5	43.4	39.20
46.0	47.6	43.10
49.0	51.7	46.52
53.0	55.7	50.40
57.0	60.7	54.90
65.5	68.9	62.20
71.5	72.6	65.70
77.0	78.6	71.10
87.0	83.2	75.20
97.0	85.7	77.50
107.0	88.9	80.40
117.0	94.3	85.20
127.0	96.4	87.20
138.0	98.7	89.40
152.0	101.0	91.30
160.0	103.0	93.20
169.0	104.4	94.50
180.0	105.8	95.70
186.0	107.4	97.20
206.0	108.9	98.50
223.0	109.3	98.90

TABLE 3--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
248.0	111.0	100.50
258.0	111.0	100.50

Observed pressure 745 mm.
Observed temperature 23.5°C.

TABLE 4

COURSE OF THE REACTION WITH NORMAL OCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.0	0.0	0.00
1.0	0.4	0.36
3.0	0.9	0.81
5.5	1.7	1.56
8.5	3.5	3.14
12.0	6.4	5.76
18.0	9.8	8.90
21.0	13.0	11.70
26.0	17.7	15.91
30.0	22.0	19.80
32.0	25.3	22.75
38.0	32.0	28.80
42.0	37.2	33.42
44.0	40.5	36.40
49.2	48.0	43.20
52.0	52.7	46.50
55.0	58.0	52.10
59.0	65.4	58.80
64.0	75.1	66.60
69.0	84.7	75.20
75.0	95.4	85.90
78.0	100.0	90.00

TABLE 4--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
83.0	101.2	91.10
95.0	103.0	92.70
98.0	104.2	93.90
106.0	105.4	95.00
109.0	106.3	95.80
115.0	107.5	97.00
135.0	108.6	97.70
142.0	110.0	99.00
152.0	111.4	100.30
162.0	112.3	101.00
172.0	112.3	101.00

Observed pressure 744 mm.^o
 Observed temperature 25.0° C.

TABLE 5

COURSE OF THE REACTION WITH NORMAL DECANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.00	0.0	0.00
5.00	3.7	3.08
7.00	10.7	9.73
9.00	19.0	17.20
12.00	26.2	23.70
15.00	35.0	31.75
19.00	45.0	40.80
23.00	54.1	49.30
26.00	64.5	58.50
30.00	73.7	66.70
33.00	85.0	77.20
37.00	95.5	86.50
38.50	100.5	90.70
41.75	105.8	95.70

TABLE 5--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
44.00	111.6	100.50
46.50	117.5	106.50
49.00	122.5	111.30
54.00	132.8	120.30
57.00	139.6	126.50
62.00	149.1	134.70
73.00	162.7	147.50
79.00	179.0	162.50
89.00	191.0	173.50
95.00	199.5	181.00
102.00	208.5	188.50
107.00	216.5	196.60
112.00	224.8	201.80
119.00	234.0	213.00
129.00	245.7	222.20
137.00	252.9	229.00
145.00	261.4	236.50
151.00	267.5	242.00
164.00	278.0	252.00
183.00	285.0	258.00
202.00	292.0	265.00
213.00	295.5	267.80
225.00	300.0	272.00
236.00	305.0	276.30
249.00	307.3	278.00
253.00	309.7	280.00

Observed pressure 752 mm.
Observed temperature 26°C.

TABLE 6

COURSE OF THE REACTION WITH NORMAL TETRADECANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0	0.0	0.00
18	0.2	0.08
41	2.0	0.82

TABLE 6--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
69	6.4	5.83
87	10.8	9.85
103	15.2	13.68
113	20.1	18.10
143	24.5	22.40
164	28.5	25.78
181	32.8	29.70
197	35.7	32.60
215	38.4	35.10
228	42.0	38.00
248	47.8	43.30
268	51.2	46.30
283	56.4	51.00
293	59.8	54.10
310	64.2	57.10
346	75.0	67.80
370	79.7	72.20
431	89.1	80.60
473	97.0	87.80
481	100.0	90.50
575	116.8	105.60
605	124.0	112.10
636	128.0	115.80
663	132.2	119.50
683	136.0	123.00
708	139.7	126.50
720	140.1	126.90

Observed pressure 753.3 mm.
Observed temperature 24.5°C.

TABLE 7
COURSE OF THE REACTION WITH 2-METHYLBUTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.0	0.0	0.00
3.0	12.5	11.09
4.0	28.5	25.22
5.0	46.5	41.30
7.0	74.2	65.90
9.0	100.0	88.70
10.5	124.0	110.50
12.0	142.5	126.40
14.0	158.0	140.50
15.5	170.1	151.00
17.0	179.0	159.00
19.0	188.8	168.00
21.0	200.0	177.00
23.0	205.8	183.00
24.5	210.5	187.00
26.0	216.5	192.00
27.5	219.7	195.00
29.0	225.8	200.00
33.0	231.4	205.00
38.0	238.0	211.00
44.0	245.6	218.00
50.0	251.0	223.00
58.0	257.5	228.00
68.0	261.2	231.50
78.0	264.3	235.00
88.0	266.3	236.20
100.0	268.2	238.00

Observed pressure 744 mm.
Observed temperature 27.5°C.

TABLE 8

COURSE OF THE REACTION WITH 2, 2, 4-TRIMETHYLPENTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.00	0.0	0.0
2.00	2.2	2.0
3.50	3.2	7.4
4.50	16.3	14.7
5.75	36.7	33.0
7.00	55.5	50.0
8.00	89.1	80.2
8.50	102.0	92.0
10.75	109.0	98.1
11.00	118.3	106.7
11.50	125.7	113.3
12.00	134.9	121.5
13.00	151.5	136.5
14.00	154.7	139.3
15.16	156.7	140.2
17.00	159.6	143.7
18.75	160.2	144.4
25.50	162.6	146.5
26.80	163.0	146.9
32.00	164.6	148.1
36.75	164.7	148.2
41.50	164.7	148.2

Observed pressure 744.6 mm.
Observed temperature 24.0 °C.

TABLE 9

COURSE OF THE REACTION WITH 2, 7-DIMETHYLOCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.0	0.0	0.0
2.0	1.5	1.4
3.5	3.2	2.9

TABLE 9--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
6.5	5.5	4.9
8.0	8.5	7.6
9.5	11.8	10.6
11.5	16.1	14.5
13.0	20.0	18.0
14.5	23.8	22.1
16.0	29.0	26.1
18.0	33.0	29.7
18.5	38.0	34.2
19.5	43.0	38.6
21.5	51.2	46.1
22.0	58.7	52.8
23.0	66.5	59.8
24.5	71.5	64.2
25.0	77.6	69.3
26.0	85.8	77.2
27.0	93.2	84.9
28.0	103.0	92.8
32.0	103.8	93.5
33.0	106.4	96.4
34.0	109.8	98.4
35.0	112.8	101.4
36.0	116.4	104.8
37.5	121.3	109.0
38.0	125.7	113.0
39.5	132.8	119.4
41.0	133.4	120.1
43.0	137.0	123.2
44.0	139.8	125.6
45.5	142.5	128.1
47.0	146.2	131.7
49.0	148.0	133.5
50.5	150.5	135.5
52.0	152.5	137.2
55.1	154.5	138.0
58.0	157.0	141.1
63.0	157.7	141.9
68.0	159.2	143.2
72.0	159.9	143.8
88.0	159.9	143.8

Observed pressure 739.5 mm.
 Observed temperature 23.5°C.

TABLE 10
COURSE OF THE REACTION WITH CYCLOHEXANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0	0.0	0.00
8	7.5	6.66
13	12.5	11.30
19	20.7	18.13
24	27.7	24.90
28	34.4	30.60
33	42.0	37.40
38	49.3	43.80
41	54.6	48.60
47	61.0	54.30
56	68.5	61.00
61	71.5	62.60
69	75.5	67.10
77	78.3	69.60
86	80.5	71.60
97	82.0	73.00
116	83.5	74.20
129	84.7	75.30

Observed pressure 748 mm.
Observed temperature 28.3°C.

TABLE 11
COURSE OF THE REACTION WITH METHYLCYCLOHEXANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.0	0.0	0.0
2.0	1.5	1.3
5.0	6.0	5.4
7.0	11.6	10.4
8.0	20.6	18.5
9.0	32.5	29.2
10.0	43.0	38.6

TABLE 11--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
10.5	53.0	47.6
12.0	64.6	58.0
13.0	76.5	69.6
14.0	90.0	80.7
15.0	100.0	89.6
18.0	115.0	103.0
19.0	121.5	109.0
19.8	129.5	117.0
21.0	140.5	124.5
22.0	148.4	133.0
23.0	156.2	140.0
24.5	166.5	149.0
25.5	175.0	157.2
27.0	186.5	167.0
28.0	194.3	174.0
29.0	200.0	179.0
31.3	206.5	184.5
32.3	213.0	190.8
34.0	223.5	200.0
35.0	231.5	207.0
36.3	239.5	214.0
38.0	248.0	222.1
39.0	254.5	228.0
40.5	260.6	233.0
42.3	269.5	240.9
44.3	279.2	249.0
46.3	285.9	256.0
47.3	294.2	264.0
48.3	298.0	267.0
49.0	302.0	270.0
51.3	306.7	274.0
53.0	312.5	270.0
54.0	318.5	285.0
56.0	325.9	292.0
58.0	332.9	298.0
59.3	340.0	304.0
61.0	347.2	310.0
62.5	354.3	317.0
64.5	361.9	324.0
66.0	368.0	333.0
67.0	373.2	337.6
69.0	382.0	342.1

TABLE 11--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
72.0	393.1	351.8
73.8	399.0	351.0
74.5	403.0	360.0
79.0	408.0	365.6
80.0	413.4	370.0
82.0	418.5	375.0
84.5	425.0	380.2
88.0	431.5	386.0
90.0	437.0	391.0
91.8	441.5	395.0
95.5	447.0	400.0
98.0	450.5	404.0
100.0	453.5	406.0
103.0	458.0	410.0
105.8	461.0	413.0
109.0	462.8	414.0
112.0	464.5	416.0
117.0	468.0	420.0
121.0	470.7	422.0
124.0	472.5	424.0
129.0	472.5	424.0

Observed pressure 742.7 mm.
Observed temperature 25.2°C.

TABLE 12

COURSE OF THE REACTION WITH A 5:1 MIXTURE OF
2, 2, 4-TRIMETHYLPENTANE AND NORMAL OCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.00	0.0	0.00
2.00	5.1	4.69
4.00	12.0	10.80
6.00	24.5	22.00
6.50	31.3	28.17

TABLE 12--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
9.00	53.0	47.70
10.00	70.0	63.00
12.00	88.8	79.25
13.00	98.0	88.20
15.00	110.0	99.10
15.50	119.3	107.50
16.00	128.0	115.10
17.00	136.3	123.50
18.50	144.5	130.00
20.00	152.8	137.30
21.00	160.0	143.90
22.00	166.5	149.80
23.50	170.5	153.30
25.00	175.5	158.00
26.50	182.0	163.70
28.50	191.0	172.00
29.00	195.2	175.60
29.25	198.0	178.20
33.00	205.0	184.70
34.00	211.0	189.70
35.75	217.0	195.20
37.00	222.5	200.00
38.75	227.0	204.50
40.50	232.2	209.00
42.50	239.0	213.00
44.00	240.5	216.50
48.00	248.7	223.90
50.50	254.9	229.30
52.50	259.5	233.80
57.50	268.2	241.50
61.00	272.5	245.30
63.00	276.5	249.50
66.50	281.4	253.00
72.00	287.2	258.40
79.00	293.7	264.00
88.00	301.0	271.00
91.00	304.0	273.70
107.00	313.5	282.00
121.00	319.5	287.50
138.00	325.0	292.30
152.00	329.0	295.90
168.00	332.2	299.00

TABLE 12--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
183.00	335.5	302.00
195.00	337.0	303.50
205.00	337.4	303.80

Observed pressure 750 mm.
Observed temperature 26°C.

TABLE 13

COURSE OF THE REACTION WITH A 2:1 MIXTURE OF
2, 2, 4-TRIMETHYLPENTANE AND NORMAL OCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.00	0.0	0.00
2.00	5.8	4.47
4.00	13.0	11.65
5.25	13.1	16.20
8.00	30.0	26.35
9.25	41.5	37.18
11.00	51.9	46.40
13.00	63.0	56.40
15.00	78.3	70.00
16.50	87.5	79.40
18.50	100.0	89.50
20.50	112.0	100.10
23.50	124.3	111.30
25.50	135.0	120.80
27.00	146.8	131.10
29.00	158.5	142.00
31.50	170.2	154.00
33.00	180.0	161.00
35.25	193.0	172.80
37.00	200.0	179.00
38.75	209.4	182.30

TABLE 13--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
41.00	220.7	197.70
43.50	228.8	205.00
45.00	235.0	210.00
48.00	244.0	218.50
49.50	249.0	223.00
51.50	253.5	226.80
54.50	260.0	232.70
56.00	263.5	235.80
62.00	276.6	247.80
66.50	288.1	258.50
74.50	299.6	268.00
78.00	305.0	273.00
82.00	311.0	278.50
84.00	313.9	281.00
99.50	318.5	285.00
93.00	322.7	289.00
98.00	326.0	291.70
104.00	329.8	295.00
108.00	333.9	298.50
151.00	342.8	306.50

Observed pressure 746.5 mm.
Observed temperature 26.5°C.

TABLE 14

COURSE OF THE REACTION WITH A 1:1 MIXTURE OF
2, 2, 4-TRIMETHYLPENTANE AND NORMAL OCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.0	0.0	0.00
1.5	8.8	7.85
3.0	29.0	25.80
4.0	39.3	35.00
5.0	52.5	46.70
7.0	65.6	58.40

TABLE 14--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
8.0	72.8	64.70
9.0	81.2	72.40
10.0	88.0	78.40
11.0	96.7	86.00
11.5	100.5	89.60
14.5	110.9	98.00
16.0	120.3	106.00
18.0	129.9	114.70
20.0	141.1	124.50
24.0	159.5	141.00
26.0	170.4	149.00
28.0	178.3	157.90
30.0	188.7	166.80
32.5	200.5	177.50
35.0	208.5	184.50
36.5	211.5	188.00
39.5	228.0	201.00
43.0	243.1	215.50
45.0	250.7	221.00
48.5	259.5	227.20
52.5	269.8	239.10
56.0	278.3	246.50
61.0	287.5	254.80
65.0	293.9	257.70
69.0	300.5	266.50
74.0	305.8	271.50
79.0	312.9	277.00
82.5	315.8	280.50
87.0	319.3	284.00
90.0	322.2	285.70
96.5	326.5	289.00
115.0	333.9	296.00
125.0	340.3	300.90
137.5	342.5	304.00
149.0	347.3	308.20
166.0	351.0	311.50
177.0	354.9	315.00
187.0	356.6	316.00
201.0	358.0	317.50
201.0	358.1	317.50

Observed pressure 742 mm.
Observed temperature 26.5°C.

TABLE 15

COURSE OF THE REACTION WITH A 1:2 MIXTURE OF
2, 2, 4-TRIMETHYLPENTANE AND NORMAL OCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.00	0.0	0.00
2.00	5.5	4.92
4.00	13.5	11.91
6.00	23.5	21.00
7.50	33.3	29.85
8.50	43.8	39.20
11.00	51.5	46.20
13.00	62.0	55.50
15.50	74.9	67.00
18.00	82.5	79.40
19.00	100.0	89.50
22.00	111.4	100.00
24.00	122.7	109.70
26.50	136.0	121.70
28.00	144.9	129.50
29.50	152.9	136.80
32.00	168.1	140.50
34.00	180.1	161.30
37.75	190.4	170.80
39.75	197.0	176.30
40.25	200.0	179.20
42.00	205.0	183.50
49.00	221.1	197.70
53.00	231.3	206.80
56.00	238.3	213.00
60.00	245.8	219.50
64.00	253.6	227.00
68.00	260.5	233.00
72.00	268.0	240.00
78.00	274.3	249.00
82.00	280.5	255.00
91.00	292.3	262.00
94.00	300.0	268.00
111.00	308.0	275.50
120.00	312.1	279.50
137.00	319.5	286.00
144.00	323.5	289.50
160.00	330.0	295.20
184.00	337.0	308.30

TABLE 15--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
193.00	340.5	304.50
203.00	344.2	308.00
212.00	345.0	309.00

Observed pressure 742.5 mm.
Observed temperature 25.5°C.

TABLE 16

COURSE OF THE REACTION WITH A 1:5 MIXTURE OF
2, 2, 4-TRIMETHYLPENTANE AND NORMAL OCTANE

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
0.00	0.0	0.0
2.00	7.7	6.2
3.00	20.2	18.1
4.50	26.2	23.3
5.50	30.7	27.2
8.00	38.7	34.3
9.00	44.1	39.7
11.00	52.8	46.3
11.75	58.4	51.9
15.00	70.1	62.3
18.50	80.0	70.9
20.00	89.6	79.5
21.25	95.5	84.6
22.00	100.0	88.8
24.50	110.0	97.9
26.00	122.0	108.3
28.00	130.2	115.7
31.00	143.3	126.7
34.00	156.5	139.0
37.00	166.6	147.0
39.00	174.5	155.0
43.00	187.0	166.0

TABLE 16--Continued

Time (min.)	Observed Volume (ml.)	Corrected Volume (ml.)
46.00	195.4	173.0
47.00	200.0	177.2
49.00	203.5	180.5
50.50	208.0	185.0
54.50	217.2	193.0
57.00	222.4	197.5
59.00	228.2	203.0
61.00	233.5	206.5
67.50	245.0	217.5
73.50	256.8	228.2
85.00	270.0	240.0
95.00	280.4	249.5
99.00	285.8	253.0
111.00	296.6	264.0
127.00	305.0	271.5
131.00	314.0	278.5
144.00	319.5	284.0
156.00	324.6	288.0
170.00	330.2	293.5
195.00	337.7	300.0
210.00	342.1	304.5
236.00	348.0	309.0
260.00	351.0	312.0

Observed pressure 740.4 mm.
 Observed temperature 26.0°C.

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