5-31-1964

Esterification of oleic acid with oleyl alcohol

Robert Persurance
New Jersey Institute of Technology

Recommended Citation

Persurance, Robert, "Esterification of oleic acid with oleyl alcohol" (1964). *Theses*. 2136.
https://digitalcommons.njit.edu/theses/2136

ESTERIFICATION OF OLEIC ACID WITH OLEYL ALCOHOL

BY

ROBERT PERSURANCE

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

NEWARK, NEW JERSEY

1964

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________________

____

____

NEWARK, NEW JERSEY

MAY, 1964

ACKNOWLEDGEMENTS

The author wishes to acknowledge his indebtedness to Dr. Saul I. Kreps, of Newark College of Engineering, for his invaluable assistance with this project.

ABSTRACT

ESTERIFICATION OF OLEIC ACID WITH OLEYL ALCOHOL

The esterification of oleic acid with oleyl alcohol was studied. A literature search showed that the chemical kinetics for this reaction had not been studied previously.

In the temperature range of 150 to 200°C. and up to a conversion of about 85 per cent, the esterification was found to be a second order reaction when the water of reaction was removed from the system by simple distillation.

Para-toluenesulfonic acid is an effective catalyst for this system, and the observed specific rate constant is a linear function of the catalyst concentration.

The effect of temperature on the specific rate constant for the uncatalyzed reaction is given by the equation

$$\ln k_1 = -\frac{6.88 \times 10^3}{T} + 10.5$$

where k_1 is in units of l./(g.-mole) (min.) and T is in degrees Kelvin. For the catalyzed reaction, the equation is

$$\ln k_2 = -\frac{4.90 \times 10^3}{T} + 14.7$$

Energies of activation for the uncatalyzed and catalyzed reactions were graphically evaluated to be 13,650 calories per gram-mole and 9730 calories per gram-mole, respectively.

An empirical rate equation was derived for this system. Using the values of the frequency factors and energies of activation determined from the experimental data, the rate equation becomes

$$r = (2.35e^{-6.88\times10^3/T} + 2.69e^{-4.90\times10^3/T} C_C)\ C_A\ C_B$$

where r = reaction rate, (g.-moles)/(l.) (min.)

C_A, C_B, C_C = concentrations of oleic acid, oleyl alcohol, and catalyst, respectively, m./l.

T = absolute temperature, °K.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

INTRODUCTION

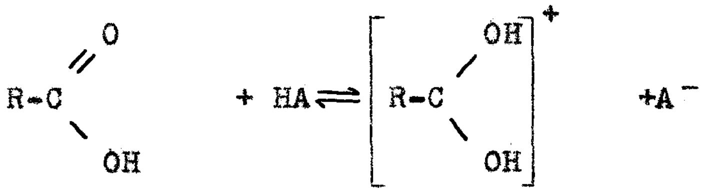
Esterification may be defined as the formation of an ester by the substitution of an organic radical for the acid hydrogen of an acid. There are many ways of producing an ester. The method studied in this paper is the direct reaction of an acid with an alcohol. The equation for this type of reaction may be written

(1) $RCOOH + R'OH \longrightarrow RCOOR' + H_2O$

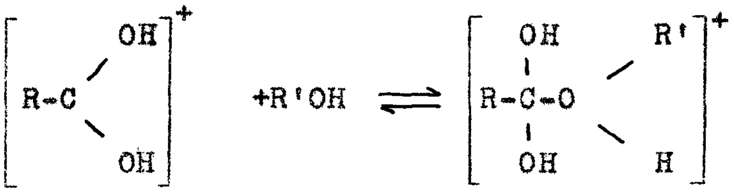
where R and R' are the acid and alcohol radicals, respectively.

The esterification is believed to be a hydrogen ion catalyzed reaction. When an acid catalyst is used, the hydrogen ions are supplied by the catalyst. If no catalyst is present, the hydrogen ions are supplied by the organic acid undergoing esterification. The esterification is thought to proceed in the following steps:

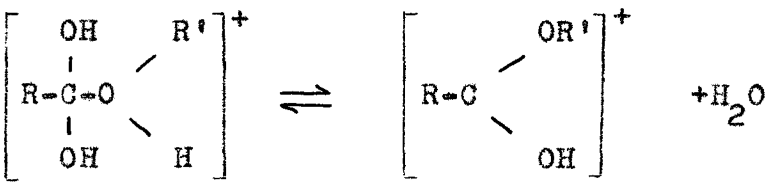
(2)



(3)



(4)



(5)

The rate of a chemical reaction is the rate at which the concentration of the reactants change with time. Mathematically, this definition can be written

$$r = -\frac{dC}{dt} \qquad (1)$$

where r is the rate of reaction, C is the concentration of one of the reactants, and t is the time.

For homogeneous chemical reactions, the rate is proportional to the concentration of the reactants. In the reaction

$$A + B \longrightarrow \text{Products}$$

the rate equation is

$$r = k\, C_A^a C_B^b \qquad (2)$$

where r = rate of reaction

k = proportionality constant

C_A, C_B = concentrations of reactants A and B, respectively

a, b = exponents to which the concentration terms must be raised

The proportionality constant, k, in the rate equation is known as the specific rate constant. This constant can be evaluated from experimental data if the order of the reaction is known. By definition, the order of a reaction is the sum of the exponents of the concentration terms in the rate equation.

If a catalyst is present, more than one reaction takes place. For the case of the second order bimolecular reaction between reactants A and B in the presence of catalyst C, the reactions occurring are

(6) A + B $\longrightarrow$ Products

(7) A + B + C $\longrightarrow$ Products + C

The rate equation for the uncatalyzed reaction (6) is

$$r_1 = k_1 \; C_A C_B \qquad (3)$$

and for the catalyzed reaction (7)

$$r_2 = k_2 C_A C_B C_C^n \qquad (4)$$

where n is the exponent to which the catalyst concentration must be raised. Since the observed reaction rate is equal to the sum of the rates of the catalyzed and uncatalyzed reactions, it follows that

$$r = (k_1 + k_2 C_C^n) \; C_A C_B \qquad (5)$$

In terms of the observed specific rate constant, k, the rate equation is

$$r = k \; C_A C_B \qquad (6)$$

Combining equations (5) and (6) gives

$$k = k_1 + k_2 C_C^n \qquad (7)$$

Thus, a plot of the observed specific rate constant against the catalyst concentration raised to the nth power should give a straight line having a slope equal to the specific rate constant for the catalyzed reaction. The intercept at C_C equal to zero will be k_1, the specific rate constant of the uncatalyzed reaction.

For a chemical reaction to occur, the molecules of the reactants must be in an activated state when they collide. The additional amount of energy that the molecules must possess, in excess of the average amount, in order to become activated is known as the energy of activation. Using the Arrhenius equation, the energy of activation for a reaction can be calculated. This equation can be written

$$k = Ae^{-E/RT} \qquad (8A)$$

where k = specific rate constant

A = frequency factor

E = energy of activation

R = gas constant

T = absolute temperature

For evaluating A and E, equation (8A) can be written in a more convenient form:

$$\ln k = -\frac{E}{RT} + \ln A \qquad (8B)$$

When ln k is plotted against 1/T, the value of $-\frac{E}{R}$ can be obtained from the slope of the straight line. Since the intercept is equal to ln A, the frequency factor can be evaluated from the same plot.

EXPERIMENTAL PROCEDURE

Esterification

The esterification was carried out in a one liter, three neck, round bottom flask equipped with an agitator, condenser, heated addition funnel, thermometer, and heating mantle. An I^2R temperature controller was used to maintain constant temperature. On the average, the temperature was controlled to within ± 1 °C.

All of the reacting materials used in the experiment were of industrial grade. Based on average molecular weights, the purities of the oleic acid and oleyl alcohol were 98 and 95 per cent, respectively.

After being heated, the alcohol was placed in the heated addition funnel, and the acid was placed in the round bottom flask. In the catalyzed runs, the catalyst was dissolved in the acid. When the reactants reached reaction temperature, the alcohol was added to the acid.

Vigorous agitation was maintained during the experimental runs. The water that formed distilled out of the reaction mixture and was removed from the system through the condenser.

During the reaction, samples of the reaction mixture were pipetted from the round bottom flask and transferred to stoppered flasks which were immediately placed on ice.

For analysis, the chilled samples were weighed into tared flasks and mixed with 50 ml. of reagent grade methanol. The resulting solutions were titrated for acid content with 0.5N sodium hydroxide solution and phenolphthalein indicator.

Density

In order to convert concentrations into the form of moles per liter, it was necessary to know the density of the reaction mixture.

The density of the mixture decreased with increase in temperature and increased with increase in ester concentration. The effect of temperature and composition on density was determined experimentally. Mixtures of different compositions of acid, alcohol, and ester were heated to various temperatures, without catalyst, and 100 ml. samples of the mixtures were pipetted into tared flasks.

The experimental results are shown in graphical form in Figure 23.

EXPERIMENTAL CALCULATIONS

The experimental results and calculations are presented in Tables 1A through 16. A sample calculation will serve to illustrate the method used in making the computations.

Run No. R-1

Sample A:

Data:

(1) Reaction temperature = 200°C.

(2) Molar ratio of acid to alcohol = 1

(3) Sample time = 10 minutes

(4) Concentration of NaOH solution = 0.498 N

Calculations:

Based on the average of three titrations, 2.88 ml. of NaOH solution were required per gram of reaction mixture. Moles of oleic acid per gram of reaction mixture = (2.88/1000) x (0.498) = 0.001434. From Figure 23, the density of this sample at 200°C. is 0.765 g./ml. Therefore, the concentration of oleic acid in this sample = 0.001434 x 0.765 x 1000 = 1.098 m./l. The reciprocal of the oleic acid concentration = 1/1.098 = 0.911 l./m.

The calculated data for this run are plotted in Figure 1A.

Table 1A

Experimental Data - Run No. R-1

Temperature: 200°C.

Catalyst Concentration: 0 m./l.

C_{A_o} = 1.408 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm.Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	2.88	0.001434	0.765	1.098	0.911	0.220
B	30	2.02	0.001007	0.769	0.774	1.292	0.450
C	60	1.425	0.000710	0.772	0.548	1.825	0.611
D	120	0.958	0.000477	0.773	0.369	2.71	0.738

0.498 N NaOH solution.

C_E = concentration of ester, m./l.

Table 1B

Experimental Data - Run No. R-1

Temperature: 200°C.

Catalyst Concentration: 0 m./l.

$C_{A_o} = 1.408$ m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	C_A^2 ($m.^2/l.^2$)	$1/C_A^2$ ($l.^2/m.^2$)	Conversion C_E/C_{A_o}
A	10	2.88	0.001434	0.765	1.098	1.207	0.830	0.220
B	30	2.02	0.001007	0.769	0.774	0.599	1.670	0.450
C	60	1.425	0.000710	0.772	0.548	0.301	3.33	0.611
D	120	0.958	0.000477	0.773	0.369	0.1361	7.35	0.738

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 2A

Experimental Data - Run No. R-2

Temperature: 200°C.

Catalyst Concentration: 0.00399 m./l.

C_{A_o} = 1.408 m./l.

Sample	Time	Vol. NaOH Soln. per Gm.Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	0.827	0.000412	0.774	0.319	3.14	0.774
B	30	0.397	0.0001978	0.775	0.1532	6.52	0.892
C	60	0.339	0.0001689	0.775	0.1310	7.64	0.906
D	120	0.326	0.0001624	0.775	0.1260	7.94	0.912

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 2B

Experimental Data - Run No. R-2

Temperature: 200°C.

Catalyst Concentration: 0.00399 m./l.

C_{A_o} = 1.408 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	ln C_A	Conversion C_E/C_{A_o}
A	10	0.827	0.000412	0.774	0.319	-1.141	0.774
B	30	0.397	0.0001978	0.775	0.1532	-1.878	0.892
C	60	0.339	0.0001689	0.775	0.1310	-2.04	0.906
D	120	0.326	0.0001624	0.775	0.1260	-2.07	0.912

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 2C

Experimental Data - Run No. R-2

Temperature: 200°C.

Catalyst Concentration: 0.00399 m./l.

$C_{A_o} = 1.408$ m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	C_A^2 ($m.^2/l.^2$)	$1/C_A^2$ ($l.^2/m.^2$)	Conversion C_E/C_{A_o}
A	10	0.827	0.000412	0.774	0.319	0.1018	9.84	0.774
B	30	0.397	0.0001978	0.775	0.1532	0.0235	42.5	0.892
C	60	0.339	0.0001689	0.775	0.1310	0.01717	58.4	0.906
D	120	0.326	0.0001624	0.775	0.1260	0.0159	62.9	0.912

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 3A

Experimental Data - Run No. R-3

Temperature: 150°C.

Catalyst Concentration: 0 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	3.50	0.001744	0.786	1.371	0.729	0.0551
B	30	3.18	0.001585	0.788	1.249	0.801	0.1390
C	60	2.81	0.001400	0.790	1.107	0.904	0.237
D	120	2.34	0.001167	0.793	0.925	1.081	0.362
E	180	1.985	0.000989	0.795	0.786	1.271	0.458
F	240	1.746	0.000870	0.796	0.693	1.442	0.522
G	300	1.563	0.000777	0.797	0.619	1.617	0.574

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 3B

Experimental Data - Run No. R-3

Temperature: 150°C.

Catalyst Concentration: 0 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	C_A^2 ($m.^2/l.^2$)	$1/C_A^2$ ($l.^2/m.^2$)	Conversion C_E/C_{A_o}
A	10	3.50	0.001744	0.786	1.371	1.880	0.531	0.0551
B	30	3.18	0.001585	0.788	1.249	1.560	0.641	0.1390
C	60	2.81	0.001400	0.790	1.107	1.226	0.816	0.237
D	120	2.34	0.001167	0.793	0.925	0.855	1.170	0.362
E	180	1.985	0.000989	0.795	0.786	0.618	1.619	0.458
F	240	1.746	0.000870	0.796	0.693	0.480	2.08	0.522
G	300	1.563	0.000777	0.797	0.619	0.383	2.61	0.574

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 4A

Experimental Data - Run No. R-4

Temperature: 150°C.

Catalyst Concentration: 0.00411 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	1.465	0.000730	0.797	0.581	1.72	0.599
B	30	0.671	0.000334	0.801	0.268	3.73	0.815
C	60	0.425	0.000212	0.802	0.170	5.89	0.884
D	120	0.407	0.000203	0.802	0.1629	6.15	0.886
E	180	0.382	0.0001903	0.802	0.1528	6.55	0.894
F	240	0.355	0.0001770	0.802	0.1420	7.04	0.901

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 4B

Experimental Data - Run No. R-4

Temperature: 150°C.

Catalyst Concentration: 0.00411 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	ln C_A	Conversion C_E/C_{A_o}
A	10	1.465	0.000730	0.797	0.581	-0.541	0.599
B	30	0.671	0.000334	0.801	0.268	-1.317	0.815
C	60	0.425	0.000212	0.802	0.170	-1.77	0.884
D	120	0.407	0.000203	0.802	0.1629	-1.812	0.886
E	180	0.382	0.0001903	0.802	0.1528	-1.878	0.894
F	240	0.355	0.0001770	0.802	0.1420	-1.950	0.901

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 4C

Experimental Data - Run No. R-4

Temperature: 150°C.

Catalyst Concentration: 0.00411 m./l.

$C_{A_o} = 1.451$ m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	C_A^2 ($m.^2/l.^2$)	$1/C_A^2$ ($l.^2/m.^2$)	Conversion C_E/C_{A_o}
A	10	1.465	0.000730	0.797	0.581	0.338	2.96	0.599
B	30	0.671	0.000334	0.801	0.268	0.0719	13.91	0.815
C	60	0.425	0.000212	0.802	0.170	0.0289	34.6	0.884
D	120	0.407	0.000203	0.802	0.1629	0.0265	37.8	0.886
E	180	0.382	0.0001903	0.802	0.1528	0.0234	42.7	0.894
F	240	0.355	0.0001770	0.802	0.1420	0.0202	49.5	0.901

0.498 N NaOH solution

C_E = concentration of ester, m./l.

Table 5A

Experimental Data - Run No. R-5

Temperature: 175°C.

Catalyst Concentration: 0 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	3.09	0.001591	0.775	1.234	0.810	0.1369
B	30	2.59	0.001333	0.778	1.038	0.964	0.274
C	60	2.06	0.001061	0.781	0.829	1.208	0.420
D	120	1.506	0.000776	0.783	0.608	1.643	0.575
E	180	1.202	0.000619	0.785	0.486	2.06	0.660
F	240	1.010	0.000520	0.786	0.409	2.45	0.715
G	300	0.873	0.000450	0.786	0.354	2.82	0.754

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 5B

Experimental Data - Run No. R-5

Temperature: 175°C.

Catalyst Concentration: 0 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	C_A^2 ($m.^2/l.^2$)	$1/C_A^2$ ($l.^2/m.^2$)	Conversion C_E/C_{A_o}
A	10	3.09	0.001591	0.775	1.234	1.521	0.657	0.1369
B	30	2.59	0.001333	0.778	1.038	1.079	0.927	0.274
C	60	2.06	0.001061	0.781	0.829	0.687	1.458	0.420
D	120	1.506	0.000776	0.783	0.608	0.368	2.72	0.575
E	180	1.202	0.000619	0.785	0.486	0.236	4.24	0.660
F	240	1.010	0.000520	0.786	0.409	0.1672	5.98	0.715
G	300	0.873	0.000450	0.786	0.354	0.1252	7.99	0.754

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 6A

Experimental Data - Run No. R-6

Temperature: 175°C.

Catalyst Concentration: 0.00406 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	1.089	0.000560	0.785	0.440	2.28	0.694
B	30	0.406	0.000209	0.788	0.1650	6.06	0.886
C	60	0.305	0.0001570	0.788	0.1238	8.08	0.915
D	120	0.248	0.0001278	0.789	0.1008	9.92	0.930
E	180	0.231	0.0001190	0.789	0.0940	10.63	0.935
F	240	0.218	0.0001122	0.789	0.0885	11.30	0.940
G	300	0.211	0.0001088	0.789	0.0858	11.66	0.941

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 6B

Experimental Data - Run No. R-6

Temperature: 175°C.

Catalyst Concentration: 0.00406 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	ln C_A	Conversion C_E/C_{A_o}
A	10	1.089	0.000560	0.785	0.440	-0.820	0.694
B	30	0.406	0.000209	0.788	0.1650	-1.800	0.886
C	60	0.305	0.0001570	0.788	0.1238	-2.08	0.915
D	120	0.248	0.0001278	0.789	0.1008	-2.29	0.930
E	180	0.231	0.0001190	0.789	0.0940	-2.36	0.935
F	240	0.218	0.0001122	0.789	0.0885	-2.42	0.940
G	300	0.211	0.0001088	0.789	0.0858	-2.46	0.941

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 6C

Experimental Data - Run No. R-6

Temperature: 175°C.

Catalyst Concentration: 0.00406 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm.Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	C_A^2 ($m.^2/l.^2$)	$1/C_A^2$ ($l.^2/m.^2$)	Conversion C_E/C_{A_o}
A	10	1.089	0.000560	0.785	0.440	0.1935	5.17	0.694
B	30	0.406	0.000209	0.788	0.1650	0.0272	36.8	0.886
C	60	0.305	0.0001570	0.788	0.1238	0.01531	65.3	0.915
D	120	0.248	0.0001278	0.789	0.1008	0.01018	98.4	0.930
E	180	0.231	0.0001190	0.789	0.0940	0.00884	113.1	0.935
F	240	0.218	0.0001122	0.789	0.0885	0.00784	127.8	0.940
G	300	0.211	0.0001088	0.789	0.0858	0.00736	135.9	0.941

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 7

Experimental Data - Run No. R-7

Temperature: 175°C.

Catalyst Concentration: 0.00406 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	0.935	0.000481	0.786	0.378	2.64	0.737
B	30	0.405	0.000209	0.788	0.1648	6.07	0.887
C	60	0.300	0.0001547	0.788	0.1219	8.21	0.915
D	120	0.278	0.0001431	0.789	0.1130	8.85	0.921
E	180	0.261	0.0001345	0.789	0.1061	9.42	0.928

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 8

Experimental Data - Run No. R-8

Temperature: 175°C.

Catalyst Concentration: 0.00406 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	10	0.963	0.000496	0.786	0.390	2.56	0.728
B	30	0.427	0.000220	0.788	0.1735	5.76	0.880
C	60	0.308	0.0001588	0.788	0.1251	7.99	0.915
D	120	0.284	0.0001464	0.789	0.1156	8.65	0.920
E	180	0.263	0.0001355	0.789	0.1070	9.35	0.927

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 9

Experimental Data - Run No. R-9

Temperature: 150°C.

Catalyst Concentration: 0.000413 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	1	3.54	0.001822	0.785	1.431	0.698	0.0138
B	3	3.50	0.001801	0.785	1.415	0.707	0.0248
C	6	3.44	0.001770	0.786	1.392	0.718	0.0406
D	10	3.36	0.001730	0.786	1.360	0.735	0.0626
E	15	3.27	0.001689	0.787	1.328	0.754	0.0846
F	30	3.03	0.001560	0.788	1.229	0.814	0.1530
G	60	2.61	0.001344	0.791	1.063	0.940	0.267
H	120	1.993	0.001027	0.794	0.815	1.228	0.439

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 10

Experimental Data - Run No. R-10

Temperature: 150°C.

Catalyst Concentration: 0.00086 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	1	3.54	0.001822	0.785	1.430	0.700	0.0145
B	3	3.48	0.001791	0.785	1.408	0.710	0.0296
C	6	3.37	0.001737	0.786	1.364	0.734	0.0600
D	10	3.20	0.001649	0.787	1.298	0.771	0.1054
E	15	2.99	0.001540	0.789	1.215	0.823	0.1630
F	30	2.42	0.001247	0.792	0.986	1.013	0.320
G	60	1.684	0.000868	0.796	0.691	1.449	0.524
H	120	1.100	0.000566	0.799	0.452	2.22	0.689

0.515 N NaOH solution

C_E = concentration of ester m./l.

Table 11

Experimental Data - Run No. R-11

Temperature: 150°C.

Catalyst Concentration: 0.00200 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. Per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	2	3.16	0.001629	0.788	1.282	0.780	0.1163
B	4	2.78	0.001432	0.790	1.131	0.884	0.220
C	7	2.54	0.001309	0.791	1.034	0.966	0.287
D	10	2.24	0.001151	0.793	0.914	1.095	0.370
E	15	1.801	0.000927	0.795	0.737	1.358	0.490
F	30	1.134	0.000584	0.798	0.466	2.14	0.677
G	60	0.630	0.000324	0.801	0.260	3.84	0.820
H	120	0.360	0.0001851	0.802	0.1487	6.73	0.897

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 12

Experimental Data - Run No. R-12

Temperature: 175°C.

Catalyst Concentration: 0.000778 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	2	3.28	0.001690	0.774	1.309	0.764	0.0841
B	4	3.04	0.001567	0.775	1.213	0.824	0.1510
C	7	2.74	0.001411	0.777	1.098	0.911	0.232
D	10	2.44	0.001257	0.779	0.979	1.021	0.316
E	15	2.12	0.001091	0.781	0.852	1.173	0.405
F	30	1.490	0.000767	0.784	0.602	1.662	0.580
G	60	0.922	0.000475	0.786	0.374	2.68	0.740
H	120	0.534	0.000275	0.788	0.217	4.61	0.850

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 13

Experimental Data - Run No. R-13

Temperature: 200°C.

Catalyst Concentration: 0.000649 m./l.

C_{A_o} = 1.408 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	2	3.16	0.001629	0.763	1.242	0.805	0.118
B	4	2.82	0.001451	0.765	1.110	0.901	0.212
C	7	2.36	0.001215	0.767	0.931	1.073	0.339
D	10	2.03	0.001046	0.769	0.804	1.245	0.429
E	15	1.738	0.000894	0.770	0.688	1.453	0.511
F	30	1.184	0.000610	0.772	0.471	2.12	0.665
G	60	0.744	0.000382	0.774	0.296	3.38	0.790
H	120	0.476	0.000245	0.774	0.1898	5.27	0.864

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 14

Experimental Data - Run No. R-14

Temperature: 150°C.

Catalyst Concentration: 0.0031 m./l.

C_{A_o} = 1.451 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (1./m.)	Conversion C_E/C_{A_o}
A	2	3.02	0.001555	0.789	1.228	0.815	0.1535
B	4	2.63	0.001355	0.791	1.072	0.934	0.261
C	7	2.20	0.001132	0.793	0.898	1.113	0.381
D	10	1.834	0.000945	0.795	0.751	1.330	0.482
E	15	1.374	0.000708	0.797	0.565	1.770	0.610
F	30	0.747	0.000385	0.800	0.308	3.24	0.786
G	60	0.403	0.000208	0.801	0.1668	6.00	0.884
H	120	0.288	0.0001483	0.802	0.1190	8.40	0.919

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 15

Experimental Data - Run No. R-15

Temperature: 175°C.

Catalyst Concentration: 0.00232 m./l.

C_{A_o} = 1.429 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	5	2.07	0.001067	0.781	0.833	1.200	0.418
B	10	1.384	0.000714	0.784	0.560	1.787	0.608
C	15	1.009	0.000519	0.786	0.408	2.45	0.715
D	30	0.538	0.000277	0.788	0.218	4.59	0.850
E	60	0.282	0.0001451	0.789	0.1146	8.73	0.920
F	120	0.216	0.0001111	0.789	0.0877	11.40	0.940

0.515 N NaOH solution

C_E = concentration of ester, m./l.

Table 16

Experimental Data - Run No. R-16

Temperature: 200°C.

Catalyst Concentration: 0.00203 m./l.

C_{A_o} = 1.408 m./l.

Sample	Time (min.)	Vol. NaOH Soln. per Gm. Sample (ml.)	Moles Acid per g. Sample	Density (g./ml.)	Acid Conc., C_A (m./l.)	$1/C_A$ (l./m.)	Conversion C_E/C_{A_o}
A	3	2.27	0.001170	0.768	0.899	1.112	0.362
B	7	1.369	0.00705	0.772	0.544	1.840	0.614
C	10	1.048	0.00054	0.773	0.417	2.40	0.705
D	15	0.746	0.000384	0.774	0.297	3.37	0.790
E	30	0.392	0.000202	0.775	0.1566	6.39	0.890
F	60	0.222	0.0001142	0.775	0.0885	11.30	0.939

0.515 N NaOH solution

C_E = concentration of ester, m./l.

DISCUSSION

The chemical reaction studied was the reaction of oleic acid with oleyl alcohol to form oleyl oleate and water:

$$(3)\quad CH_3(CH_2)_7CH = CH(CH_2)_7COOH + CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH \longrightarrow$$
$$CH_3(CH_2)_7CH = CH(CH_2)_7COOCH_2(CH_2)_7CH{=}CH(CH_2)_7CH_3 + H_2O$$

Swern, Billen, and Knight [14] produced oleyl oleate by this direct reaction, but they did not study the reaction kinetics.

The order of this reaction was determined graphically by plotting different functions of acid concentration, C_A, against time. The concentration functions which were plotted were ln C_A, $1/C_A$, and $1/C_A^2$ which should give straight lines for first, second, and third order reactions, respectively.

From the plots made, both the catalyzed and uncatalyzed reactions were found to be second order at low conversions. At high conversions, above 85 per cent, the reaction no longer appears to be second order.

These results are in disagreement with those obtained by Flory [4,5] who studied the kinetics of esterifications and polyesterifications. Flory found that uncatalyzed esterifications were third order reactions. However, the second order plots in figures 1A, 3A, and 5A for the uncatalyzed reactions are definitely more linear than the third order plots in figures 1B, 3B, and 5B. Other investigators[3,10,11,13] who studied different oleic acid esterifications also found the catalyzed and uncatalyzed reactions to be second order. The explanation of why different orders were reported for the same type of reaction may be found when the extent of ester conversion is studied. At low conversions, the esterification is a second order reaction, but at high conversions, the order of the reaction may change to third order.

For this reaction, the rate equation is

$$-\frac{dC_A}{dt} = k\, C_A C_B \tag{9}$$

where C_A and C_B are the concentrations of oleic acid and oleyl alcohol, respectively. In the experiments, the acid and alcohol were present in equal concentrations. Therefore, the rate equation becomes

$$-\frac{dC_A}{dt} = k\, C_A^2 \tag{10}$$

Integration gives

$$\frac{1}{C_A} = kt + C' \tag{11}$$

where C' is the constant of integration. At zero time, the concentration of oleic acid is equal to its initial concentration, C_{A_o}. Thus

$$\frac{1}{C_A} = kt + \frac{1}{C_{A_o}} \tag{12}$$

A plot of $1/C_A$ against t gives a straight line having a slope equal to the specific rate constant, k.

The specific rate constants were determined graphically. These constants are summarized in Tables 17 and 18.

TABLE 17

EXPERIMENTALLY DETERMINED SPECIFIC RATE CONSTANTS

Run No.	Temperature °C.	Catalyst Conc., m./l.	k l./(g.-mole)(min.)
R-3	150	0	0.00325
R-9	150	0.000413	0.00441
R-10	150	0.00086	0.0133
R-11	150	0.00200	0.0500
R-14	150	0.00310	0.0889
R-4	150	0.00411	0.105
R-5	175	0	0.00715
R-12	175	0.000778	0.0333
R-15	175	0.00232	0.133
R-6	175	0.00406	0.175
R-7	175	0.00406	0.175
R-8	175	0.00406	0.172
R-1	200	0	0.0184
R-13	200	0.000649	0.0500
R-16	200	0.00203	0.187
R-2	200	0.00399	0.33

TABLE 18

CATALYZED REACTION SPECIFIC RATE CONSTANTS

Temperature $^{o}C.$	k $l.^2/(g.\text{-mole})^2$ min.
150	22.8
175	40.0
200	77.1

In determining the specific rate constants, the reverse reaction was assumed to be negligible. This assumption is valid at low conversions because the rate of the reverse reaction is proportional to the concentration of ester and water, and at low conversions the ester is present in small quantities. Since the water was removed from the system, the reverse reaction was made even more negligible. Theoretically, if the water were completely removed the instant it formed, there would be no reverse reaction. At high conversions, the assumption is no longer valid. An appreciable reverse reaction takes place because of the high concentration of ester and the presence of water which was not completely removed from the system.

To avoid the complications of the reverse reaction, the slopes of the lines were measured at low conversions.

In addition to the esterification reaction and reverse reaction, side reactions occurred. The side reactions included the reaction of the impurities present in the reactants and the reaction of atmospheric oxygen with the reactants.

When oleic acid and oleyl alcohol are heated separately in open beakers, both with and without the catalyst, each reactant becomes dark in color, indicating that a reaction takes place. If the heating is continued, the reactants become very dark and thicken when they cool to room temperature. This change appears to occur more quickly when catalyst is present.

The changes that were observed can be attributed to the reaction of oxygen with the reactants. Henderson and Young[8] studied the rate of reaction of oleic acid with oxygen and found that the reaction took place readily even at moderate temperatures.

Deatherage and Mattill[2], and Hamilton and Olcott[7] found that the reaction of oleic acid and oleyl alcohol with oxygen was complex and that many products were formed. The products that formed were peroxide, aldehyde, carboxyl, and hydroxyl compounds.

Because more than one reaction was possible, it seemed desirable to determine whether the experimental procedure yields reproducible results. As a test, three identical runs were made, R-6, R-7, and R-8. By comparing the specific rate constants for these runs in Table 17, it can be seen that the results are reproducible.

Some of the second order plots are linear initially but become curved as the conversion to ester increases. In almost every case, the curvature begins at a 1/C valve of 4 to 7 l./m., corresponding to an ester conversion of 83 to 91 per cent, respectively. The curvature does not begin at exactly the same ester conversion for every run. The reason for this is that the reactants, after being heated separately, were held for different lengths of time before being reacted together.

This deviation from linearity at high ester conversions may be caused by side reactions, a change in reaction order, or the reverse reaction, which can not be completely eliminated because it is difficult to drive out all of the water from the reaction mixture. More studies would have to be made to determine the principal cause for the deviation.

When the specific rate constants were plotted against the catalyst concentration, a linear relation was observed. These plots are shown in Figures 17, 18, and 19. The same relation was found by Levesque and Craig[9] and by Othmer and Rao[12] for their catalyzed oleic acid esterifications.

The effect of temperature on the slope of the lines is shown in Figure 20.

To calculate the energy of activation, the Arrhenius equation in the form of equation (8B) was used. The plot of the natural logarithm of the specific rate constant against the reciprocal of absolute temperature for the uncatalyzed reaction is shown in Figure 21, and the plot for the catalyzed reaction is shown in Figure 22.

From the slopes of the straight lines obtained, the energy of activation was calculated to be 13,650 calories per gram-mole for the uncatalyzed reaction and 9730 calories per gram-mole for the catalyzed reaction. Ling and Geankoplis[11] determined the energy of activation for the uncatalyzed oleic acid-isobutyl alcohol esterification to be 14,100 calories per gram-mole.

By substituting data at different temperatures into

Equation (8B), the following equation relating the specific rate constant to the temperature for the uncatalyzed reaction was obtained:

$$\ln k_1 = -\frac{6.88\text{x}10^3}{T} + 10.5 \qquad (9)$$

where the units of k_1 are 1./(g.-mole)(min.) and T is expressed in degrees Kelvin. For the catalyzed reaction, the equation is

$$\ln k_2 = -\frac{4.90\text{x}10^3}{T} + 14.7 \qquad (10)$$

Using the data in Equations (9) and (10), the frequency factors, A_1 and A_2, for the uncatalyzed and catalyzed reactions were found to be 2.35 and 2.69 respectively.

An empirical equation relating the reaction rate with reactant concentration, catalyst concentration, and temperature can be written by combining equations (6), (7), and (8A):

$$r = (A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT} C_C)\ C_A C_B \qquad (11A)$$

Substitution of known values into Equation (11A) gives

$$r = (2.35e^{-6.88\text{x}10^3/T} + 2.69e^{-4.90\text{x}10^3/T} C_C)\ C_A C_B \qquad (11B)$$

CONCLUSIONS

1. In the temperature range of 150 to 200°C., the esterification of oleic acid with oleyl alcohol appears to be a second order reaction up to about 85 per cent conversion, both in the presence and absence of catalyst. Beyond this conversion, side reactions complicate the kinetics.

2. The observed specific rate constant for the para-toluene-sulfonic acid catalyzed reaction is a linear function of the catalyst concentration.

3. The relation of the specific rate constant with temperature is described by the Arrhenius equation.

4. The empirical equation derived can be used to predict the reaction rate when the temperature and the concentrations of the reactants and catalyst are known.

RECOMMENDATIONS

From an academic point of view, it might be desirable to use purified rather than industrial grade oleic acid and oleyl alcohol.

An inert gas atmosphere should be used in the reaction flask. The inert atmosphere would prevent the reaction of oleic acid and oleyl alcohol with atmospheric oxygen. This would then eliminate one of the side reactions that can take place.

If inert gas were introduced into the flask by passing it through the reaction mixture, it would aid in the removal of water. The extent to which the reverse reaction takes place depends on the amount of water present in the system.

Additional work should be done to study the reaction at conversions of ester above 80 per cent.

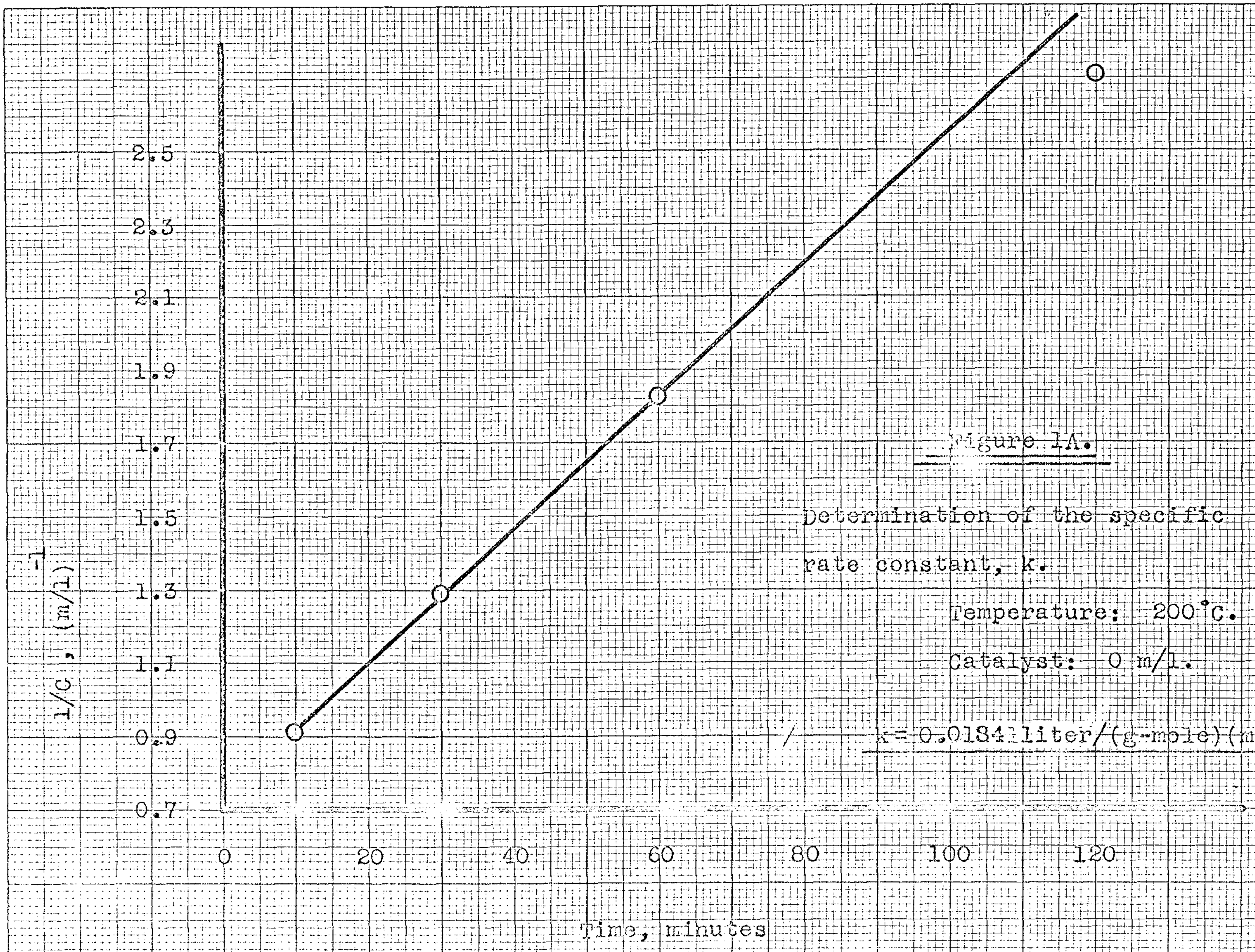


Figure 1A.

Determination of the specific rate constant, k.

Temperature: 200°C.

Catalyst: 0 m/l.

k = 0.0184 liter/(g-mole)(min)

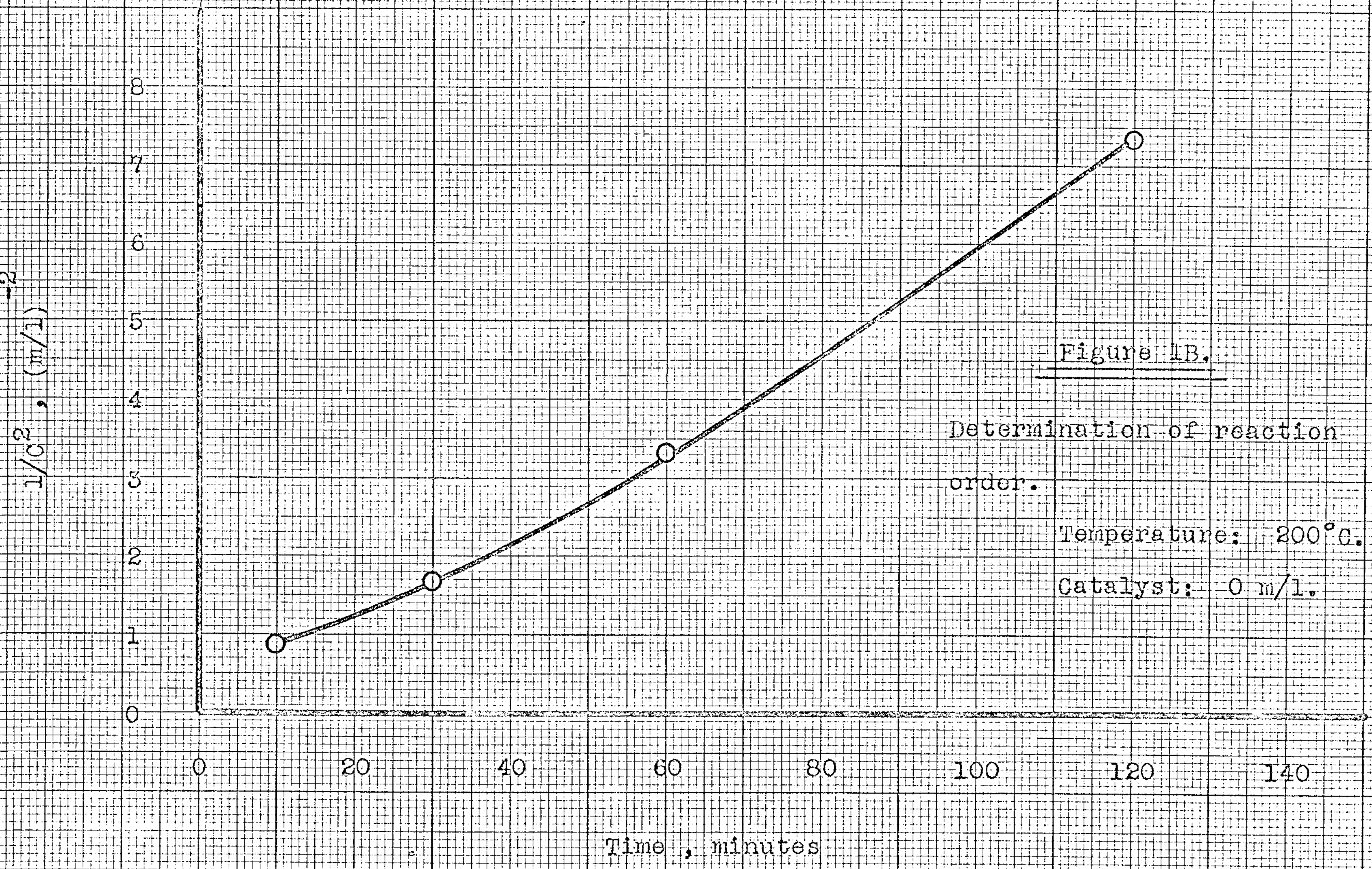


Figure 1B.

Determination of reaction order.

Temperature: 200°C.

Catalyst: 0 m/l.

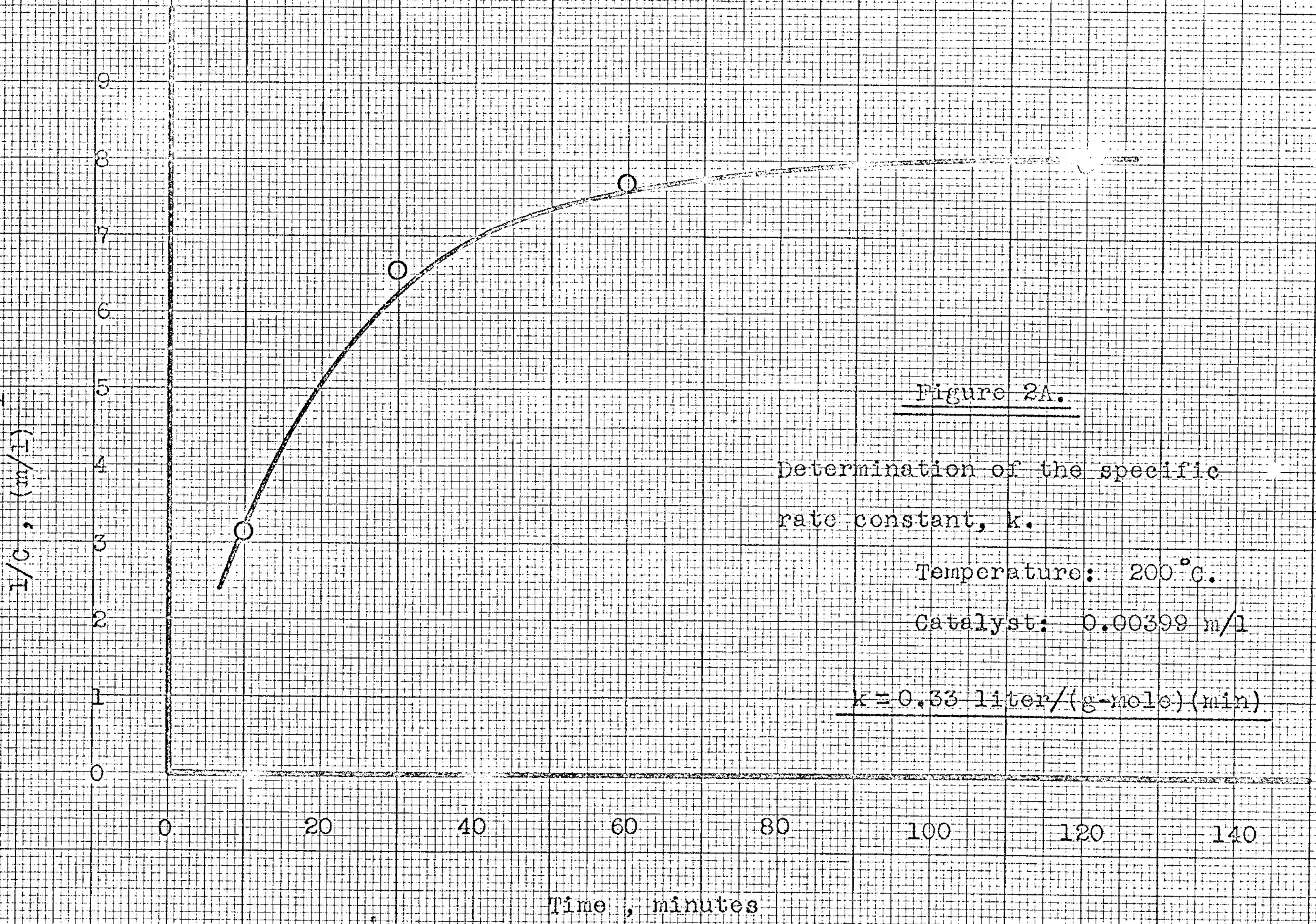


Figure 2A.

Determination of the specific rate constant, k.

Temperature: 200 °C.

Catalyst: 0.00399 m/l

$k = 0.33$ liter/(g-mole)(min)

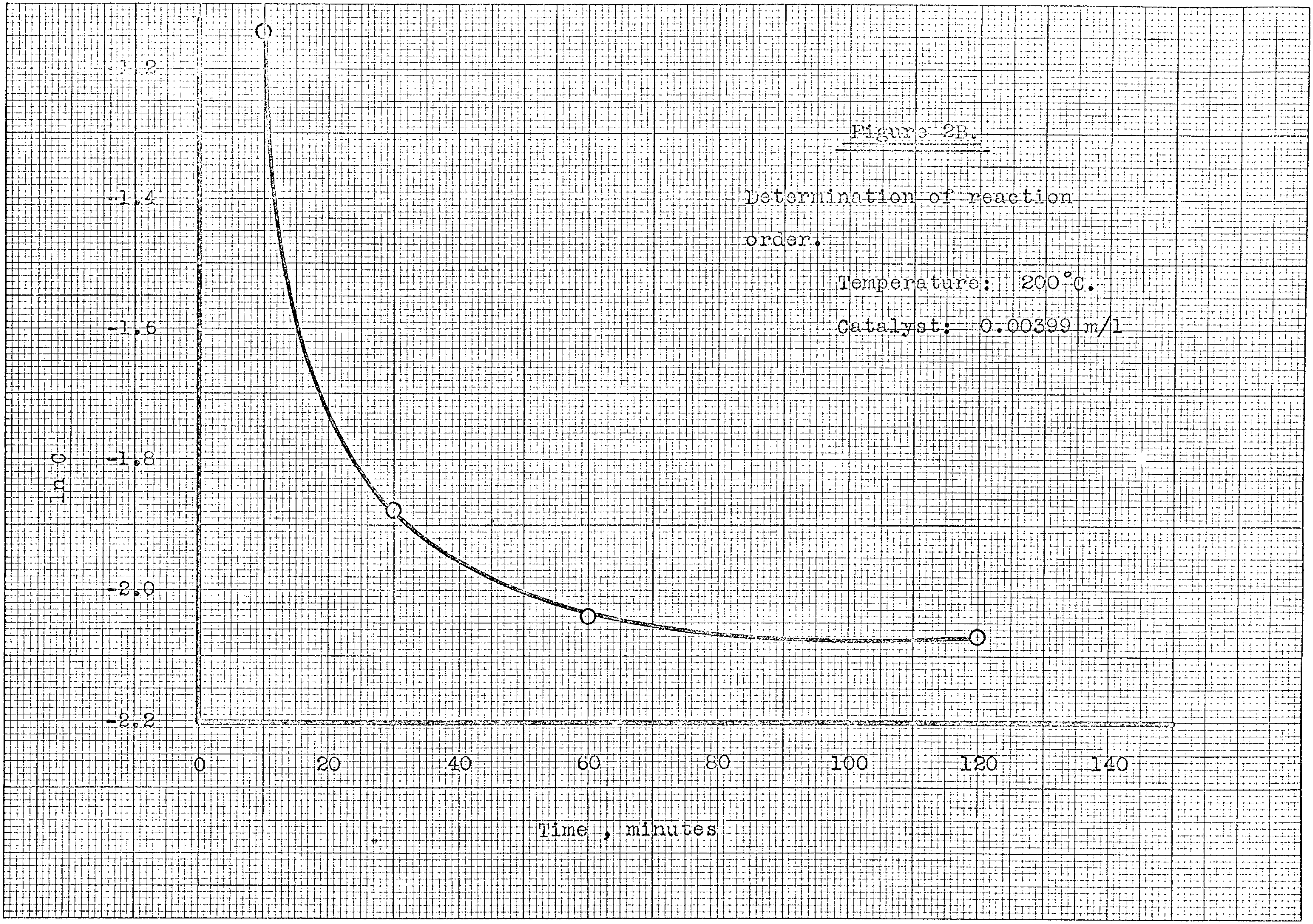


Figure 2B.

Determination of reaction order.

Temperature: 200°C.

Catalyst: 0.00399 m/l

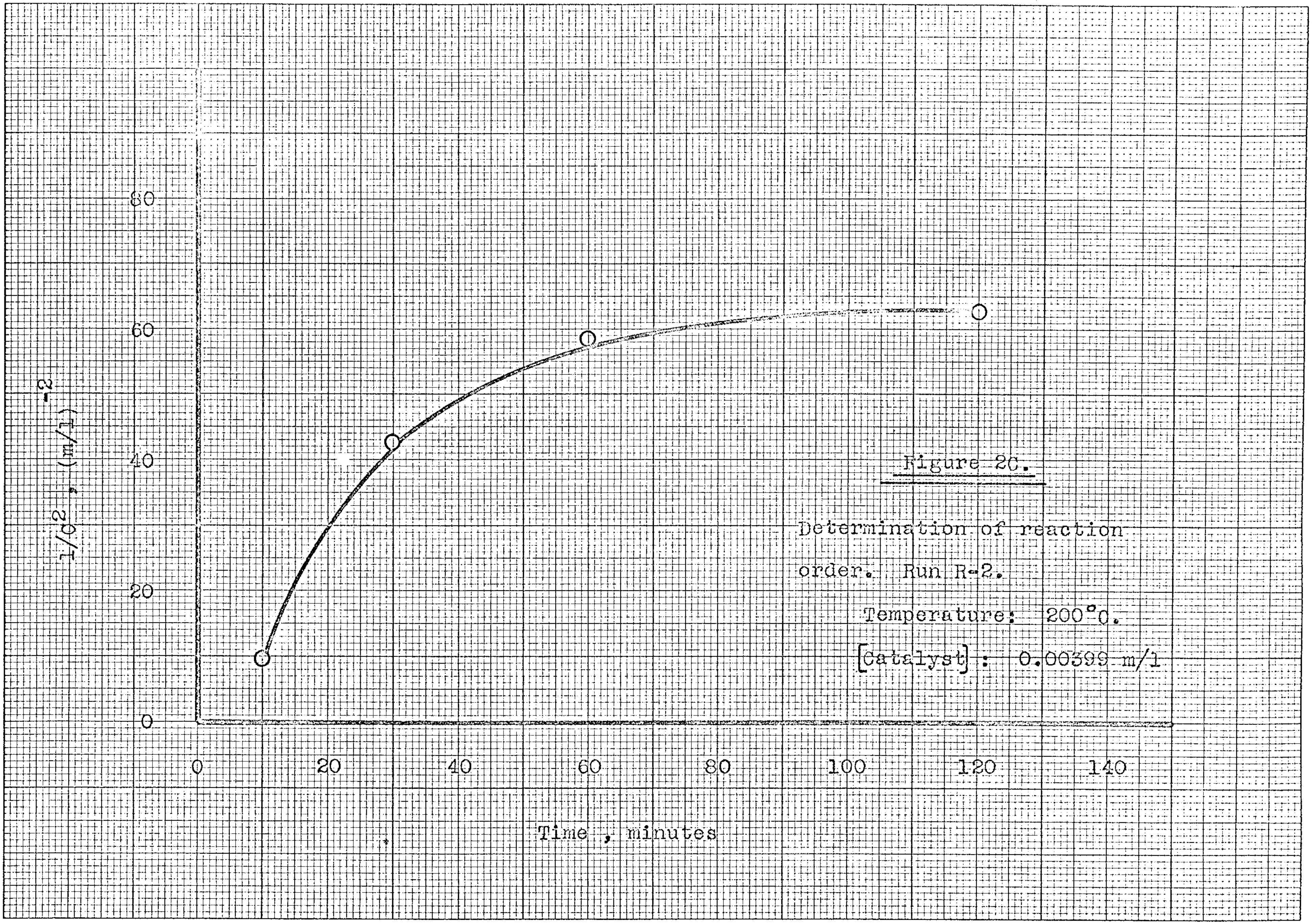


Figure 20.

Determination of reaction order. Run R-2.

Temperature: 200°C.

[Catalyst] : 0.00399 m/l

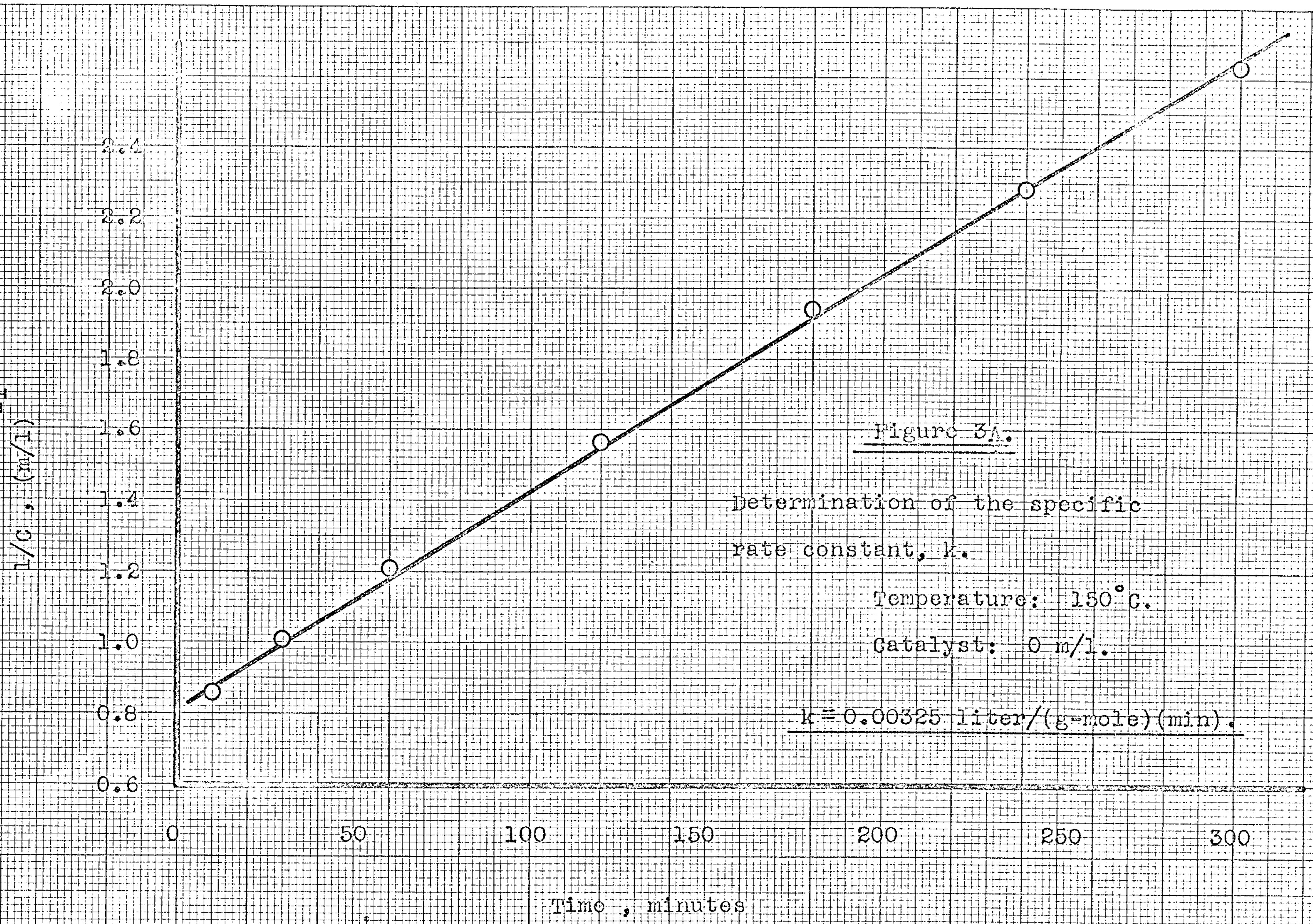


Figure 3A.

Determination of the specific rate constant, k.

Temperature: 150°C.

Catalyst: 0 m/l.

$k = 0.00325$ liter/(g-mole)(min).

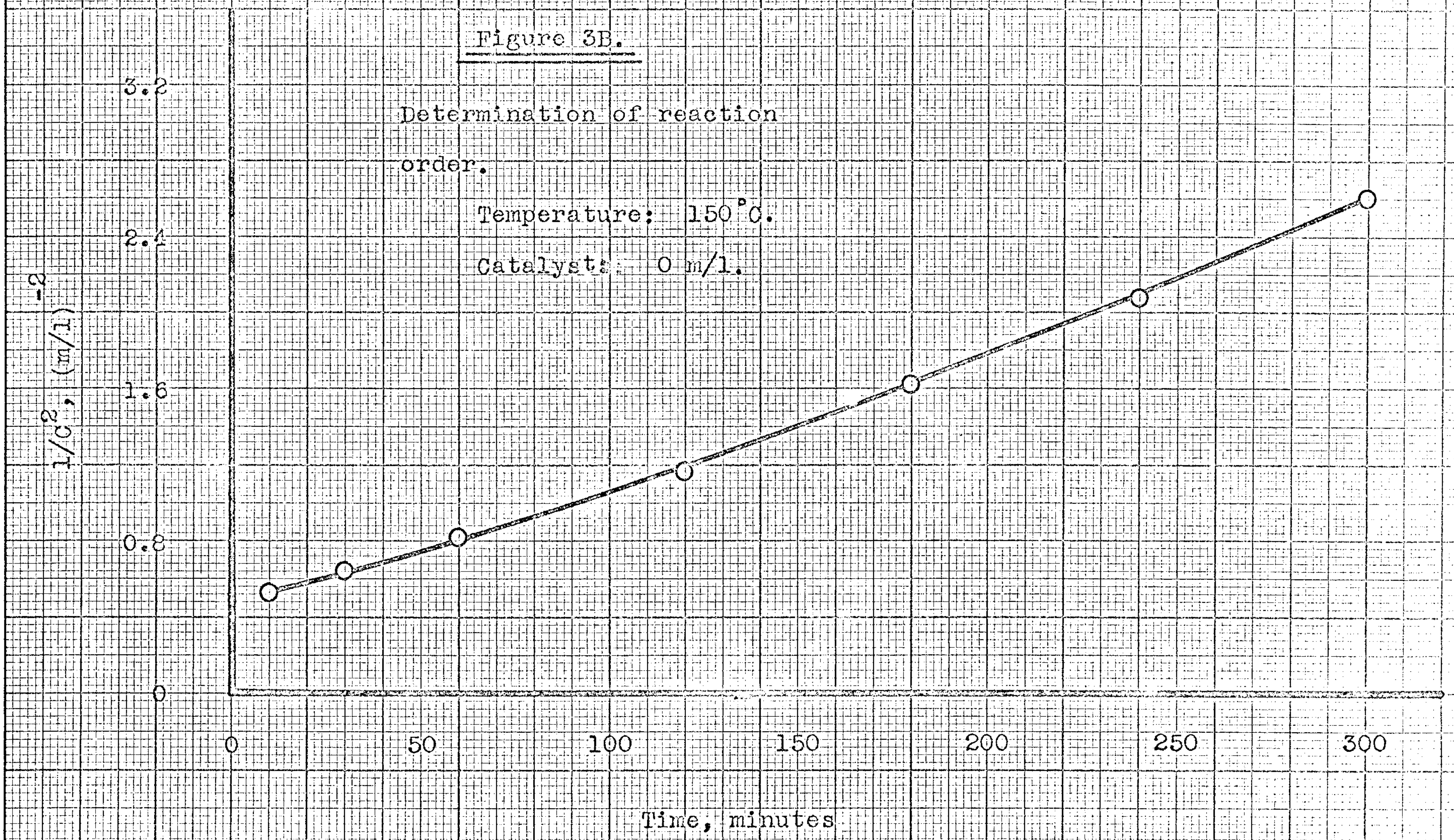


Figure 3B.
Determination of reaction order.
Temperature: 150°C.
Catalyst: 0 m/l.
$1/C^2$, $(m/l)^{-2}$
3.2
2.4
1.6
0.8
0
0
50
100
150
200
250
300
Time, minutes

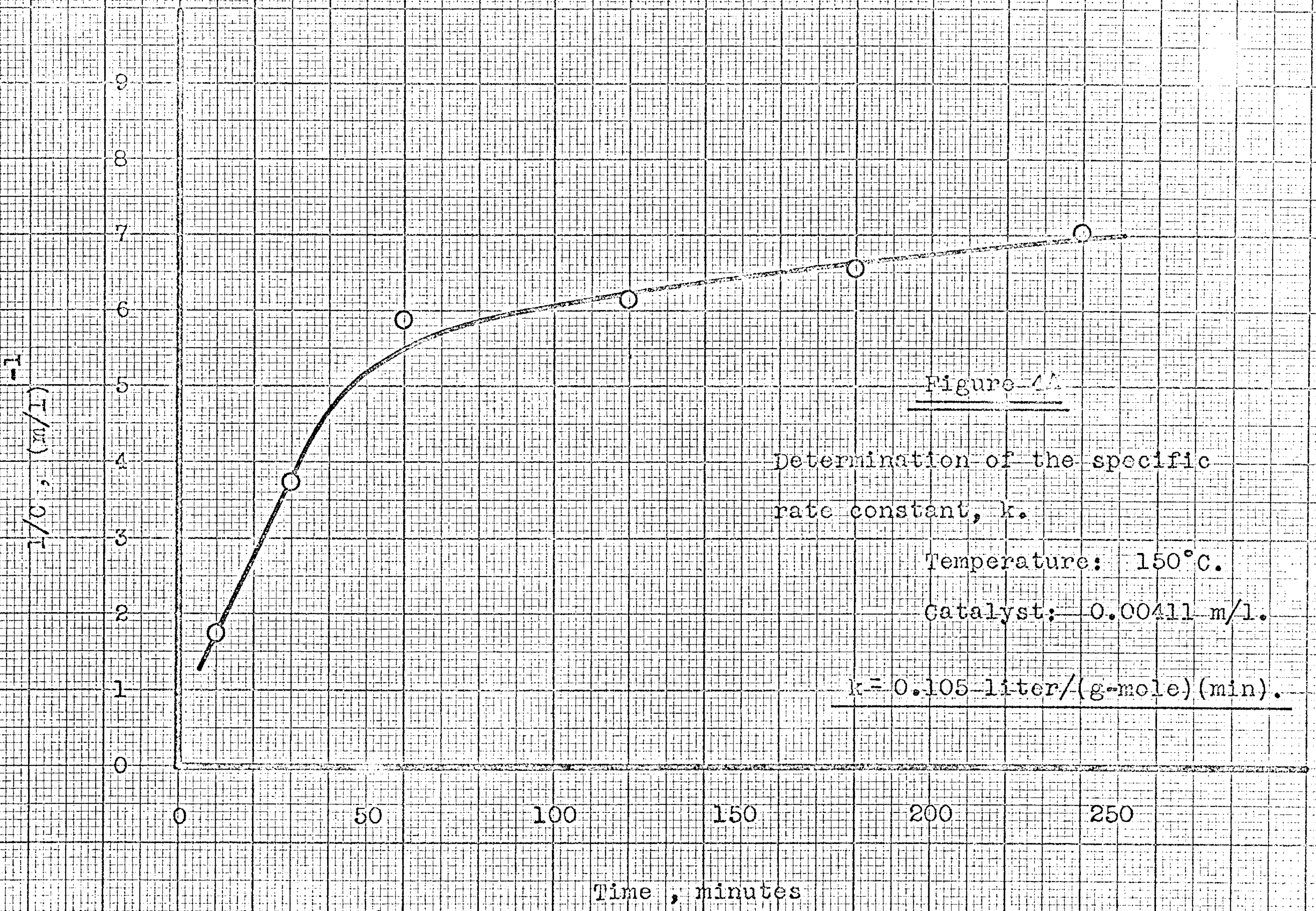


Figure 4A

Determination of the specific rate constant, k.

Temperature: 150°C.

Catalyst: 0.00411 m/l.

k = 0.105 liter/(g-mole)(min).

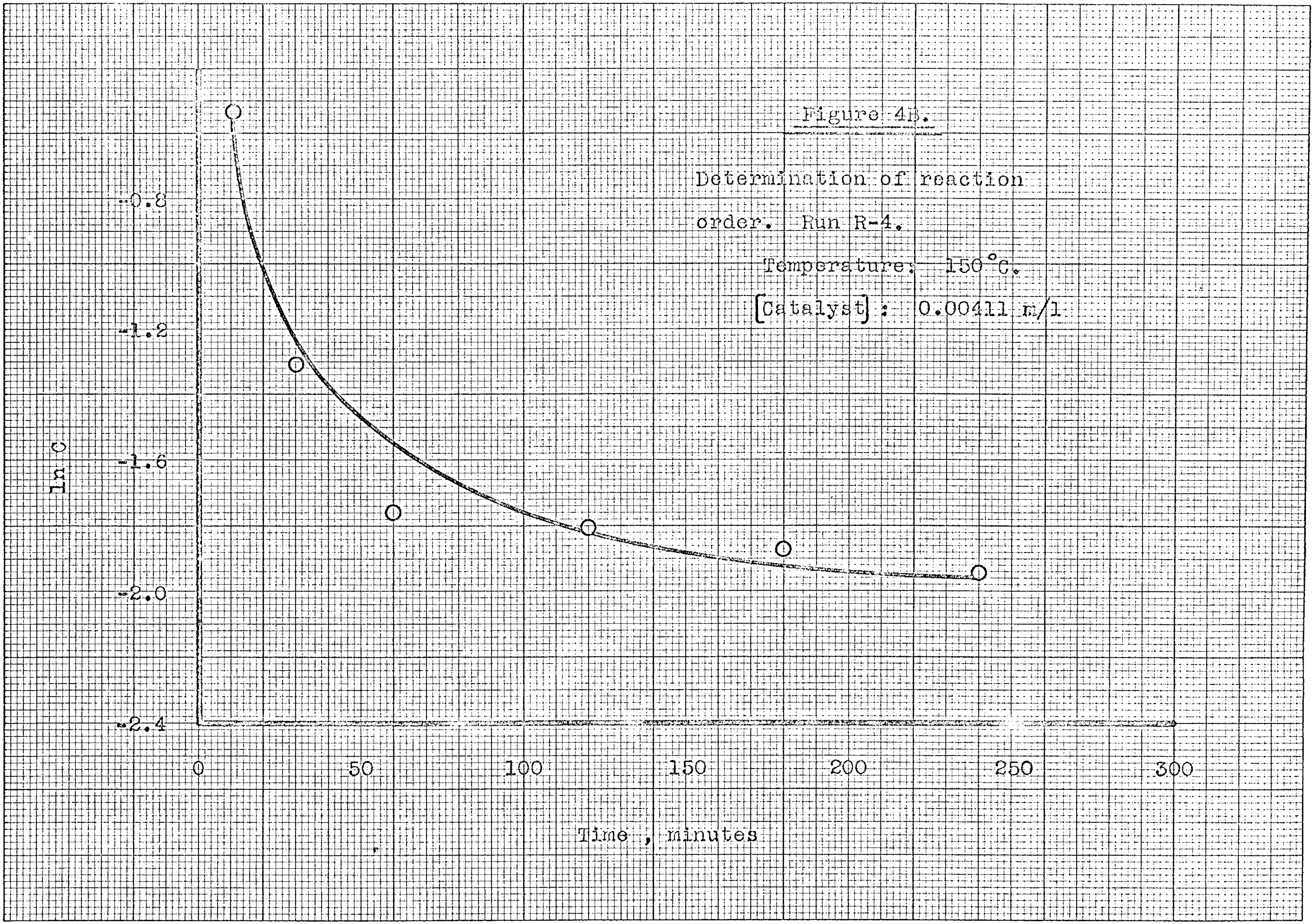


Figure 4B.

Determination of reaction order. Run R-4.

Temperature: 150°C.

[Catalyst] : 0.00411 m/l

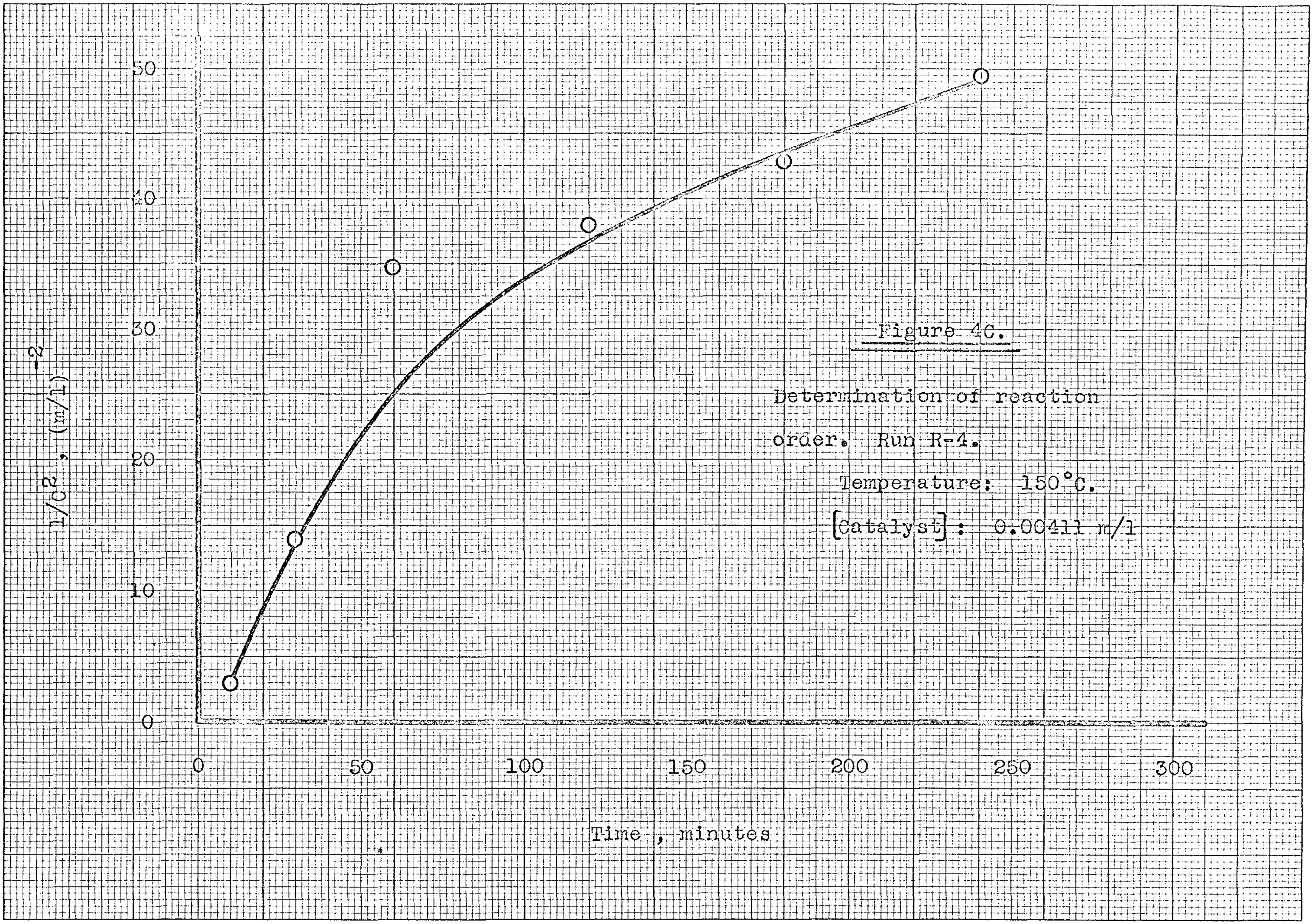


Figure 4C.

Determination of reaction order. Run R-4.

Temperature: 150°C.

[Catalyst]: 0.00411 m/l

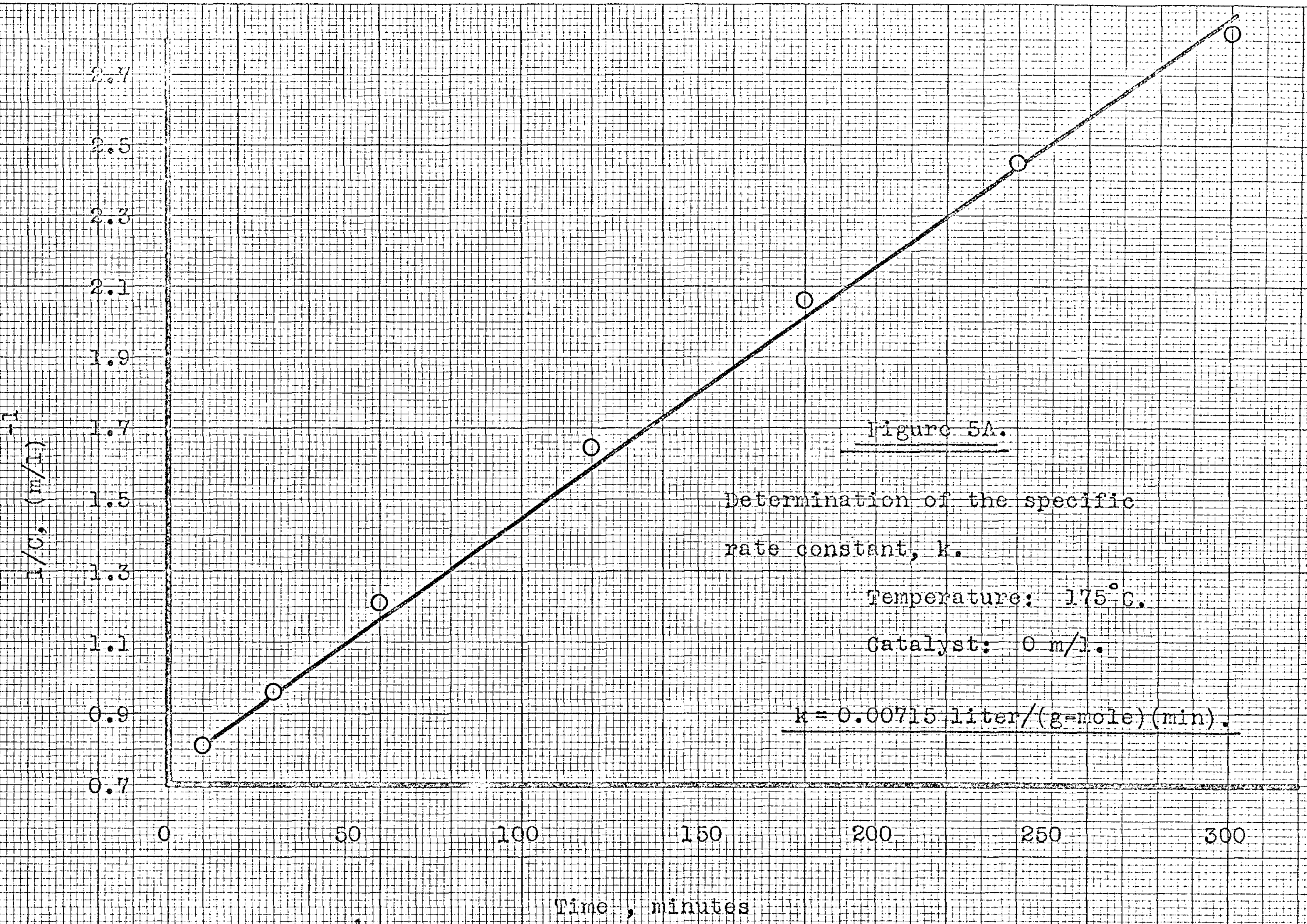


Figure 5A.

Determination of the specific rate constant, k.

Temperature: 175°C.

Catalyst: 0 m/l.

k = 0.00715 liter/(g-mole)(min).

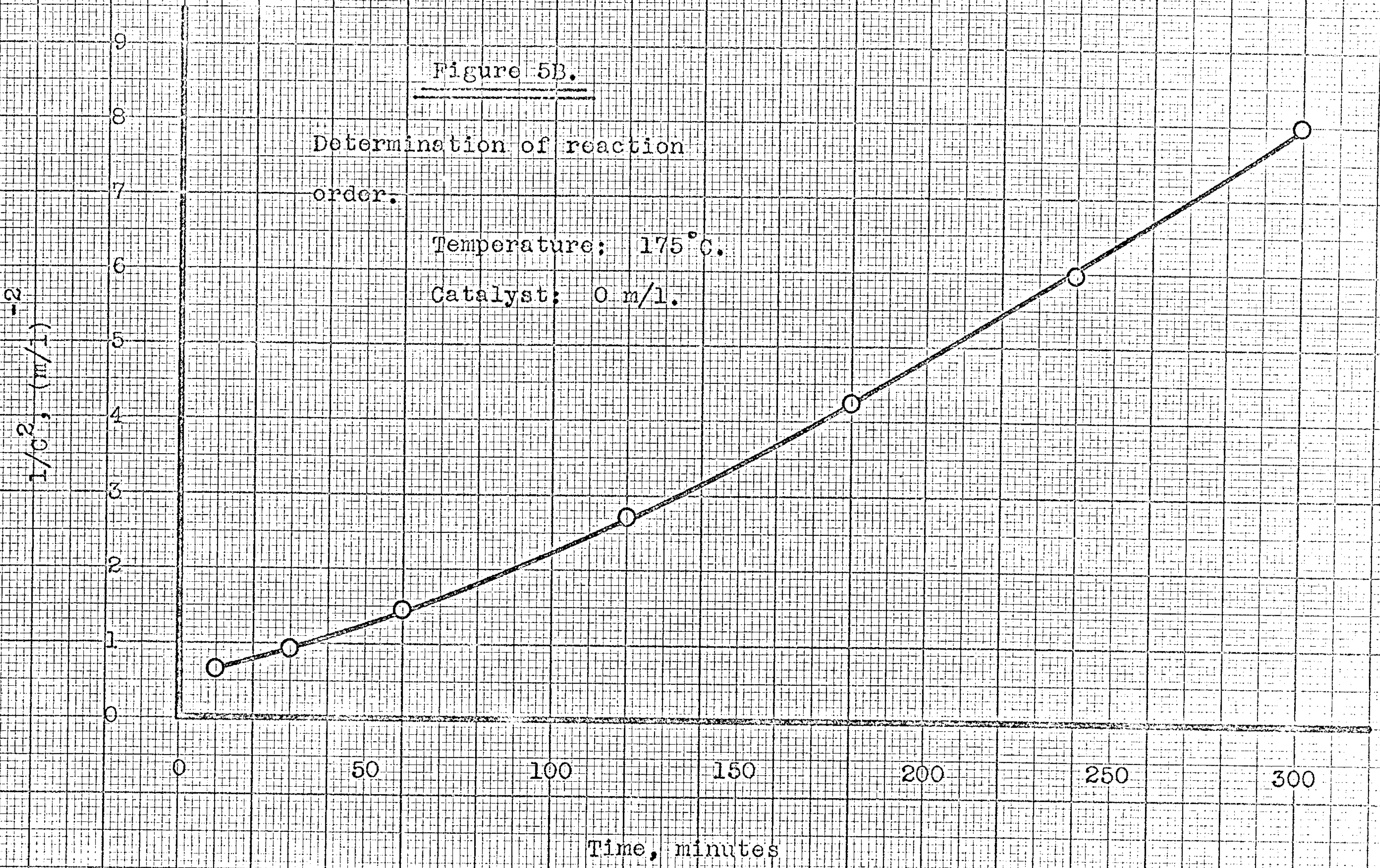


Figure 5B.

Determination of reaction order.

Temperature: 175°C.

Catalyst: 0 m/l.

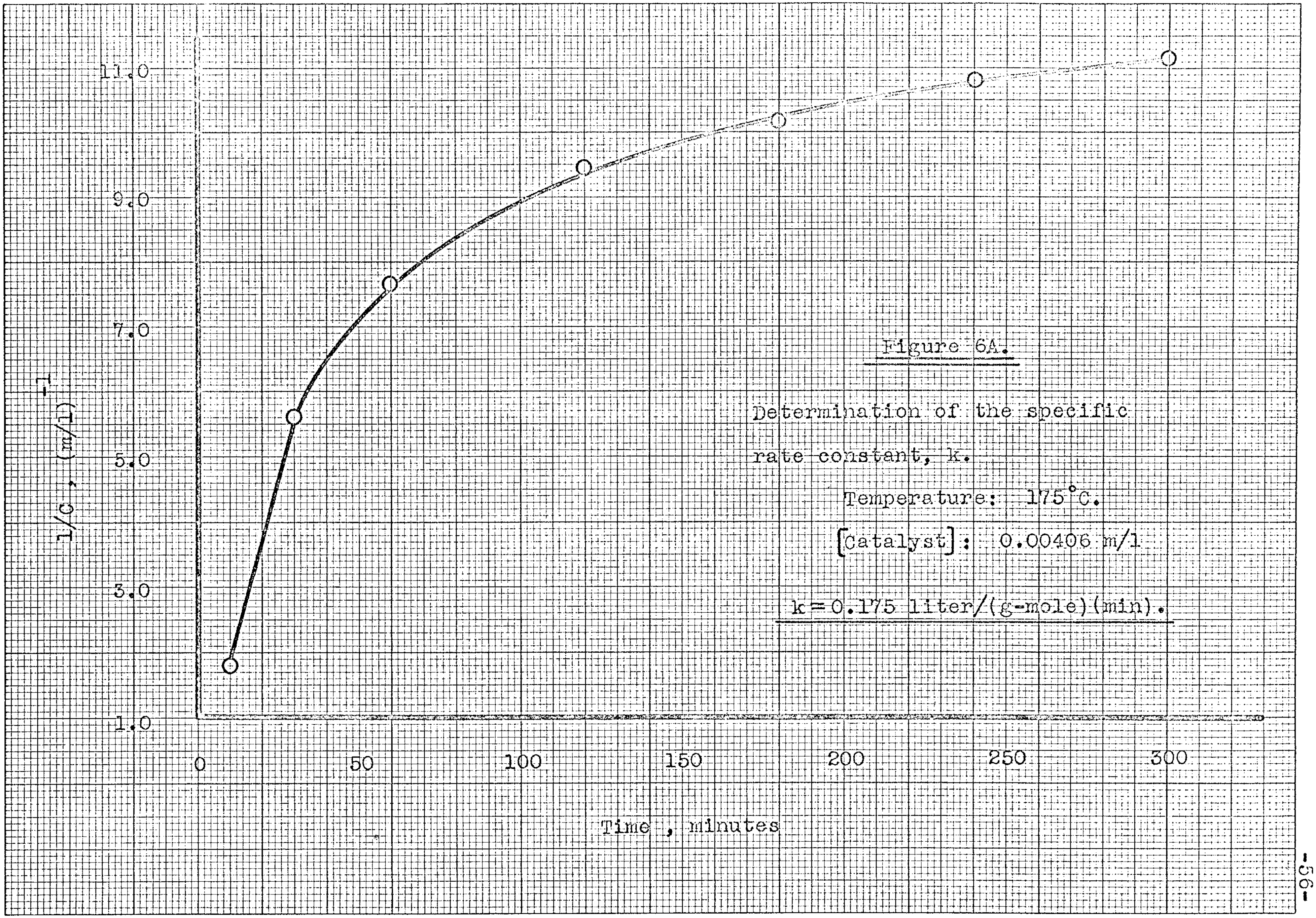


Figure 6A.

Determination of the specific rate constant, k.

Temperature: 175 °C.

[Catalyst]: 0.00406 m/l

k = 0.175 liter/(g-mole)(min).

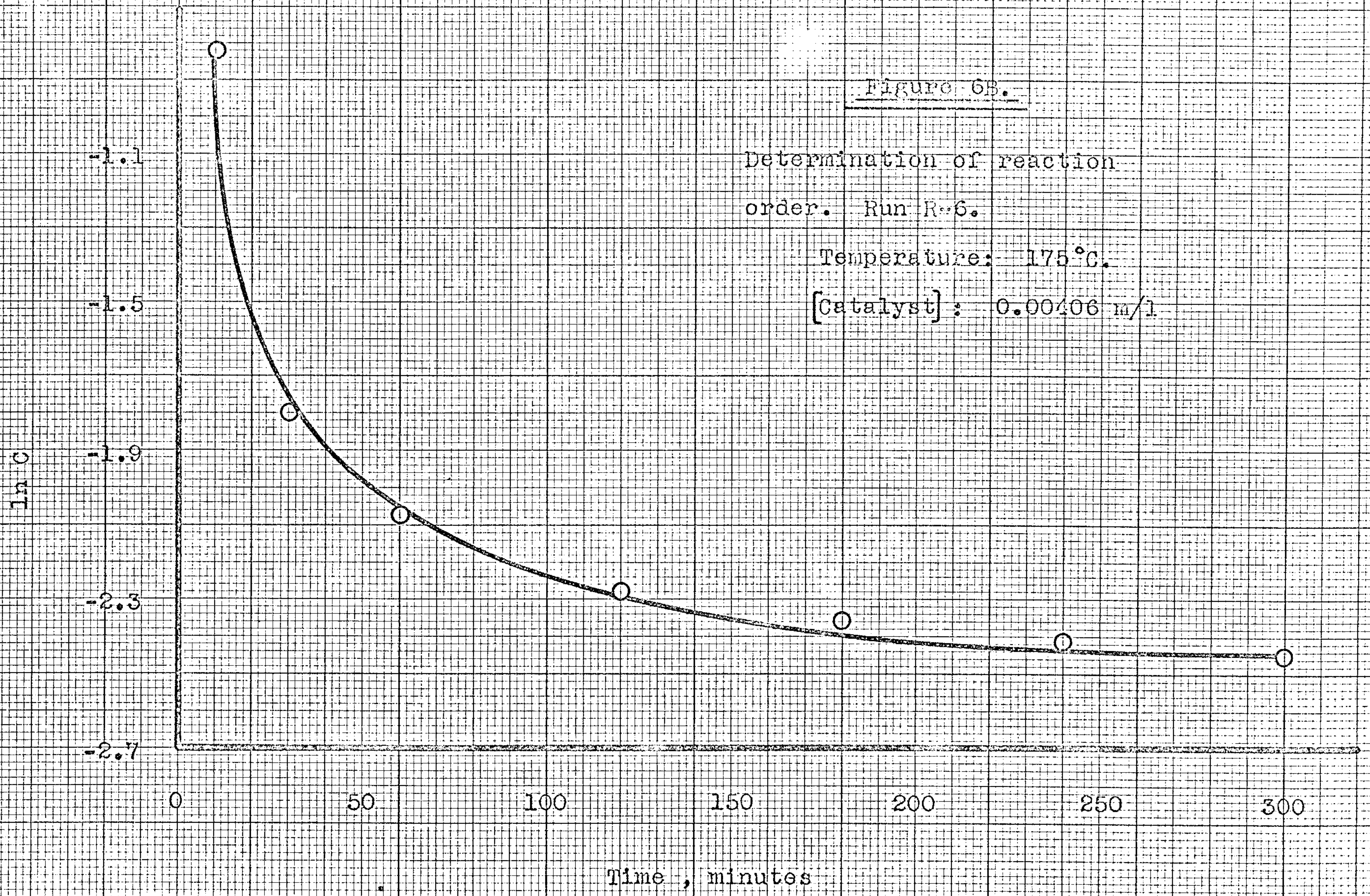


Figure 6B.

Determination of reaction order. Run R-6.

Temperature: 175 °C.

[Catalyst] : 0.00406 m/l

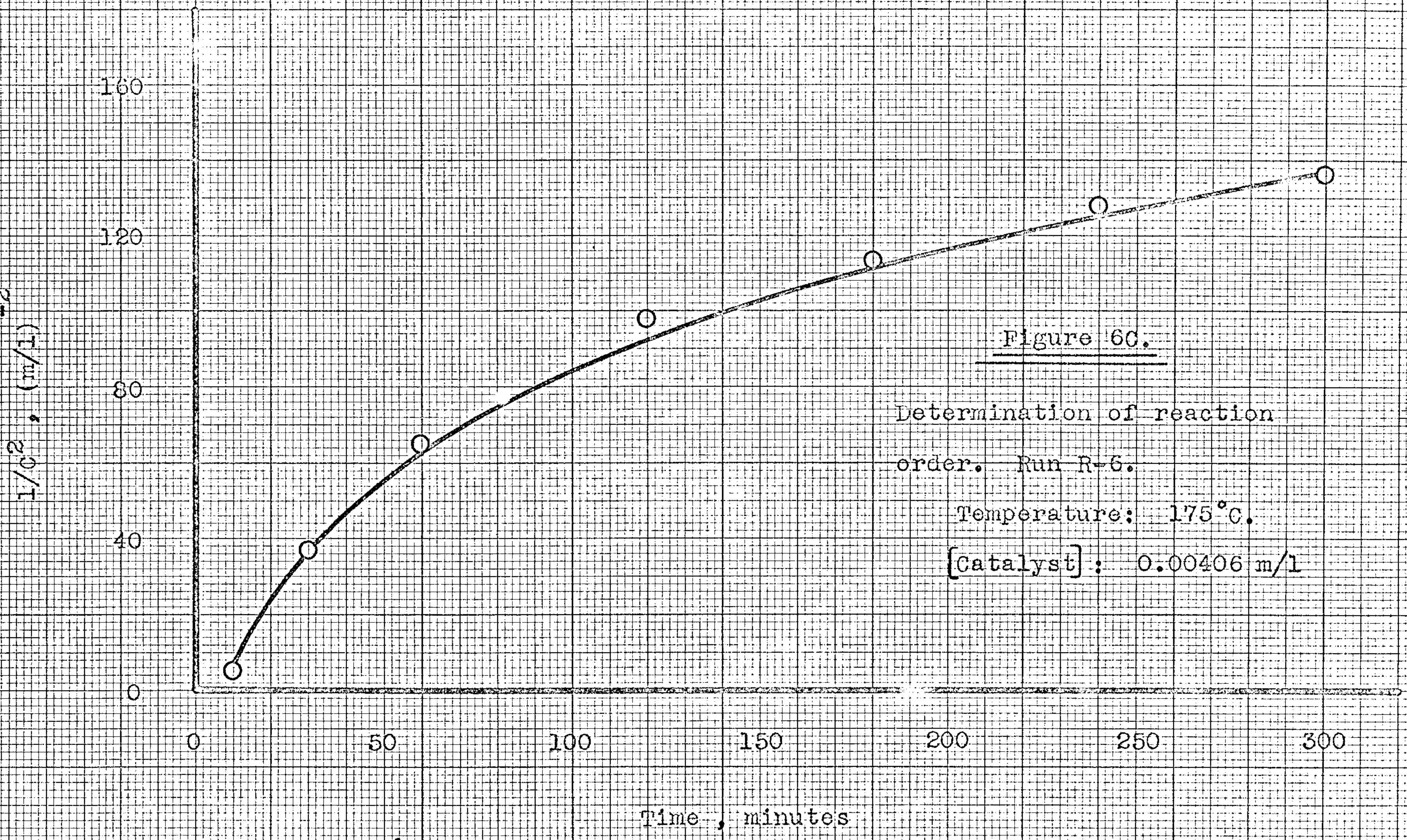


Figure 6C.

Determination of reaction order. Run R-6.

Temperature: 175°C.

[Catalyst] : 0.00406 m/l

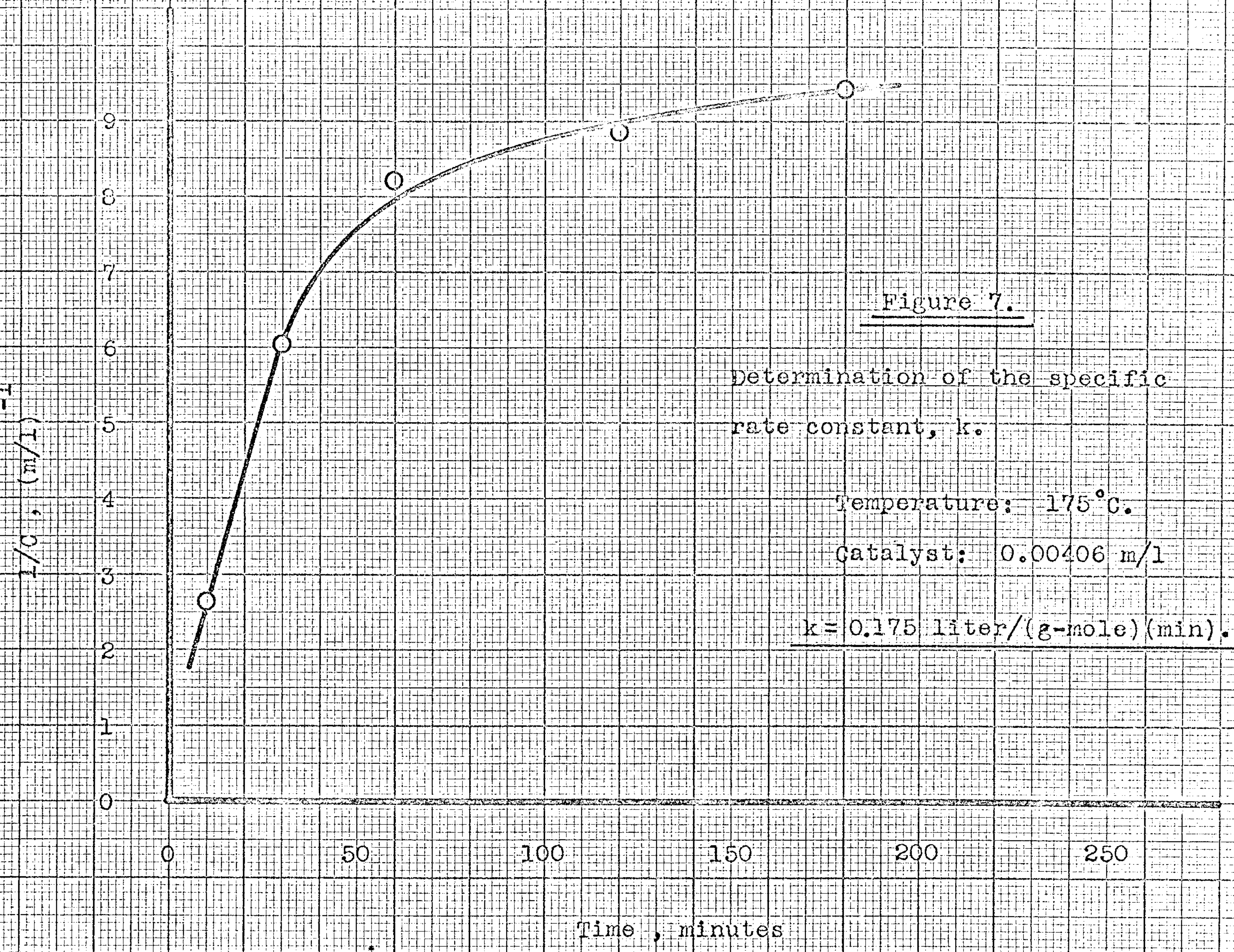


Figure 7.

Determination of the specific rate constant, k.

Temperature: 175°C.

Catalyst: 0.00406 m/l

k = 0.175 liter/(g-mole)(min).

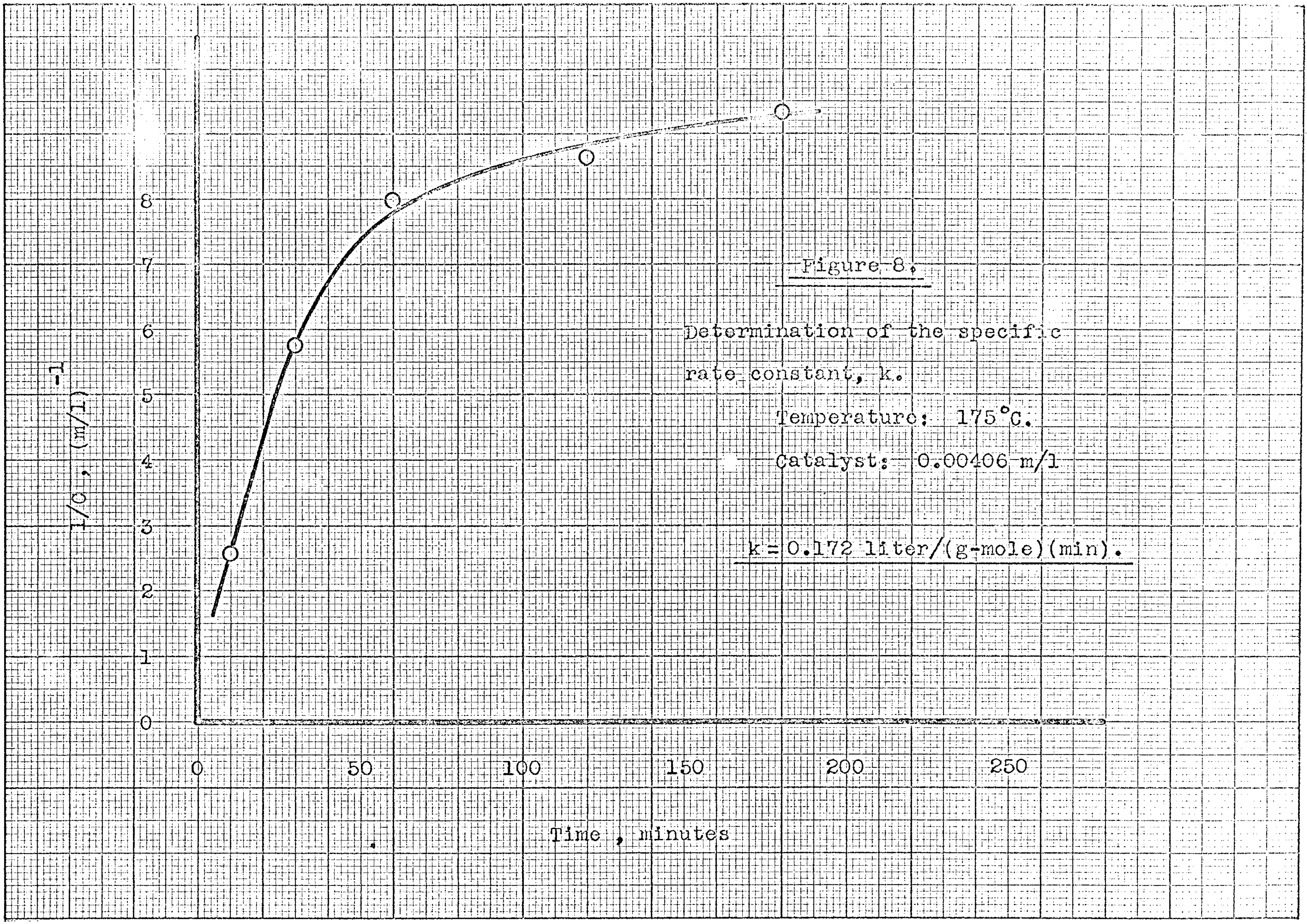


Figure 8.

Determination of the specific rate constant, k.

Temperature: 175°C.

Catalyst: 0.00406 m/l

k = 0.172 liter/(g-mole)(min).

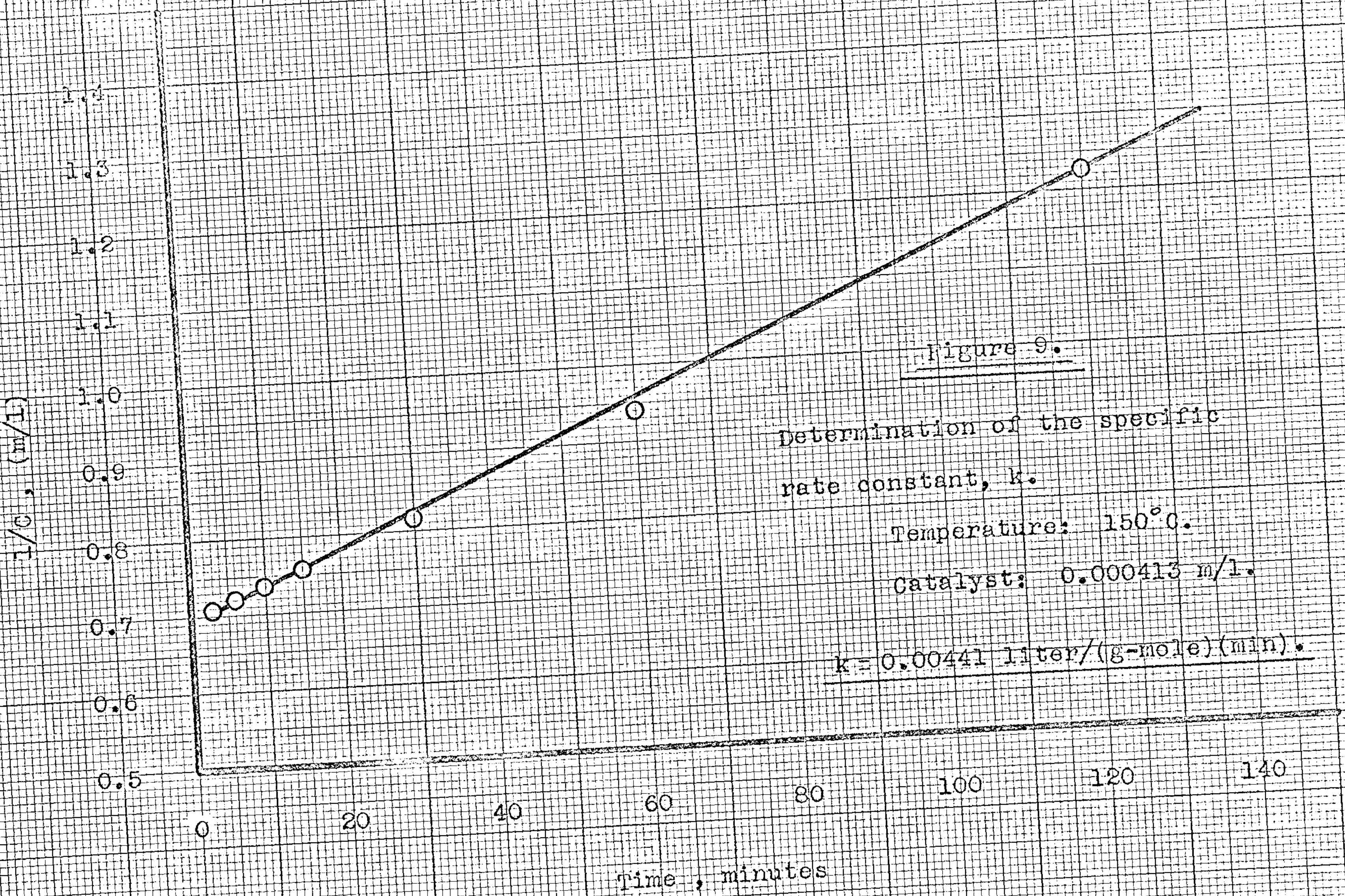


Figure 9.

Determination of the specific rate constant, k.

Temperature: 150°C.

Catalyst: 0.000413 m/l.

k = 0.00441 liter/(g-mole)(min).

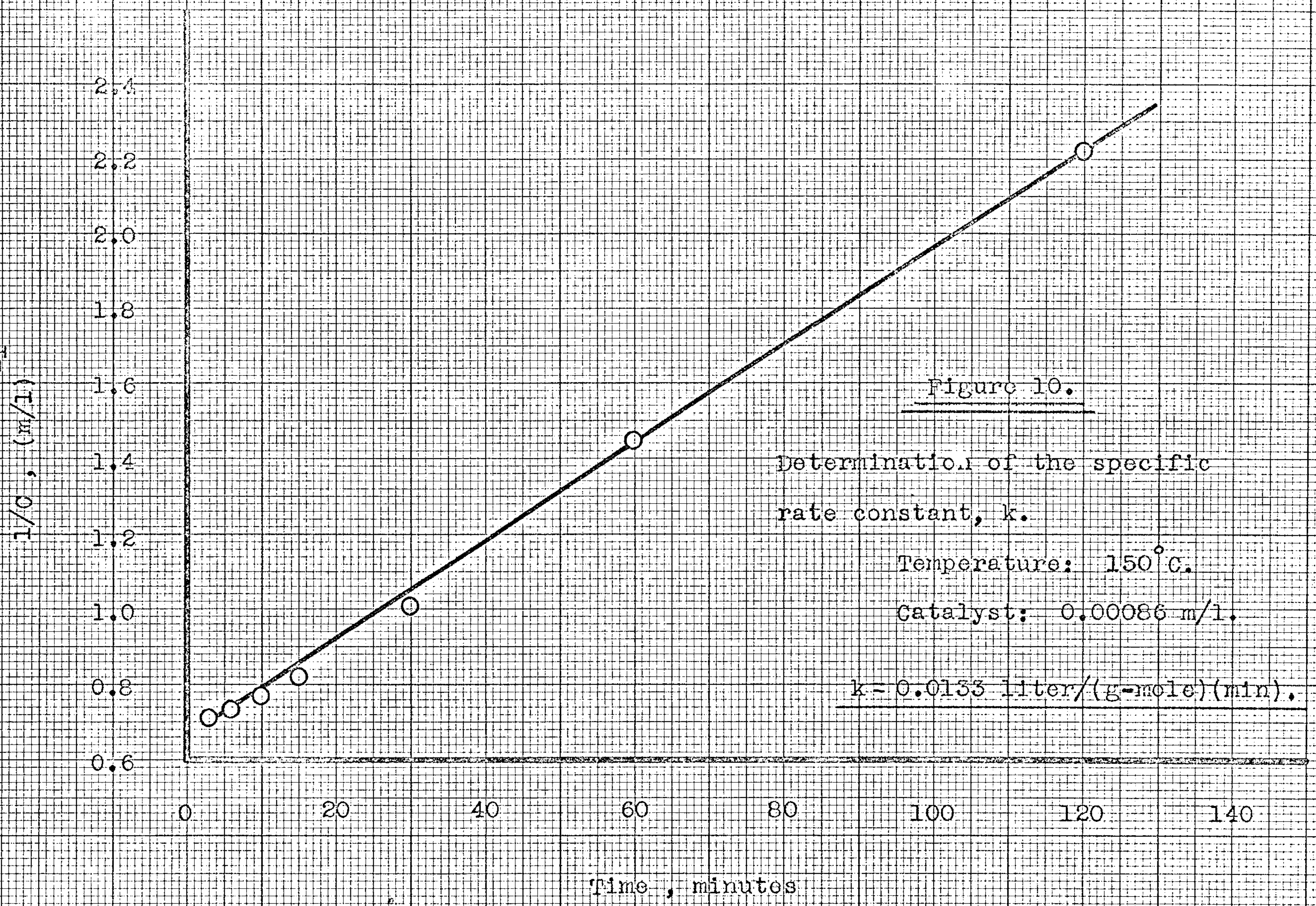


Figure 10.

Determination of the specific rate constant, k.

Temperature: 150°C.

Catalyst: 0.00086 m/l.

k = 0.0133 liter/(g-mole)(min).

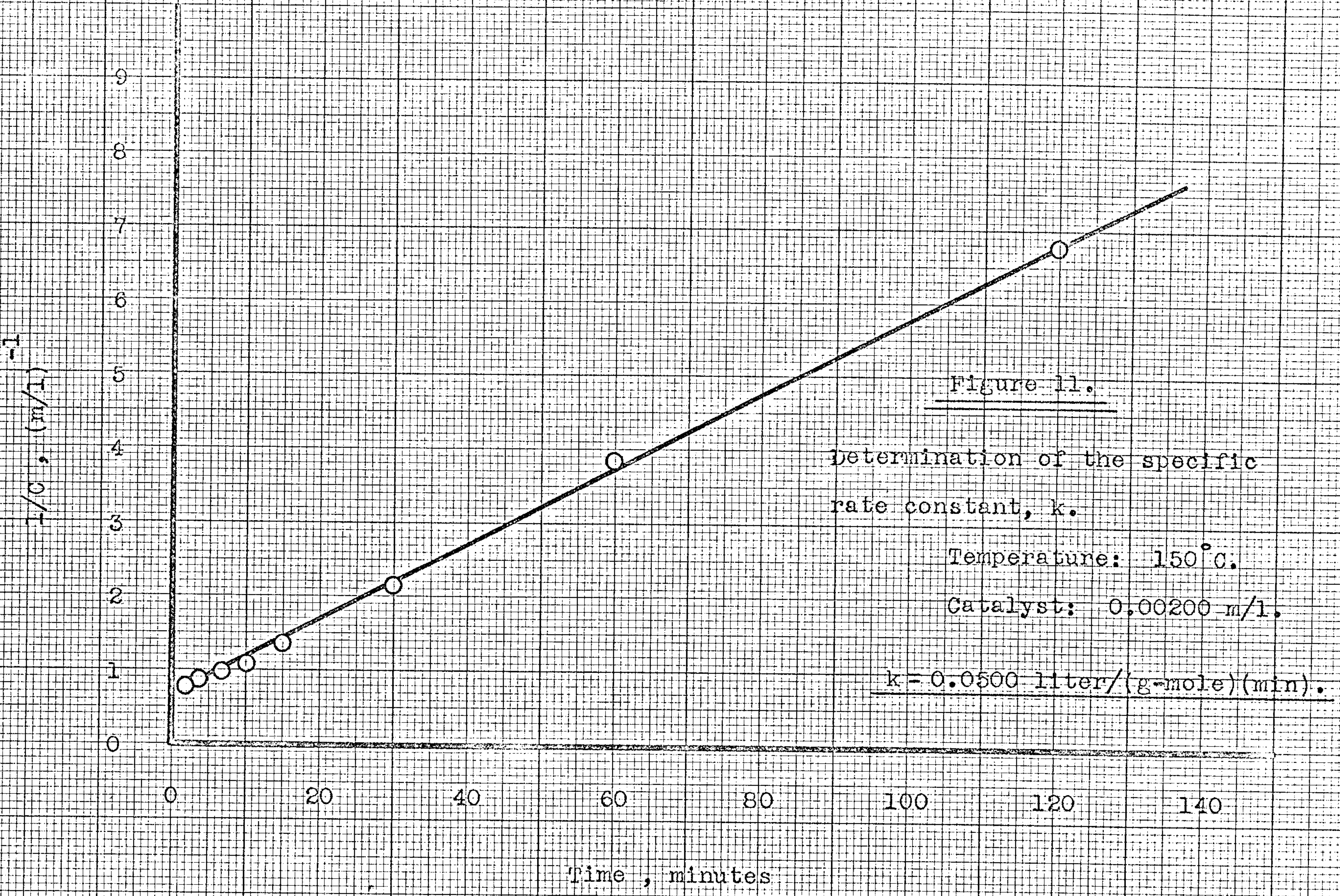


Figure 11.

Determination of the specific rate constant, k.

Temperature: 150 °C.

Catalyst: 0.00200 m/l.

k = 0.0500 liter/(g-mole)(min).

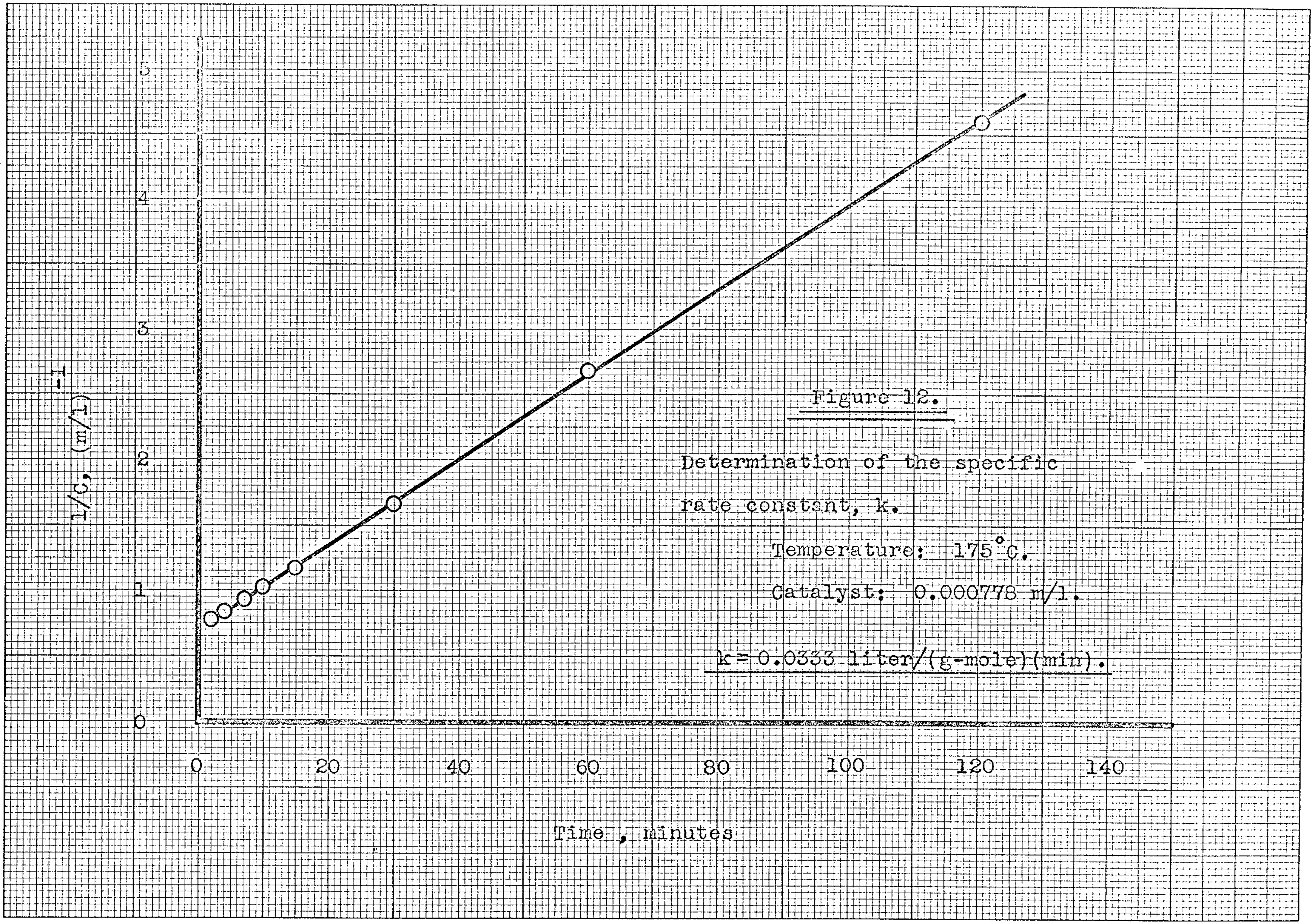


Figure 12.

Determination of the specific rate constant, k.

Temperature: 175°C.

Catalyst: 0.000778 m/l.

k = 0.0333 liter/(g-mole)(min).

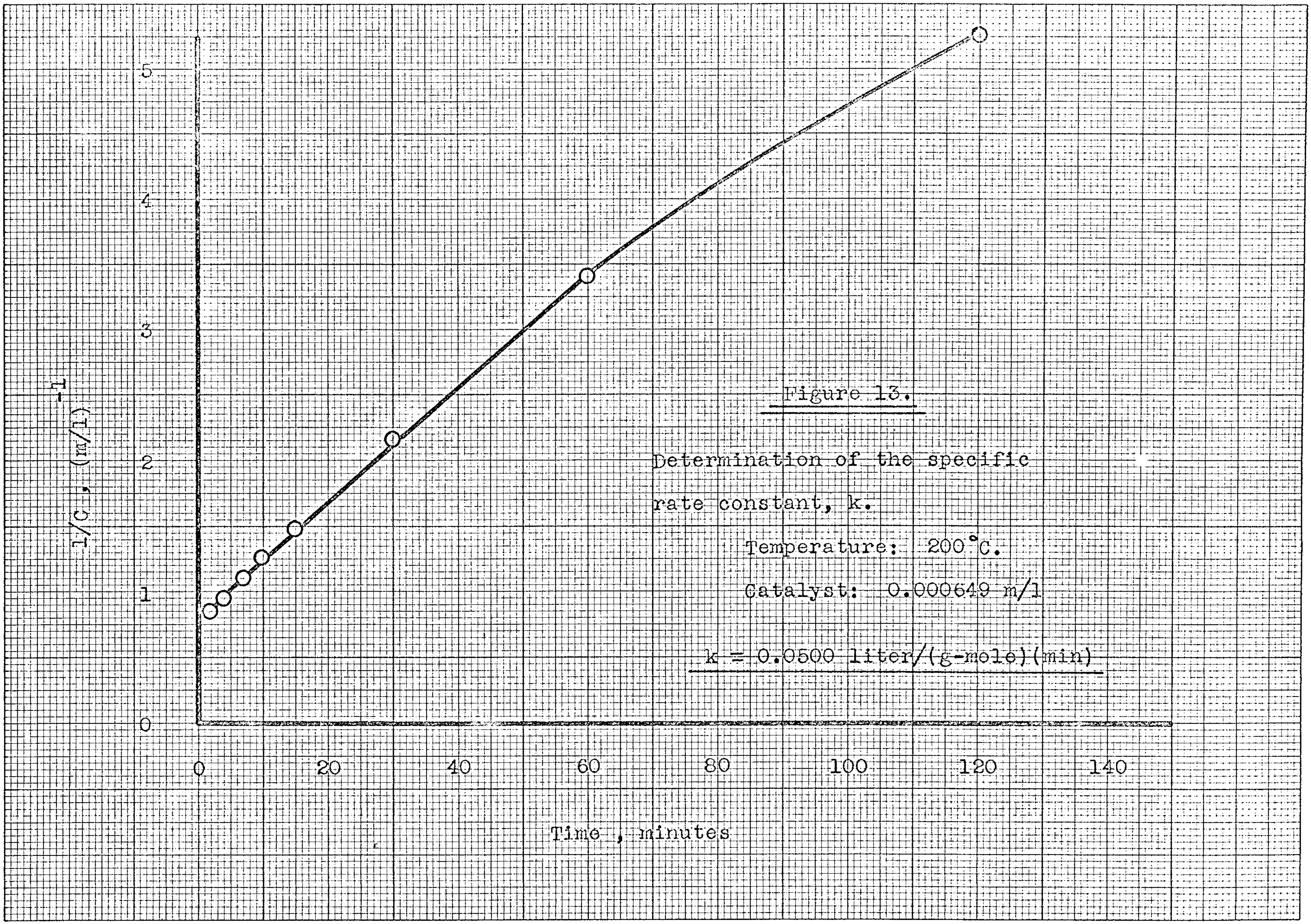


Figure 13.

Determination of the specific rate constant, k.

Temperature: 200°C.

Catalyst: 0.000649 m/l

k = 0.0500 liter/(g-mole)(min)

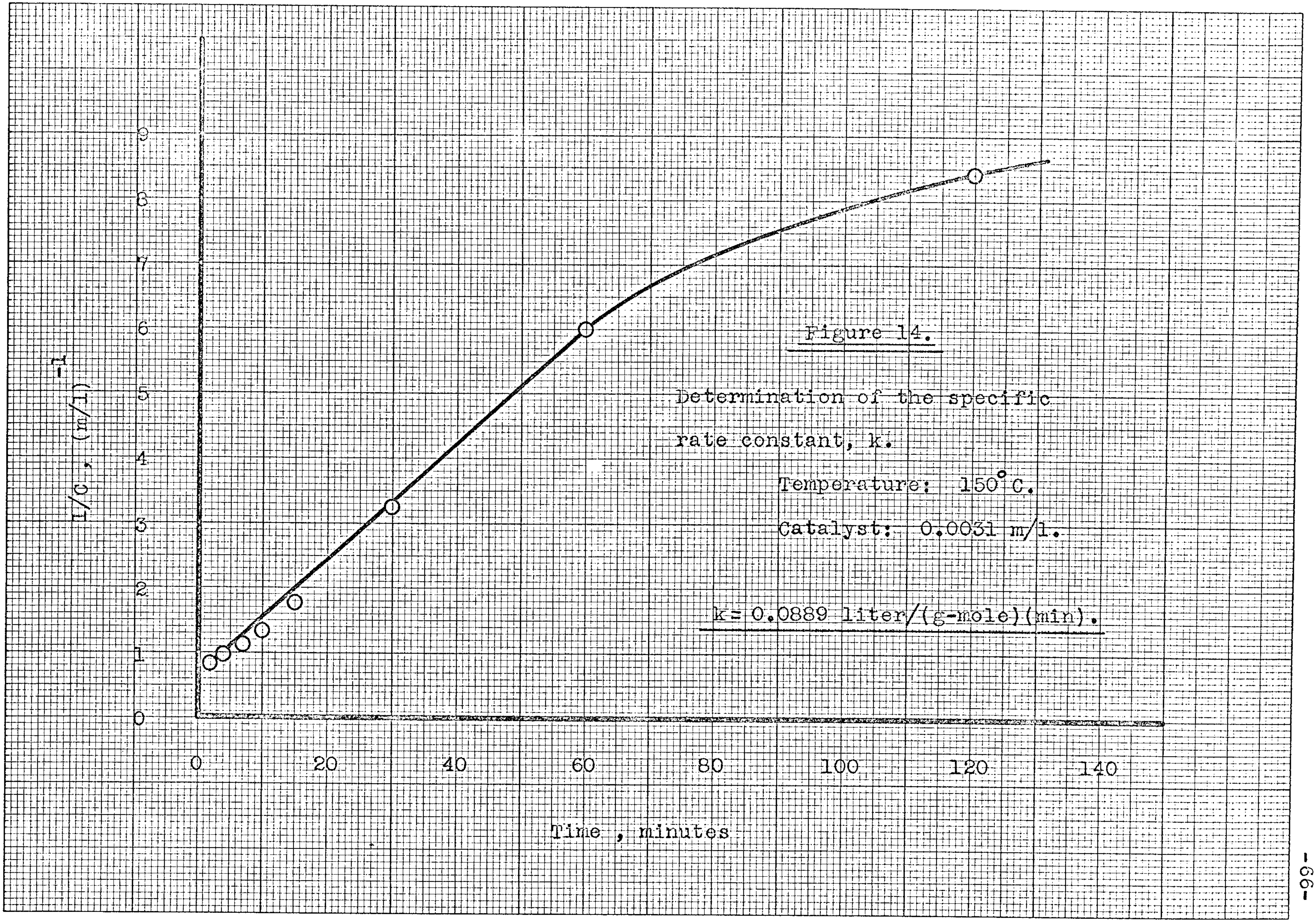


Figure 14.

Determination of the specific rate constant, k.

Temperature: 150° C.

Catalyst: 0.0031 m/l.

k= 0.0889 liter/(g-mole)(min).

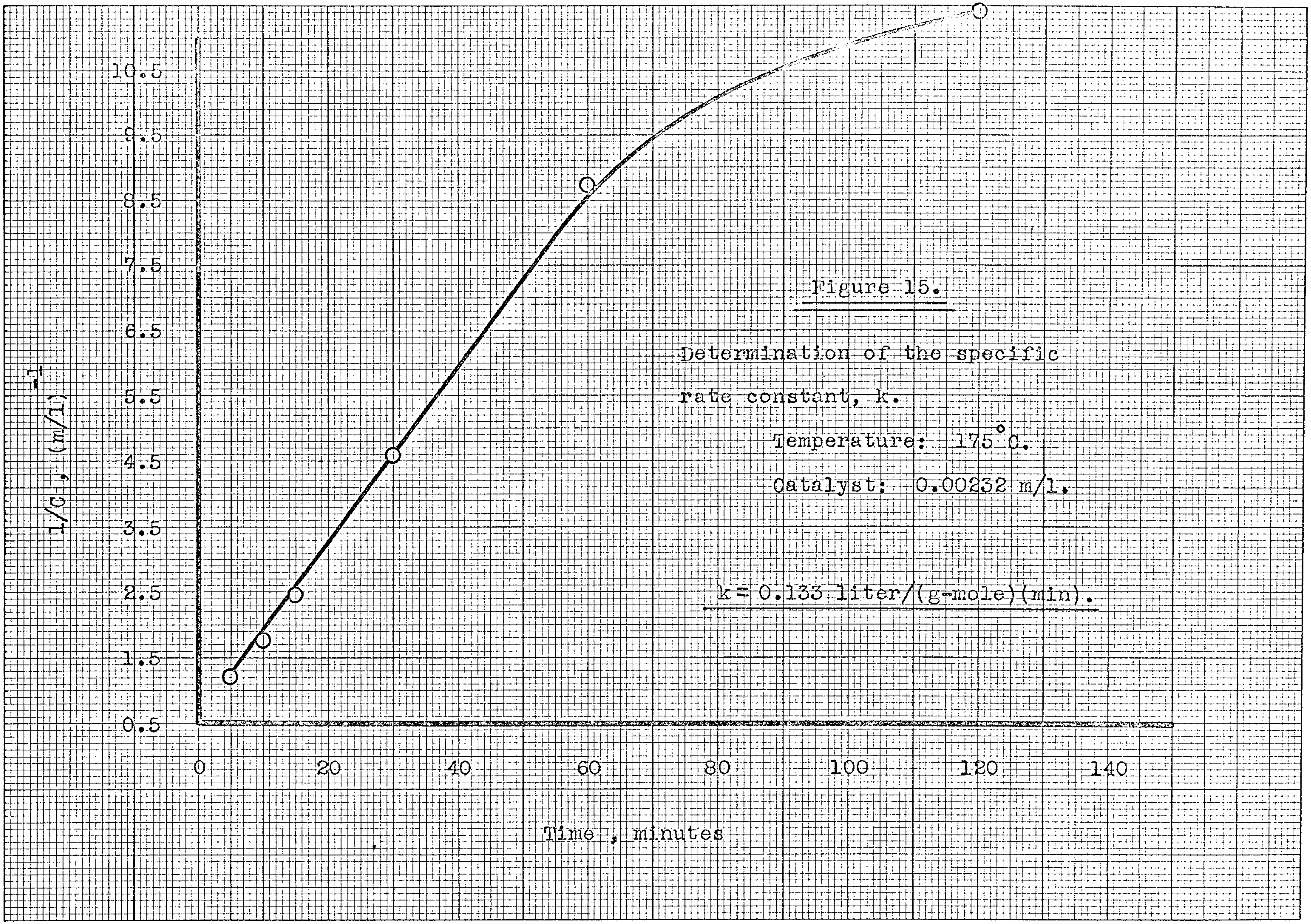


Figure 15.

Determination of the specific rate constant, k.

Temperature: 175°C.

Catalyst: 0.00232 m/l.

k = 0.133 liter/(g-mole)(min).

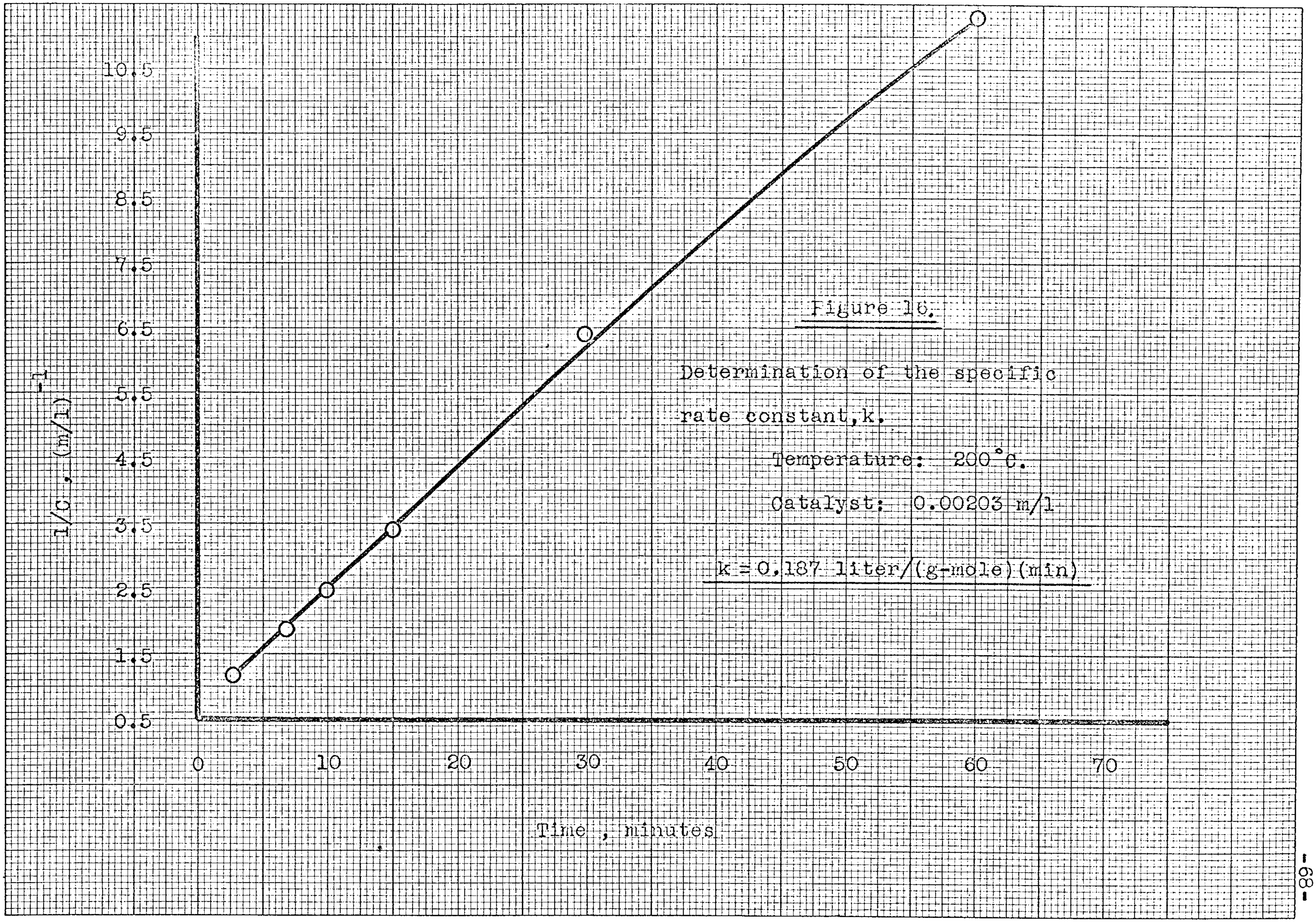


Figure 16.

Determination of the specific rate constant, k.

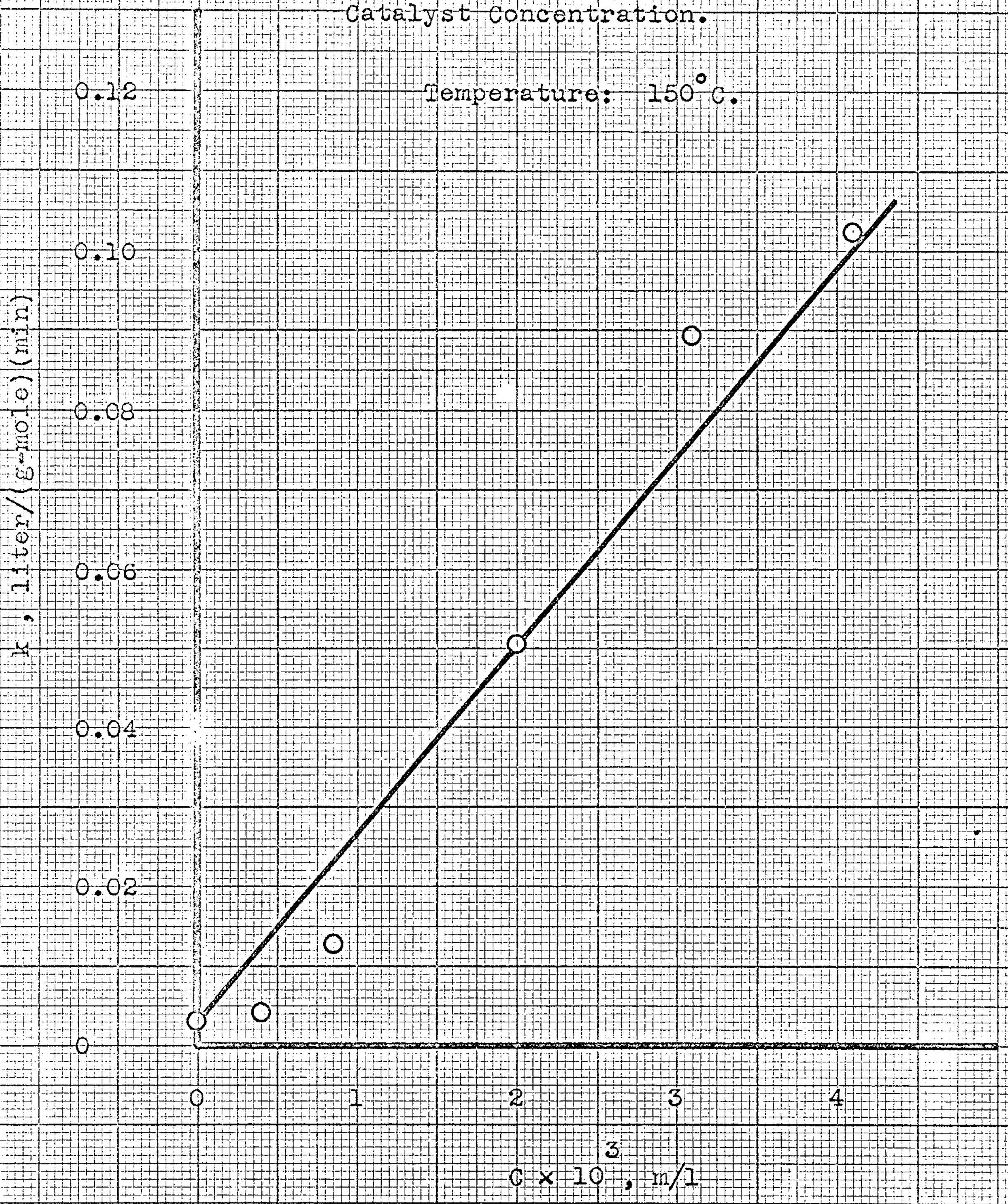
Temperature: 200°C.

Catalyst: 0.00203 m/l

k = 0.187 liter/(g-mole)(min)

Figure 17.

Reaction Rate as a Function of Catalyst Concentration.



Temperature: 150°C.

Figure 18.

Reaction Rate as a Function of Catalyst Concentration.

Temperature: 175°C.

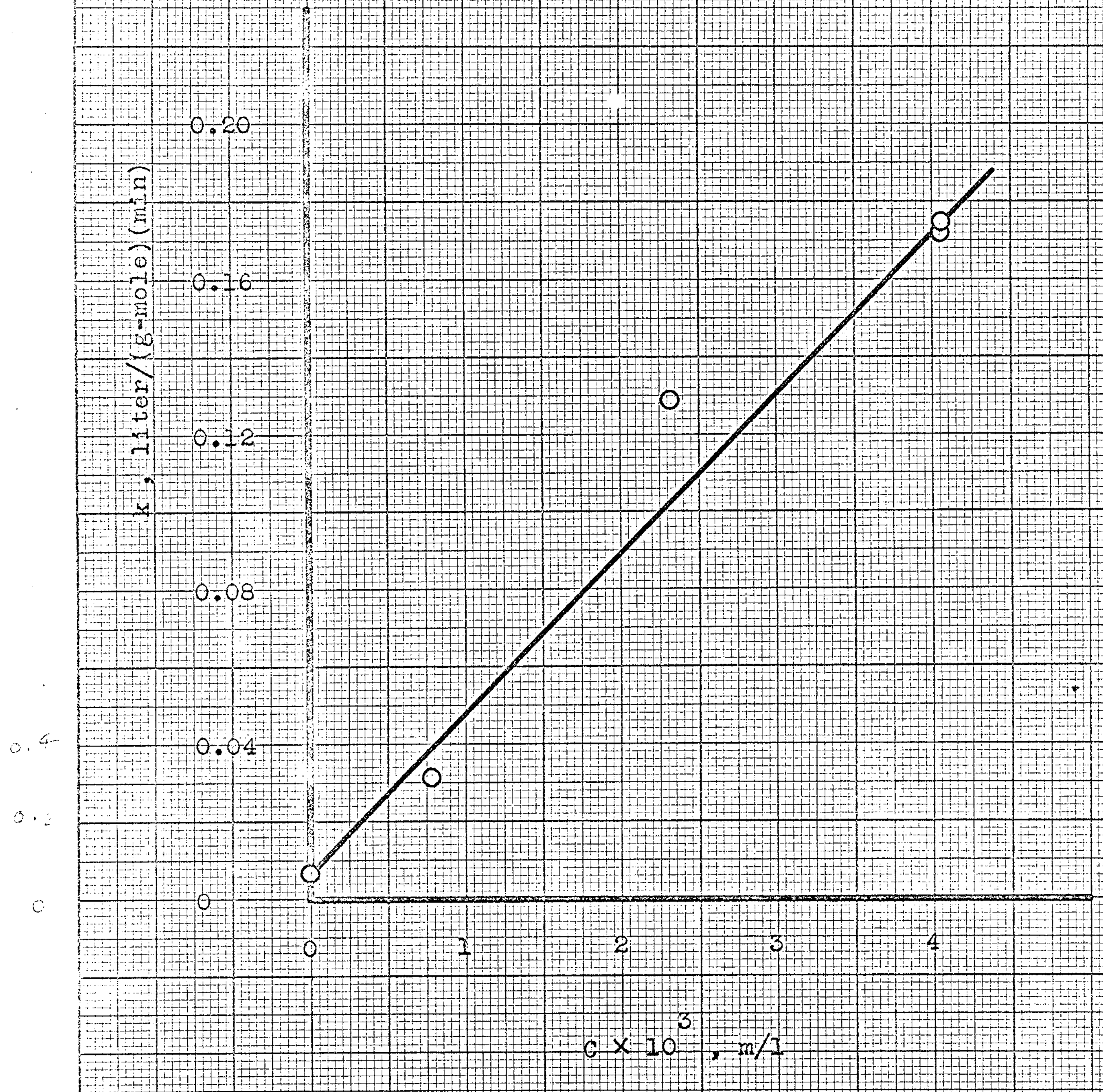


Figure 19.

Reaction Rate as a Function of Catalyst Concentration.

Temperature: 200°C.

Figure 20.

Reaction Rate as a Function of Catalyst Concentration at Different Temperatures, From Figures 17, 18, and 19.

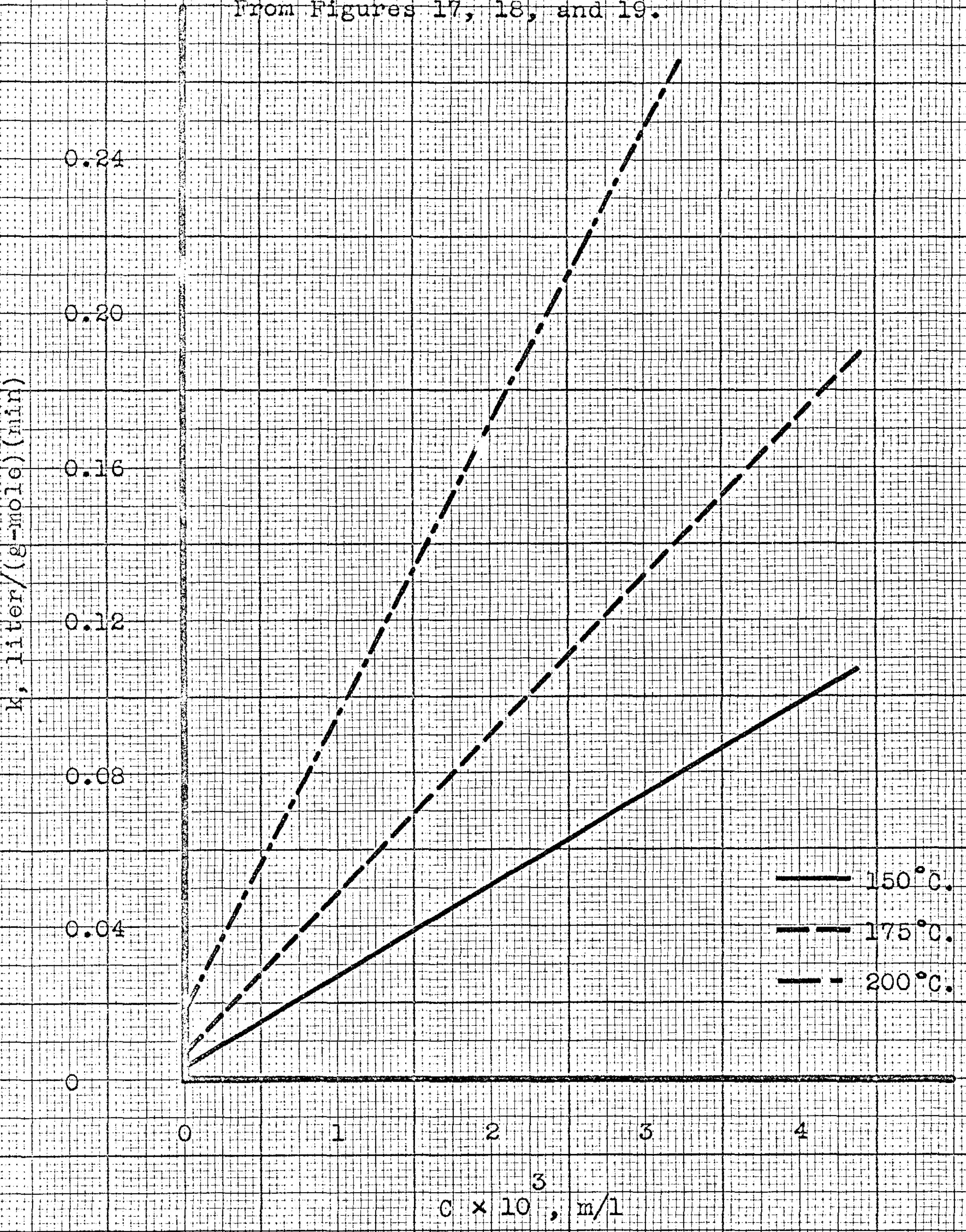


Figure 21.

Variation of Uncatalyzed Reaction Rate With Temperature

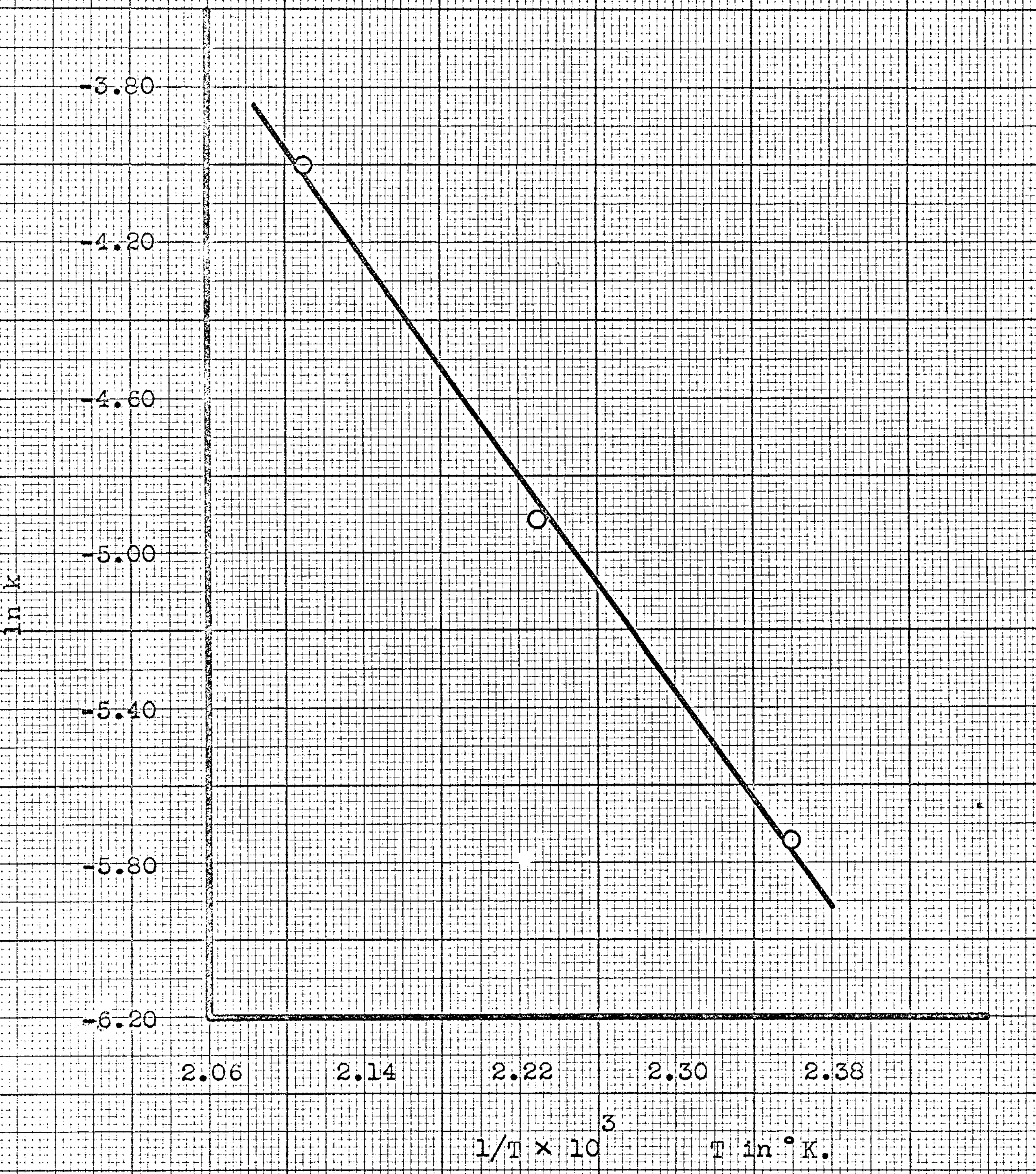
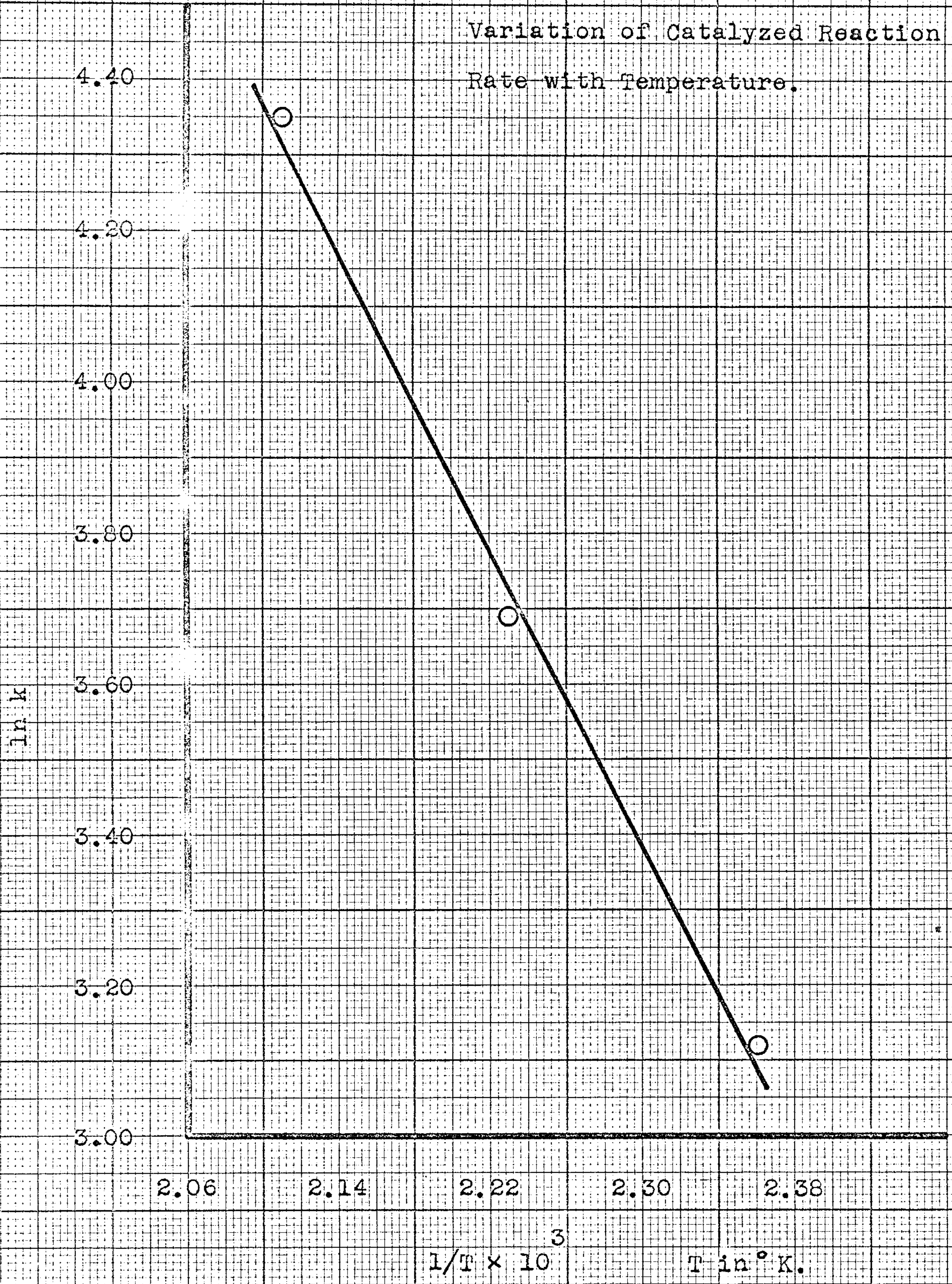


Figure 22.



Variation of Catalyzed Reaction Rate with Temperature.

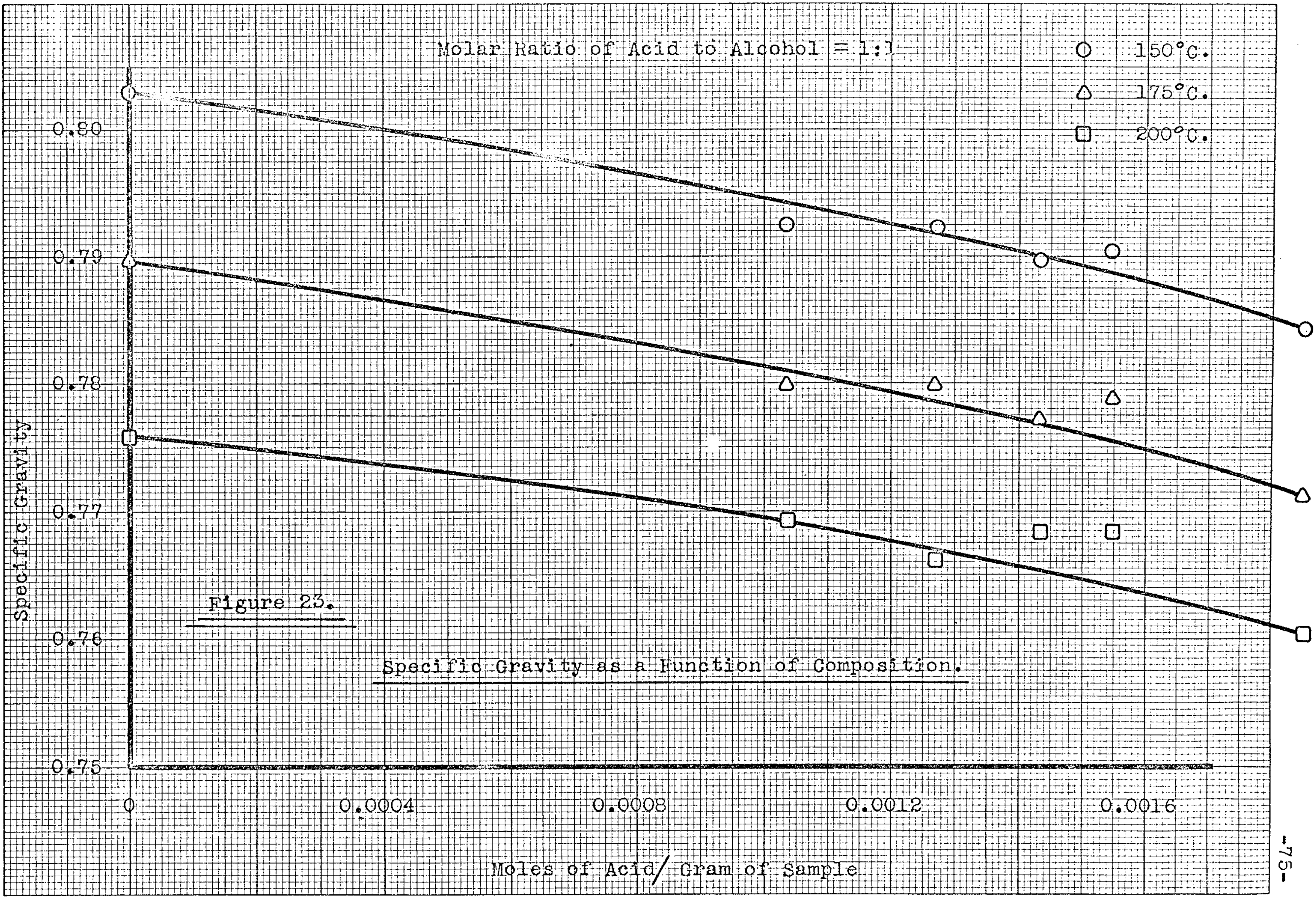


Figure 23.

Specific Gravity as a Function of Composition.

REFERENCES

1. Daniels, Farrington. Chemical Kinetics. New York: Cornell University Press, 1938. p. 18-21.

2. Deatherage, F. E. and Mattill, H. A. American Oil Chemists' Society Journal. 31:1425-31. November, 1939.

3. Dunlap, L. H. and Heckles, J. S. American Oil Chemists' Society Journal. 37:281-5. June, 1960.

4. Flory, Paul J. American Chemical Society Journal. 61:3334-3340. December, 1939.

5. Flory, Paul J. American Chemical Society Journal. 62:2261-2264. September, 1940.

6. Groggins, P. H. Unit Processes in Organic Synthesis. New York: McGraw-Hill Book Company, Inc. 1958, p.22-31, 694-705.

7. Hamilton, L. A. and Olcott, H. S. Industrial and Engineering Chemistry. 31:1425-31. November, 1939.

8. Henderson, J. L. and Young, H. A. Journal of Physical Chemistry. 46:670-84. June, 1942.

9. Hill, G. A. and Kelly, L. Organic Chemistry. Philadelphia; The Blakiston Company. 1943. p. 271-273.

10. Levesque, C. L. and Craig, A. M. Industrial and Engineering Chemistry. 40:96-9. January, 1948.

11. Ling, W. C. and Geankoplis, C. J. Industrial and Engineering Chemistry. 50:939-42. June, 1958.

12. Moelwyn-Hughes, E. A. The Kinetics of Reactions in Solution. Oxford: The Clarendon Press. 1933. p. 29-34, 223-229.

13. Othmer, D. F. and Rao, S. A. Industrial and Engineering Chemistry. 42:1912-19. September, 1950.

14. Swern, D., Billen, G. N., and Knight, H. B. American Chemical Society Journal. 37:281-5. June, 1960.