Thesis

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Degree of Doctor of Philosophy

by

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Physicochemical Studies on Polymerisation.

The Polymerisation of Methyl Acrylate.

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The Polymerisation of Methyl Acrylate.

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Introduction.

Introduction.

Much work has been done in recent years in the study of the kinetics of vinyl polymerisation using non-stationary state methods[1]. Some difficulty has been encountered, however, in the kinetic measurement of the polymerisation of methyl acrylate, although some information has been obtained through refractive index and dielectric constant methods. This present work has therefore been devoted to the elucidation of the polymerisation kinetics of methyl acrylate.

Rates and the corresponding lifetimes of the kinetic chain were determined by two non-stationary state methods hitherto untried with methyl acrylate polymerisation, the adiabatic dilatometer method and the thermocouple method. These results, combined with measurements of rates of initiation gave velocity coefficients which agreed with results obtained by other workers; it was found too, that there was reasonable agreement between activation energies measured in this work and those of other experimenters.

However, this comparison has been limited to the early stages of the reaction as very little is known about the later stages. These later stages have now been examined in more detail, although difficulty was encountered with variations from one experiment to another, due probably to trace impurities causing varying degrees of gelling. Therefore, to study this latter effect, a chain transfer agent, trichlorobromomethane was added to delay gelling to a later stage in the reaction.

The results of this work enables a comparison to be drawn between the dilatometer and thermocouple non-stationary state methods; some preliminary results were also obtained from apparatus designed to incorporate both methods using the one reaction mixture.

To clarify the data dealt with in this thesis, a general survey of vinyl polymerisation is given in the following pages.

The Mechanisms Involved in Addition Polymerisation.

Addition polymerisations, such as the polymerisation of methyl acrylate, proceed by four steps: initiation, propagation, transfer and termination. Each of these steps will now be examined.

a) Initiation.

Initiation of addition polymerisation may take place through various agences: heat, radiation and thermal breakdown of a number of organic compounds.

Thermal Initiation.

In the absence of a free radical producing initiator, thermal polymerisation is initiated through the formation of a dimeric radical[2,3]. This being so, the termination reaction will probably be intra- rather than intermolecular[4] with the result that large rings are formed and the reaction mixture gels. However, all thermal polymerisations do not produce gels e.g. styrene, so that the above mechanism is not universal. This may be due to the diradicals giving two monoradicals as in photochemical polymerisation.

Photochemical Initiation.

Irradiation of most monomers with ultraviolet light results in fairly rapid polymerisation. The mechanism of this initiation is probably through an electron shift at the double bond to give an unsymetrical diradical. This, however, would again lead to ring formation with subsequent gel formation. In general, this has not been found and it is thought that the diradical rapidly stabilizes itself by hydrogen atom transfer to the diradical from a neighbouring molecule so that two monoradicals are formed.

Decomposition of Organic Peroxide and Azo-compounds.

The decomposition of free radical producing compounds is effective as a method of initiating polymerisation reactions.

Peroxides generally decompose as follows:

$$R\text{-}CO\text{-}O\text{-}O\text{-}OC\text{-}R' \rightarrow R\text{-}COO\text{-} + R'\text{-}COO\text{-}$$

i.e. two monoradicals are produced.

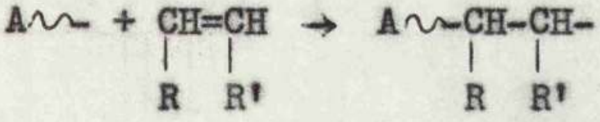
Azo-compounds decompose similarly to give two monoradicals:

$$\mathrm{A{-}N{=}N{-}A} \rightarrow \mathrm{A{-}N{=}N{-}} + \mathrm{A{-}} \rightarrow 2\mathrm{A{-}} + \mathrm{N_2}$$

and the efficiency of initiation, which in practice lies between 50 and 100%, depends on the reactivity ratios of the radical-monomer and the radical-radical reactions.

b) <u>Propagation.</u>

The propagation step in radical addition polymerisation consists merely of the attack of a growing polymer radical upon the monomer double bond which is opened:



$$\mathrm{A}\sim\!\sim - + \underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}{=}\underset{\mathrm{R'}}{\underset{|}{\mathrm{CH}}} \rightarrow \mathrm{A}\sim\!\sim\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}{-}\underset{\mathrm{R'}}{\underset{|}{\mathrm{CH}}}{-}$$

c) <u>Chain Transfer.</u>

Interaction of a growing polymer radical with a monomer or solvent can result in the free radical character of the growing chain being destroyed, while the molecule attacked forms a new free radical and is capable of initiating a new polymerisation chain[5]. This involves the migration of an atom between radical and molecule.

d) Termination.

The destruction of free radicals in polymerisation is almost always through the mutual interaction of two radicals. This can take place in two distinct ways: either the two radicals combine to give a single molecule[6] or there is transfer of an atom between the radicals giving one saturated and one unsaturated molecule. The exact nature of the termination step depends very much on the experimental conditions and there is evidence to support both mechanisms.

The Kinetics of Addition Polymerisation.[7,8.]

The four stages in addition polymerisation can be summarised as follows:

		Rate.
Initiation	$M \rightarrow P_1$	I
Propagation	$P_n + M \rightarrow P_{(n+1)}$	$k_p(P)(M)$
Transfer	$P_n + M \rightarrow M_n + P_1$	$k_f(P)(M)$
Termination	$P_n + P_m \rightarrow M_n + M_m$	$k_t(P)^2$

where M_n = stable polymer of n units

Pn = monovalent radical of n units

k_p = rate constant for propagation reaction

k_f = rate constant for transfer reaction

k_t = rate constant for termination reaction

I = rate of initiation.

Assuming that the reactivity of polymer radicals is the same irrespective of chain length[9], then in the addition reaction when the stationary state is attained

$d(P)/dt = I - k_t(P_s)^2 = 0.$ . . . .(1)

where (P_s) is the concentration of free radicals i.e. the same concentration of radicals is being formed as is being destroyed.

i.e. $I = k_t(P_s)^2$ . . . . (2)

$P_s = (I/k_t)^{\frac{1}{2}}$ . . . . (3)

In the initial stages of the reaction, however, before the stationary state is reached, the concentration of free radicals will be given by

$d(P)/dt = I - k_t(P)^2$. . . . . (4)

On integration, this gives

$$\tfrac{1}{2}(k_tI)^{-\frac{1}{2}}\ln\left[\frac{(1 + (k_t/I)^{\frac{1}{2}}(P))}{(1 - (k_t/I)^{\frac{1}{2}}(P))}\right] = t + c \;\ldots\ldots \tag{5}$$

where c is the integration constant.

This reduces to

$$\tanh^{-1}(P)/(P_s) = (k_tI)^{\frac{1}{2}}t \;\ldots\ldots\ldots\ldots \tag{6}$$

since $P = 0$ when $t = 0$ and hence $c = 0$.

The lifetime of the kinetic chain, τ, is given by

$$(k_tI)^{-\frac{1}{2}} = \tau \;\ldots\ldots\ldots\ldots\ldots\ldots \tag{7}$$

Substituting for τ in equation (6) we have

$$(P) = (P_s)\tanh(t/\tau) \;\ldots\ldots\ldots\ldots\ldots \tag{8}$$

The polymerisation rate at any time is given by the equation

$$-d(M)/dt = k_p(P_s)(M)\tanh(t/\tau) \;\ldots\ldots\ldots \tag{9}$$

On integration, this gives

$$-\ln\left[(M)/(M_o)\right] = (k_p/k_t)\ln\left[\cosh(t/\tau)\right] \;\ldots\ldots \tag{10}$$

Let F be the fraction of monomer converted

i.e. $(M)/(M_o) = 1 - F \;\ldots\ldots\ldots\ldots$ (11)

Substituting in equation (10) we have

$-\ln(1 - F) = (k_p/k_t)\ln(\cosh(t/\tau))$ . . . . . . (12)

Now, if the amount of conversion is kept at a low value i.e. if $F \ll 1$, then

$-\ln(1 - F) = F$ . . . . (13)

and so

$F = (k_p/k_t)\ln\left[\cosh(t/\tau)\right]$. . . . . (14)

which approaches the line

$F = (k_p/k_t)(t/\tau - \ln 2)$ . . . . (15)

For times $t > 3\tau$, this line has a gradient of k_p/k_t and intercepts the time axis at a time $= \tau \ln 2$

Thus the lifetimes of the kinetic chain and the ratio k_p/k_t are known although the absolute values of the velocity coefficients are not.

However, by measuring rates of initiation under conditions identical to the non-stationary state ones, k_t can be derived from

$k_t = 1/(I\tau^2)$ . . . . (16)

and hence, k_p is derived from

$$k_p = k_t \tau \times F \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

Non-stationary State Methods for measuring the Kinetics of Polymerisation Reactions.

The general principle involved in measuring reaction rates is the measurement of a change in a property of the reaction mixture due to polymerisation, such as change in specific volume, refractive index or dielectric constant. Methods have been devised based on these changes but unfortunately the limitations are great mainly because of the stringent experimental conditions that must be maintained.

a) Dielectric Constant Method.[10]

Changes in the dielectric constant as monomer is converted to polymer have been measured but the experimental conditions require careful handling. As monomer is converted to polymer, the dielectric constant of the mixture changes. Counterbalancing this, there is a larger change due to temperature rise from the heat of reaction. Thus, the dielectric constant measured is the resultant value of the two effects. To measure this accurately, the system must remain adiabatic over the measuring period, for then, the rate of reaction will be directly proportional to rate of rise of temperature. Although the apparatus can detect a temperature rise of 10^{-5} C° in 10^{-4} sec., the method is limited in that the decrease in dielectric constant must be reasonably small, of the order of 0.002 at 100 MC/sec..

Only the initial stages of the reaction can be followed, for after gelling it is difficult to remove the polymer from the specially designed vessels.

b) Interferometer Method.[11]

In this the change of refractive index is being measured as monomer is being converted to polymer. Again the main change , a decrease, is from the rise in temperature due to the heat of reaction. There is also an increase in refractive index from the formation of polymer. Here, too, fast detection is required and a photoelectric recording interferometer can detect a change of 10^{-4} C° in 10^{-2} sec.; by using cine photographic methods, the resolving power in time can be increased. As with the dielectric constant method, specially designed reaction vessels are used and so the reaction mixture must be removed before gelling.

c) Thermistor Method.[12,13]

Similar to the thermocouple method, the thermistor method measures directly the temperature rise due to the heat of reaction. A bridge is used consisting of two thermistors one of which is located at the centre of the reaction vessel and the other at the centre of a standard vessel. Again, adiabatic conditions are essential during the measuring period. It is claimed by Miyama[12] that this method is more sensitive to temperature changes than the thermocouple method[14].

d) The Adiabatic Dilatometer and Thermocouple Methods.

These two methods have been examined in detail in a later section.

Other Methods for Measuring the Kinetics of a Polymerisation Reaction.

a) Dilatometer Method.

In this method, the rate of contraction of reaction mixture is measured as monomer is converted into polymer. Heat of reaction is dissipated to the surroundings and so only the change in specific volume is being measured. A polymerisation reaction cannot be followed into the gel state by this method as reaction mixture in the stem of the vessel distorts and makes volume readings impossible. However, because of the large difference between the specific volumes of monomer and polymer, this method is highly sensitive although only measuring reaction rates.

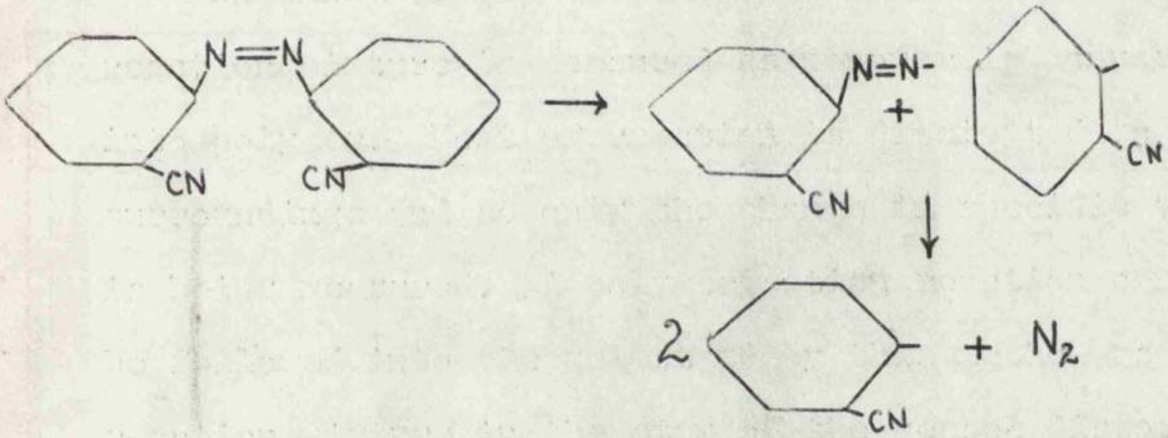
A dilatometer method has been used[41,42] for following the non-stationary state of polymerisation reactions using the post-irradiation effect to measure τ. By allowing for heat losses, the system did not require to be adiabatic.

b) Rotating Sector Method.[15]

The simple dilatometer method described above can also be used to find lifetimes of the kinetic chain. This is done by using a sector rotating at different speeds between the light source and the dilatometer. The measurements from this type of experiment are made over a large section of the reaction - of the order of 3 - 5% - with perhaps a large change in reaction rate and a corresponding change in τ.

Rates of Initiation.

Using 1,1'azo-bis-cyclohexane carbonitrile as photoinitiator, polymerisation reactions may be initiated through the formation of two monoradicals



Each of these free radicals joins onto a monomer molecule initiating a polymer chain. To calculate rates of initiation, the free radicals formed can be removed by reaction with some inhibitor and the rate of disappearance of the inhibitor measured.

Inhibitor concentration can be measured colorametrically and an inhibitor suitable for this method is $\alpha\alpha'$diphenyl β picryl hydrazyl (D.P.P.H.) which has a deep violet colour. Also, D.P.P.H. on combining with a free radical from the catalyst used forms a colourless or pale yellow compound.

Another method of measuring rate of disappearance of inhibitor is to regard the point at which the reaction commences as the point when last traces of inhibitor have been used up. However, results[16] have shown that an inhibitor is formed as D.P.P.H. combines with a free radical and that the inhibitor retards the polymerisation reaction further.

Other methods which can be used are osmometry and radioactive tracer techniques.

Previous Work on Methyl Acrylate.

Matheson[17] and co-workers have studied the early stages of the photopolymerisation of methyl acrylate using the sector method; 1,1'azo*bis*isobutyronitrile was used as initiator and each experiment covered from 3 to 5% of the reaction. Some trouble was encountered through formation of "popcorn" - white opaque polymer with gas pockets which damages the reaction vessel and gives very large errors in dilatometer measurements.

Rates of initiation were measured using picric acid, benzoquinone and tetrachloroquinone as inhibitors.

Results show a rate acceleration from the very initial stages due to the early gelling. To check that the acceleration was from the gel effect, the system was kept fluid by adding a small amount of transfer agent (n-butyl mercaptan). Under these conditions there was no acceleration.

Velocity coefficients have also been studied by Sinitsyna and Bagdasar'yan[18] using the sector method and rates of initiation were determined from the induction period in the presence of D.P.P.H..

The values obtained from the sector experiments are compared with other values in the discussion section.

Ross[19] measured the direct photopolymerisation reaction (i.e. no photosensitizer) at 25°C using the sector method. He found that the rate only accelerated at conversions greater than 7%. However, the method gave a large variation in values for the lifetimes of the kinetic chain and trouble was also encountered with "popcorn" formation. The cause of this was said to be traces of oxygen in the system. It was also found that benzoquinone acted as a photoactivator and not as an inhibitor in this reaction.

Ross also studied molecular weights of polymethyl acrylate by osmometry to obtain rates of initiation.

Reaction rates and values of τ for methyl acrylate polymerisation have been measured using the dielectric constant[10] and interferometer[11] methods but unfortunately rates of initiation were not measured. Thus, although values of k_p/k_t were obtained, no values for the individual velocity coefficients were available from this source.

The procedure used in the dilatometer and thermocouple non-stationary state methods will now be described.

The Adiabatic Dilatometer Method for Following the Polymerisation Reaction of Methyl Acrylate.

Experimental.

Materials.

Purification of Methyl Acrylate.

Methyl acrylate, as supplied by L. Light & Co. Ltd. contained hydroquinone as a stabiliser which was removed as follows.

The monomer was washed several times with 10% aqueous sodium hydroxide solution until the washings were colourless. Any residual sodium hydroxide was neutralised by dilute hydrochloric acid (2N). It was then washed with ferrous sulphate solution to remove any peroxides, and finally with distilled water. The resultant monomer contained up to 5% water which was removed by fractional distillation; for methyl acrylate with water forms an azeotrope[20] (B.P. 71°C; 7.2% water, 92.8% methyl acrylate) which distils off before the main fraction of monomer (79°C).

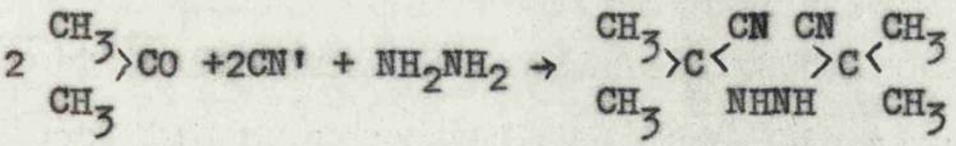
The methyl acrylate was finally prepolymerised and distilled under high vacuum before use.

To give a reasonable rate in the photoinitiated polymerisation reaction of methyl acrylate, a photosensitizer was used. Two of these were prepared: 1,1'azo*bis*isobutyronitrile and 1,1'azo*bis*cyclohexane carbonitrile.

Preparation of Photosensitizers.

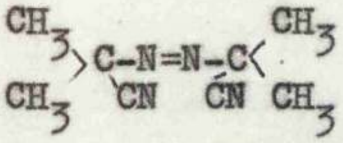
a) 1,1'azo*bis*isobutyronitrile.[21]

11.9 g. hydrazine sulphate, 9.6 g. acetone and 12 g. of potassium cyanide were mixed in aqueous solution for a period of 2 days during which time a crystalline compound was formed, i.e. the disubstituted hydrazine.



$$2\ \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\mathrm{CO} + 2\mathrm{CN'} + \mathrm{NH_2NH_2} \rightarrow \begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!>\mathrm{C}\!<\begin{matrix}\mathrm{CN}\quad\mathrm{CN}\\\mathrm{NHNH}\end{matrix}\!>\mathrm{C}\!<\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}$$

This product was removed by filtration and added to a 1 litre round-bottomed flask. After addition of 50 ml. dilute hydrochloric acid and 50 ml. ethanol, the flask was cooled in an ice bath and stirred during the addition of bromine water; the hydrazine was oxidised[22] by the bromine water to give

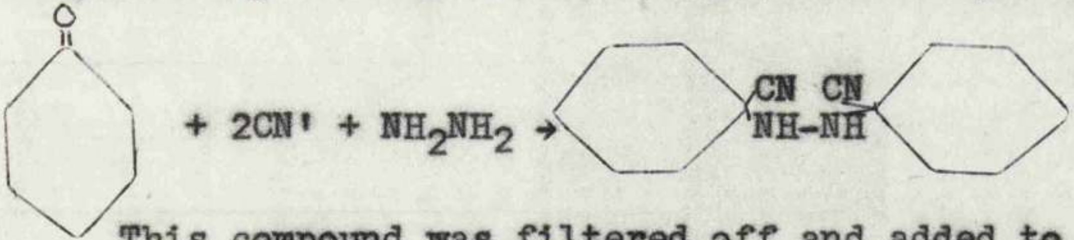


$$\mathrm{(CH_3)_2C(CN){-}N{=}N{-}C(CN)(CH_3)_2}$$

This was filtered off and recrystallised twice from ether. The final product, white needle crystals, gave a melting point of 103°C.

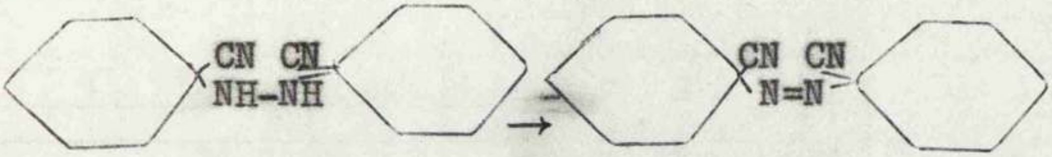
b) <u>1,1' azobiscyclohexane carbonitrile.</u>

11.9 g. of hydrazine sulphate, 16.2 g. of cyclohexanone and 12 g. potassium cyanide were mixed in aqueous solution for 2 days. Blobs of a yellow compound separated out - the disubstituted hydrazine.



This compound was filtered off and added to a 2 litre round-bottomed flask together with 25 ml. ethanol and 50 ml. dilute hydrochloric acid. The flask was cooled in an ice bath during the addition of bromine water, vigorous stirring being employed.

The white compound which separated out was filtered and recrystallised twice from 95% ethanol. This was the 1,1'azo<u>bis</u>cyclohexane carbonitrile.



The melting point of the recrystallised product - white crystalline plates - was found to be 115°C.

Catalyst Solution.

An accurately weighed amount of 1,1'azo*bis*cyclohexane carbonitrile was dissolved in freshly distilled chloroform and made up to 100 ml. The concentration of this solution was 0.005044 g. moles/L., and such solutions could be used for a few weeks if kept stoppered and in the dark.

Preparation of $\alpha\alpha'$diphenylβpicryl hydrazyl.[23,24] (D.P.P.H.)

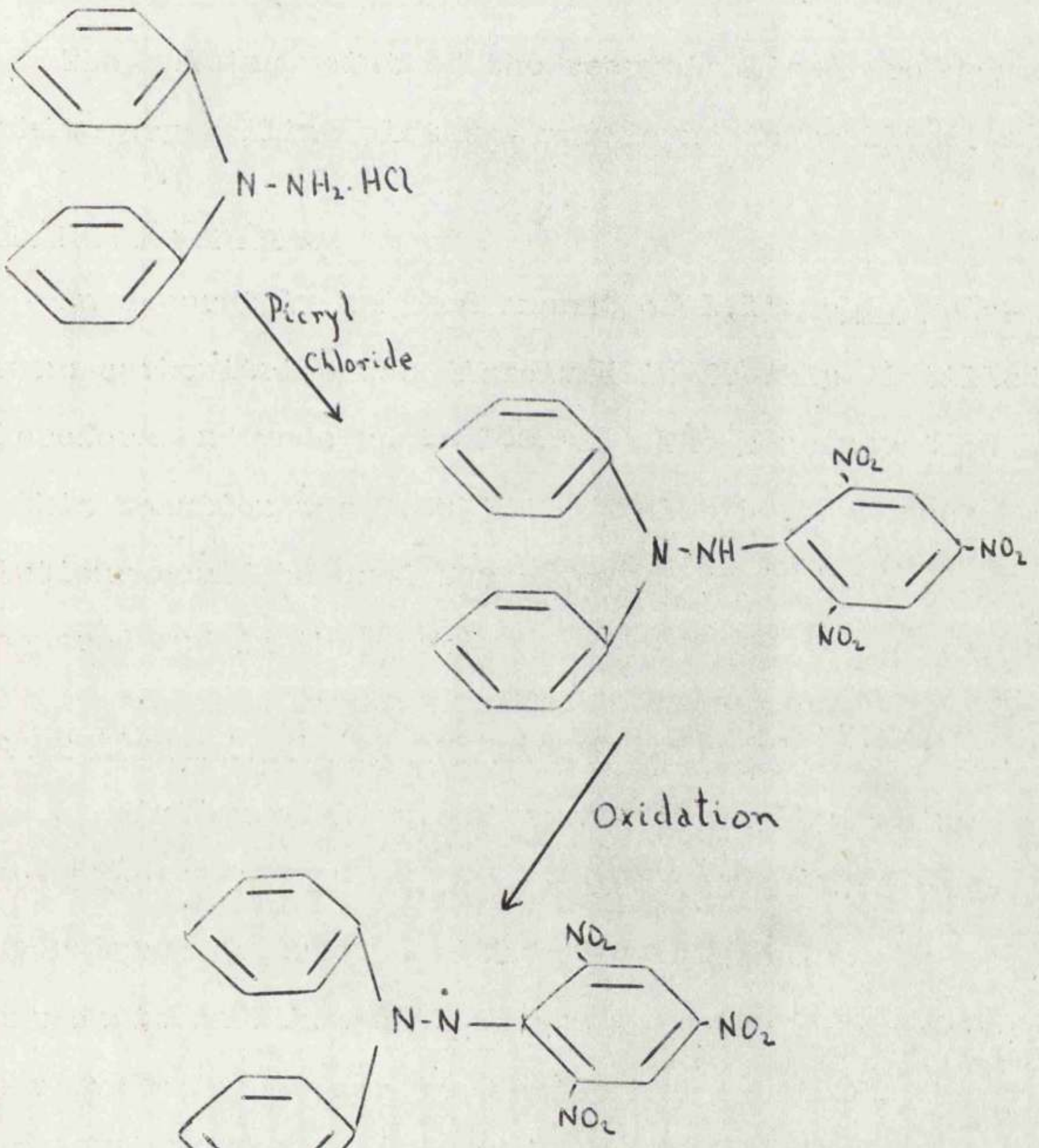
A solution of 10 g. of unsym-diphenylhydrazine hydrochloride in 115 ml. of absolute ethanol at room temperature was treated with 9.5 g. of sodium bicarbonate and then with 11.3 g. of picryl chloride. After evolution of carbon dioxide had subsided, the mixture - now red - was boiled gently for 15 minutes. An equivalent volume of chloroform was added and the solid residue filtered off while the mixture was still warm.

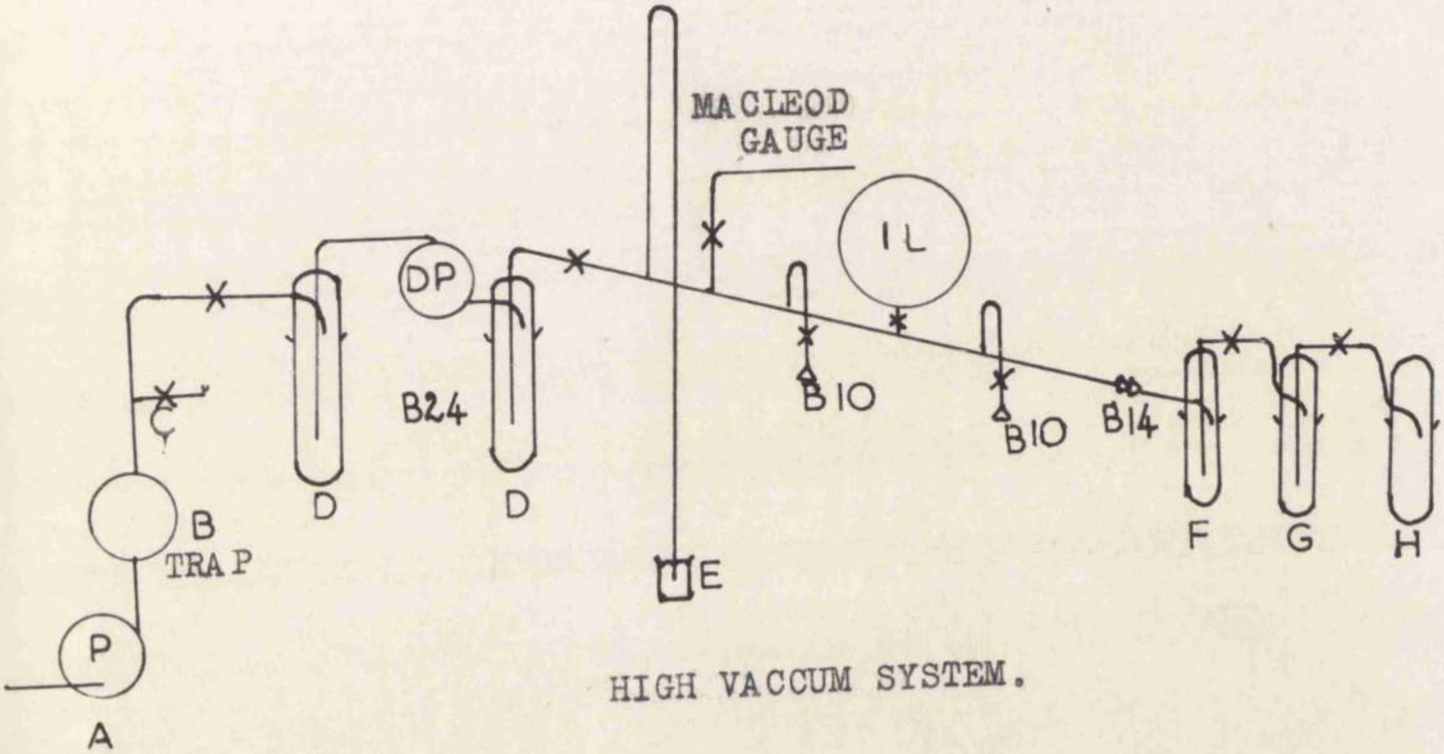
The filtrate, after washing with two 115 ml. portions of water, was concentrated on a steam bath to about 70 ml. and diluted with 70 ml. warm absolute ethanol. On standing at room temperature overnight, brick red prisms separated (M.P. 169°C.). This was the αα'diphenylβpicryl hydrazine.

5.1 g. of this compound, 5.1 g. of anhydrous sodium sulphate and 31.4 g. of lead peroxide were shaken in 100 ml. of purified benzene for 2 hours. The solid résidue was removed from the dense violet solution by filtration through a fine grain paper. The filtrate was evaporated to dryness under vacuum.

The dark coloured residue gave large violet prisms. These were recrystallised from a benzene-ligroin (2:1) mixture.

The overall reaction is





HIGH VACCUM SYSTEM.

SIMPLE DILATOMETER

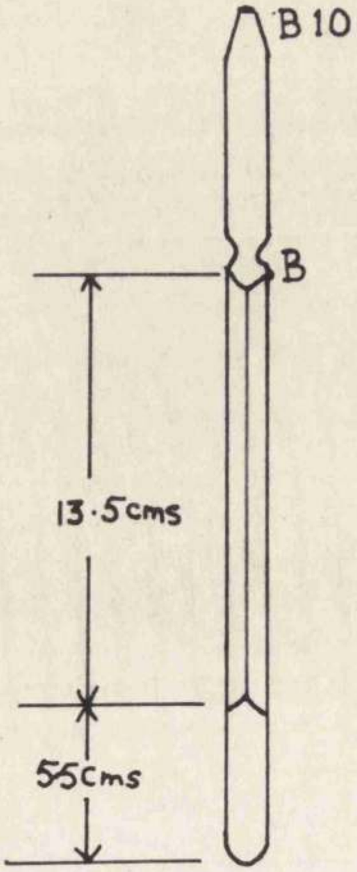
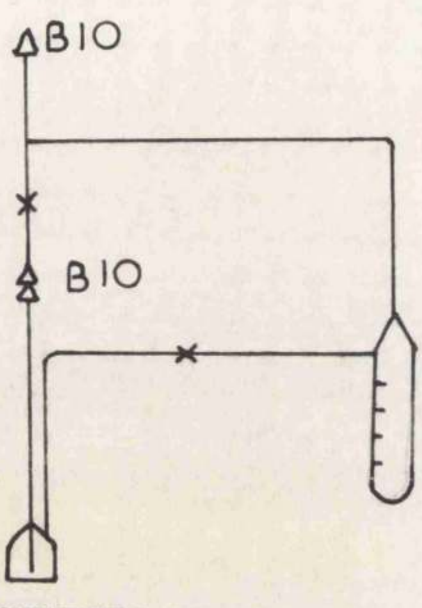
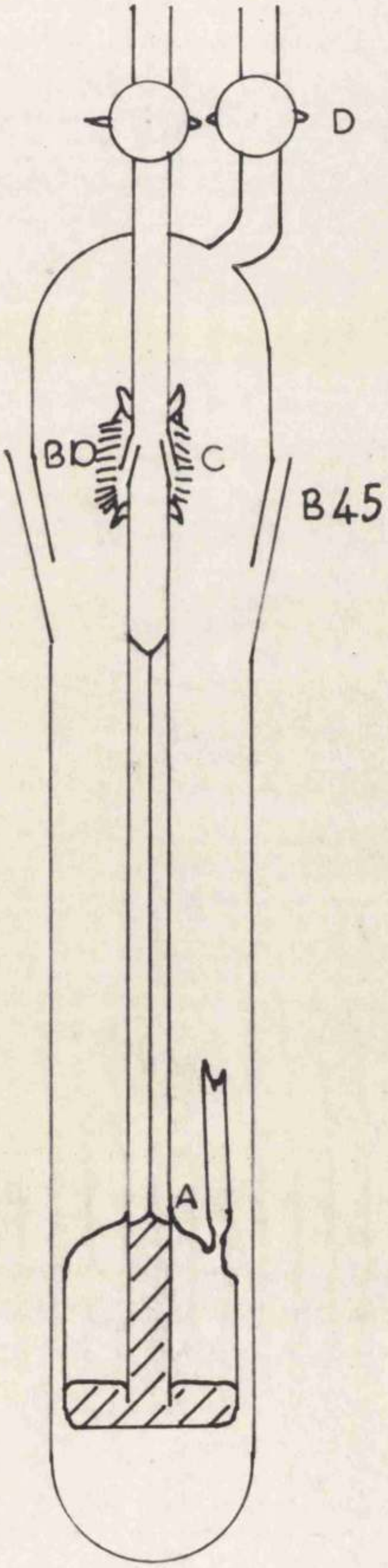


Figure 1.



DILATOMETER MEASURING SYSTEM.



DILATOMETER
AND
CASING

Figure 2.

Apparatus.

Dilatometers.

a) Dilatometers for preliminary Experiments.

Figure 1 is a diagram of one of these dilatometers. The constriction at B, above the safety bulb, is for sealing purposes and the vessel is made in Pyrex glass.

b) Dilatometers for Non-stationary State measurements.

(See fig. 2.)

Each dilatometer has a bulb of about 10 to 15 ml. capacity connected to a capillary of Veridia tubing 0.40 mm. in diameter. An extension of this tubing almost touches the bottom of the bulb whereas the other end is fused to a B.10 Quickfit cone. To help hold the dilatometer in place in the surrounding casing, two steel springs are clipped onto the glass lugs near the cone and socket joint.

The casing is constructed in two parts, the lower part being a test-tube shaped jacket fitted with a B.45 Quickfit socket while the upper part, which holds the dilatometer in position, fits into this tube

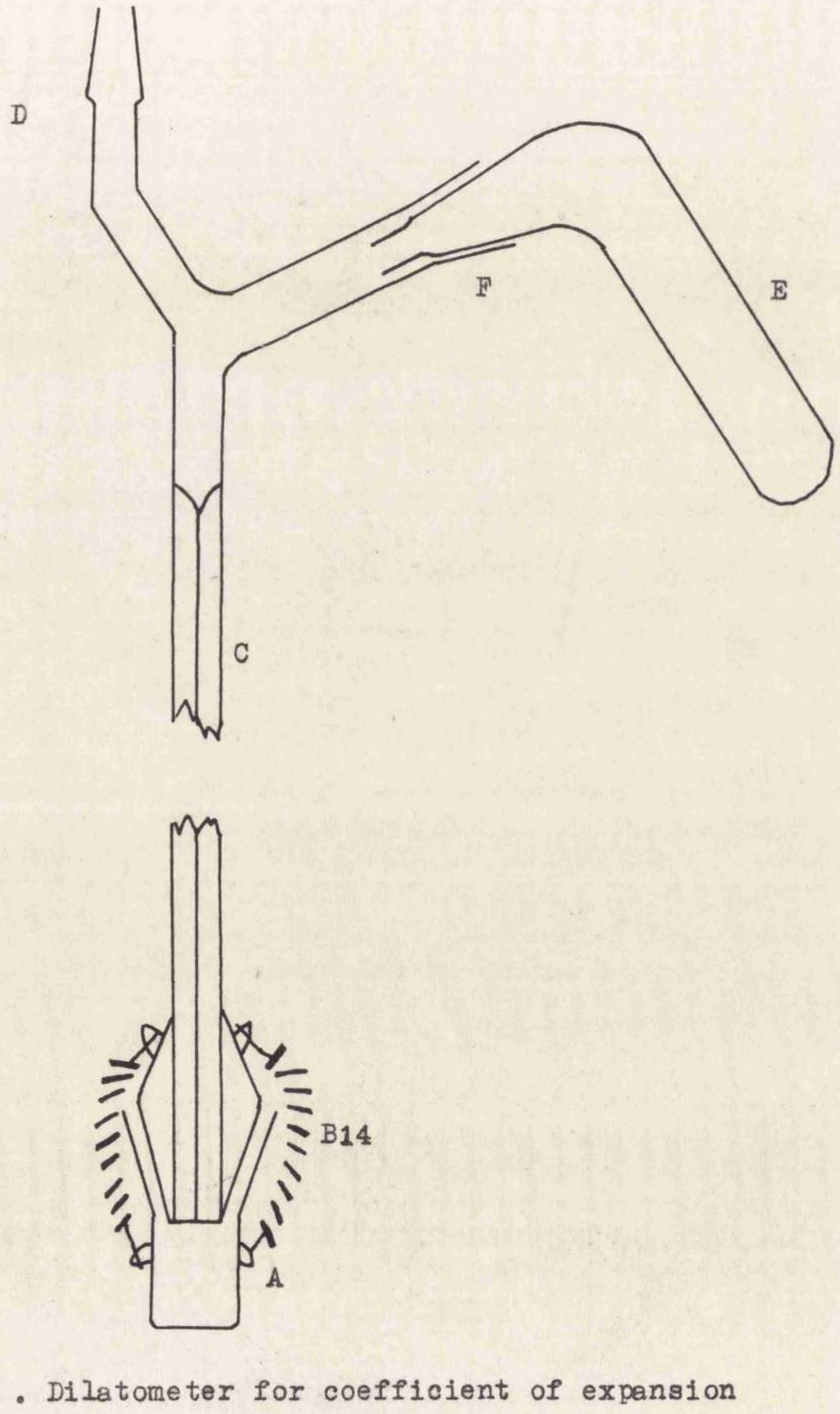


Figure 3 . Dilatometer for coefficient of expansion measurements.

through the B.45 cone. The ground glass joints are firmly held by Picene wax and the outer jacket can be evacuated through the side arm D.

c) Dilatometer for Coefficient of Expansion measurements.

This is shown in fig. 3 and consists of a detachable vessel, A, fitted by a B.14 Quickfit cone and socket to a length of Veridia tubing, C, of 1.50 mm. bore. The capillary is sealed to the narrow end of the cone and steel springs hold the vessel securely in position. The L-shaped vessel is designed to introduce mercury, free from grease, into the dilatometer while the system is under vacuum.

Vessels for Rates of Initiation Measurements.

These vessels are simply cylindrical bulbs 2.5 cm. long and 1.0 cm. in diameter with a stem for filling purposes. They are made in Pyrex glass.

High Vacuum System.

The high vacuum system (shown in fig.1) consists of a 2 stage mercury diffusion pump (D.P.) backed by a Speedivac rotary oil pump (type 2) which is protected by cold traps, DD. A series of traps, F,G and H are used for the distillation of monomers and reaction vessels are filled from the stopcocks marked B.10.

The apparatus is made in Pyrex glass with Quickfit joints and hollow vacuum stopcocks greased with Apiezon L.

Thermostatically Controlled Tank and Fittings.

Kinetic measurements were made in a thermostatically controlled tank, 12 inches by 12 inches by 15 inches deep, constructed from copper sheeting and lagged with ¾ inch expanded ebonite. Two long vertical slit windows are cut in opposite sides for observation, and there are two circular windows in the other two sides for U.V. irradiation. The outsides of these latter windows have slot holders attached for filters.

The tank is filled to a set mark with clean water which is changed regularly to cut down irradiation losses due to light scattering from suspended dust particles. The water is raised to the required temperature by a 1.5 kilowatt immersion ring heater after which the power is switched to a 100 watt copper sulphate tube-heater controlled by a toluene regulator through a relay. The bath is agitated by an electric motor and can be controlled to ± 0.015C° (measured by a Beckmann thermometer).

For photoinitiation, a 125 watt Osira ultra violet lamp (with the envelope removed) is used. This is set in a hard asbestos cylindrical casing with a slit window in the wall. Before any runs are photoinitiated using this lamp, it is switched on for at least half an hour and allowed to settle to a constant temperature - temperature affects the output from this type of lamp.

Between the lamp and the tank, there is an electro-magnetically operated shutter controlled by a push button switch. To cut out extraneous wavelengths and leave that of 3650Å, a Chance OX1 filter is used.

Meniscus levels in the capillaries of dilatometers in the tank are observed by a travelling microscope measuring to 0.001 cm.. When small changes in meniscus

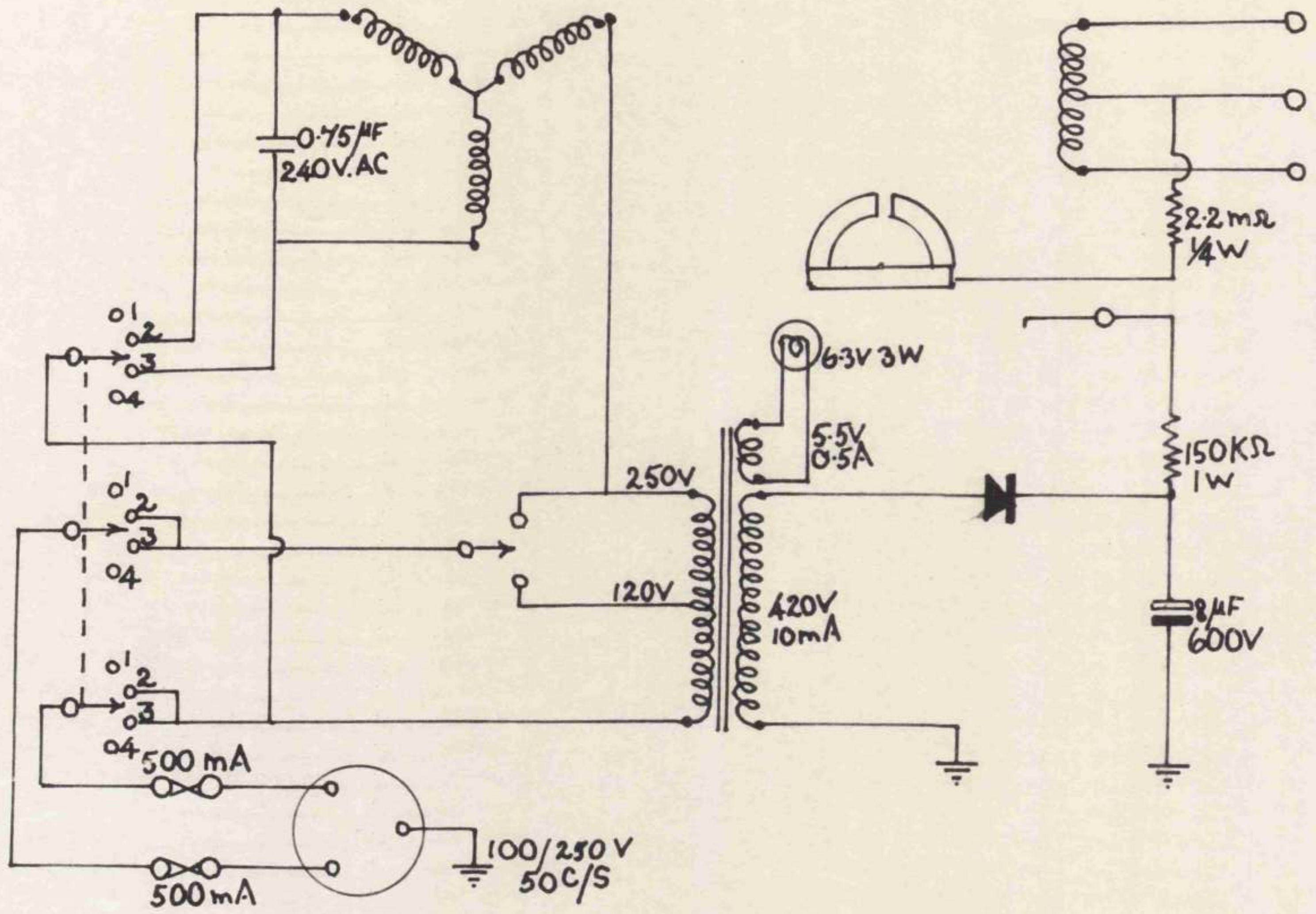


Figure 4 . Kelvin & Hughes recorder wiring diagram.

level have to be measured very quickly, the cross-wire of the cathetometer is replaced by a film microscale divided into 0.01 cm. divisions.

Recording Instruments.

In preliminary experiments, a Smith's Timer stopclock is used to time readings. When, however, readings have to be taken very quickly, a high speed recorder is used - Kelvin & Hughes Ltd., Model mark V, high speed single channel recorder- the wiring diagram is shown, fig.4. Using this instrument, a changing meniscus level passing the scale can be recorded by depressing, at each division, a tapping key to complete the circuit to the recorder; this gives a mark on a recording chart, the speed of which is 2.5 cm./sec..

The recorder was kindly lent for a period of 1 year by the Admiralty.

After this period, the recorder was replaced by another, an Elliot pen recording voltmeter. It was found that with the Elliot recorder, since the instrument response period was fairly large (ca. 1 second) it was better to have the circuit closed for the normal position of the tapping key and to break the circuit to make a recording mark. The speed of this recording chart was 12 inches per minute i.e. approximately 1/5 the speed of the first recorder.

Intensity Screens.

To cut down the intensity of the U.V. light by known factors, screens were made by exposing photographic plates for different periods. However, these were found to be unsuitable since there was high absorption of light in the U.V. region because of the plate emulsion.

To replace these, a nickel gauze screen (40 mesh) set in a copper frame was used. The transmission of the gauze was calculated by measuring, with and without the screen interjected, light intensity from a fixed source (100 watt tungsten filament lamp) using a photoelectric cell coupled to a microammeter.

Procedure.

Preliminary Experiments.

To obtain an idea of polymerisation rates corresponding to different catalyst concentrations and thence to choose a suitable concentration for a required rate, a series of simple type dilatometers were made with a capacity of about 2 ml.. These dilatometers were calibrated using acetone[25]. The requisite amount of catalyst solution was then introduced into the dilatometer and the solvent, chloroform, was pumped off.

Meanwhile, 20 ml. of freshly distilled and dried methyl acrylate were prepolymerised in trap G and distilled under vacuum into trap F (fig.1). With the dilatometer containing catalyst still in position on the vacuum line, monomer was distilled in from trap F. After adjusting the monomer level, the dilatometer was sealed by a hand torch using a coal gas/oxygen flame.

The reaction vessel was then ready for kinetic measurements to be made and was kept frozen in solid carbon dioxide until required.

The filled and sealed dilatometer, placed in a fixed position in the thermostat at a fixed distance, (23 cm. from centre to centre) from the mercury vapour U.V. lamp, was allowed to settle to the temperature of the water (25°C).

After initiating the reaction by opening the shutter to the U.V. lamp, the meniscus level was followed with the cathetometer, readings being taken at minute intervals.

This experiment was repeated at different catalyst concentrations.

Non-stationary State Measurements.

No direct method of calibration was used with the dilatometers for the non-stationary state measurements. The bore of the Veridia capillary was known to be 0.40 mm.. Also, a measured amount of monomer was distilled into the bulb and so the volume of monomer in the reaction vessel was also known.

a) Fillings of Dilatometers.

The requisite amount of catalyst solution was introduced through the side arm and evaporated to dryness in the upper half of the bulb. This was to ensure that all the catalyst would be dissolved in subsequent monomer in the bulb and not masked by the confining mercury pool. 2.5 ml. of mercury were placed in the bulb and the side arm joined to a graduated section which in turn was attached to the vacuum line. The position is shown in fig. 2b.

The mercury was drawn up the capillary until only a small amount, enough to seal the end of the tube, was left in the bulb. The mercury was frozen to keep it in this position and the whole system evacuated.

Methyl acrylate, previously purified, was distilled under vacuum into the graduated section until a set mark (at 25°C) was reached. This volume was then distilled into the dilatometer and isolated there by sealing the side arm. The reaction vessel was kept in Drikold until required.

b) <u>Non-stationary Kinetic Measurements.</u>

With the dilatometer set in the casing as shown in fig.2, the whole apparatus was fixed in position in the thermostat and allowed to settle to the bath temperature. When temperature equilibrium was obtained, excess mercury above the capillary was removed using a glass dropper, and the outer casing evacuated.

The cathetometer was focused on the meniscus level and the shutter opened to the U.V. lamp; simultaneously, a recording mark was registered with the pen recorder. A mark was also recorded when the meniscus passed each division on the microscale as the volume in the vessel expanded.

After each experiment, the dilatometer was heated a little to bring the mercury column to the top of the capillary so that more mercury could be introduced to compensate for contraction of reaction mixture due to polymerisation. Hence, experiments could be carried out at different stages of conversion.

c) Intensity Exponent.

Also, by inserting the nickel screen during various stages in the reaction, rates can be compared at different light intensity to give the intensity exponent and from this, the order of the termination reaction is obtained.

Estimation of Extent of Reaction.

By weighing the amount of mercury introduced into the dilatometer at each stage, the volume contraction of monomer can be calculated knowing the density of mercury. Now, for 100% polymerisation at 25°C the reacting mixture contracts 22.63%. Hence, the extent of reaction can be estimated.

Reaction Rates from Contraction Measurements.

Contraction measurements can also be made using the above type of dilatometer. It has been said in the introduction that the overall effect will be one of expansion as long as conditions remain adiabatic, the expansion being the difference between the heating effect (heat of reaction) and the specific volume change. However, as adiabatic conditions break down, the heating effect becomes less until it is balanced by the rate of heat lost. At this stage specific volume change will be the only effect measured i.e. rate of contraction.

Thus, if the shutter is kept open for a long period until the mercury meniscus is falling at a steady rate, rates of reaction can be measured and compared to rates measured from expansion experiments carried out immediately before and after using the same reaction vessel.

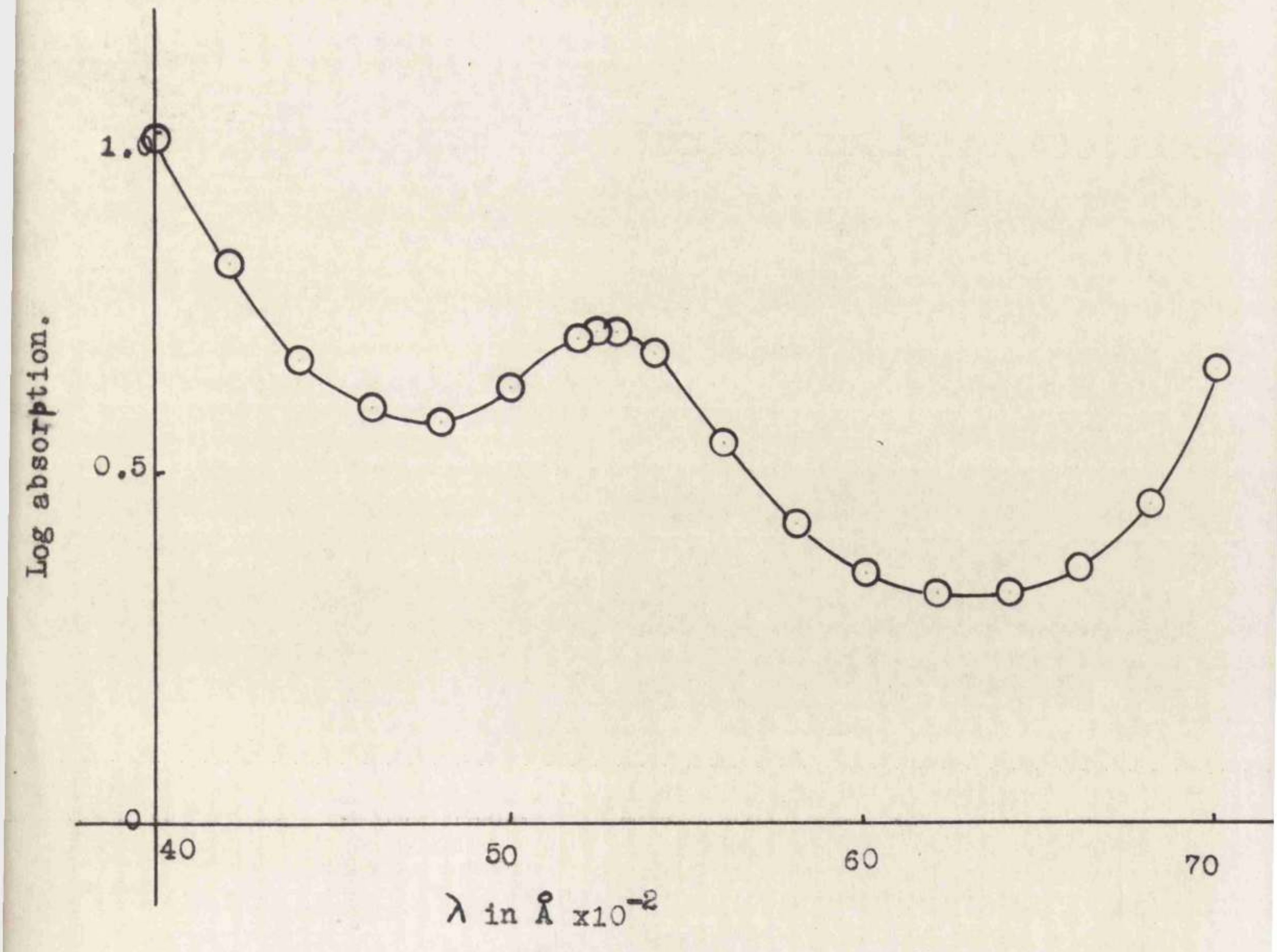


Figure 5 . Light absorption curve for 5×10^{-5} M/L D.P.P.H. in chloroform.

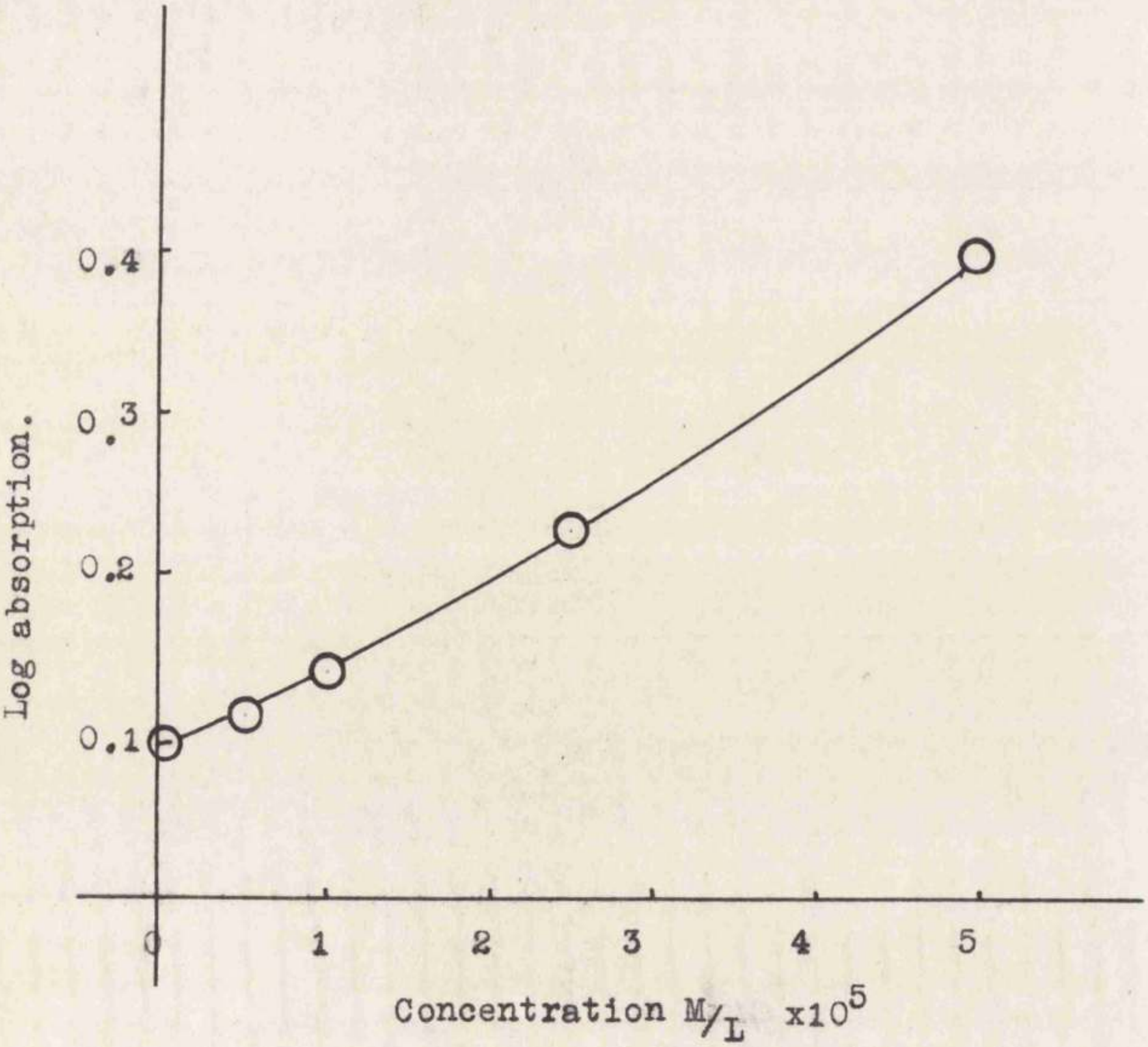


Figure 6. D.P.P.H. - relationship between concentration and absorption ($\lambda = 5250$ Å).

Rates of Initiation.

A solution of D.P.P.H. was placed in the vessel described earlier. The absorption spectrum between 4000 Å and 6000 Å was measured using a Unicam S.P.600 to find a suitable peak wavelength at which subsequent absorption measurements can be made. This was found to be 5250 Å (fig. 5).

Using standard flasks, solutions of D.P.P.H. in chloroform were made up of various strengths ranging from 1×10^{-4} g.moles/L. to 0.5×10^{-5} g.moles/L.. Absorption readings were noted for these solutions using the same vessel as before and a plot of log absorption against concentration made to be used later for estimation of strengths of solutions (fig.6).

One of the reaction vessels containing a solution of D.P.P.H. in methyl acrylate with catalyst (8.45×10^{-4} g.moles/L.) and sealed under vacuum, was placed in the same position in the thermostat as that occupied by a dilatometer during an experiment. The solution was irradiated by U.V. light and absorption readings at 5250 Å made every 2 minutes. Simultaneously, contraction measurements were observed using a cathetometer focused on the stem of the vessel. These readings were continued for a period after the last traces of purple colour had disappeared from the solution.

Also, a series of experiments were made under the same conditions replacing the methyl acrylate with chloroform. To check on fading by U.V. light without catalyst, a solution of D.P.P.H. in chloroform was irradiated for 1 hour. There was no change in absorption readings.

Coefficients of Expansion of Different Monomer/Polymer Mixtures.

Using the apparatus shown in fig. 3 with mercury in the reservoir, E, monomer/polymer mixture was frozen in A for several minutes and the system evacuated as quickly as possible to prevent loss of monomer. The reservoir was tilted and the mercury allowed to fill the dead space in the vessel and to come some way up the capillary. The dilatometer was weighed before and after the process to find the volume of mercury present.

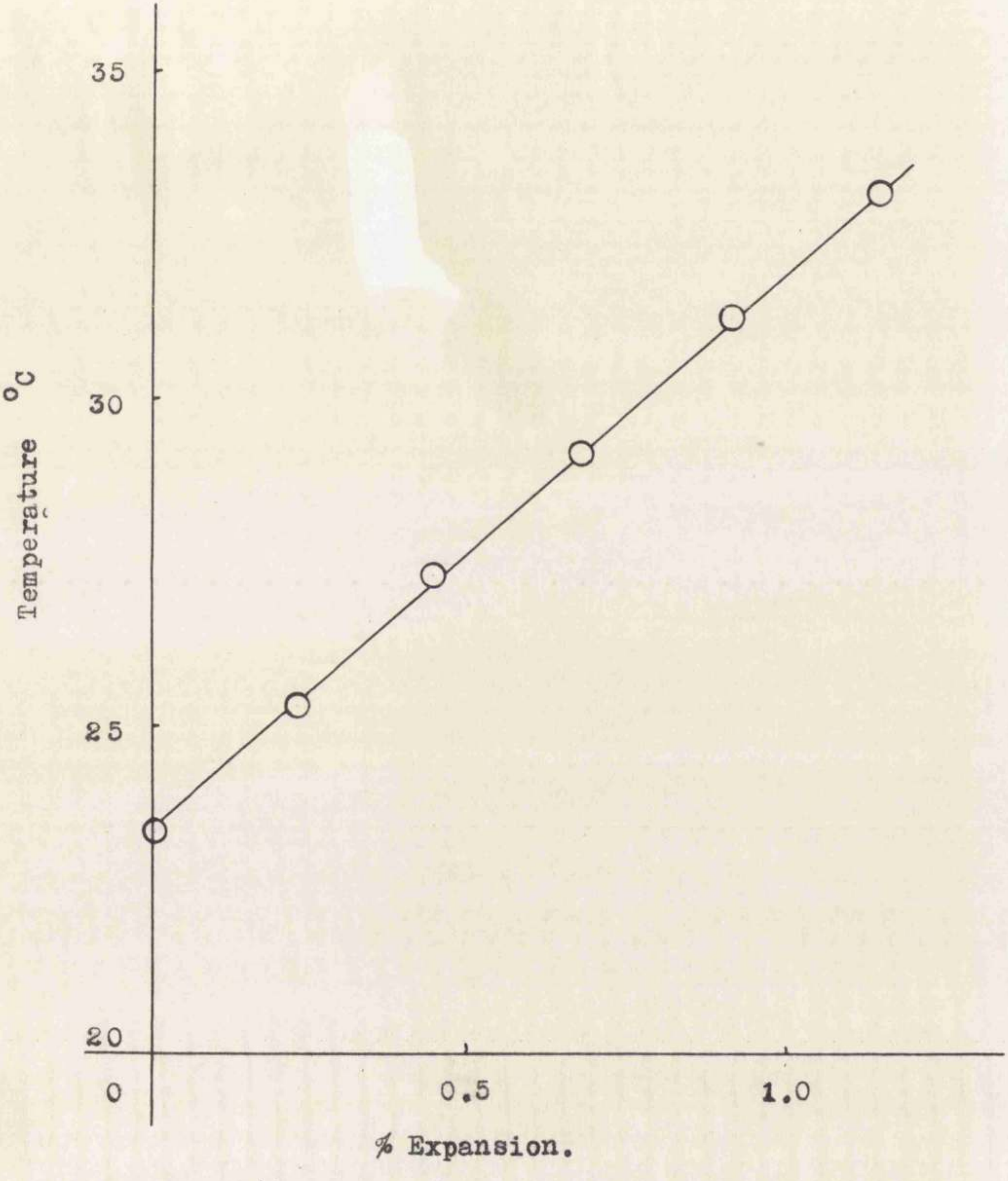


Figure 7. The coefficient of expansion of methyl acrylate polymer at 25% conversion.

With the dilatometer placed in a thermostat, expansion measurements were made over a range of 15 C°.

A graph was constructed of expansion against temperature, fig.7 and from the slope, the combined coefficient of expansion of mercury, monomer and polymer was measured.

Note: The polymer used had been formed by polymerising, as far as possible, methyl acrylate using U.V. light and then leaving the reaction vessel unbroken (i.e. under vacuum) in daylight for a period of 1 year. No traces of monomer could be detected after that time and it was therefore presumed that 100% polymer was being used.

Also, a little hydroquinone inhibitor was left in the monomer used for making up the monomer/polymer mixtures to prevent further polymerisation in the mixture while expansion measurements were being made.

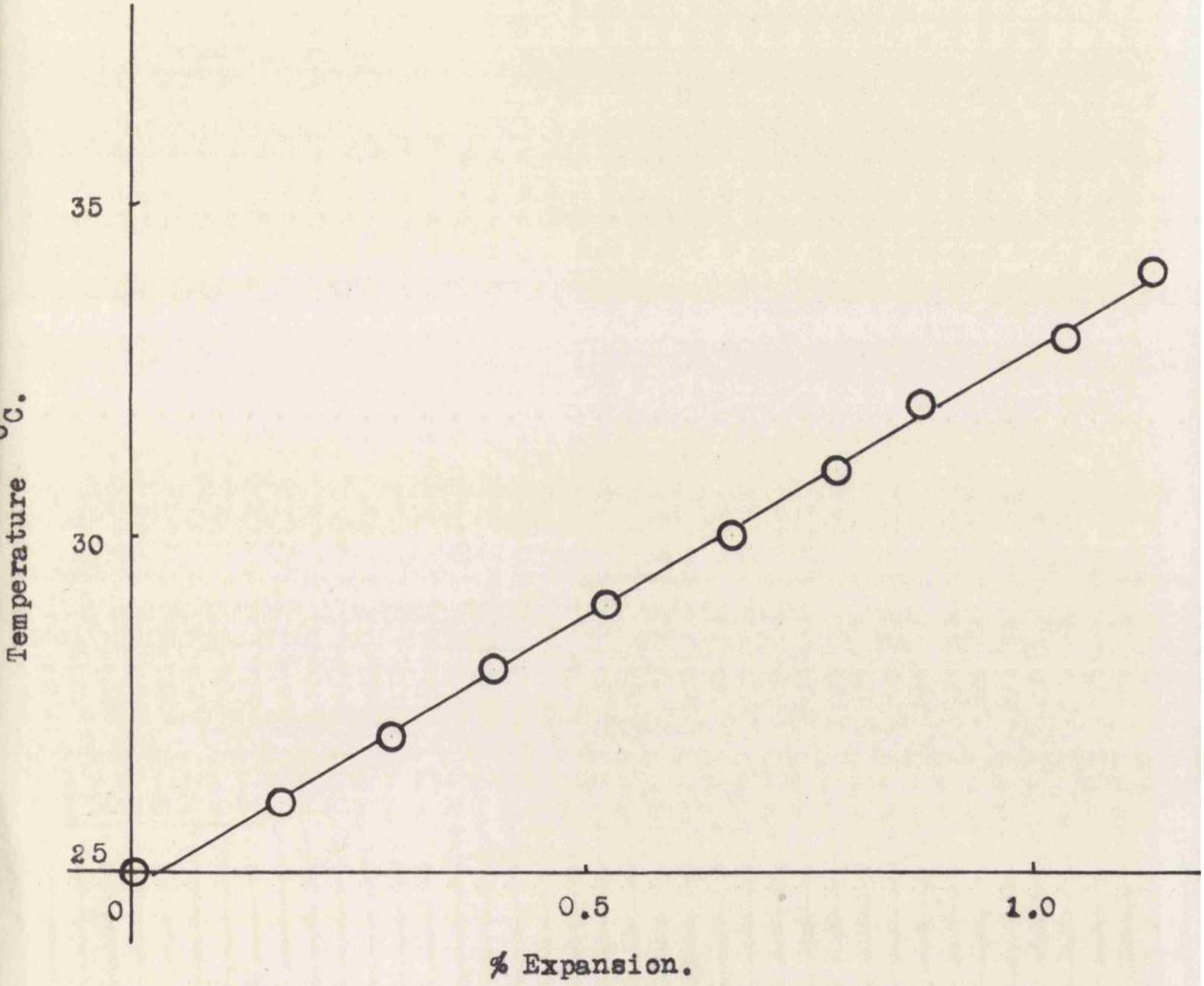


Figure 8. The coefficient of expansion of pure methyl acrylate.

The coefficient of expansion of methyl acrylate monomer measured over the range 25°C to 35°C (fig.8) was found to be 1.26×10^{-3} deg.$^{-1}$. This agrees well with Matheson's values[17], 1.28×10^{-3} deg.$^{-1}$ derived from density measurements at different temperatures.

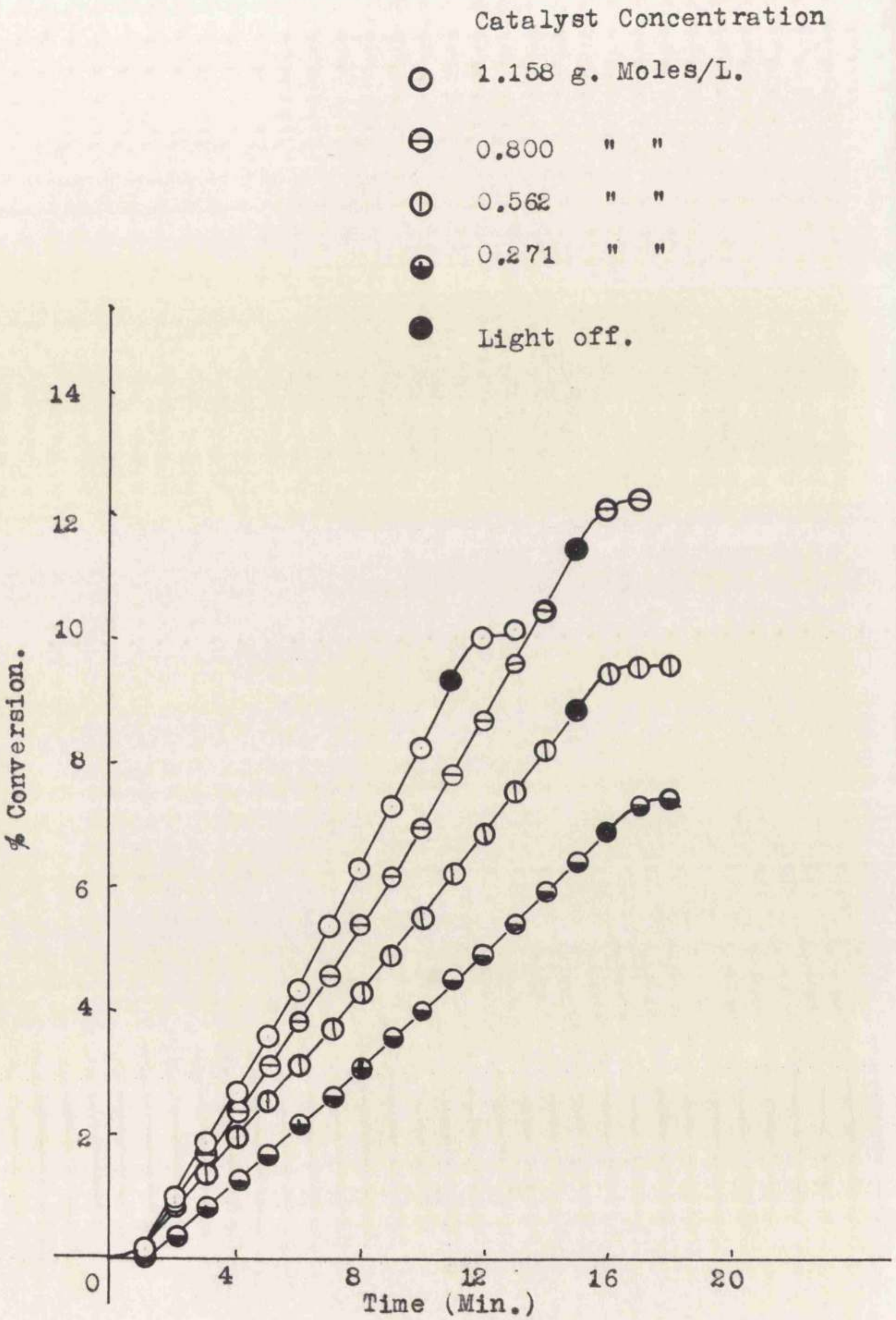


Figure 9 . Rate curves for methyl acrylate polymerisation at different catalyst concentrations.

Results.

Preliminary Experiments.

Some preliminary experiments were designed to give guidance for further, more comprehensive experiments. The preliminary results give an indication of the rates to be expected under different conditions and from these results suitable experimental conditions can be chosen.

Fig.9 shows polymerisation rate curves for different catalyst concentrations using simple dilatometers. These rates are given in table I.

Table I.

The variation of rate with catalyst concentration for the polymerisation of methyl acrylate at 25°C.

Catalyst concentration g.moles/L. x 10^3	Polymerisation rate %/h.
1.483	53.5
1.373	45.7
1.158	49.4
0.800	41.5
0.562	33.0
0.271	23.4
0.262	22.3
No catalyst	4.1

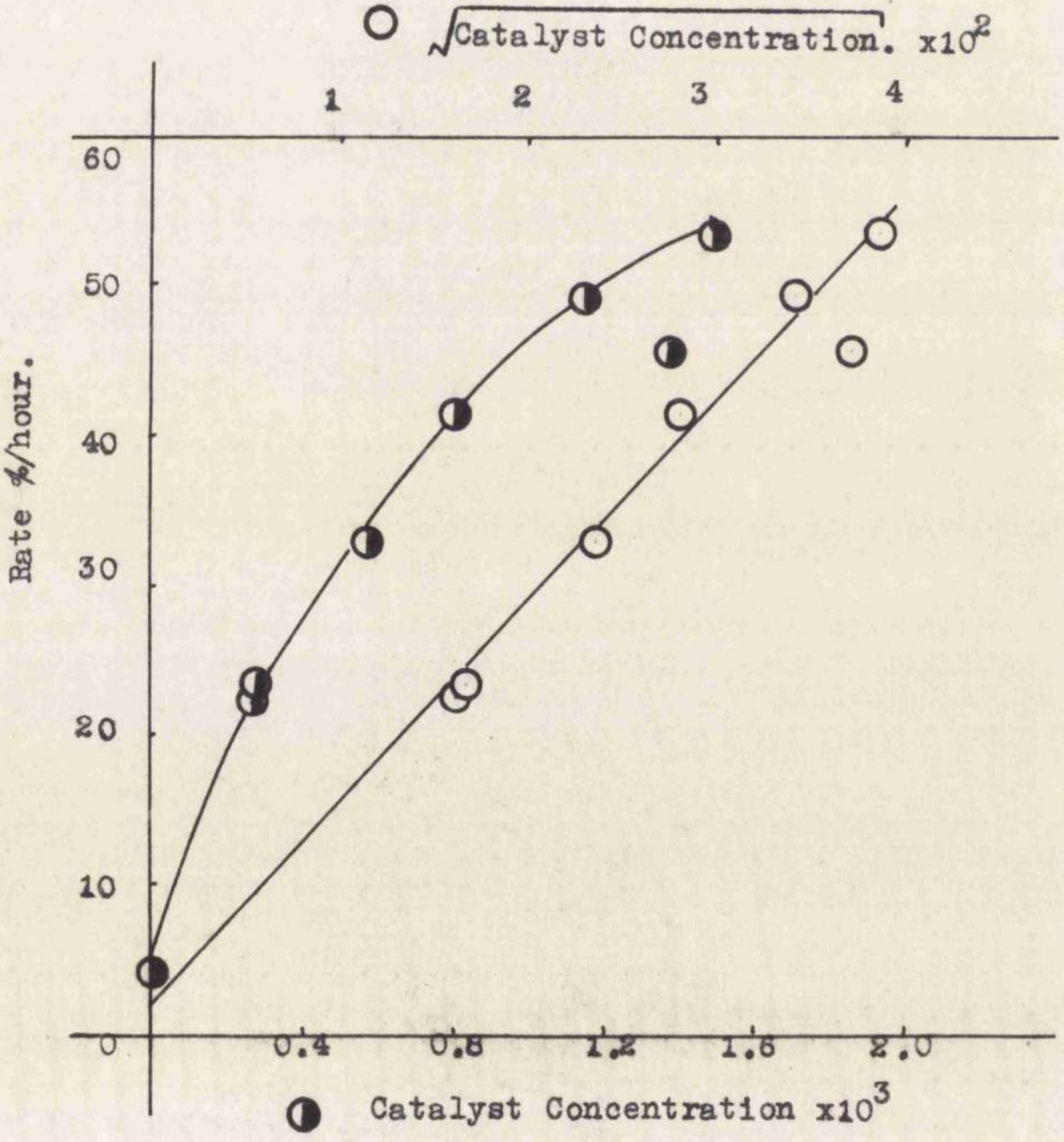


Figure 10. The relationship between rate and catalyst concentration in the polymerisation of methyl acrylate.

From table I a plot of catalyst concentration against polymerisation rate has been drawn (fig. 10) and in the same figure, the plot of the square root of the catalyst concentration against rate is seen to be linear. From table I a catalyst concentration of 0.800×10^{-3} g.moles/L. was chosen for subsequent experiments.

The Order of the Termination Reaction.

The straight line relationship between polymerisation rate and the square root of catalyst concentration shown in fig. 10, is an indication of second order termination reaction. It can be seen, however, that there is some scatter of points in this plot and confirmation of second order termination is required. To this end, further experiments at different light intensity were carried out.

Using the simple type of dilatometer with constant catalyst concentration, the rates of polymerisation at different light intensities were followed. By measuring the gradient of the plot of contraction

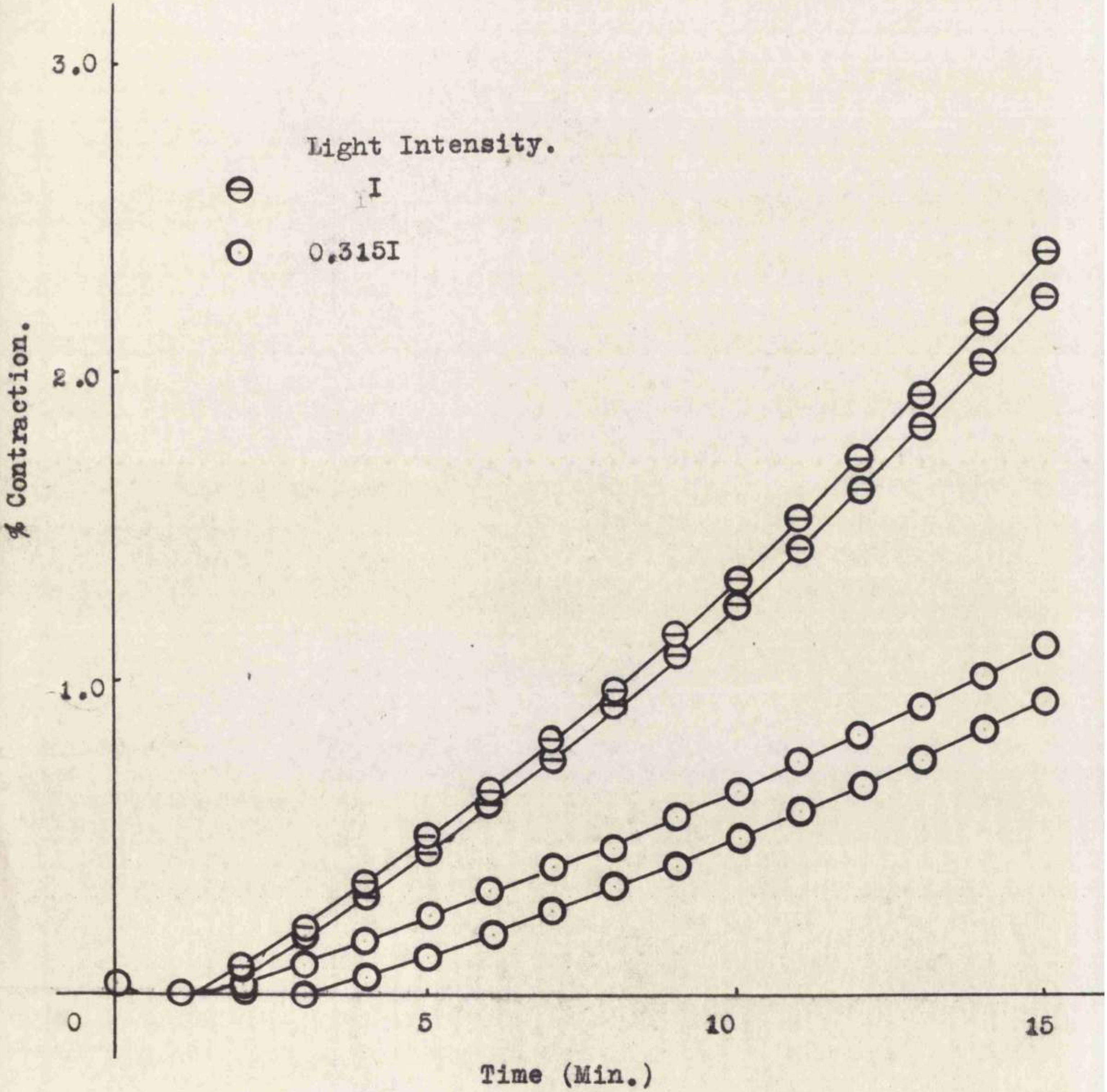


Figure 11. Methyl acrylate polymerisation rates at different light intensities.

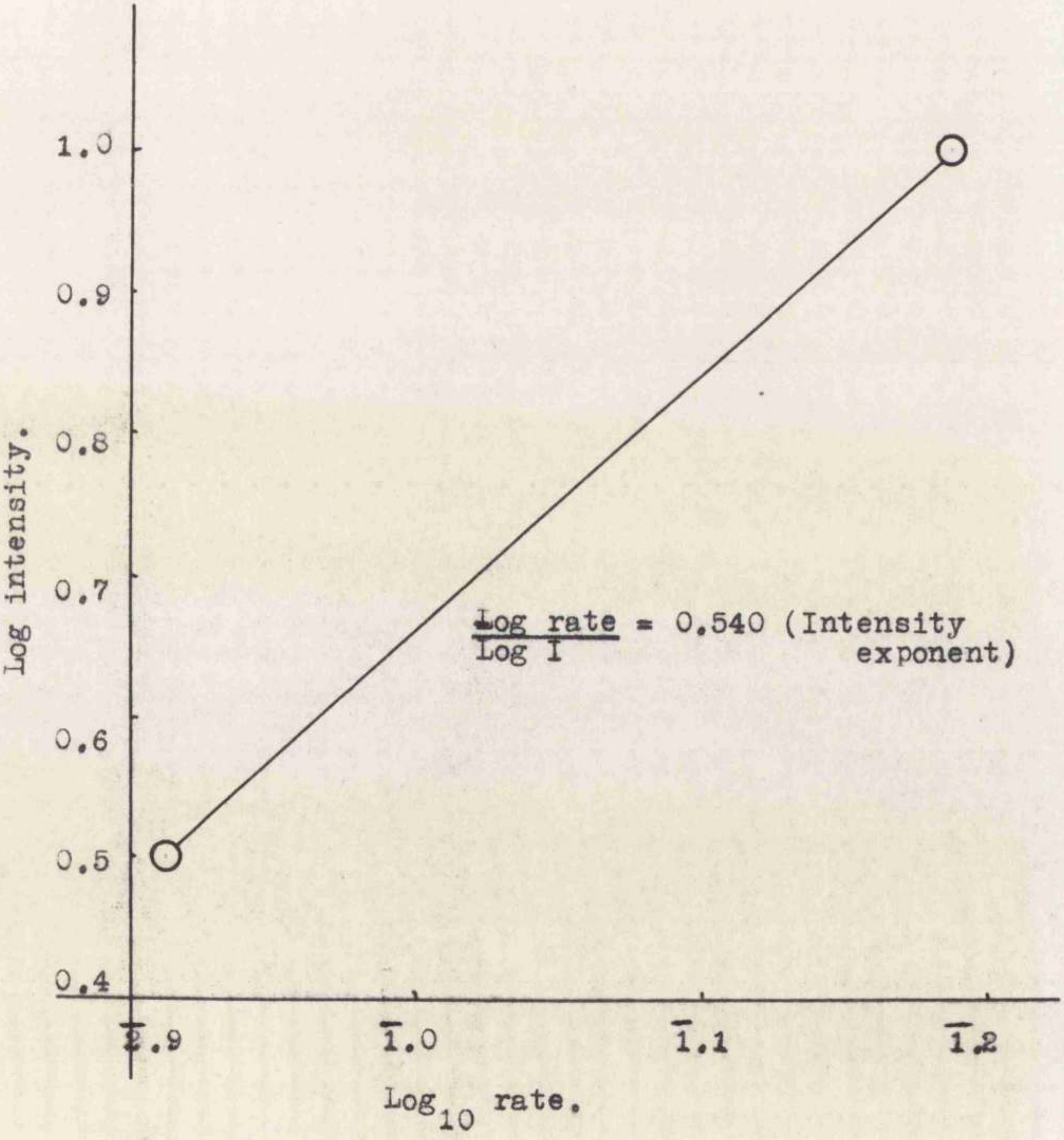


Figure 12. Intensity exponent.

against time (fig. 11), the intensity exponent can be calculated from

$$\text{Intensity exponent} = \frac{\text{Log}\ (m_a/m_b)}{\text{Log}(I_a/I_b)} \quad (\text{ see fig. 12.})$$

where m_a and m_b are the polymerisation rates at the different light intensities I_a and I_b respectively.

Table II

Intensity exponent for the polymerisation of methyl acrylate at 25°C.

m_a (maximum intensity I_a)	m_b (reduced intensity $I_b = 0.315I_a$)	Intensity exponent
0.156 0.156	0.0829 0.0815	0.545 0.550

From table II it can be seen that the termination reaction is almost second order.

A further check on the order of the termination reaction,using non-stationary state methods (dilatometer and thermocouple methods) for following the rate of reaction,gave varied results according to the extent of polymerisation. Table III which is divided into three sections, very early stages ($<2\%$ conversion of monomer to polymer), early stages ($>$ 2% conversion) and later stages (when the reaction mixture has gelled), shows the variation in intensity exponent at the different stages of the reaction. This table makes use of the results of several experiments, 'D' denoting the dilatometer method and 'T' denoting the thermocouple method (described in detail later).

Table III

The variation of intensity exponent at different extents in the polymerisation of methyl acrylate using non-stationary state (dilatometer and thermocouple) methods for measuring the rates of reaction.

Experiment number	% conversion	Polymerisation rate (%/h.) Intensity		Intensity Exponent
		Maximum (I_a)	Reduced ($0.315I_a$)	
D6	0	18.9	7.2	0.83
D3	0	18.5	8.0	0.73
D3	0	20.8	5.5	1.15
D9	1.9	19.9	4.2	1.35
D9	2.0	16.0	5.0	1.01
T8	2	19.3	9.2	0.64
T8	2	18.4	9.2	0.60
D6	3	14.0	7.2	0.57
T2	4	41.4	23.9	0.48
T2	4	40.2	22.8	0.49
T9	17	16.2	8.1	0.60
T9	17	16.0	8.9	0.51
D6	22	19.5	8.9	0.68
D6	22	18.9	8.7	0.67
T7	50	5.3	2.1	0.80
T9	60	24.2	7.9	0.95

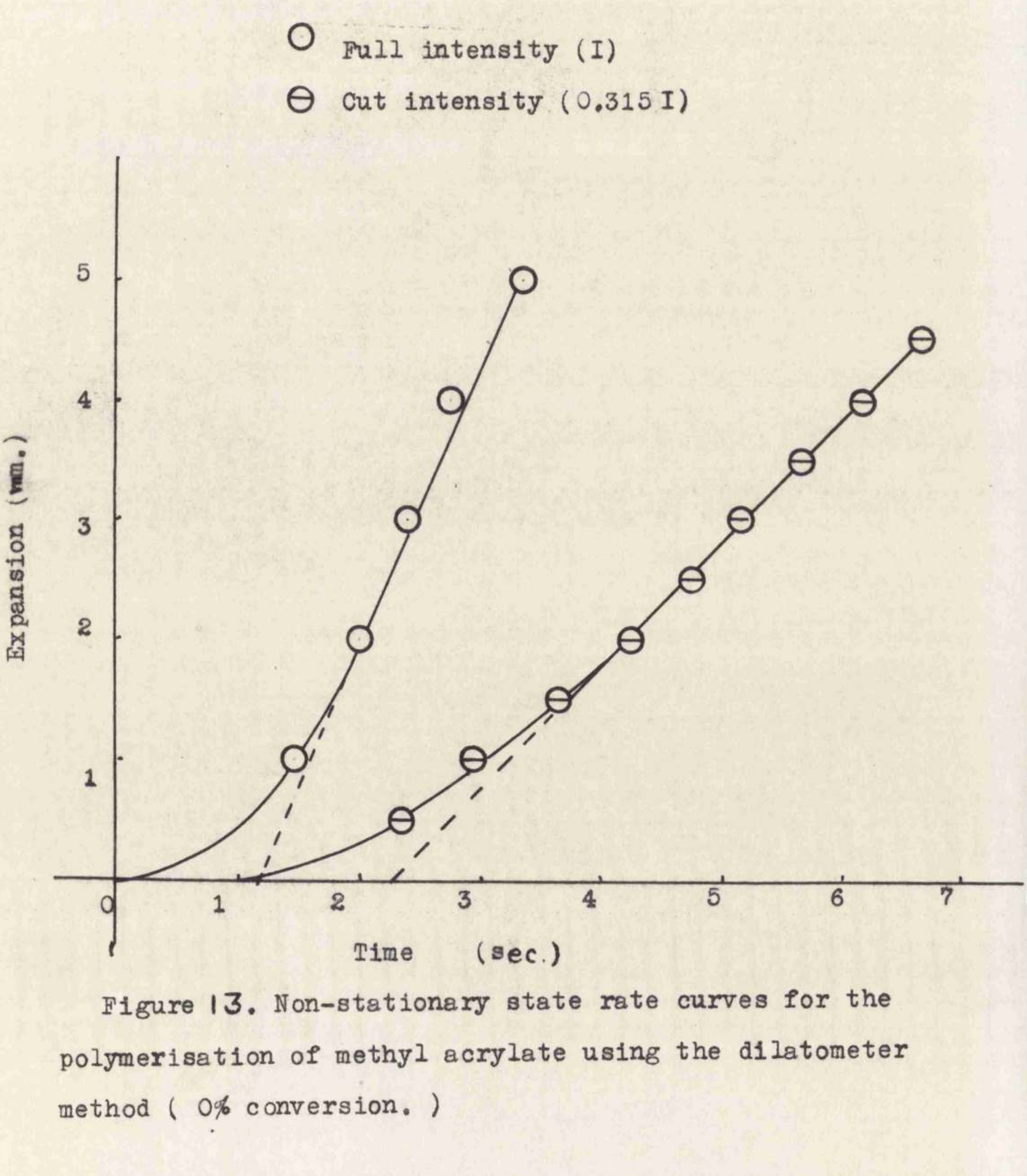


Figure 13. Non-stationary state rate curves for the polymerisation of methyl acrylate using the dilatometer method (0% conversion.)

Since, in the polymerisation of methyl acrylate, there is lack of reproducibility and also a large deviation from second order termination in the very initial measurements, these have been neglected as far as accurate determinations are concerned.

After the very initial stage, however, the intensity exponent is almost 0.5 i.e. the termination reaction is almost second order. At later stages in the reaction, there is again deviation from second order termination. These measurements are discussed later.

From non-stationary measurements made by the dilatometer method, plots of expansion against time during the first 10 seconds following the commencement of irradiation have been made (fig. 13).

Polymerisation rates and the corresponding values for the lifetimes of the kinetic chain (τ) are shown in table IV.

Table IV.

The dependence of the rate of polymerisation and τ upon the intensity of the irradiation for the photosensitized polymerisation of methyl acrylate at 25°C.

Rate (%/h.)	τ (sec.)	Intensity of irradiation (I, arbitrary)	Rate x $I^{-0.5}$	$I^{0.5}\tau$
14.0	2.3	1	14.0	2.3
7.2	3.8	0.315	12.9	2.1

From table IV it can be seen that the rate of polymerisation is proportional to the square root of the intensity of irradiation while τ is inversely proportional to the square root of the intensity. Both of these results confirm that the termination reaction is second order, thus indicating that the termination proceeds by mutual interaction of growing polymer radicals.

Table V.

Values for the rates of polymerisation and τ for the photosensitized polymerisation of methyl acrylate at 25°C using different catalyst concentrations.

τ (sec.)	Rate (%/h.)	$(k_p/k_t) \times 10^5$	Catalyst conc. (g.moles/L.)
2.6	13.6	9.83	0.800×10^{-3}
2.3	14.3	9.14	"
7.1	5.8	11.5	0.800×10^{-4}
5.9	6.1	10.0	"
10.4	3.5	10.1	0
14.2	2.3	9.07	0

The results in table V were obtained from non-stationary experiments using the dilatometer method, and whereas catalyst concentration has been altered from one experiment to another, the light intensity is kept constant. From these experiments, it is seen that the ratio k_p/k_t remains constant. Also, polymerisation rate is almost dependent on the square root of catalyst concentration although at the lower concentration the rate is a little high. Direct photorate (i.e. the polymerisation rate with no added catalyst) will affect polymerisation rates at the lower catalyst concentrations since

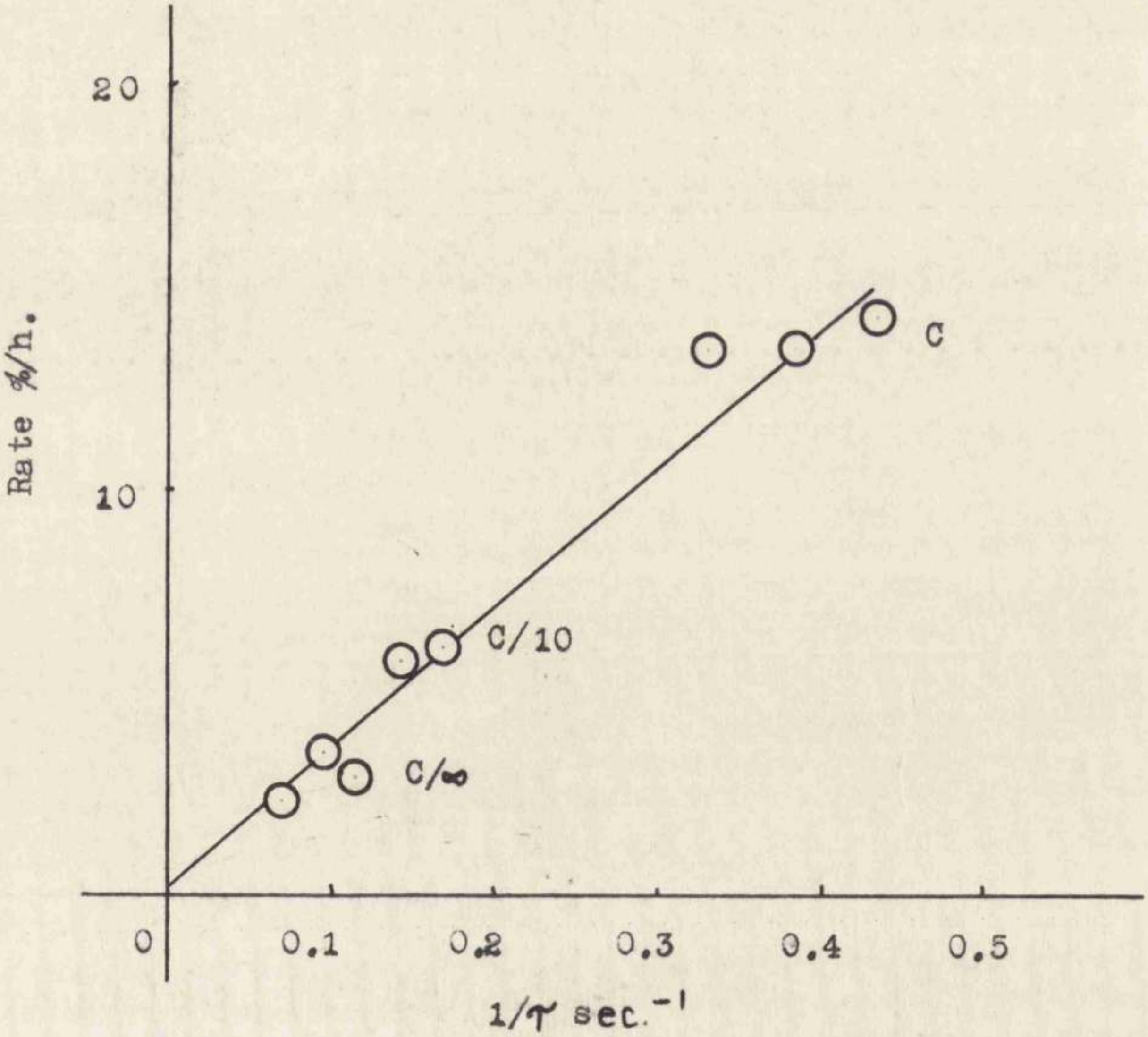


Figure 14. Comparison of rate and 1/τ at different catalyst concentrations in the polymerisation of methyl acrylate.

both sets of rates are of the same order. This near dependence, however, of polymerisation on root catalyst concentration is an indication of a second order termination reaction.

Values for τ, Polymerisation Reaction Rate and k_p/k_t.

To show the constancy of the ratio k_p/k_t, the values, from table V, of $1/\tau$ and polymerisation rate have been plotted against each other (fig. 14). This plot shows a straight line relationship between $1/\tau$ and rate:

i.e. $1/\tau \propto$ rate.

i.e. rate $\times \tau =$ constant

where the constant is k_p/k_t.

A number of polymerisations were carried out at 25°C and 35°C, and from values of τ and rates of polymerisation, the ratio k_p/k_t was calculated. A range of values of k_p/k_t from these experiments is given in table VI together with the relative data.

Table VI.

Values of rate, τ and k_p/k_t for polymerisation of methyl acrylate photosensitized with 1,1'azo<u>bis</u>-cyclohexane carbonitrile at 25°C and 35°C. (The results are divided by the horizontal lines into 5 groups corresponding to 5 different dilatometers.)

Temperature (°C.)	Rate (%/h.)	τ (sec.)	$(k_p/k_t) \times 10^5$
25	14.3	2.3	9.1
25	13.6	2.6	9.8
25	12.9	2.4	8.6
25	11.0	2.7	8.3
25	12.1	2.5	8.4
25	11.4	2.8	8.9
25	14.2	2.3	9.1
35	17.9	2.2	11.0
35	15.9	3.2	14.1
35	16.8	1.9	8.9
35	19.5	2.9	15.7

It can be seen from table VI that the variation in value of the ratio k_p/k_t is greater at 35°C than it is at 25°C.

Figure 15. Rate of decomposition of D.P.P.H. compared to its inhibitor effect in the polymerisation of methyl acrylate.

Rates of Initiation.

Rates of initiation for the photopolymerisation of methyl acrylate have been measured on two different principles using D.P.P.H..

a) The rate of disappearance of the violet colour of the D.P.P.H. has been measured using an absorptiometer [26,27].

b) By adding a known amount of D.P.P.H. inhibitor, the point when contraction begins can be taken as the end of the inhibition period [28].

Both principles have been incorporated into the one experiment and fig. 15 shows a typical plot from one of these experiments. Light absorption at $\lambda = 5250$ Å has been plotted against time of irradiation and the slope of this curve gives the rate at which D.P.P.H. is removed by reaction with radicals. In the same figure, a plot of contraction against time is given. By extrapolating the linear portion of this latter curve to the time axis, an inhibition period of 82 minutes is found. The former curve, however, gives an inhibition period

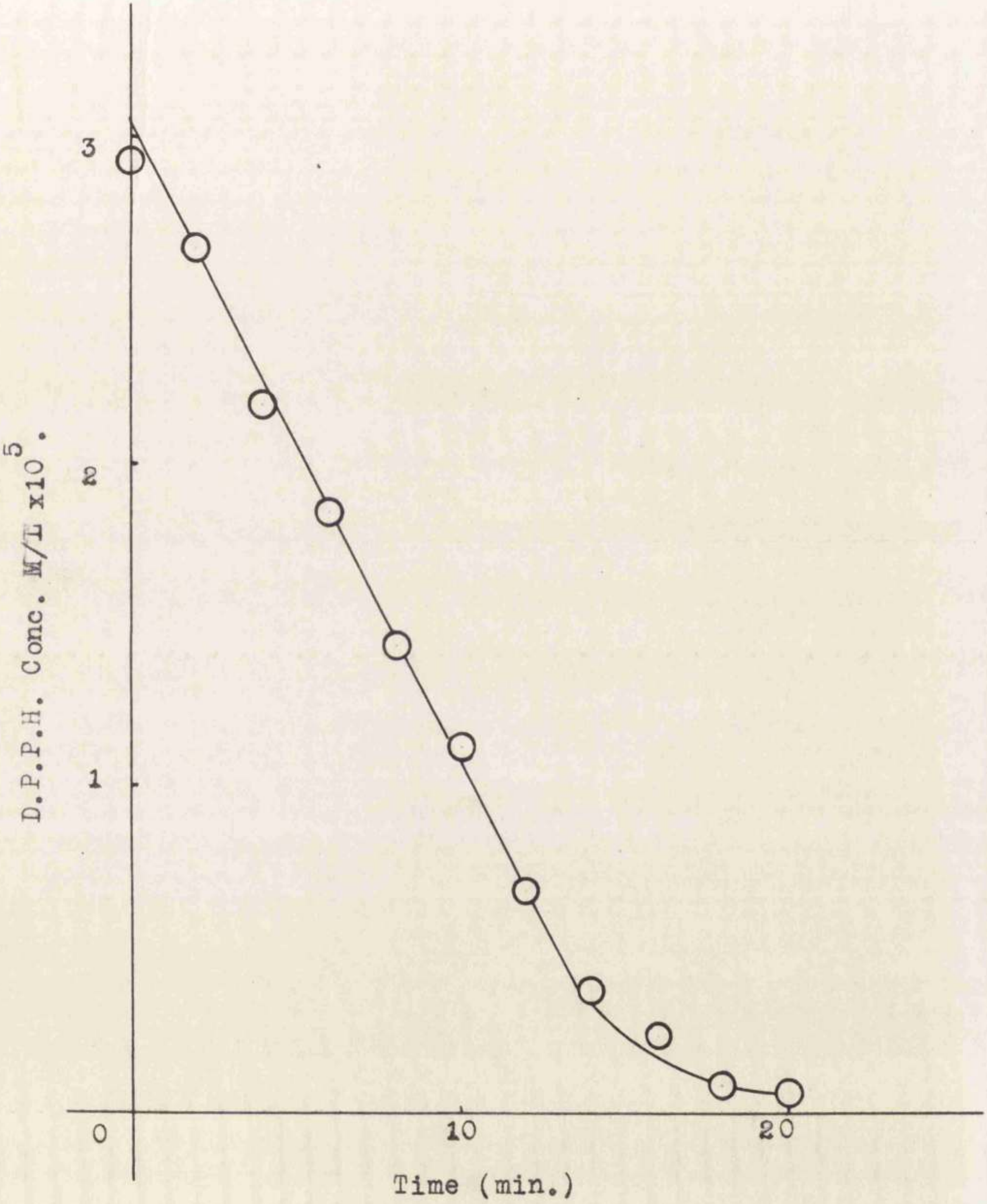


Figure 16. The rate of decomposition of D.P.P.H.

of 42.5 minutes. This difference of a factor of 2 between the two methods is probably caused by the formation, during the D.P.P.H. removal, of another inhibitor [29] which has to be removed before polymerisation occurs. Because of this effect, colorametric determinations of rates of initiation were used.

Also, since decomposition of 1,1' azo<u>bis</u>cyclohexane carbonitrile is nearly independent of solvent[30], rates of initiation using this catalyst, were studied in chloroform solution.

A plot of decrease in D.P.P.H. concentration with time under normal experimental conditions is shown in fig. 16. This is very close to plots from duplicate experiments.

From the slope of the linear portion of the curve (fig. 16),

$$\text{moles D.P.P.H. removed} = \frac{3.72 \times 10^{-6}}{60} \text{ moles/L./sec.}$$

Assuming 50% efficiency,

$$I = \frac{1.86 \times 10^{-6}}{60}$$

$$= 3.1 \times 10^{-8} \text{ moles/L./sec.}$$

Note: Since these experiments were carried out in chloroform, the direct photopolymerisation rate of methyl acrylate has been neglected. This, however, is of the order of 10% of the total rate and therefore affects the results to a small degree only.

Values for Velocity Coefficients.

Having obtained a value for rate of initiation of the reaction under the conditions of the experiment, the velocity coefficients for the propagation and termination rates, k_p and k_t respectively, can be calculated. It can be seen from table VI, however, that there is a variation in the values for rates of reaction. This variation may be the result of changes in rate of initiation although the dilatometers were clamped in the same position in the water thermostat. It is possible, however, that slight errors in the position of the dilatometers combined with slight differences in photosensitizer concentration and fluctuations in the intensity of the irradiation from the Osira lamp are responsible for the variations in the values of the rate of reaction. Values of k_p and k_t have been calculated therefore on the basis of two assumptions:

a) The variation in rate was due to variation in the rate of initiation.

b) The rate of initiation was constant for all determinations.

Values of k_p and k_t are listed in table VII, the values in brackets having been calculated on the basis of a constant rate of initiation.

Table VII.

Values of the velocity coefficients for the propagation and termination reactions of the photosensitized polymerisation of methyl acrylate at 25°C.

k_p L.mole^{-1}sec.$^{-1}$	$k_t \times 10^{-6}$ L.mole^{-1}sec.$^{-1}$	$(k_p/k_t) \times 10^5$
520 (520)	6.1 (6.1)	8.5
520 (470)	5.3 (4.8)	9.8
600 (440)	6.9 (5.2)	8.6
620 (360)	7.5 (4.4)	8.3
610 (440)	7.3 (5.2)	8.4
580 (360)	6.5 (4.1)	8.9
560 (550)	6.2 (6.1)	9.1

These values have been calculated from measurements taken on several experiments made on the initial stages of the reaction i.e. before the rates had accelerated. As can be seen from table VII, there is less variation in the values of k_p if they are calculated on the basis that the rate of initiation varied in each determination. Reproducibility is good for these early stages, although some experiments at the very early stages gave anomolous results as mentioned earlier.

The average value of k_p calculated on the assumption that rate of initiation varied, is 580 L. mole^{-1} sec.$^{-1}$ and the average value of k_t is 6.5×10^6 L.mole^{-1} sec.$^{-1}$ at 25°C.

Table VIII.

Values of the rate, τ , k_p, k_t and k_p/k_t for the photosensitized polymerisation of methyl acrylate at 35°C.

Rate %/h.	τ sec.	k_p L.mole^{-1}sec.$^{-1}$	$k_t \times 10^{-6}$ L.mole^{-1} sec.$^{-1}$	$(k_p/k_t)\times10^5$
15.1	3.5	390	2.6	14.7
17.9	2.2	730	6.7	10.9
15.9	3.2	450	3.2	14.1
15.1	2.3	590	6.1	9.7
16.8	1.9	790	8.9	8.9
19.5	2.9	600	3.8	15.7
19.5	3.0	590	3.6	16.3

In the experiments at 35°C (table VIII) there is greater variation in results particularly in the measurements of τ ; results based on τ will therefore have similar variations. Thus, approximate values for the energy of activation for the termination reaction, based on the results given in table VI and table VIII, vary from 0 to 7.8 k.cal./mole.

The increase in polymerisation rate with increase in temperature indicates a positive overall activation energy. From the rate data at 25 and 35°C the overall activation energy was found to be 6.2 k.cal./mole. Thus, from $E_o = E_p - \frac{1}{2}E_t$, the value for the activation energy of the propagation reaction, E_p, lies between 6.2 and 2.3 k.cal./mole.

Later Stages of the Polymerisation Reaction.

Variations in the Coefficient of Expansion.

In calculating polymerisation rates, one of the factors involved, the coefficient of expansion of the reacting mixture, must be known accurately. It was found, however, that as the extent of polymerisation progressed, the coefficient of expansion of the monomer/polymer mixture changed. Expansion was measured over 25 to 35°C for various monomer/polymer mixtures in the apparatus described previously.

A graph was constructed of expansion against temperature (e.g. fig.7 for 25% conversion). Since the measured volume included mercury, the slope of the plot gave the combined coefficient of expansion of mercury, monomer and polymer. Knowing the individual volumes of the constituents of the measured volume, the coefficient of expansion for that monomer/polymer mixture could be calculated. An example of such a calculation is given in appendix II.

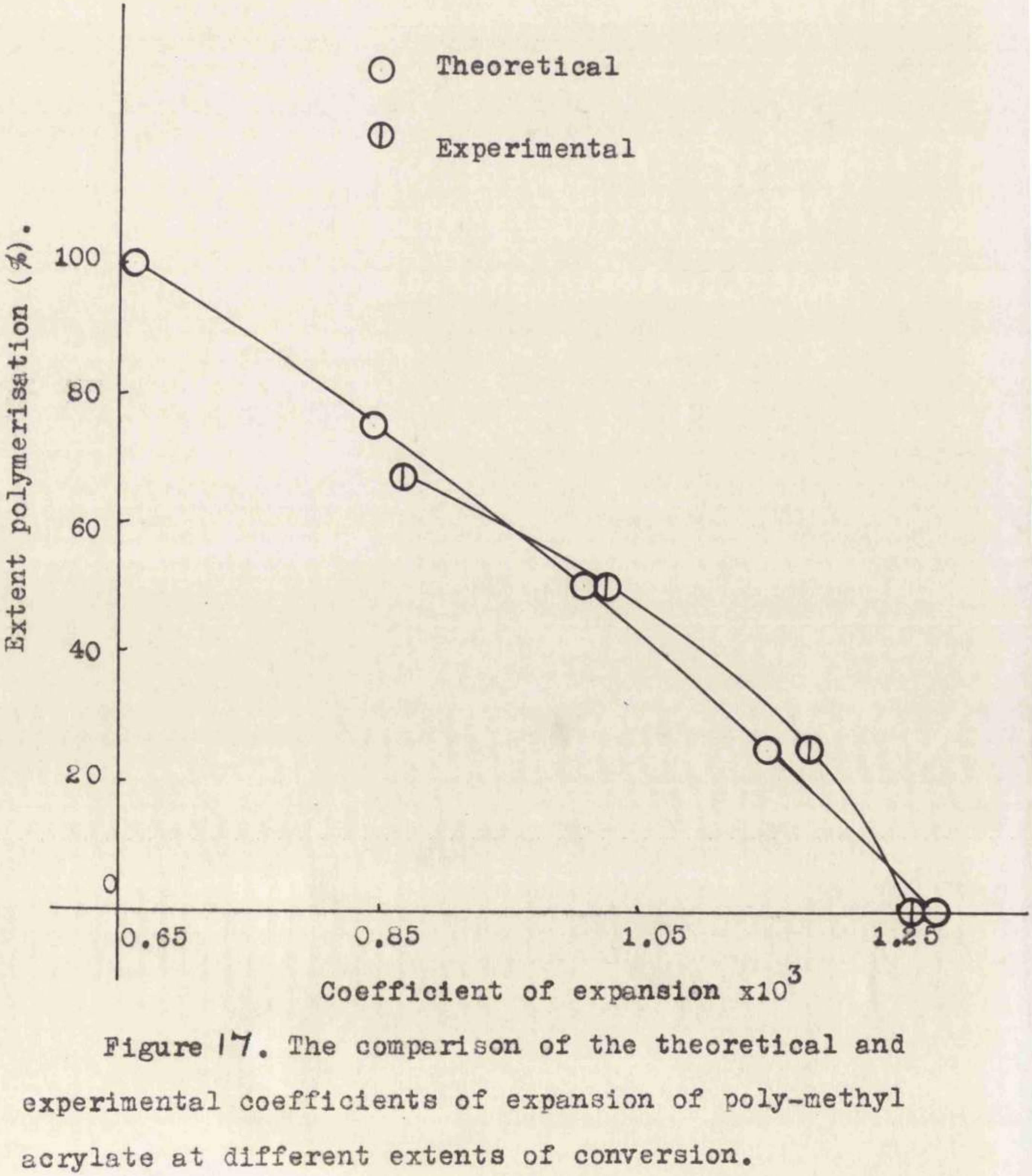


Figure 17. The comparison of the theoretical and experimental coefficients of expansion of poly-methyl acrylate at different extents of conversion.

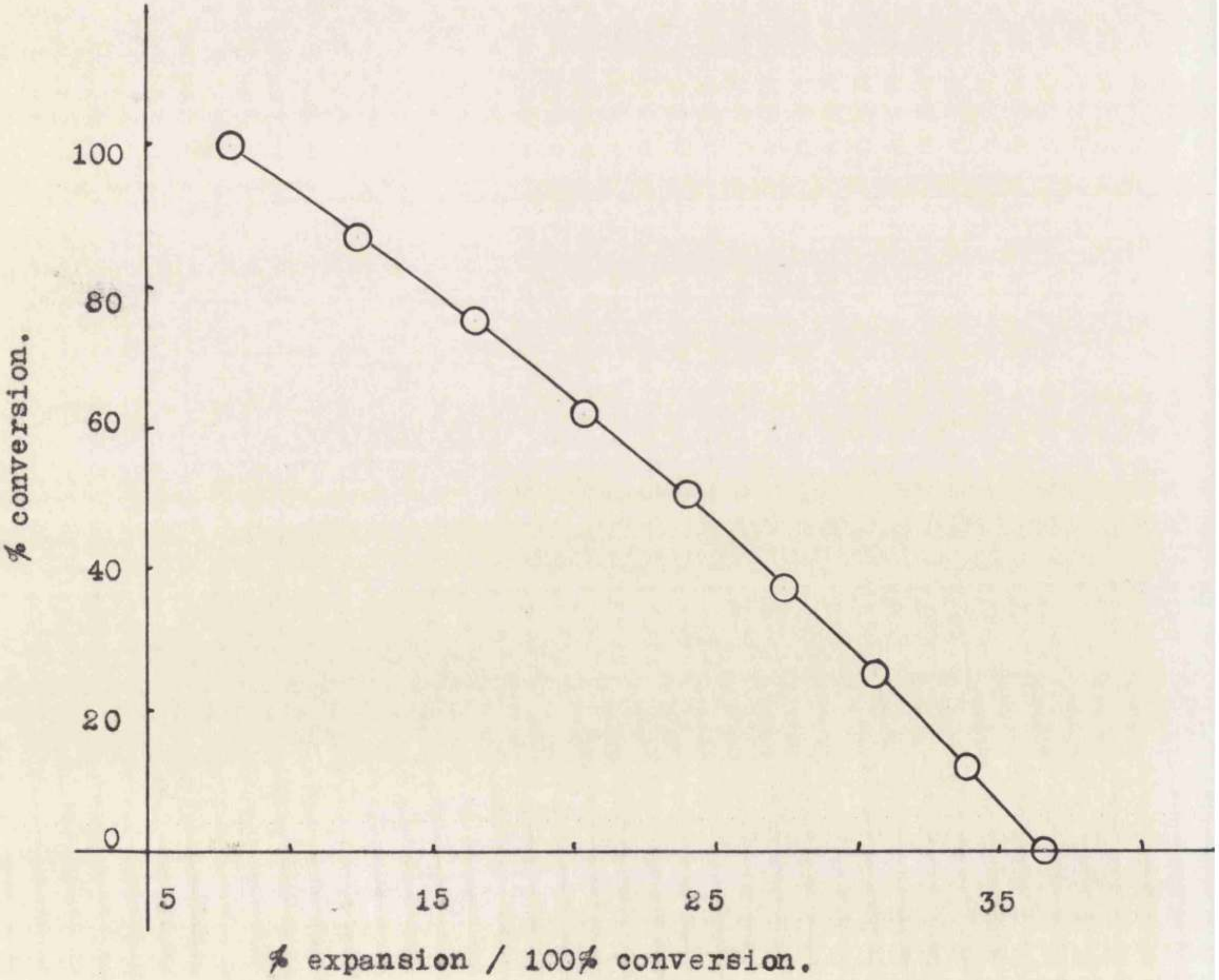


Figure 18. The variation of factor "A" with extent polymerisation.

Coefficients of expansion for various similar mixtures, were plotted against the extent of monomer to polymer conversion in fig.17. These coefficients were compared to those calculated by direct addition of the individual monomer and polymer expansion coefficients in their relative proportions. A typical calculation for this "theoretical" coefficient of expansion is given in appendix II.

From fig.17 it can be seen that the experimental curve differs from the theoretical one indicating that the expansion coefficient of polymethyl acrylate changes when it is dissolved in methyl acrylate.

The relationship

$$\text{Rate} = \frac{m \times 3600 \times 100}{A} \quad \%/\text{h}.$$

gives the rate of polymerisation from expansion data, where m is the rate of expansion (%/sec.) and A is % expansion for 100% polymerisation. The variation of A with extent polymerisation has been plotted in fig.18.

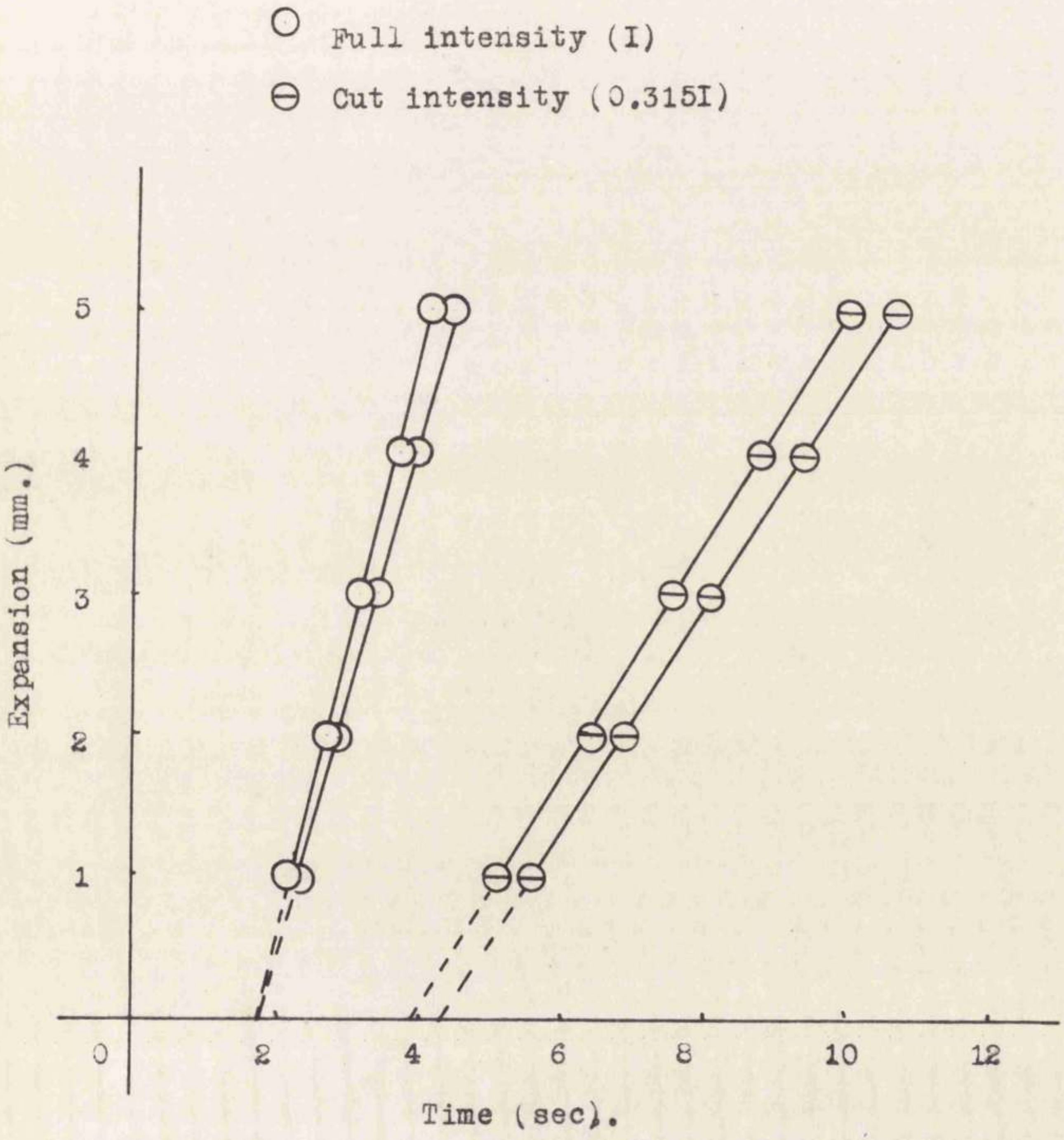


Figure 19. Non-stationary state rate curves for the polymerisation of methyl acrylate at 2 different light intensities using the dilatometer method. (22% polym.)

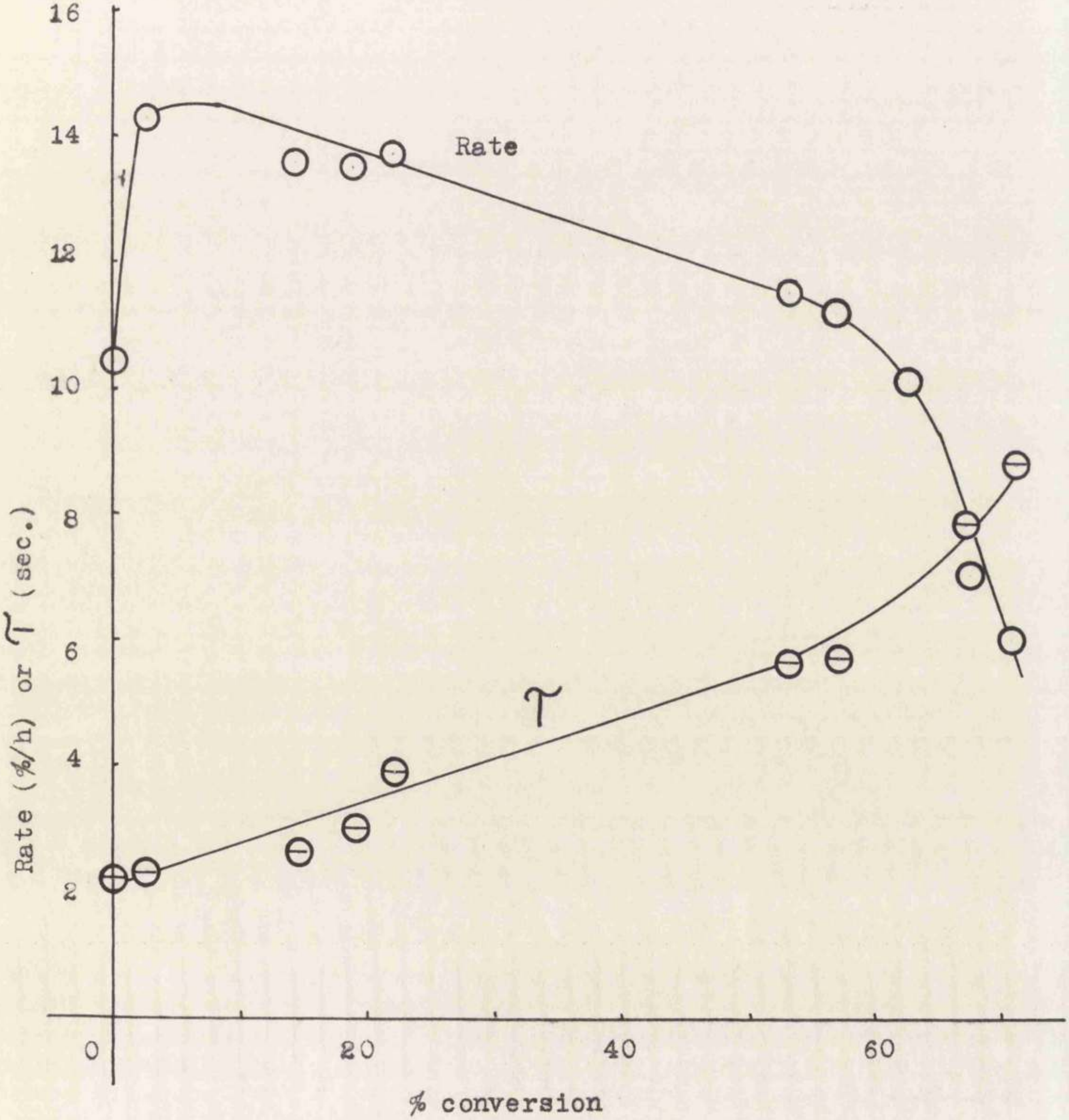


Figure 20. The variation of rate and τ with extent reaction for the polymerisation of methyl acrylate - dilatometer method.

Non-stationary Measurements at Later Stages.

Non-stationary measurements were made at the later stages by the dilatometer method. A typical expansion against time plot for such experiments is shown in fig.19; the reaction mixture had polymerised to 22% conversion and the measurements were made at two different light intensities. Although at this stage, the reaction mixture had gelled, reproducibility of measurements was still good.

In fig.20, the effect of extent conversion of monomer to polymer is shown. There is an initial acceleration of reaction rate followed by a gradual decrease in rate. With the plot of τ against extent polymerisation (fig.20) there is a corresponding gradual increase in values of τ as the reaction progresses. As in the initial stages of the reaction, decrease of catalyst concentration decreases the reaction rate.

Rate of polymerisation increases with increase in temperature; this was found to hold over the

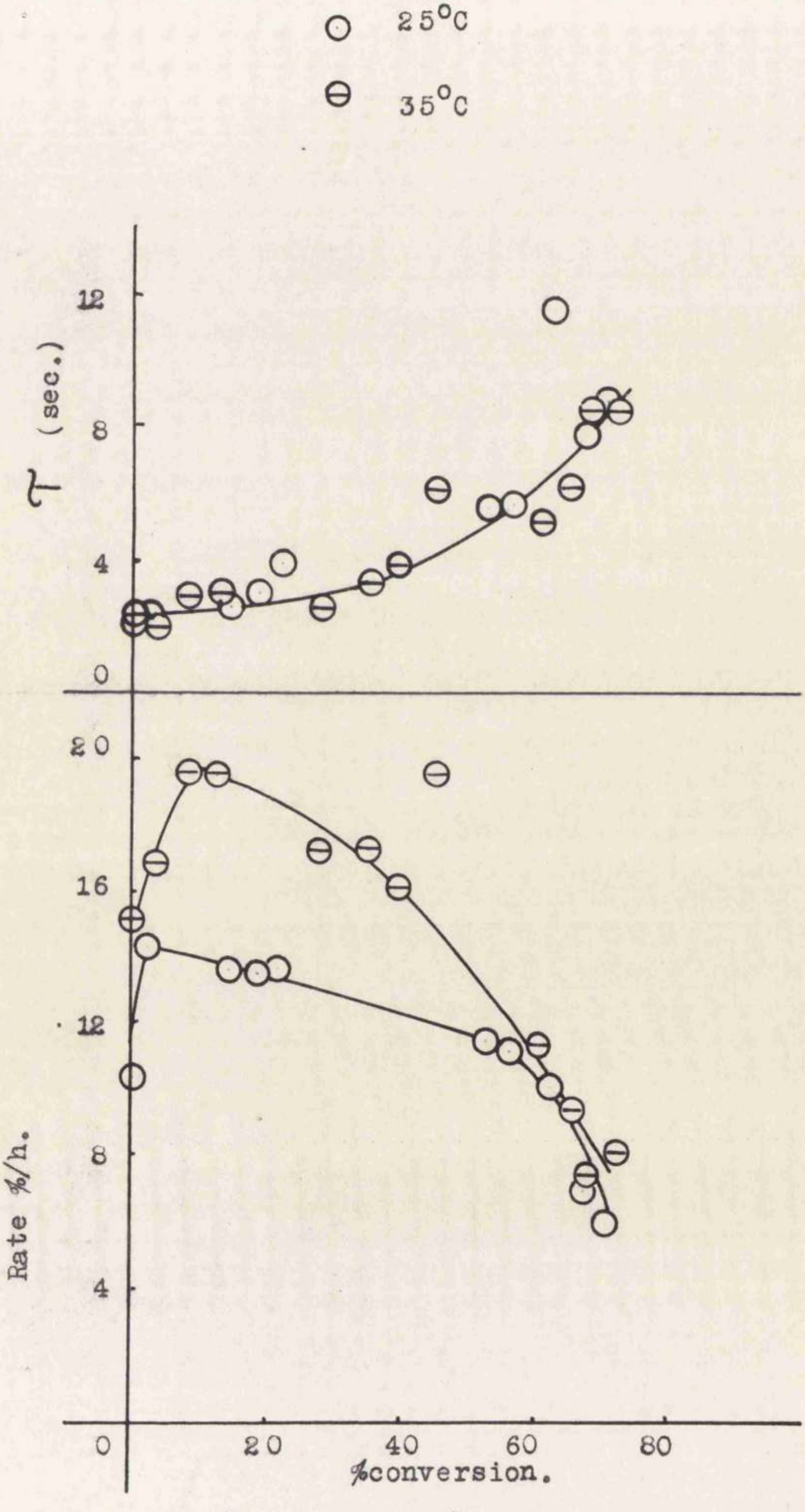


Figure 21. Rate and τ - dilatometer method.

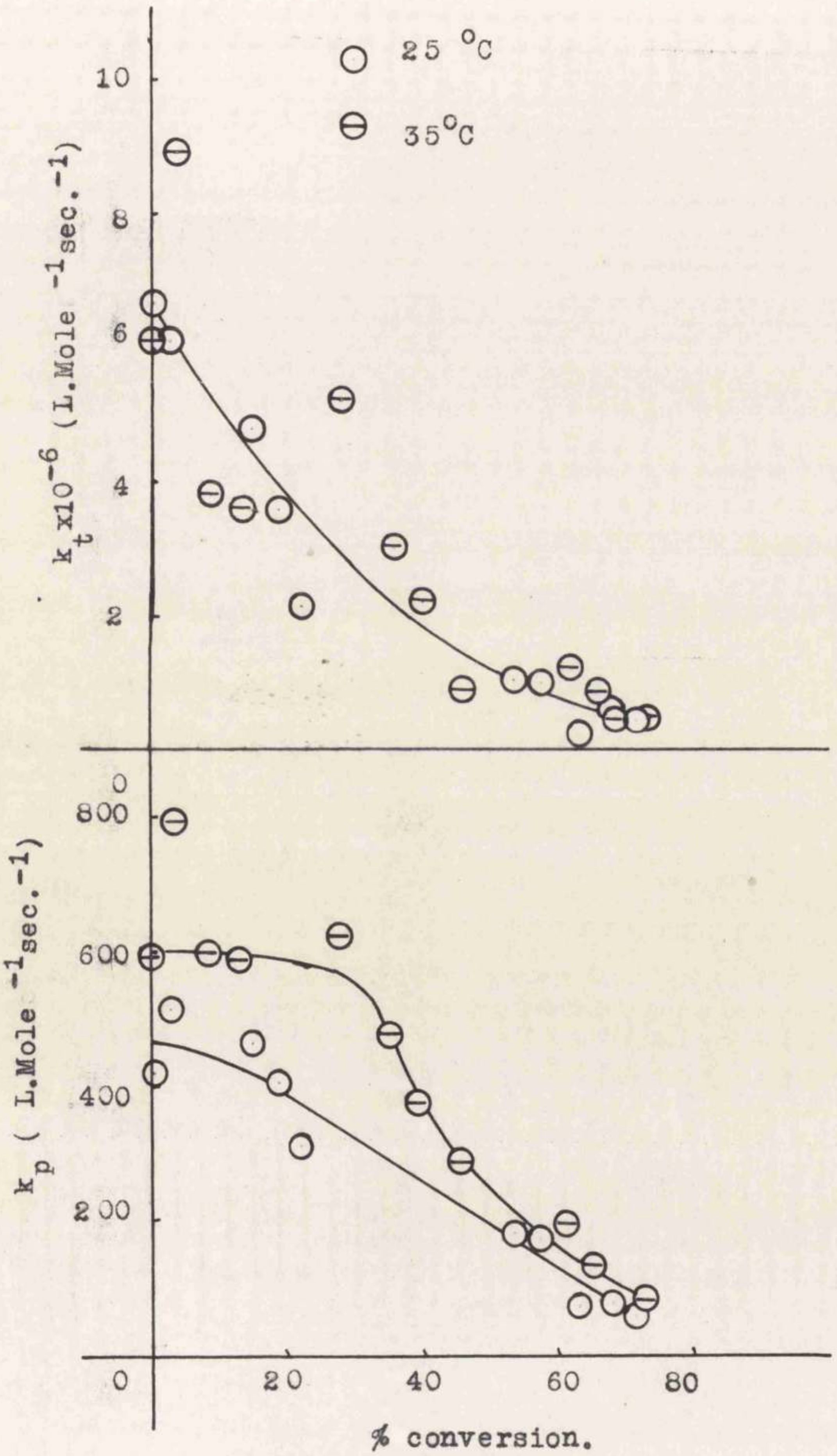


Figure 22. The variation of k_p and k_t with extent reaction at different temperatures.

range of extent of polymerisation measured (up to 70% conversion) indicating a positive overall activation energy, (fig.21) although the value of this E_o decreases with extent conversion; this is indicated in fig.21 by the convergence of the plots for results at 25°C and 35°C.

From fig.21, however, the plot of τ against extent conversion for experiments conducted at 2 different temperatures, it can be seen that temperature has very little effect on values of τ i.e. an indication of zero energy of activation for the termination reaction.

The effect of extent conversion on the kinetic constants, k_p and k_t, has been studied from fig.22. Both k_p and k_t decrease with extent polymerisation.

Again, the effect of temperature is to increase k_p but to have little effect on k_t. There is also convergence of the 2 plots of k_p against extent conversion (at 2 different temperatures) similar to the experience of rate in fig.21.

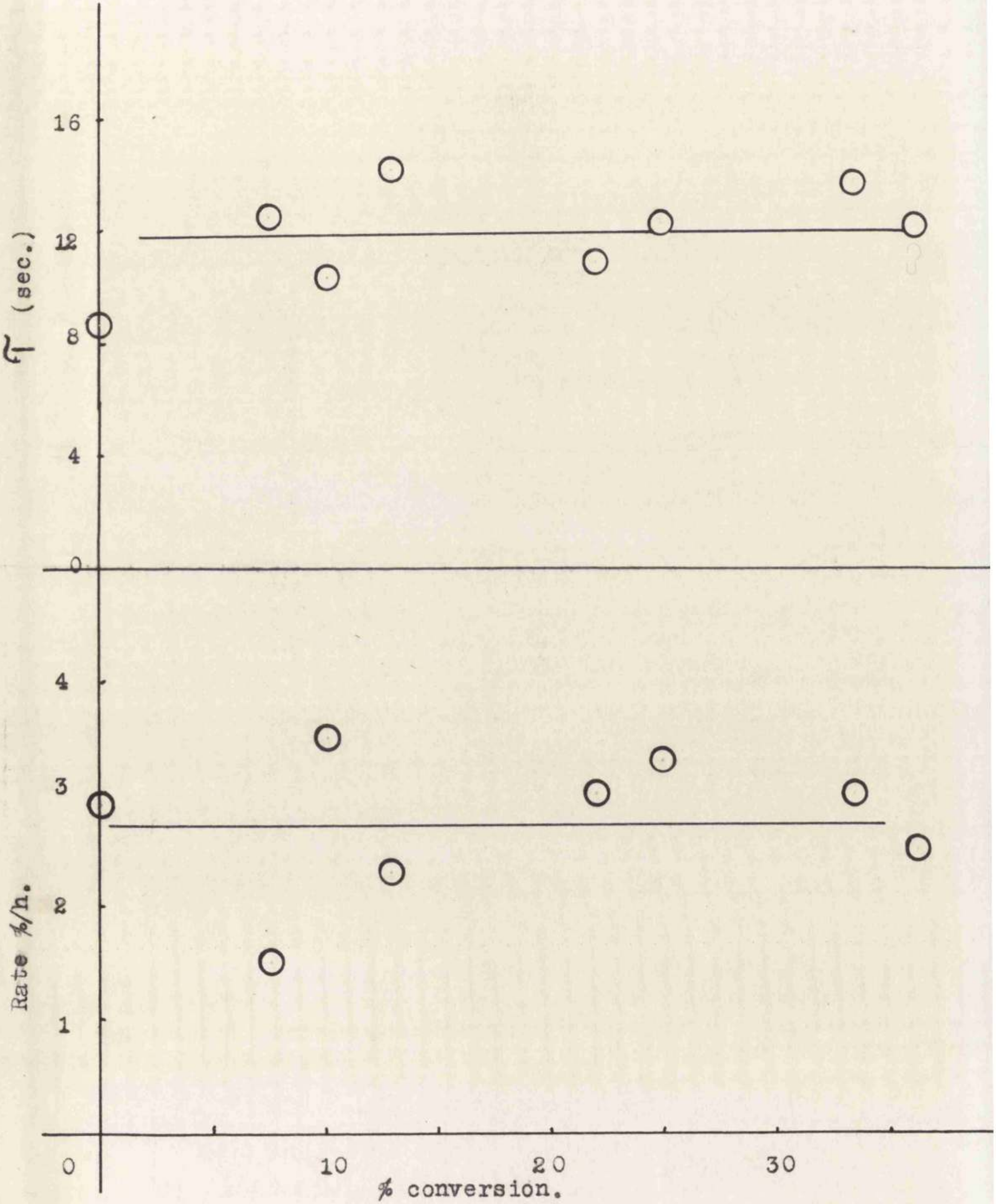


Figure 23. Rate and τ with no catalyst present.

Although it can be seen that there is a positive overall energy of activation, the value for this cannot be determined accurately at the latter stages because of the scatter of points. Similarly, there is a large scatter of values of τ at the later stages making the determination of E_t impossible.

Non-stationary State Experiments with No Catalyst.

Using the non-stationary state dilatometer method, reaction rates and values of τ were measured for the polymerisation of methyl acrylate without catalyst. As was expected, this direct photorate was much smaller than the rate for the catalysed reaction (*ca*.1/4 to 1/5 the rate at normal catalyst concentration). There was a corresponding increase in values of τ.

There was, however, no rate fall off with increase in extent conversion as fig.23 shows. Also, fig.23 (a plot of τ against extent conversion) shows that τ maintained a steady value with increased monomer to polymer conversion.

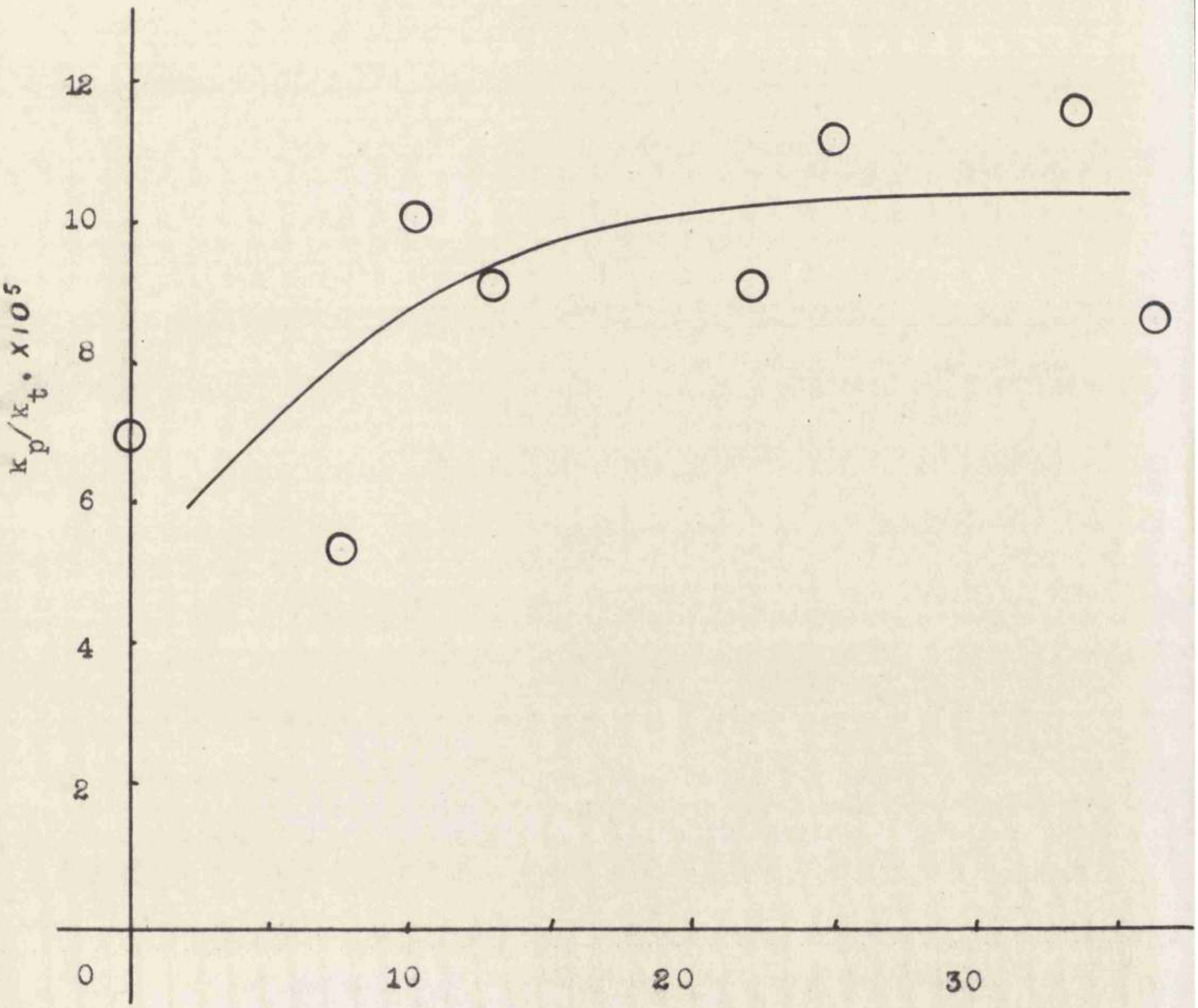


Figure 24. Variation of k_p/k_t with extent reaction for the polymerisation of methyl acrylate using no catalyst (dilatometer method.)

Also, the plot of k_p/k_t against extent conversion, fig.24 gives a line of almost zero gradient i.e. the ratio of the kinetic constants is unchanged with increased conversion. There was, however, considerable scatter in these values, the result of the large values of τ rendering rate measurements unreliable (see discussion).

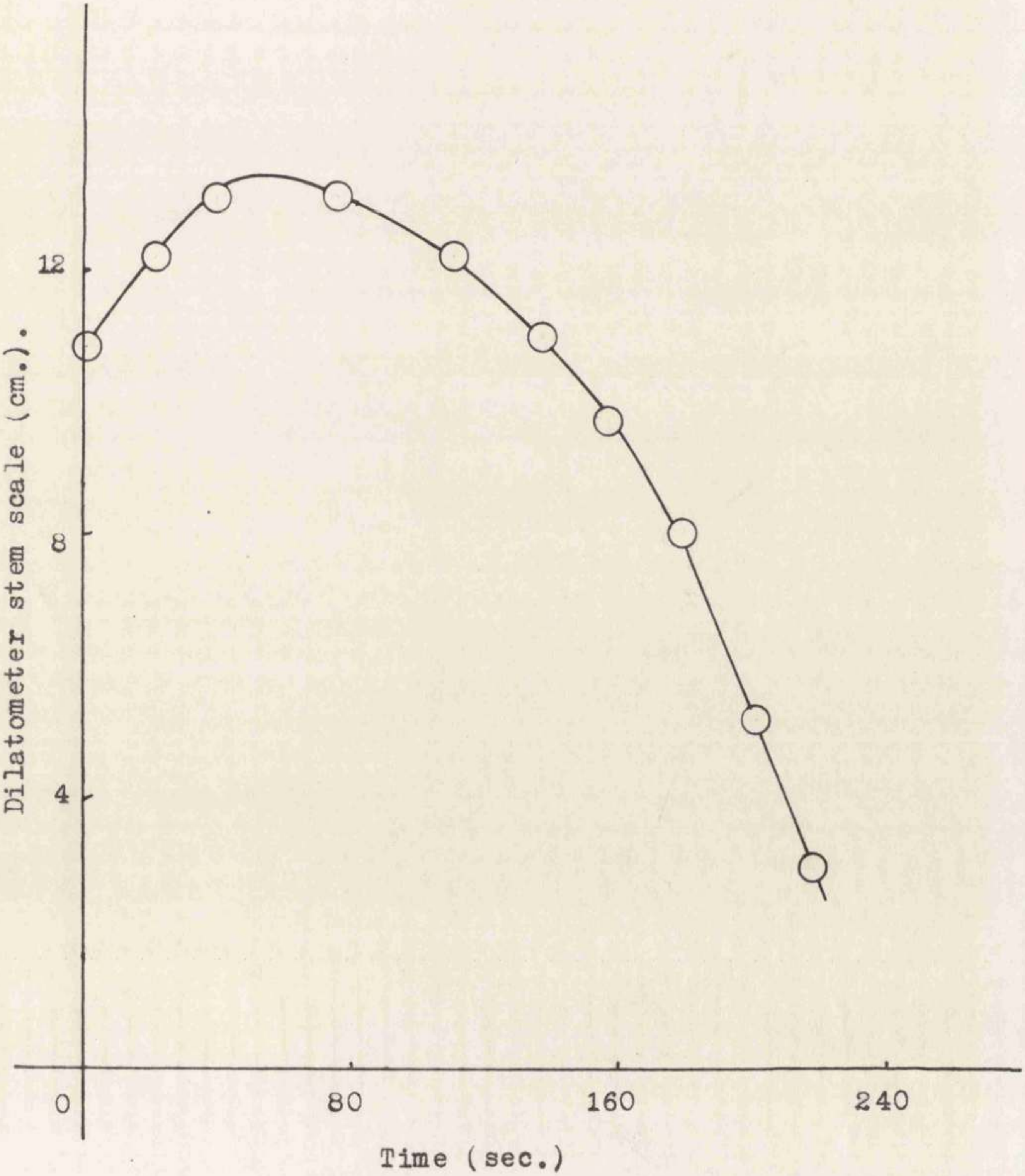


Figure 25. A continuous polymerisation experiment for the polymerisation of methyl acrylate (dilatometer method.)

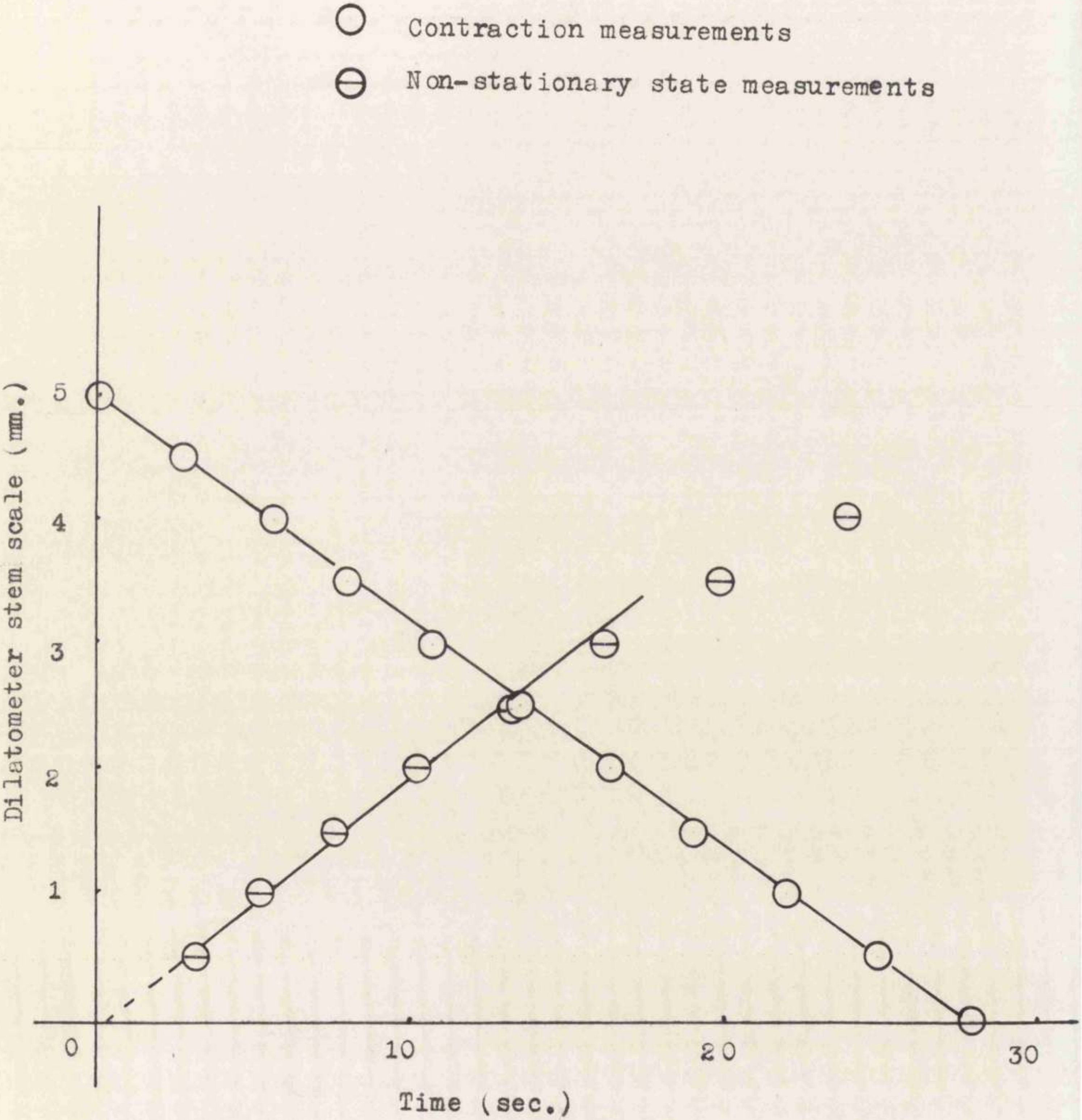


Figure 26. Comparison of contraction and non-stationary state measurements for the polymerisation of methyl acrylate.

Comparison of Expansion and Contraction Measurements.

Polymerisation rates were calculated from contraction measurements and compared directly to non-stationary measurements to check the validity of the latter values. Fig.25 shows a typical plot of height of mercury in the stem of a dilatometer against time. Non-stationary state measurements made at the very initial point of this curve are compared with contraction measurements in table IX.

Table IX.

Comparison of polymerisation rates in the early stages of the reaction deduced from non-stationary state measurements and contraction.

Rate of polymerisation (%/h.)	
Non-stationary state method.	Contraction method.
18.4	25
24.3	
19.6	25

In fig.26, an example of non-stationary and

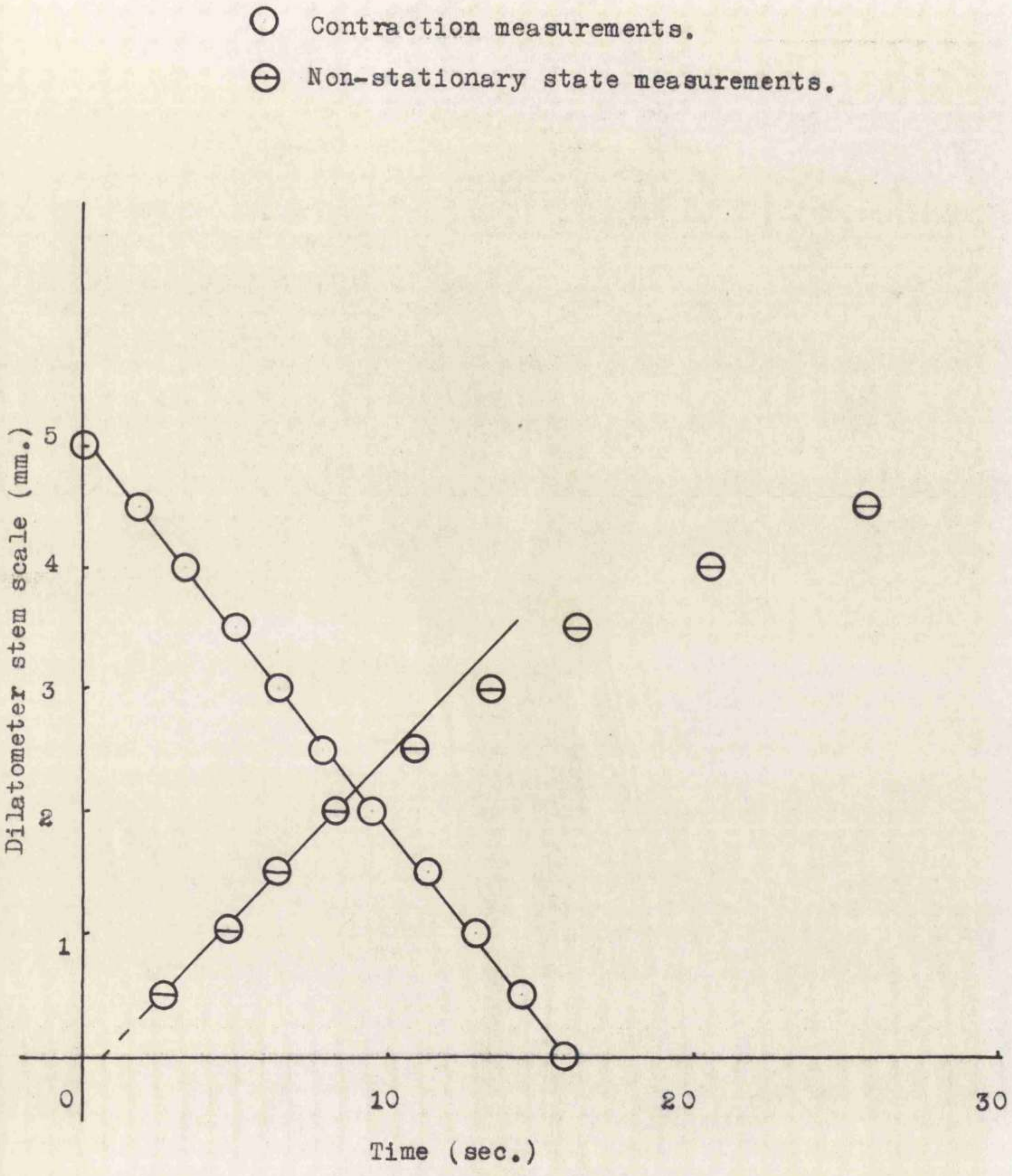


Figure 27. Comparison of contraction and non-stationary state measurements for the polymerisation of methyl acrylate at 20% conversion.

contraction measurements is given in more detail. It will be noticed that in these early stages of the reaction, the agreement between the two methods of measurement is fairly good.

When later stages in the reaction were reached and the two methods of measuring compared, it was found that there were large differences in rate measurements (fig.27); rates differed by as much as a factor of 2. Table X shows some of these results at later stages.

Table X.

Comparison of polymerisation rates in the later stages of the reaction deduced from non-stationary state measurements and contraction measurements.

Extent conversion %	Rates of reaction (%/h.)	
	Non-stationary method.	Contraction method.
0	19.6	25
7.9	27.0	39.7
19.7	28.9 28.1	46.1
35.3	23.1 20.8	47.1

The above difference in results from the

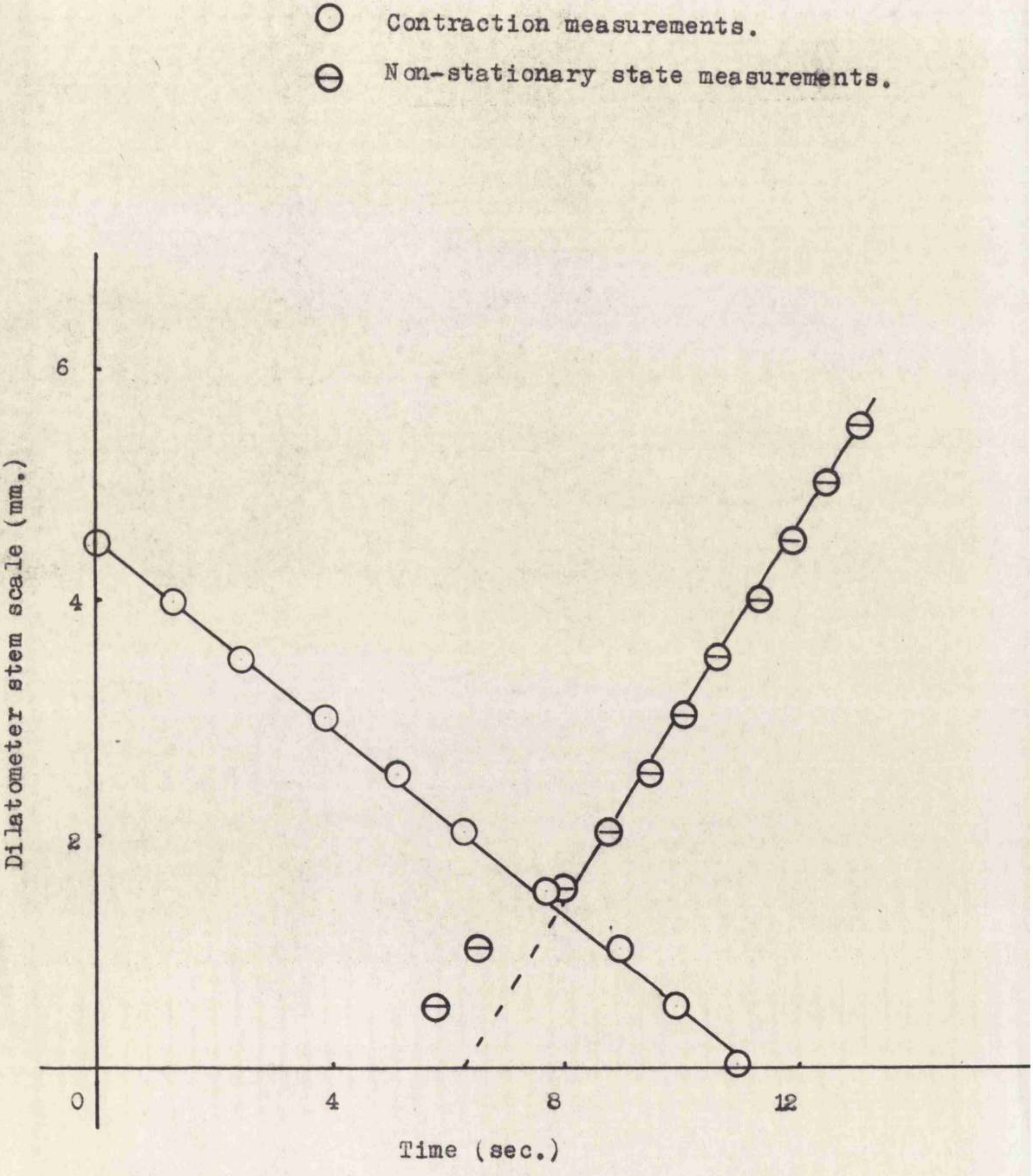


Figure 28. Comparison of contraction and non-stationary state measurements for the polymerisation of methyl acrylate using a catalyst concentration of 0.800x10^{-4} M/L.

different methods may be due to a heating effect (see discussion) from the heat of reaction. This effect can be reduced by using 1/10th catalyst concentration. An example of resulting measurements is given in fig.28. In table XI, the two methods of measuring are compared at the lower rates.

Table XI.

Comparison of polymerisation rates deduced from non-stationary state measurements and contraction measurements using 1/10th catalyst concentration.

Extent conversion %.	Rates of reaction (%/h.)	
	Non-stationary method.	contraction method.
2	5.8 6.1	5.2
8	7.6 7.1	5.1
15	7.6	11.4

It can be seen that at these lower rates where the heating effect is not so marked, there is reasonable agreement between the two methods, although when conversion reaches about 15%, the variation between the two methods of measuring is as great as that found at normal catalyst concentrations.

The Thermocouple Method for following the Polymerisation Reaction of Methyl Acrylate.

Introduction.

Having studied the kinetics of polymerisation of methyl acrylate using a dilatometer method for following the reaction, another method for measuring the reaction kinetics would serve as a useful comparison. A series of experiments was therefore carried out under the same experimental conditions using the thermocouple method for measuring values of τ and polymerisation rates.

The thermocouple method was devised by Bengough and Melville[14] and used to measure the rate constants of the propagation reaction and termination reaction for vinyl polymerisation and has already been used for vinyl acetate, methyl methacrylate and butyl acrylate polymerisations. Essentially, the method is one of measuring temperature rise in the centre of a reaction vessel.

Since the whole of the reacting mixture is being heated uniformly by the reaction and cooling occurs through the walls of the vessel only, the adiabatic conditions hold for about 30 sec. at the centre of the vessel, that is, in the region of one thermocouple junction. Therefore no complicated apparatus is required to keep the whole vessel under adiabatic conditions. This is a distinct advantage over other methods[10,11,12] where a measurement is made on the average change throughout the vessel. Also, these vessels are easily replaced; subsequently, any reaction carried on into the gel state with destruction of the vessel is no great loss. This makes the method ideal for following the later stages of the reaction.

Under adiabatic conditions, the temperature rise is directly proportional to the fractional conversion and hence both the polymerisation rate and τ can be obtained directly from the temperature rise against time curve.

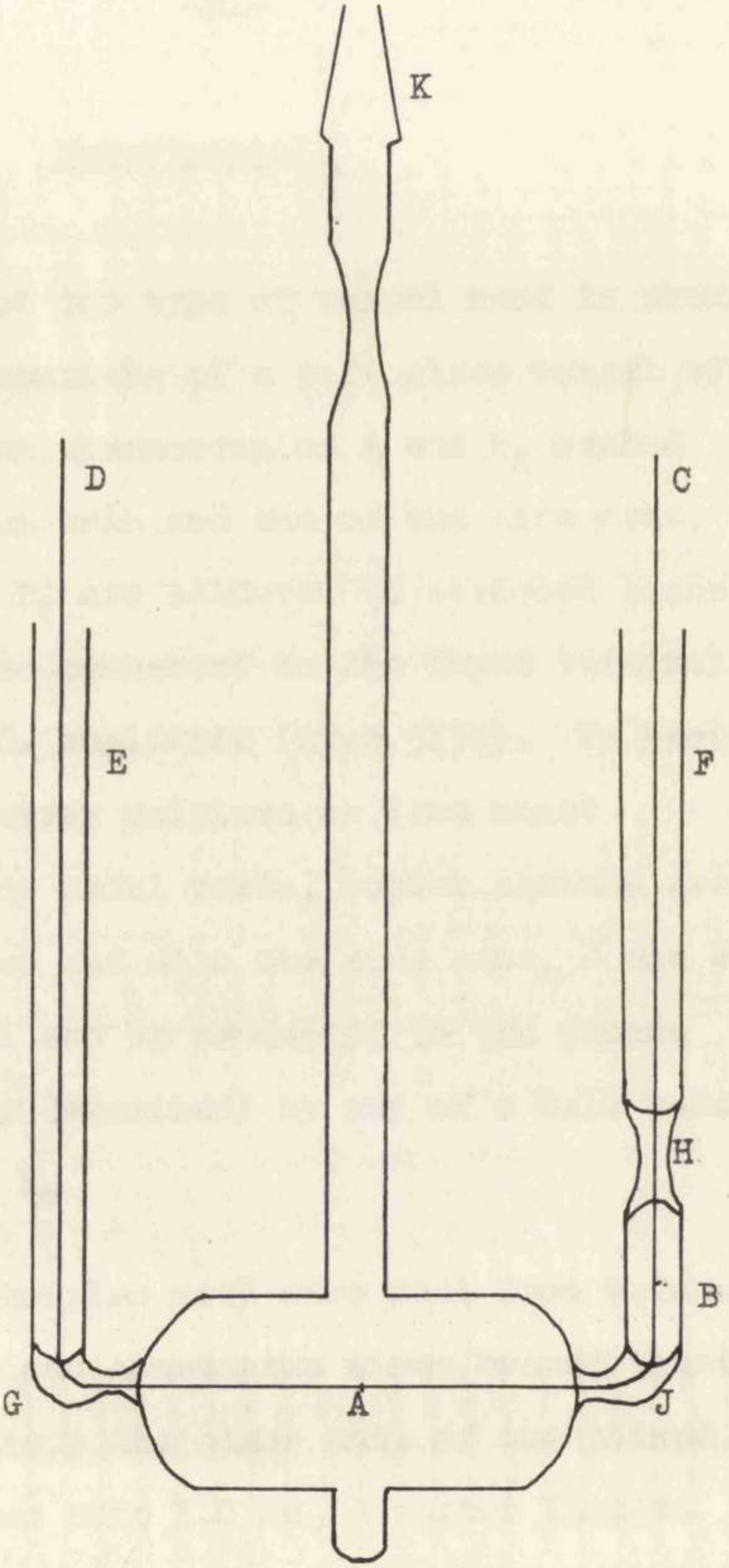


Figure 29. Reaction vessel for non-stationary state measurements by the thermocouple method.

Experimental.

Apparatus.

A diagram of the type of vessel used is shown in fig.29. It consists of a soft glass vessel with copper/constantan thermocouples A and B, sealed into the reaction bulb and one of the side arms. The wires C and D, are soldered to screened leads which in turn are connected to the input terminals of a Tinsley D.C. amplifier (type 5132). To protect the wires from stray moisture or from short circuiting on any metal parts, rubber sheaths are slipped over them and onto the side arms, E and F. The whole vessel can be connected to the vacuum line (previously described) by way of a B.10 soda Quickfit joint, K.

The thermocouples used were made from 0.2mm. diameter copper and constantan wires brazed together at a point contact; the other ends of the joined wires were brazed onto 1.0 mm. diameter Vactite borated copper clad wire for sealing into soft glass.

With the side arms primarily in a horizontal straight line, the prepared couples were slipped through and sealed at G and H, arm E being bent to the vertical position shown in the final diagram. The whole vessel was then evacuated and the seal at J completed resulting in the thermocouple at B being isolated under vacuum. Arm F was raised parallel to the others.

Procedure.

These vessels were filled in the same way as ordinary dilatometers (page 33). Clamped in position in the thermostatically controlled bath, the vessel and contents were allowed to reach temperature equilibrium with their surroundings. With the thermocouple leads connected to the input of the amplifier whose output is conducted to an Elliot voltmeter pen recorder, the system was ready for the reaction to be initiated.

Half an hour before using, the amplifier and the mercury vapour arc are switched on so that they both give steady outputs.

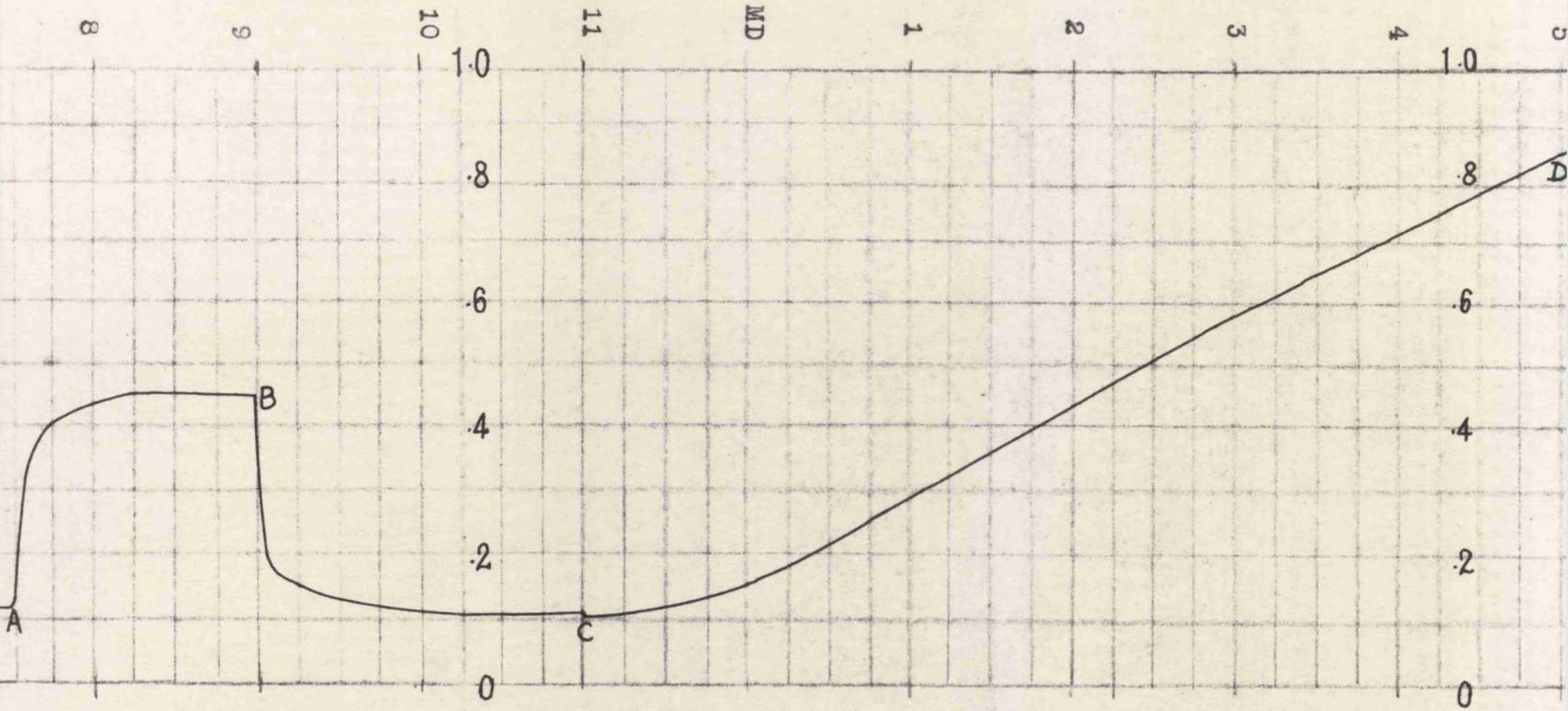


Figure 30. A typical time/temperature trace from a thermocouple method experiment.

At various stages in the reaction, the height of the monomer in the stem of the vessel was noted. Thus from the volume contraction, the bore of the stem having been measured, the extent of polymerisation could be calculated at these stages.

With the amplification adjusted to a suitable value, the test voltage was applied for 5 sec. (points A to B fig.30) and was used as a standard when making measurements from the recording chart.

Referring to fig.30, after the test voltage was cut out at point B, the shutter to the mercury vapour lamp was opened. The shutter action simultaneously produced a pip (point C) on the recording chart which was used as a starting marker. This rise in temperature was recorded (curve CD) until the rate of rise was constant. The closing of the shutter stopped the reaction and the vessel was again allowed to attain temperature equilibrium with the tank water before another experiment was recorded.

Recording Instruments.

The Tinsley D.C. amplifier (type 5132) is designed for an input impedence of less than 10Ω; it is therefore suitable for use with thermocouples. The voltage amplification is greater than 10^6, and the instrument has a coarse and fine balance control for balancing out E.M.F.s of up to 400 μV in the input circuit. This means that temperature rises of up to 10C° can be measured to an accuracy of 0.001 C°. Thus temperature changes can be followed in a continuous polymerisation as well as the non-stationary phase of the reaction. The test voltage used for calibrating the temperature rise in the reacting system is introduced into the input circuit by means of a switch and can be varied from 0.01 to 100 μV by factors of 10.

The output circuit is designed for a 500 Ω load and gives a current of up to 10 mA. The output is connected to an Elliot voltmeter pen recorder which has a resistance of 1100Ω and gives a full scale deflection when a potential difference of

1 volt is applied. The recording paper has a width 3.75 inches and was usually run at a speed of 12 inches per minute although some continuous polymerisation runs taken over a long period were recorded at 12 inches per hour. The half life of response of the instrument is 0.5 sec.

Measurement of the Kinetic Constants of Polymerisation of Methyl Acrylate in the presence of Trichlorobromomethane as Transfer Agent - Thermocouple Method.

Thermocouple experiments were also carried out using methyl acrylate in the presence of 1 mole percent of a transfer agent, trichlorobromomethane.

The trichlorobromomethane, kindly supplied by R.A.M. Thomson esq., had been purified by washing with aqueous sodium carbonate to remove free bromine, drying over anhydrous calcium chloride and distilling under vacuum (20mm. pressure).

After introducing the catalyst to the reaction vessel and pumping off solvent in the usual manner, the requisite amount of CCl_3Br was measured in and degassed. Monomer was distilled in as before.

A few primary experiments were carried out using the simple dilatometers described under the dilatometer method. It was found that the rates measured were the same as those in the initial stages of reactions in the absence of transfer agent.

Thermocouple experiments were carried out with the methyl acrylate/CCl_3Br mixture; the method of measuring values of τ and reaction rates has been described earlier in this section.

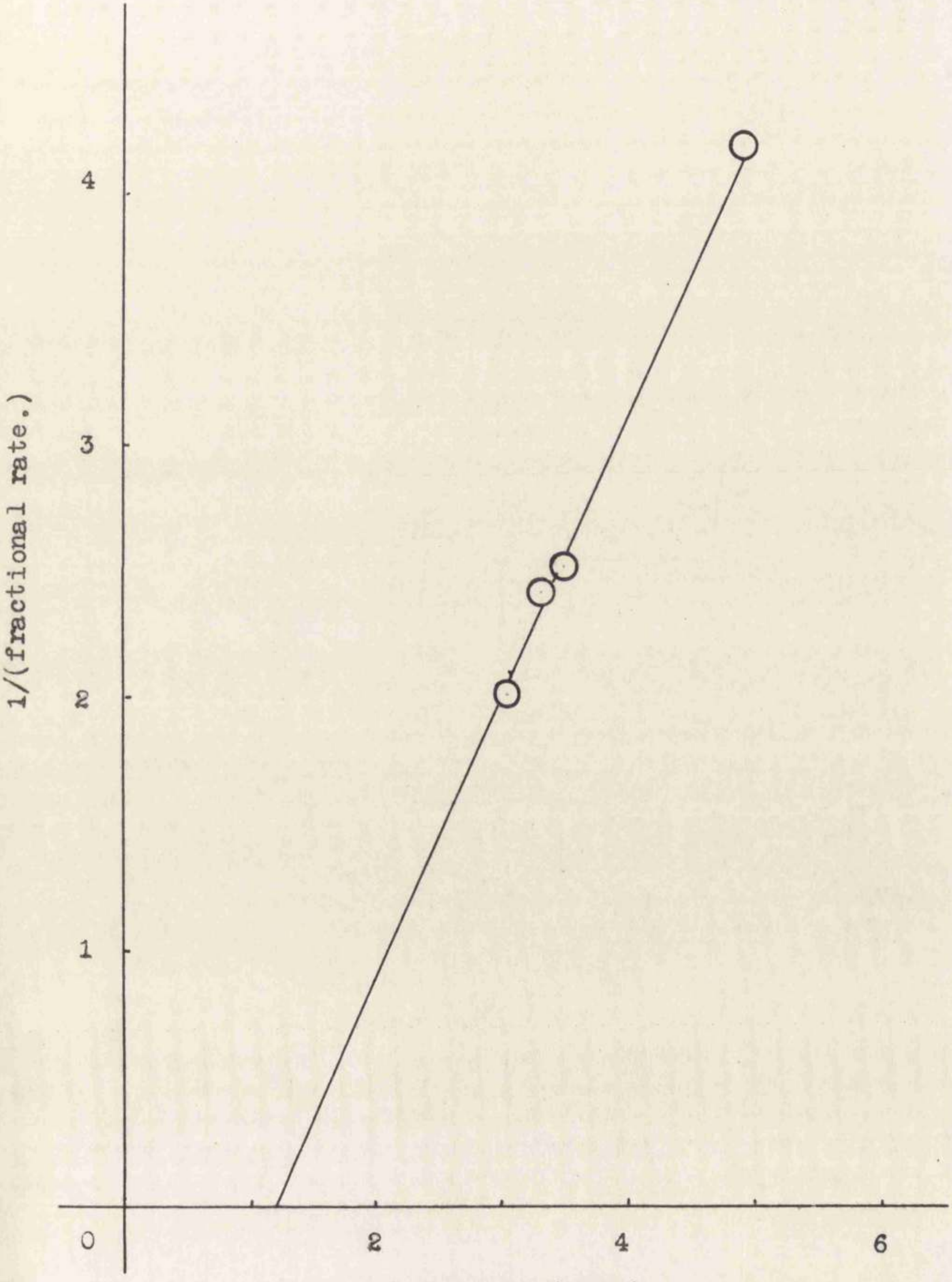


Figure 31. The calculation of instrument lag.

Results.

Early Stages of Methyl Acrylate Polymerisation.

Rate measurements were made on the early stages of the reaction by the method just described. Traces similar to that shown in fig.30 were obtained and rates of reaction were measured from these. Values for τ, however, could not be determined until the instrument lag for the total system was known.

A graph of 1/fraction rate against intercept of the trace on the time axis was plotted (fig.31) and by extrapolating to cut the intercept axis, a value of 1.3 ± 0.1 sec. was measured for the instrument lag. This value was subtracted from the intercept of the trace on the time axis before any calculations were made for the lifetimes of the kinetic chain. Also, the gradient of the line is proportional to k_t/k_p.

Intensity Exponent.

Intensity exponents have been discussed for the dilatometer method and it was found that in the thermocouple method, values for intensity exponents followed a similar pattern (see page 46).

Also ,from fig.31 it can be seen that the plot of 1/fractional rate against intercept on the time axis of the experimental trace, gives a straight line i.e. the lifetime of the kinetic chain varies with rate. This is an indication that the terminatinn reaction is second order, for with first order termination there is no variation of τ with rate.

Values for Velocity Coefficients.

Table XII shows some values of rate constants, rates and lifetimes of the kinetic chains. These values have been measured in the early stages of the reaction and measurements made on the same dilatometer have been grouped together.

Table XII.

Values of reaction rates, lifetimes of the kinetic chains and rate constants for the polymerisation of methyl acrylate reaction, measured by the thermocouple method.

Rate %/h.	τ sec.	k_p L.mole^{-1}sec.$^{-1}$	$k_t \times 10^{-6}$ L.mole^{-1}sec.$^{-1}$	k_p/k_t x10^5.
16.4	3.7	400	2.4	17
21.0	3.2	590	3.2	19
24.0	3.0	720	3.6	20
17.4	2.7	580	4.4	13
24.3	3.8	570	2.2	26
20.8	2.8	660	4.1	16

There is some variation in results from one experiment to another and even with measurements made on one dilatometer there is considerable variation. In some experiments there was marked acceleration of polymerisation rate from the very early stages of the reaction and frquently, experiments had to be abandoned because of "popcorn" formation. An example of an experiment whose rate accelerated in the early stages is shown in table XIII.

Table XIII.

Values of reaction rates, lifetimes of the kinetic chain and rate constants for the polymerisation of methyl acrylate measured by the thermocouple method; acceleration of rate in the early stages of the reaction.

Conversion %	Rate %/h.	τ sec.	k_p L.mole^{-1}sec.$^{-1}$	k_tx10^{-6} L.mole^{-1}sec.$^{-1}$	k_p/k_t x10^5
2	29	4.8	550	1.4	39
6	46	4.3	970	1.7	56
7	50	4.3	1070	1.8	60
8	53	4.4	1090	1.7	65
10	61	4.6	1190	1.5	77
13	63	5.2	1090	1.2	91
14	62	5.2	1070	1.2	90
16	61	5.0	1100	1.3	85
18	65	6.0	980	0.9	109

In this experiment, it can be seen that there is very little variation in values of τ as the rate increases.

Early gelling was a characteristic feature with

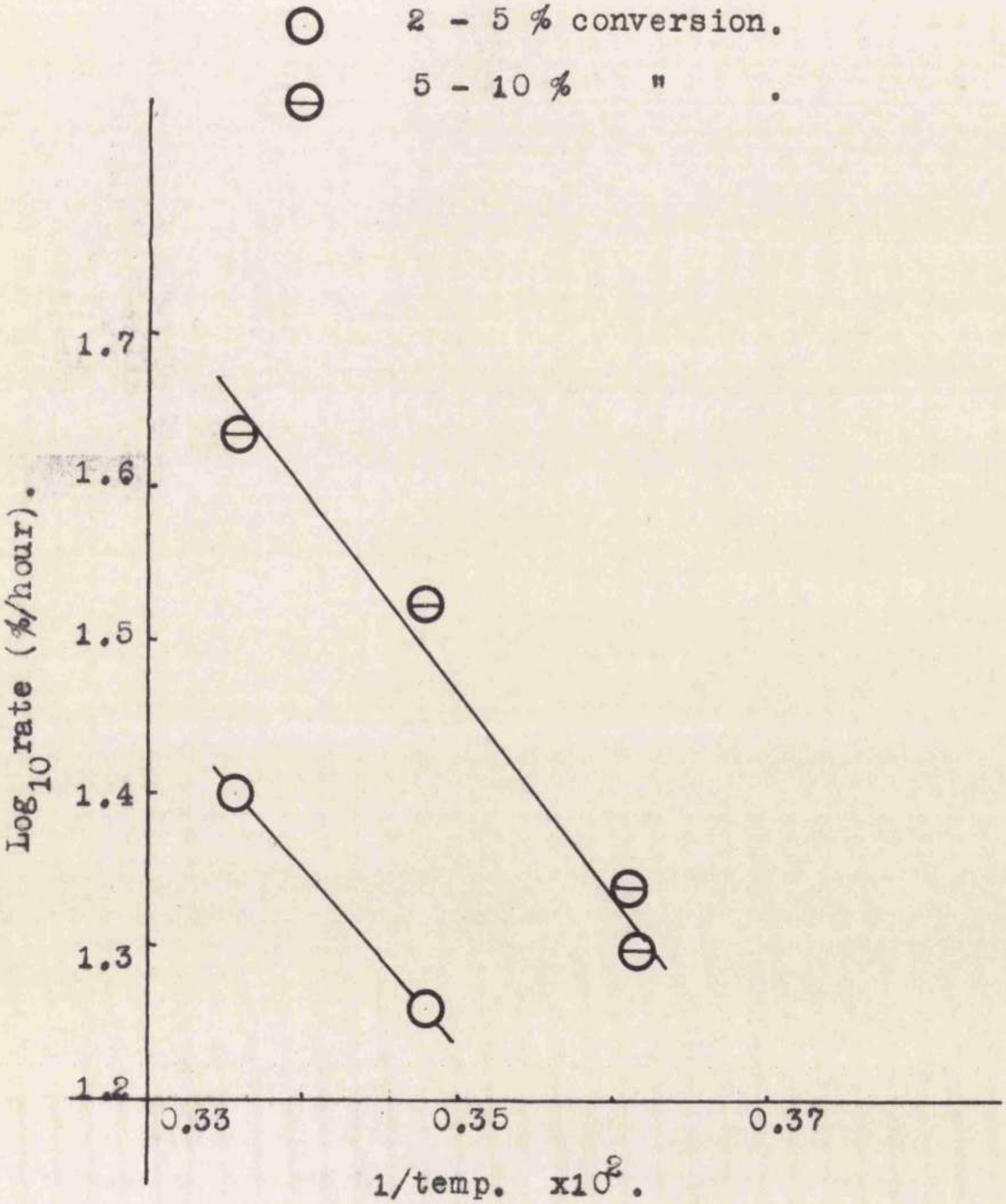


Figure 32. Measurement and comparison of E_0 at 2 different extents of reaction for the polymerisation of methyl acrylate.

many of these experiments and could readily be detected in the stem of the reaction vessel, whereas this gelling could easily pass unnoticed in the dilatometer method since there was no reaction mixture in the stem. It is suspected that this early gelling may be the preliminary stage of "popcorn" formation.

The Effect of Temperature.

As in the dilatometer method for measuring the kinetics of polymerisation of methyl acrylate, it was found that the rate increased with temperature. This is shown in fig.32 where log. rate is plotted against 1/absolute temperature.

During these experiments where rates and values of τ are being measured at different temperatures, the extent of polymerisation is continually rising. It has been seen from table XIII that rate of reaction rises sharply in the early stages of conversion; therefore, any changes in rates taking place during these experiments may not be the result of temperature alone. To check this, rates and values of τ were measured through a temperature range by

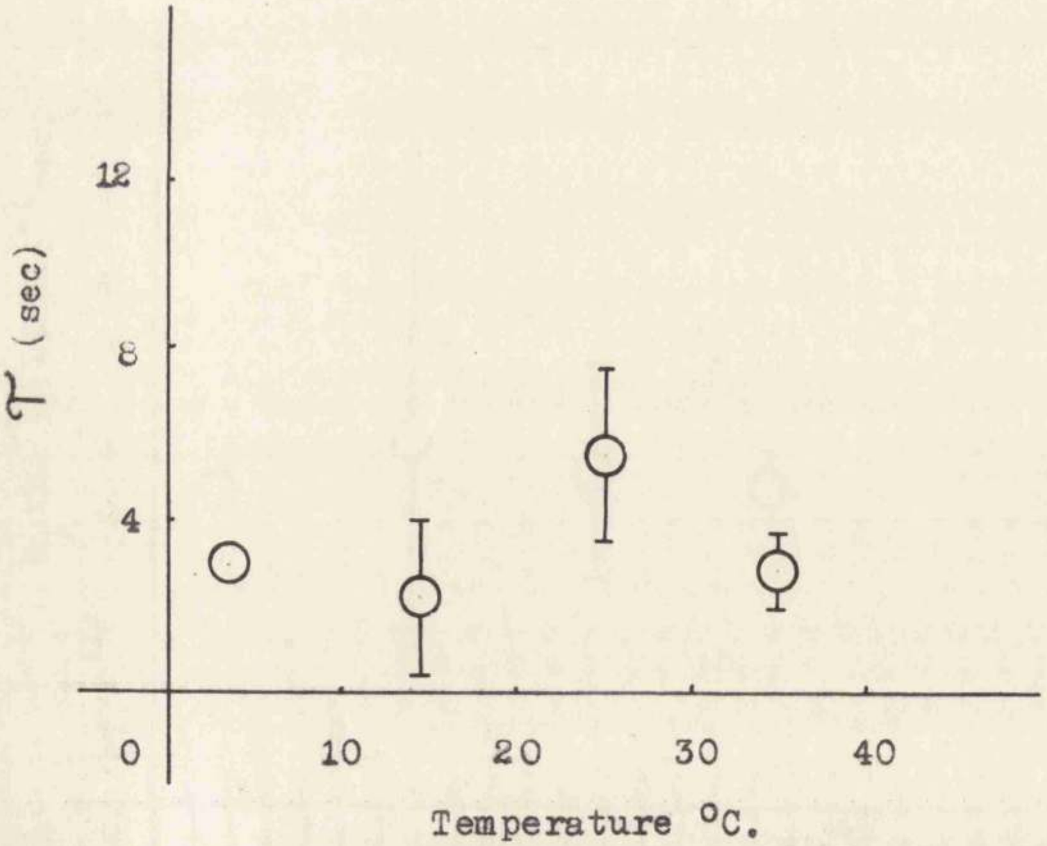


Figure 33. The variation of τ with temperature for the polymerisation of methyl acrylate - thermocouple method.

a) lowering the temperature of the reacting mass from 25°C to 14°C and

b) by raising the temperature of the reacting mass from 3°C to 25°C. In the latter series of experiments the extent conversion had increased by about 5%. It was found that series a) gave a value for E_o = 5.1 k.cal./mole whereas b) gave a value of 6.8 k.cal./mole. The difference between the two sets of results is not very great and may be accounted for by experimental error.

Values of τ have been plotted against temperature in fig.33. The indication from this is that τ is unaffected by temperature, thus indicating a value of zero for the activation energy of the termination reaction. As a result of the scatter of values of τ, the plot of k_t against temperature fig.34 is too great to be able to deduce anything positive although a line through the mean values of each group of points shows a steady value of k_t with temperature - see table XIV.

Table XIV.

Variation of k_t with temperature for the polymerisation of methyl acrylate measured by the thermocouple method.

Average $k_t \times 10^{-6}$ L.mole^{-1}sec.$^{-1}$	Temperature °C.
3.69	35
3.90	25
4.25	14.4
3.48	3.8

The irreproducibility in τ and k_t may be the result of rapid gelling in the early stages of the reaction. To avoid this early gelling, a chain transfer agent, trichlorobromomethane, was added.

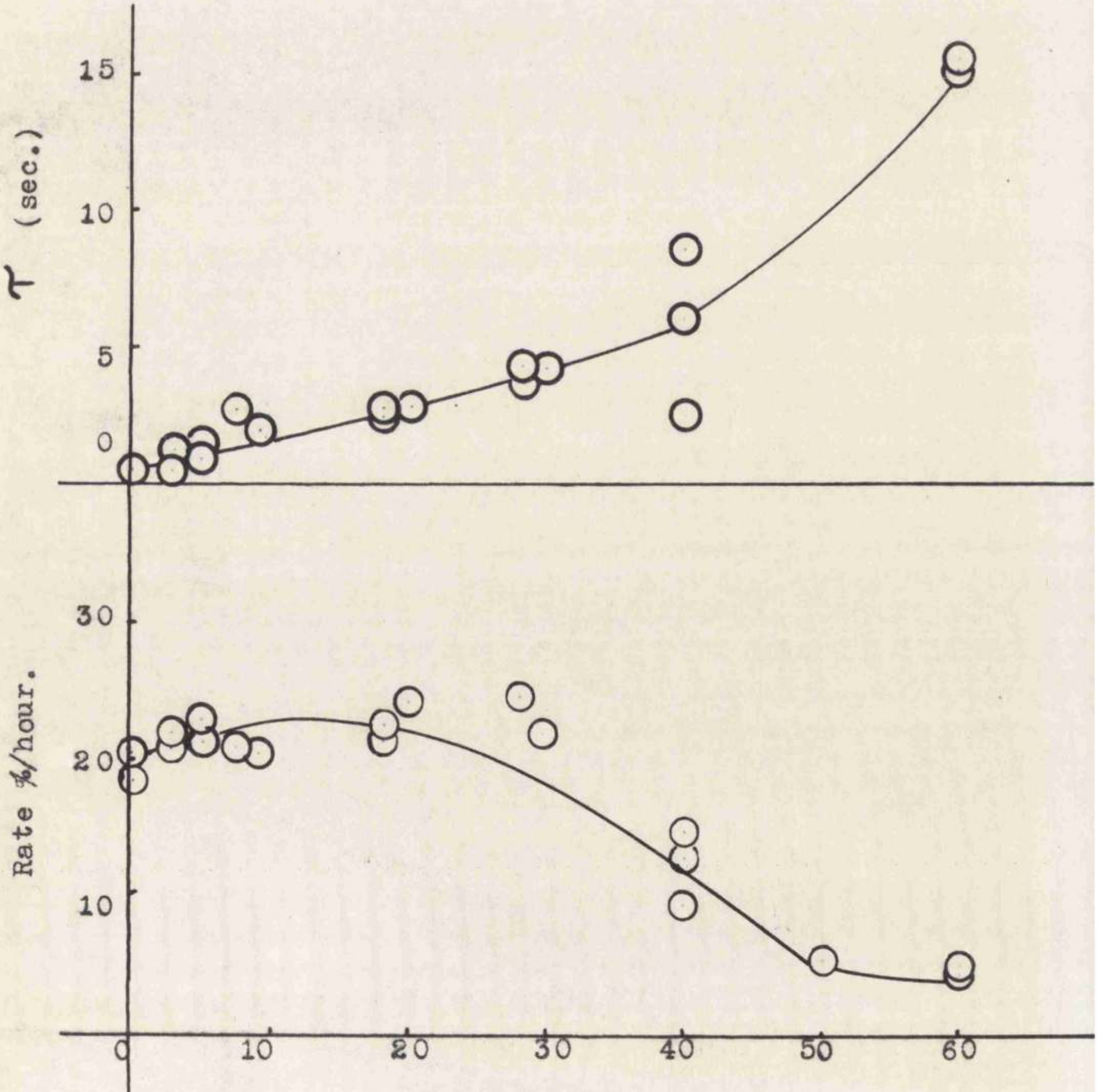


Figure 35. The variation of rate and τ with extent conversion for methyl acrylate polymerisation with transfer agent present (thermocouple method.)

Results for Polymerisation of Methyl Acrylate with Transfer Agent present.

The early gelling effect was cut down by adding 1 mole percent of the transfer agent, trichlorobromomethane. The effect of this agent was to cut down average molecular weights without affecting values of τ or rates.

Examination of polymerisation rates at 25°C (fig.35) showed that there was very little increase up to 30% conversion. It was found too that intensity exponents were in the region of 0.6 indicating mainly second order termination reaction. Some values obtained for intensity exponents are shown in table XV over the range 2% to 60% conversion.

Table XV.

Intensity exponents for the polymerisation of methyl acrylate in the presence of CCl_3Br using the thermocouple method for measuring rates.

(Table XV over.)

Table XV.

% conversion	Polymerisation rate		Intensity exponent.
	maximum intensity I_a	reduced intensity $0.315\ I_a$	
2	19.3	9.2	0.64
2	18.4	9.2	0.60
17	16.2	8.1	0.60
17	16.0	8.9	0.51
60	24.2	7.9	0.95

It can be seen that the order of the termination reaction is approaching unity in the region of 60% conversion whereas measurements of intensity exponents taken earlier in the reaction indicate second order termination.

Up to 30% conversion there is a small increase in lifetimes of the kinetic chain (fig.35). However, this increase in τ is small compared to that experienced in experiments without transfer agent. At 30% conversion there is a large increase in τ and a corresponding drop in rate of reaction.

The Effect of Temperature.

Kinetic measurements were made over a large extent of the polymerisation reaction at 25°C. Using fresh reaction vessels, the kinetics of the reaction were examined at 14°C and 35°C over the same range of the reaction. It was found, however, on plotting values for reaction rates against extent polymerisation, that there was considerable intermingling of points. It is also doubtful from the general appearance of the curves whether an absolute value can be deduced for the overall activation energy. The extent of scatter of results from one experiment to another can be seen in table XVI.

Table XVI.

Variation of reaction rate and τ with temperature at different stages in the polymerisation of methyl acrylate reaction with transfer agent present.

Conversion %	Rate of reaction (%/h.)			τ (sec.)		
	14°C.	25°C.	35°C.	14°C	25°C	35°C.
1-3	19.3	21.9	19.9	3.5	1.2	1.7
9-12	18.4	20.4	-	4.5	1.9	-
14-18	19.8	21.3	20	2.9	2.8	2.2
20-24	20.7	24.0	12.1	3.5	2.8	3.5
ca 40	24.9	9.4	22.7	4.9	8.7	6.1

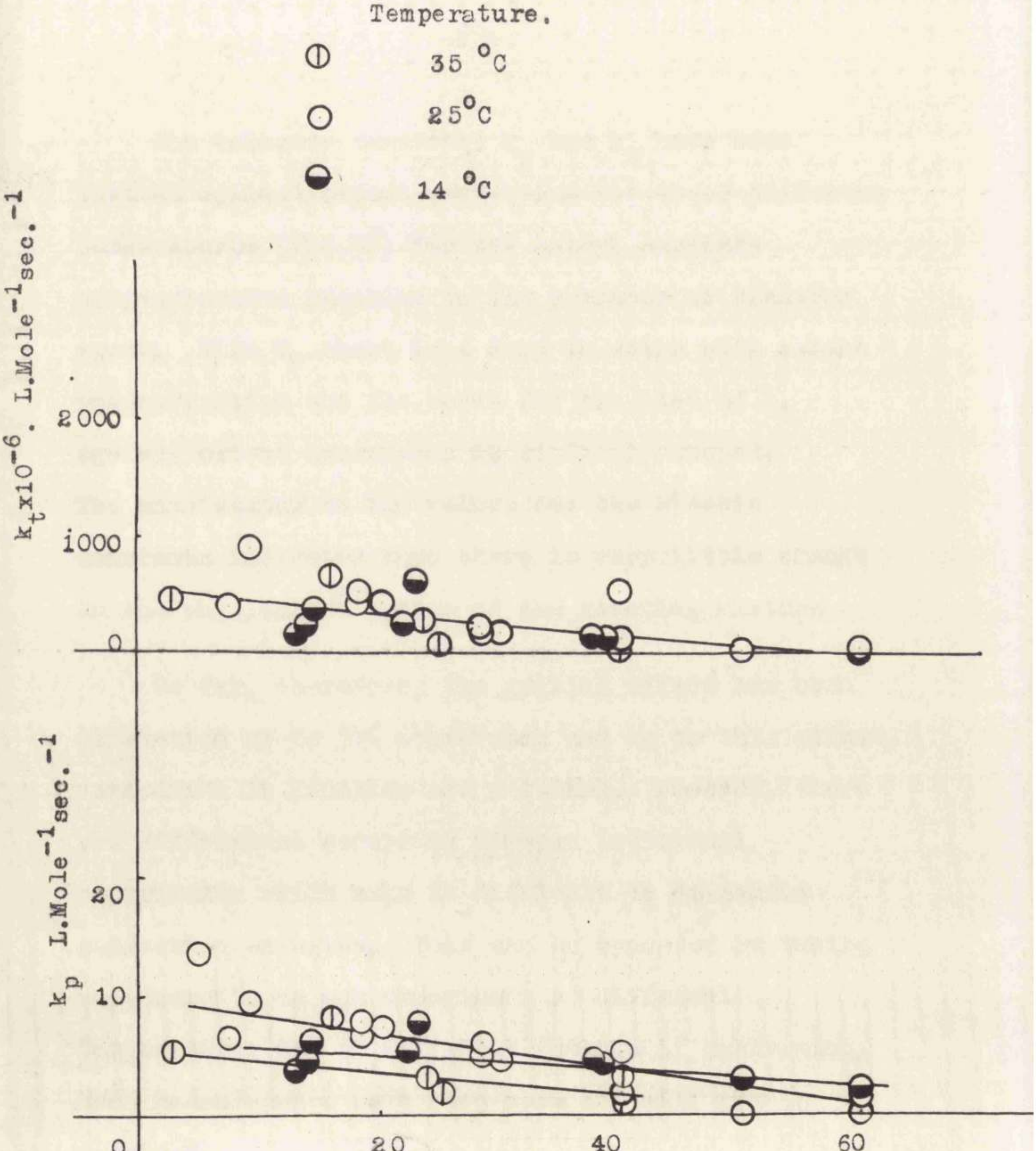


Figure 36. The variation of k_p and k_t with extent conversion in the polym. of methyl acrylate + CCl_3Br.

The velocity constants k_p and k_t have been plotted against extent conversion for three different temperatures (fig.36) for the methyl acrylate polymerisation reaction in the presence of transfer agent. With k_p there is a drop in value with extent polymerisation and the curve for the plot of k_t against extent conversion is similarly shaped. The consistency in the values for the kinetic constants indicates that there is very little change in the physical condition of the reacting mixture.

So far, therefore, the gelling effect has been eliminated up to 30% conversion and up to this extent, variations in kinetics are parallel. However, there are differences occurring between individual experiments which make it difficult to determine activation energies. This can be bypassed by taking measurements on one experiment at different temperatures and at different extents of conversion. Such measurements have been made and will now be examined.

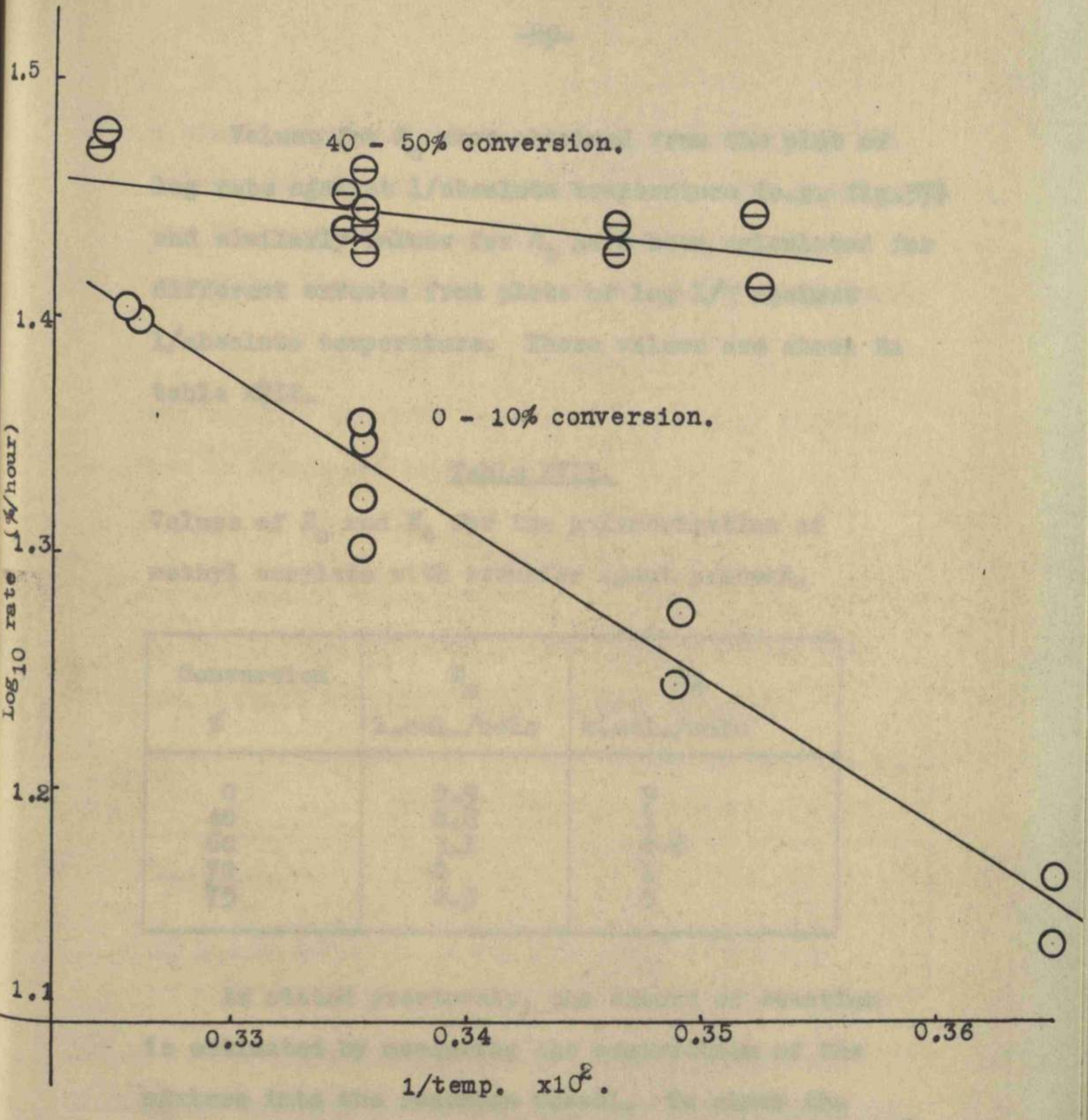


Figure 37. Values of E_0 measured for the polymerisation of methyl acrylate with CCl_3Br.

Values for E_o were obtained from the plot of log rate against 1/absolute temperature (e.g. fig.37) and similarly values for E_t have been calculated for different extents from plots of log $1/\tau$ against 1/absolute temperature. These values are shown in table XVII.

Table XVII.

Values of E_o and E_t for the polymerisation of methyl acrylate with transfer agent present.

Conversion %	E_o k.cal./mole	E_t k.cal./mole
0	2.9	9
40	0.8	1
60	3.1	0-6
70	0	1
75	2.3	5

As stated previously, the extent of reaction is estimated by measuring the contraction of the mixture into the reaction vessel. To check the final value, however, the vessel was broken open and the density of the solid polymer measured by a simple displacement experiment i.e. weighing the polymer in air and then in liquid of known density (in this case water at 20°C). Density results agreed to within 5% of the contraction measurements.

On examination of the temperature effect with and without transfer agent, the following results can be tabulated (table XVIII).

Table XVIII.

Comparison of values of reaction rate, τ, E_o and E_t for the polymerisation of methyl acrylate with and without transfer agent present (CCl_3Br).

	With CCl_3Br	Without CCl_3Br
Rate %/h.	21	21
τ sec.	2	3
E_o k.cal./mole	0 - 2.9	5.1 - 6.8
E_t k.cal./mole	0 - 9	0 - 2.9

The later stages for the polymerisation of methyl acrylate without CCl_3Br will now be examined.

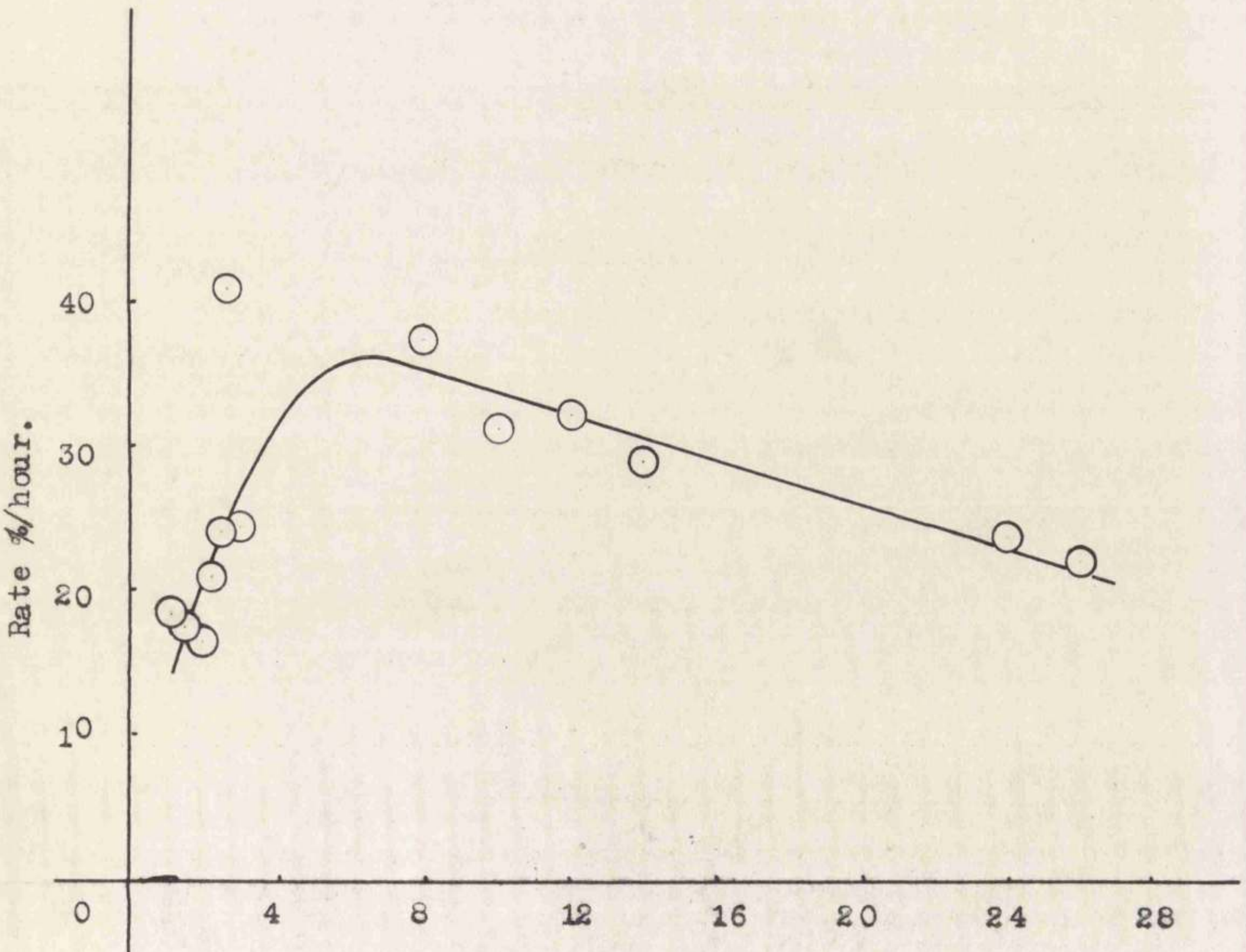


Figure 38. The effect of extent reaction on rate of methyl acrylate polymerisation (thermocouple method.)

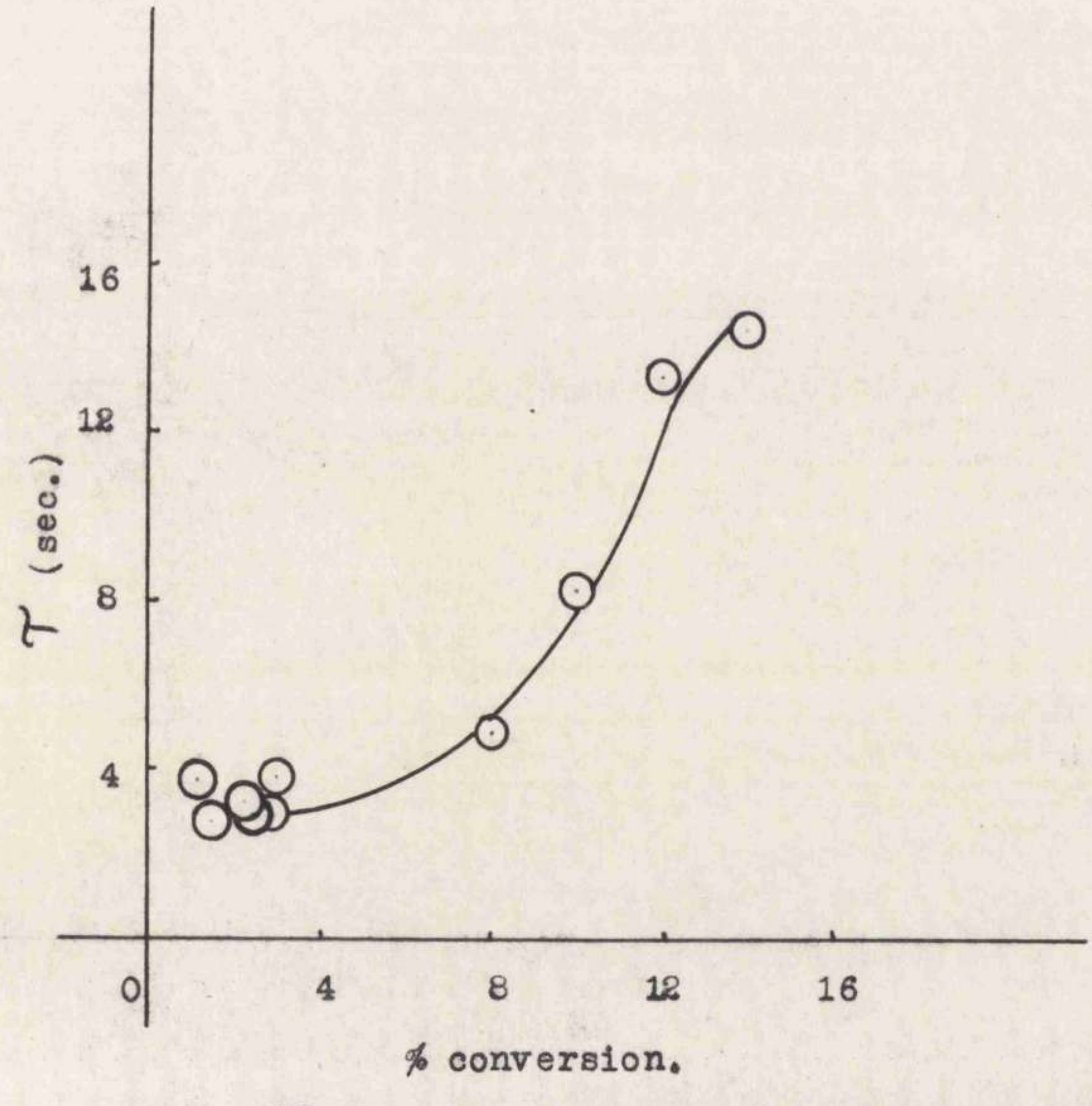


Figure 39. The effect of extent reaction on τ for methyl acrylate polymerisation (thermocouple method.)

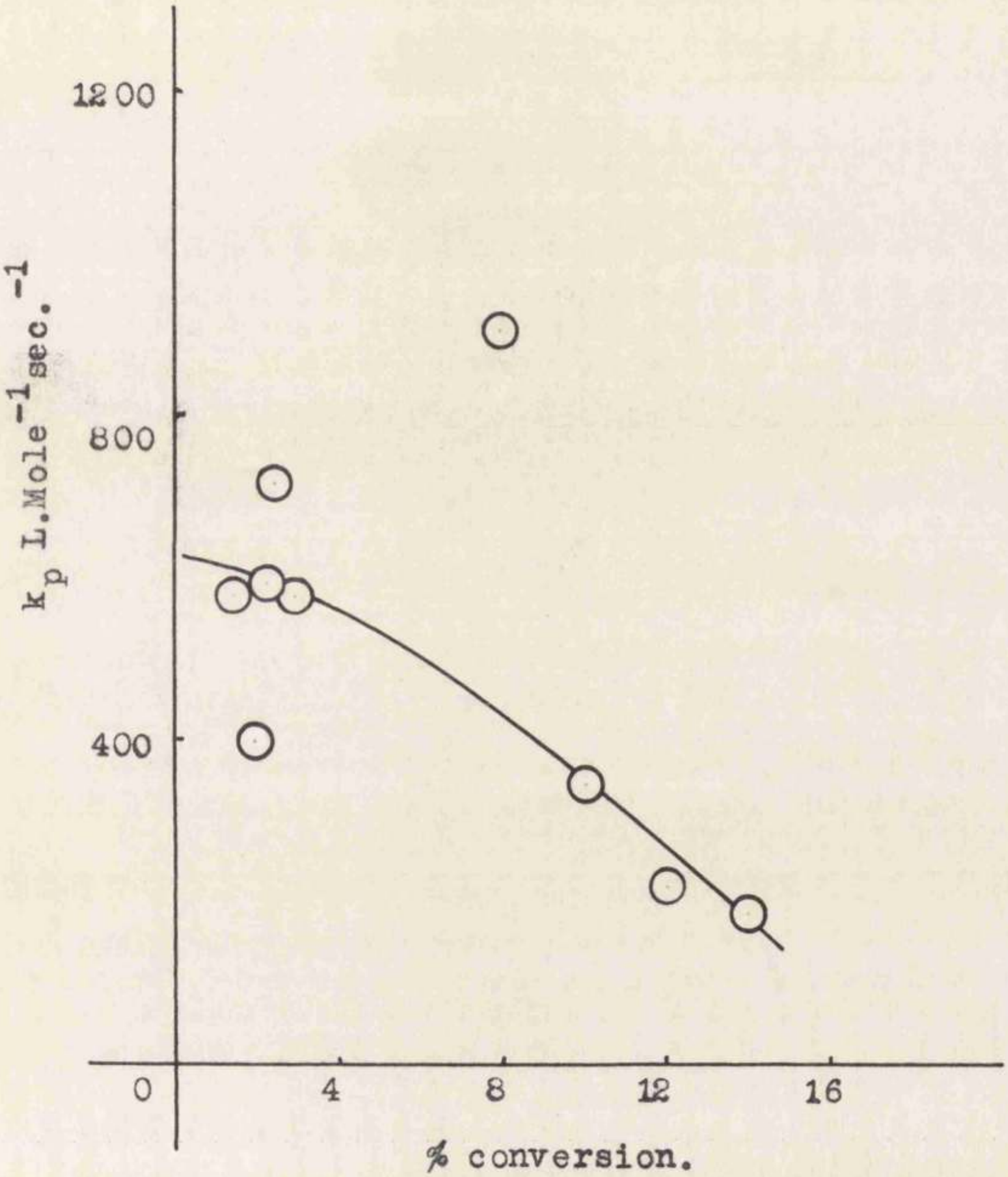


Figure 40. The effect of extent conversion on k_p for methyl acrylate polymerisation (thermocouple method.)

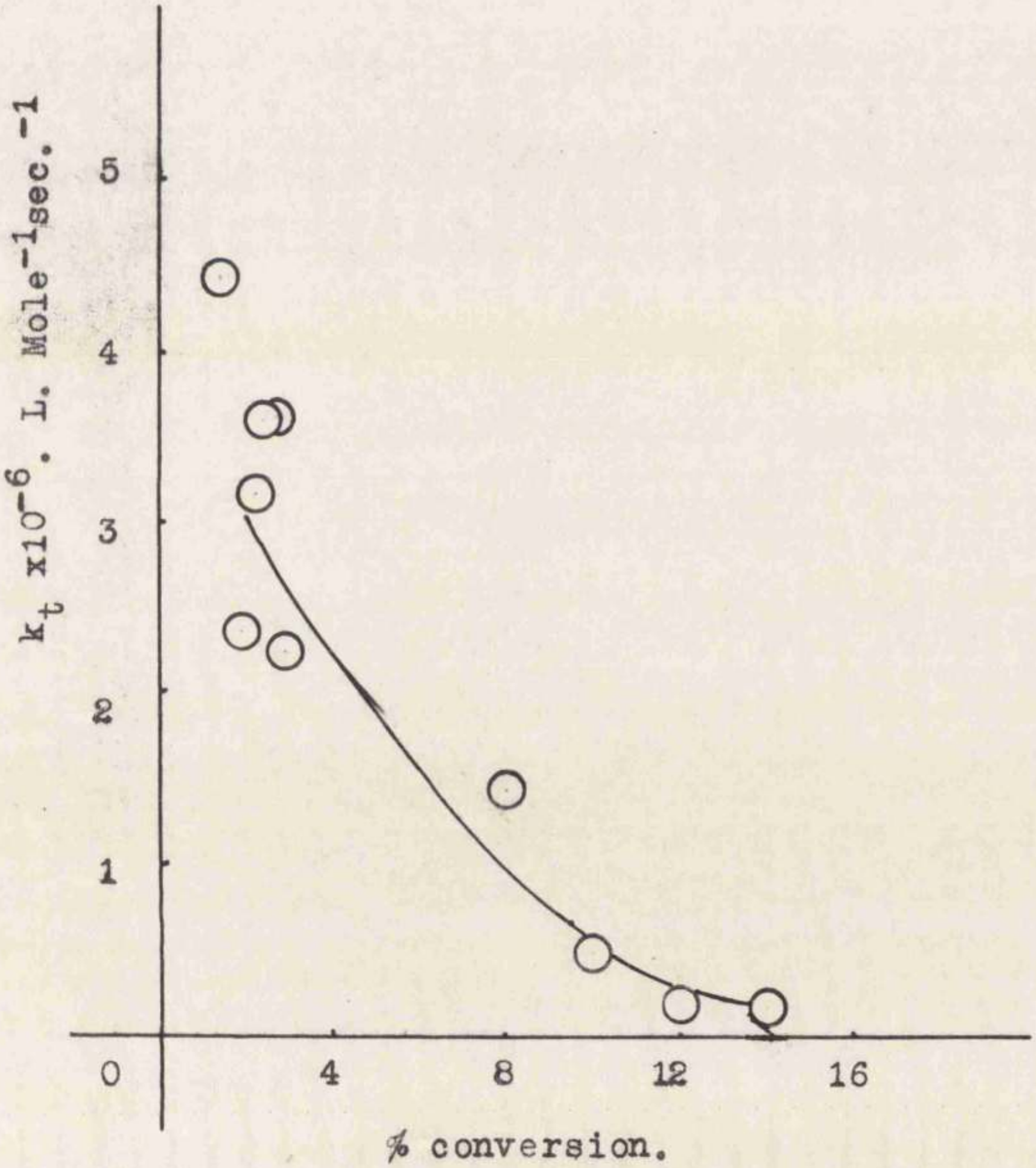


Figure 41. The effect of extent conversion on k_t for methyl acrylate polymerisation (thermocouple method.)

Results for Later Stages in the Reaction.

Although gelling and "popcorn" formation caused difficulty in the examination of the reaction at later stages, some results were obtained.

Neglecting the first 2% conversion, fig.38 shows that, after an initial rise, there is a gradual fall in polymerisation rate with increase in conversion.

Values of τ have been plotted against extent conversion in fig.39. From this it can be seen that there is an increase in values of τ as the reaction proceeds.

By plotting k_p against extent conversion (fig.40), it was seen that values for the velocity constant dropped with increased extent of reaction. There was, however, some scatter of values over the first few percent of the reaction.

In fig.41 where k_t has been plotted against extent conversion, there is also a decrease in velocity constant values with increased extent of reaction.

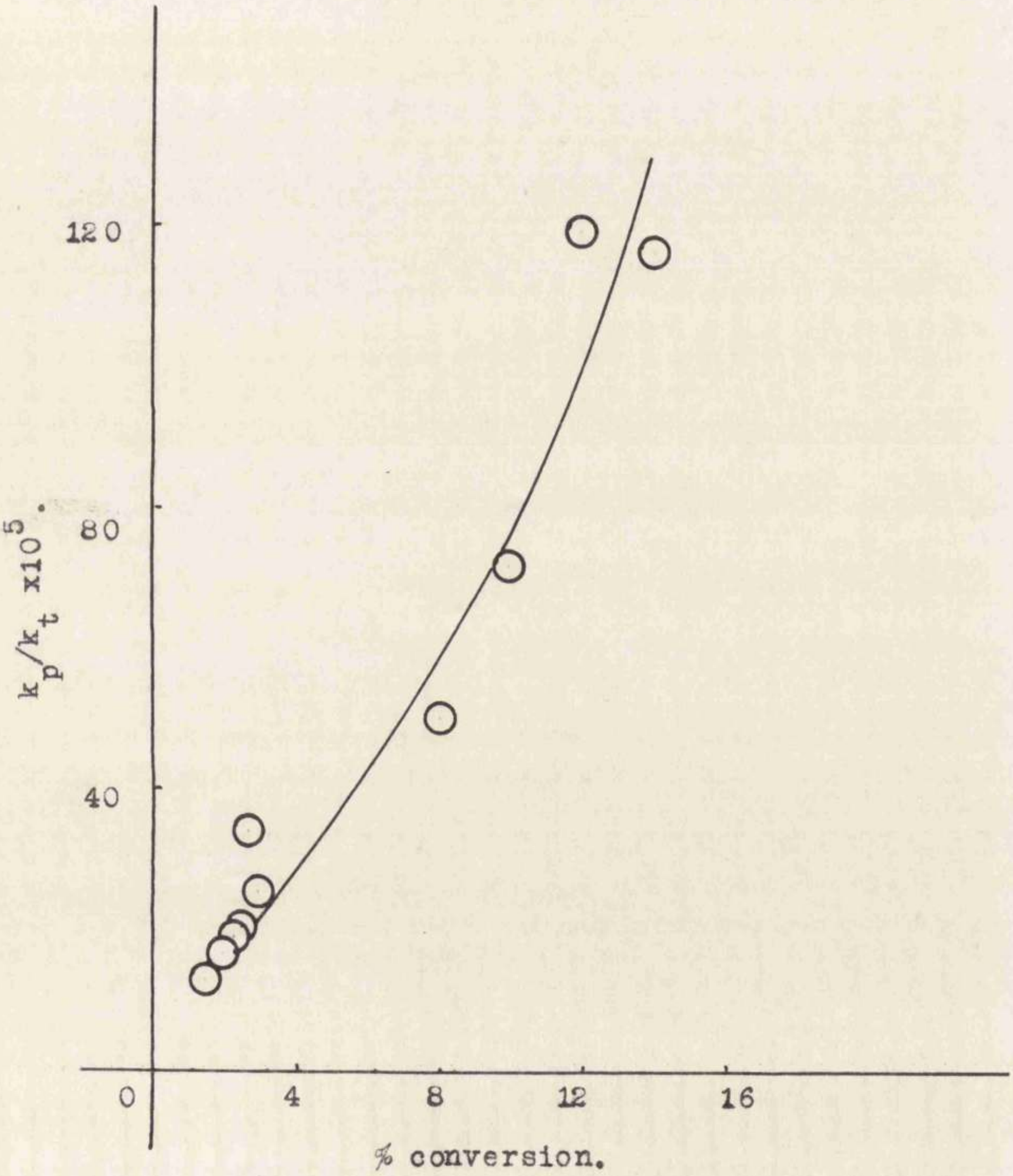


Figure 42. The effect of extent conversion on k_p/k_t for methyl acrylate polymerisation (thermocouple method.)

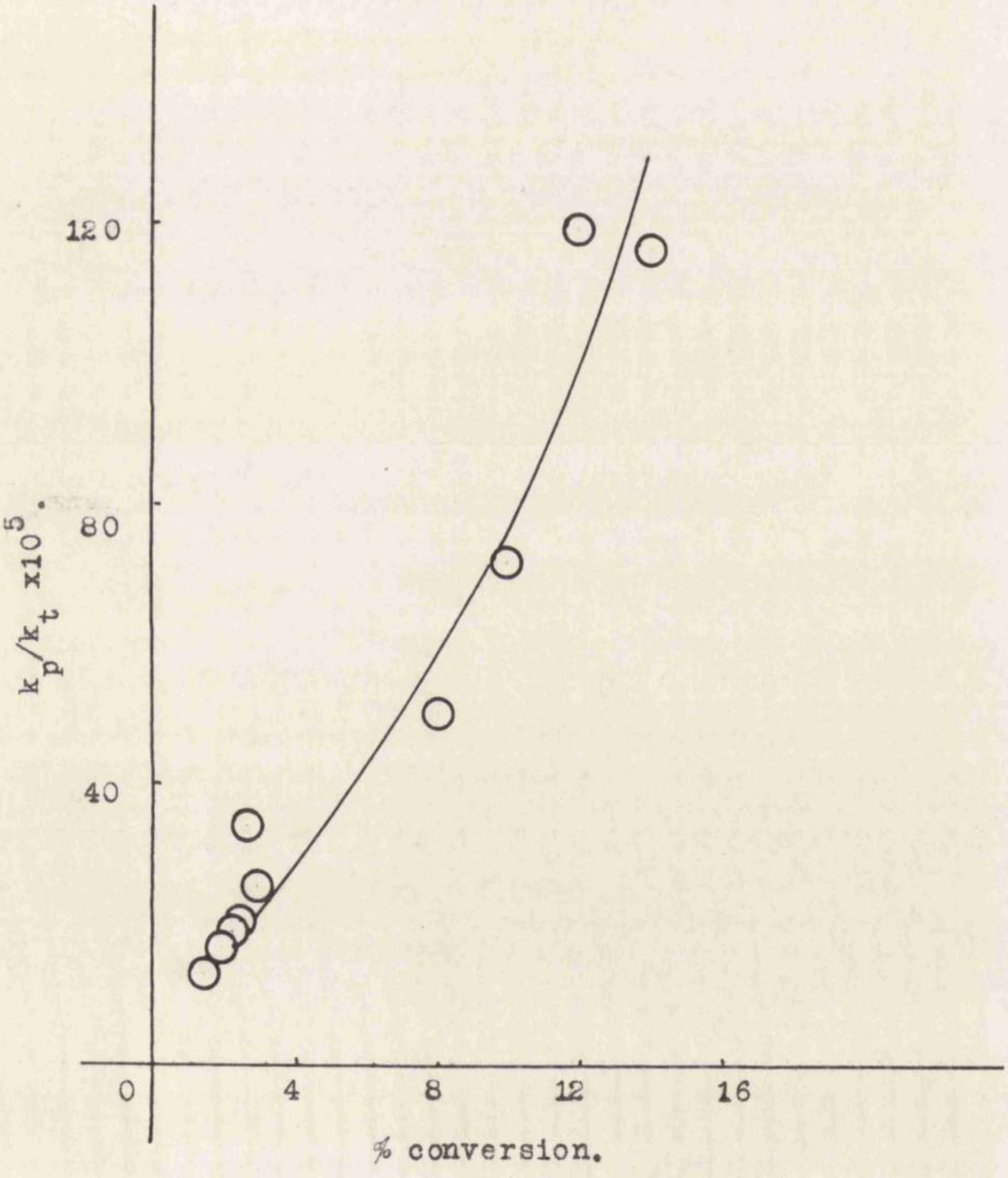


Figure 42. The effect of extent conversion on k_p/k_t for methyl acrylate polymerisation (thermo-couple method.)

The plot of the ratio k_p/k_t against conversion in fig.42 is the combined effect of extent conversion on k_p and k_t.

Although temperature effect was examined during the later stages of the reaction, the results were irreproducible and have not been included.

Discussion.

The conditions which govern the choice of reaction rate are as follows:

a) Values for the lifetime of the kinetic chain, which have to be measured, must not be greater than about one fifth of the time the reacting mixture remains approximately adiabatic. This controls the lower limit of the reaction rate since the rate varies inversely as the lifetime of the kinetic chain.

b) A further limitation on the lower rate limit is the magnitude of the thermal polymerisation, for this must be of the order of 10% or less of the main reaction rate. Therefore, the photo-initiated reaction rate must be at least 10 times the thermal rate in order that the latter effect might be neglected.

c) The upper limit of the reaction rate is controlled by the amount of heat liberated by the reaction.

Each of these points will now be examined in greater detail.

a) Factors Influencing Adiabatic Conditions Of The Reaction Vessels.

Two types of reaction vessel have been used to study the kinetics of the methyl acrylate polymerisation reaction. In the dilatometer method for non-stationary state measurements, the reaction vessel is surrounded by a vacuum jacket. From a previous study of such a system[31] it was estimated that adiabatic conditions prevail for about 30 sec.. In these dilatometers, the reaction medium is confined over mercury and there is the possibility of heat being transferred accross the interface to the mercury. A large transfer of heat from reacting mixture to the mercury is thought to be unlikely. To assess the maximum possible error from this source, however, it is assumed that the mercury volume attains the temperature of the reacting mixture. In such a case, the maximum possible error has been caculated as -17% (see appendix V).

However, conduction of heat through the monomer/polymer mixture is much less than that through mercury and so the former is the controlling factor in heat losses to the mercury. Other factors which cut down heat losses are the increasing viscosity of the system and the static nature of the film in contact with the mercury surface. It is thought, therefore, that the probable error will not be greater than 5%.

With non-stationary state measurements using the thermocouple method, it is only necessary for the reaction mixture in the region of the thermocouple junction to remain adiabatic during the period of measurement. In the early stages of the reaction prior to a gel state, the adiabatic period at the centre of the reaction vessel is of the order of 30 seconds which means that lifetimes of up to 6 seconds can be measured accurately. When, however, heat transfer is cut down as a result of a large increase of viscosity (gelling), then this adiabatic period is increased, with the resultant increase in measurable lifetimes to about 10 seconds.

b) The Dark Rate of Reaction.

Neglecting the effect of extent of reaction, at a fixed temperature there will be a set dark rate with a corresponding concentration of free radicals = R_d.

When the reaction mixture is exposed to the light source, this concentration increases by R_l, say. If, however, R_d is large and the dark rate is of the same order as the light rate, then R_l is lowered because the termination rate which depends on $(R_l + R_d)^2$ changes.

At high dark rates, therefore, the reaction rate measured will not be a true one but an overall rate = $k(R_l + R_d)$. Even if the dark rate is known and a calculation made for light rate from

$$\text{Rate} = k(R_l + R_d) - kR_d ,$$

this will be a depressed rate.

In this polymerisation reaction it was found that dark rate was normally about 1%/h. at 25°C.

To neglect the dark rate, therefore, the light rate should be greater than 10%/h..

The "dark rate" arises from two sources: thermal polymerisation which depends on the thermostat temperature and photoinitiated polymerisation from stray light; this is mainly daylight although some can be expected from the lamp used to observe the mercury meniscus.

The larger of these two sources is that of stray light, for it was found that dark rate measurements made overnight were much smaller than those made in daytime. To cut stray light down to a minimum, therefore, the surrounding tank is shielded as much as possible.

Also, activation energy studies must not be made at higher temperatures because of the larger activation energies associated with a high dark rate.

c) The Effect of Heat of Reaction.

Both the dilatometer and the thermocouple non-stationary state methods for measuring the kinetics of a polymerisation reaction depend on accurate measurement of heat of reaction. If reaction rates are high, there is a large increase in the temperature of the reacting mixture giving rise to the following errors.

In the dilatometer method, a large increase in temperature over a short period means that the position of a moving mercury meniscus will have to be recorded very quickly. This difficulty could be overcome by using a cinecamera focused on the stem of the dilatometer, but again this method of recording requires bright illumination of the mercury meniscus with a resultant increase in reaction rate from stray light. With a fast rate, too, the mercury meniscus would soon move out of the section of capillary being observed. These difficulties could be removed by either using a smaller volume of reaction mixture or larger bore capillary. In the thermocouple method, such difficulties do not arise.

A large rise in the temperature of the reaction mixture increases the thermal rate of polymerisation markedly. This increases errors from an unknown dark rate.

Taking into account these effects, the concentration of catalyst chosen was $0{,}800 \times 10^{-3}$ g.moles/L.

The Order of the Termination Reaction.

The polymerisation reaction of methyl acrylate can be divided into three stages:

a) the very early stages where the extent of reaction is less than 2%.

b) the early stages where the extent of reaction is over 2% but the reaction mixture has not reached the gel state.

c) the later stages when the reacting mixture has gelled.

From the results, it was seen that the order of the termination reaction deviated from second order at stages a) and c). The deviation from second order termination in the very early stages of the reaction was thought to be due to the presence of trace impurities which escaped the purification procedure. This is supported to some extent by the lack of reproducibility of both reaction rates and τ values at these very early stages. A similar effect has been observed in the polymerisation of vinyl acetate[32]. Also, in the early stages, measurements have been made on a reacting mixture the rate of which was rapidly increasing. Hence, reproducibility between these measurements will be poor.

In the thermocouple method, there is a marked sudden increase in the rate of polymerisation at later stages in the reaction (<u>ca</u>. 10 - 20% conversion) the rate in some cases being doubled. Other workers[17,19] have observed an increase in rate with the extent of reaction for methyl acrylate polymerisation and it is thought to be the result of reduction in the rate of termination following

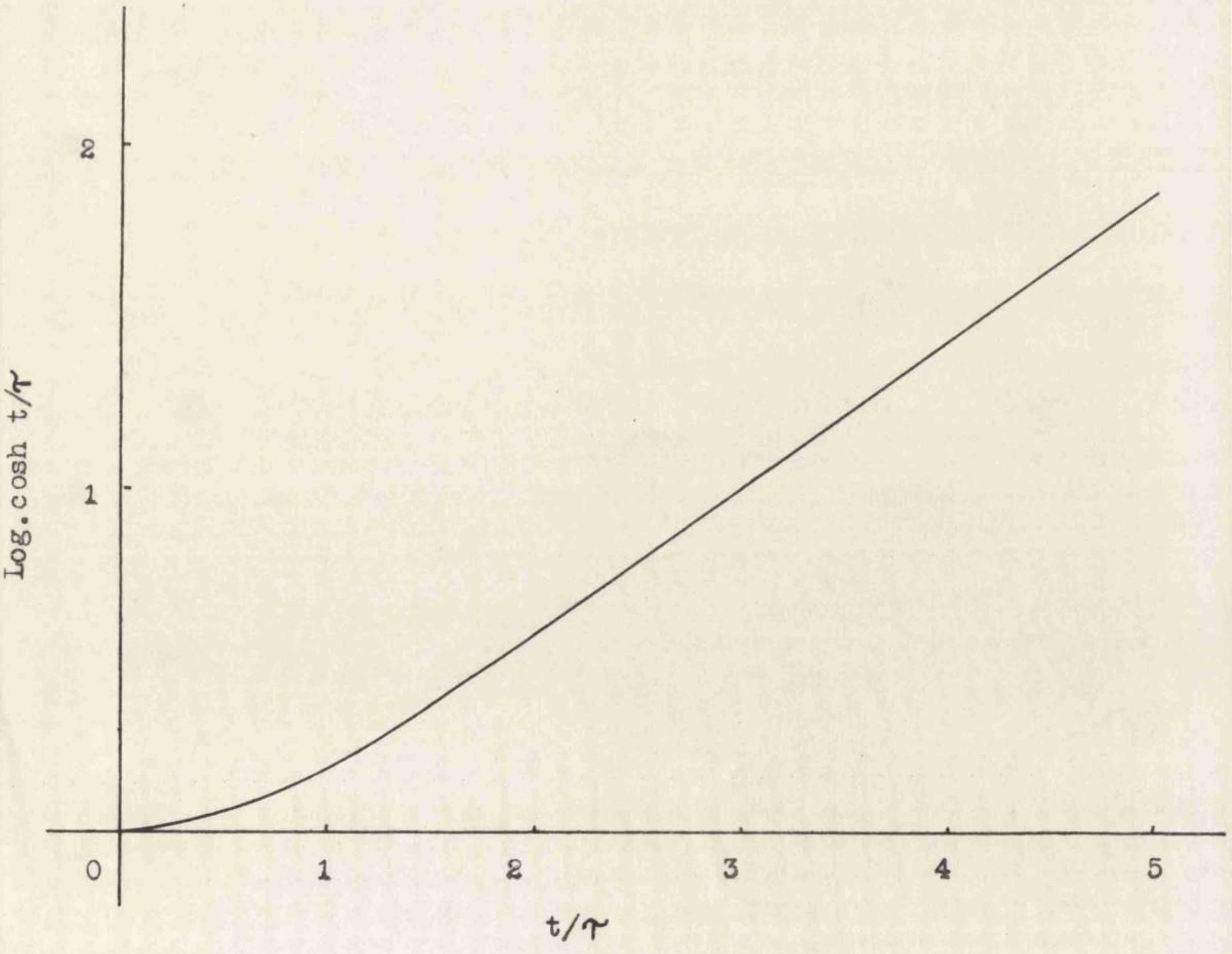


Figure 43. Theoretical plot of fractional conversion against time.

the enormous increase in the viscosity of the system[33,34].

Accompanying this large increase in reaction rate, there is a deviation from second order termination. This may be the result of occlusion of free radicals in a purely polymer medium preventing termination of these free radicals.

Again, at very late stages there is a falling off in the rate of reaction; at these stages, the order of the termination reaction is approaching one. An additional error is introduced here as a result of low rates and high values of τ; for at such rates, it is doubtful whether the straight portion of the rate curve is attained before the adiabatic conditions of the system breakdown. This leads to false values for reaction rates and τ.

This can be seen more clearly from the theoretical plot of fractional conversion against time which is shown in fig.43. Provided adiabatic

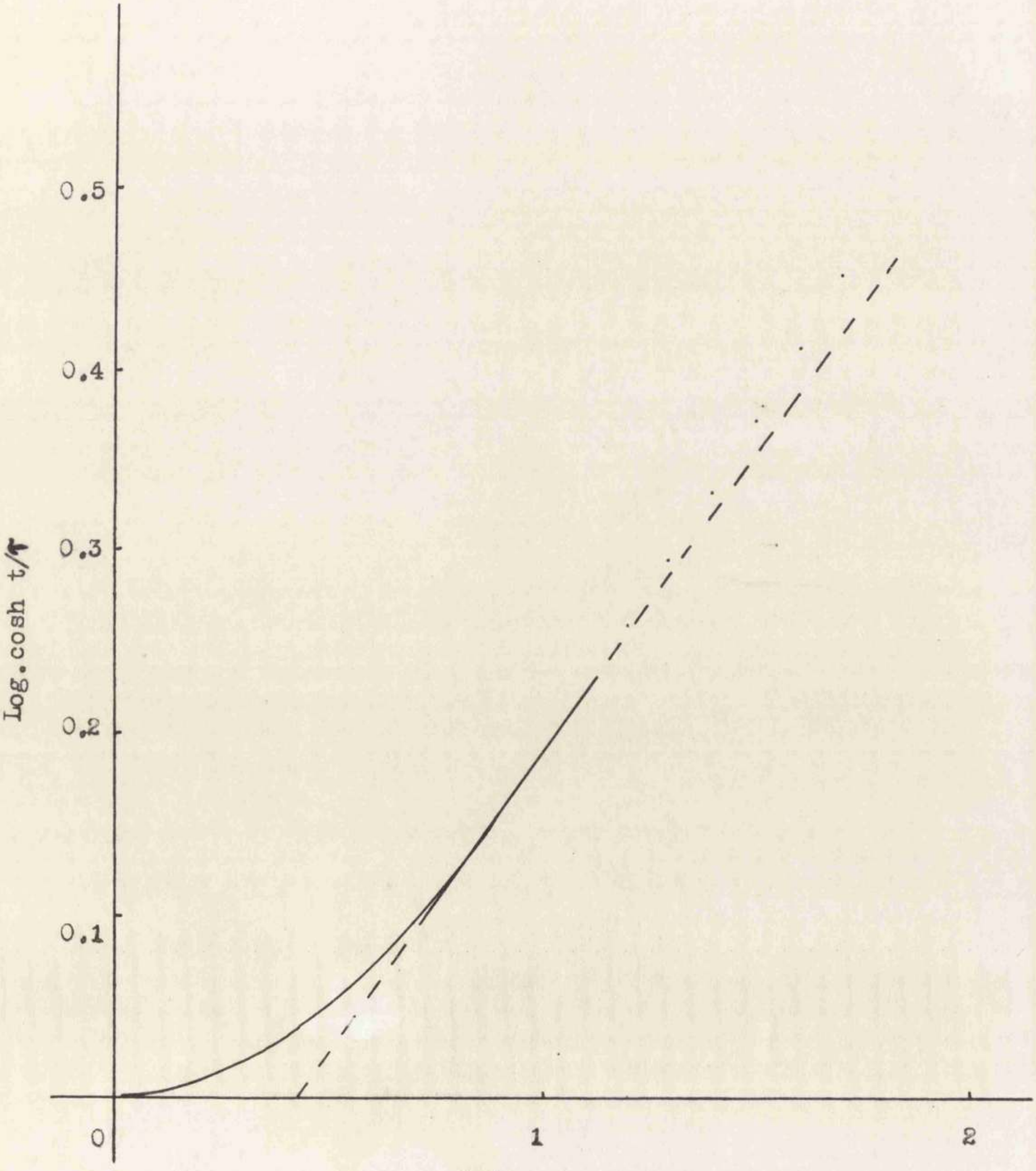


Figure 44. Theoretical plot of fractional conversion against time.

conditions exist during this reaction, the plot of temperature, or % expansion due to reaction, against time will have the same shape. After a period of time equal to 3τ the curve assumes linearity. On replotting the curve with a change of scale on the time axis so that the region of values of t/τ, 0 to 1, can be studied in greater detail (fig.44) it appears that the curve is linear at t/τ ratio = 1. On production of this section to cut the time axis, a value of $t = 0.4\tau$ is obtained i.e. this value is obtained for a reaction whose adiabatic system fails after $t = \tau$ (shown by the broken line). A continuation of the plot to $t = 3\tau$, i.e. the true straight portion of the curve, gives an intersection on the time axis $= 0.69\tau$. Thus, it can be seen that non-adiabatic conditions occuring so early in the recording of a reaction can affect the accuracy of the results to a considerable extent.

Rate of Initiation.

The calculations of the individual velocity coefficients for the propagation and termination reactions depend on the value of the rate of initiation. The method which has been employed is a combination of the methods of Bawn[27] and Bartlett[28], and is based upon the assumption that each growing polymer radical or radical produced in the photolysis of the photosensitizer reacts with one D.P.P.H. radical. If the efficiency of the reaction between the free radicals produced from the photosensitizer and monomer is known, and also that of the reaction between D.P.P.H. and the other free radicals present in the system, then the rate of initiation can be calculated from the rate of reaction of the D.P.P.H..

The rate of removal of D.P.P.H. can be measured either absorptiometrically, or from the lengths of the periods of inhibition produced when known amounts of D.P.P.H. are added to the reaction mixture. This latter method, however, was found to be unsatisfactory for the polymerisation of vinyl acetate[29], as the product of the reaction between D.P.P.H. and free radicals also inhibited the polymerisation. The former method will be satisfactory even though the D.P.P.H. plus radical reaction product is an inhibitor, provided the reaction product reacts very much more slowly with free radicals than does the D.P.P.H.. This latter supposition seems a reasonable one, since the reaction product is likely to be a substituted hydrazine which would be expected to react less rapidly with free radicals than would D.P.P.H. which is itself a free radical.

In the measurement of the rate of removal of D.P.P.H., it has been assumed that D.P.P.H. is 90% efficient as a free radical scavenger as found by Bevington[35] for radicals produced in the decomposition of 1,1 azo-bis-isobutyronitrile.

For most monomers, the efficiency of the initiation process usually lies between 50 and 100% and in the absence of data regarding the efficiency of initiation for methyl acrylate, a value of 50% has been assumed. As both the calculated values of k_p and k_t are inversely proportional to the rate of initiation, an assumption of 100% efficiency would simply halve the values of k_p and k_t.

The effect of Extent of Polymerisation on the Reaction Mixture.

As the polymerisation reaction proceeds, the physical constants of the reaction mixture are constantly changing. One such constant, the coefficient of expansion, was measured on several monomer/polymer mixtures, fig.17. Therefore, since this coefficient of expansion can be estimated from fig.17 at any stage, the kinetics of the reaction can be measured at any stage using the dilatometer method.

In a fluid medium, radical-radical and radical-molecule reactivities are governed by the same factors which govern chemical reactivity in general. At later stages in the reaction system, therefore, when the liquid medium becomes viscous, diffusion can readily become a rate controlling factor. Since radical-radical interaction is more dependent on the mobility of the surrounding medium than radical-molecule interaction because of the greater resistance to the larger species, with increased viscosity the termination process is slowed down, and the overall rate increases. If chain transfer is a controlling factor, the molecular weight of the polymer is lower and at later stages, the viscosity of the system increases to a lesser degree. Thus, the termination process may not be affected and there will be no increase in the overall rate. This was found in the reactions where CCl_3Br was added as a transfer agent.

In radical-molecule interactions, the effect of viscosity is not nearly so marked and the interaction coefficient only becomes diffusion controlled at high conversions i.e. at very late stages. This is mainly due to the higher mobility of the monomer molecule in the polymer gel. Therefore it is only at very high viscosities (gel state) that a decrease in reaction rate is apparent.

With increase in extent of reaction and the corresponding increase in viscosity, there is a rise in the value of the lifetime of the kinetic chain. Thus, in a sufficiently gelled system of polymer, the radical lifetime may become indefinitely large when the radicals are trapped in the solid; these radicals cannot grow or be destroyed. Neither of the methods can measure lifetimes of such magnitude because of breakdown of adiabatic conditions in these experiments; moreover, before such an extent can be reached, the high viscosity reaction mixture parts from the sides of the reaction vessel giving vapour pockets and no measurements can be made.

In experiments without catalyst, results do not have any definate trends within the first 30% of the reaction. This is contrary to what is expected, for with such a low concentration of free radicals it would be expected that termination rates would be low and molecular weights high. On the other hand, small concentrations of impurities will have a greater effect on the termination rate when reaction rates are small i.e. when the concentration of free radicals is low. Thus, pure methyl acrylate should gel earlier in the reaction when directly photopolymerised than it would do when a photo-initiator is present. The presence of impurities in the reaction mixture is supported by the lack of reproducibility over the first 1 to 2% of the reaction with catalyst present and also the deviation from second order termination over the same period.

When the methyl acrylate reaction system gels, the conditions for heat transfer are changed; the system has lost mobility and heat cannot be transferred by convection. Thus, heat can only be conducted or radiated away from the centre of the reacting mass and adiabatic conditions are maintained for a longer period than would normally exist for a mobile liquid. At later stages, therefore, larger values of τ can be measured.

This improvement of adiabatic conditions of the system through gelling is more apparent in the thermocouple method, for it is only necessary for the centre of the reacting mass to remain adiabatic, whereas in the dilatometer method, the whole reacting volume must remain adiabatic.

Energies of Activation - E_t and E_o.

Although the variation in values of E_t in the later stages of the reaction is great, in the early stages of the reaction the value is about 0 i.e. extremely low. This value includes the energy of activation for the diffusion of radicals together. The only obvious alternative to the radicals diffusing together prior to interaction seems to be the possibility of radicals growing together i.e. moving through the solution by growth rather than by diffusion thus explaining the low energy of activation for the reaction. If, however, it is assumed that the diffusion constant is 10^{-6}, then it can be calculated that the distance travelled by diffusion is of the order of 10^{6} times that moved by polymer growth i.e. the possibility of radicals growing together is not reasonable.

Values of E_o are compared to those of other workers later in the discussion.

"Popcorn" Polymer.

Generally, experiments were terminated by the reaction mixture shrinking and parting from the walls of the reaction vessel. In some experiments, however, "popcorn" polymer was formed in the early stages of gelling.

"Popcorn" polymer starts as a small seed of insoluble polymer which gradually grows to spread through the reaction mixture. This white puffed mass forms vapour pockets and eventually the reaction vessel breaks because of this expanding polymer. Quite frequently, too, it was found that "popcorn" polymer formed on tap grease in the high vacuum line where contact had been made only with methyl acrylate monomer vapour; this suggests that formation of this polymer took place also in the vapour phase.

Other workers[17,19] have encounered the difficulty of "popcorn" formation in methyl acrylate polymerisation and it has been suggested[19] that traces of water may be the cause. "Popcorn" polymer is also formed when traces of air are present.

Work along this line is rather difficult since there is no definite method for inducing "popcorn" formation, although it has been found[19] that subsequent polymerisation is more rapid than the normal polymerisation would be.

"Popcorn" polymer has the characteristics of a crosslinked polymer; it is insoluble in organic solvents such as benzene, chloroform and acetone although such solvents swell the polymer mass. It is stable for several days to heating in vacuo at 160°C but heating in the presence of air gives, within an hour, a syrup which is soluble in benzene i.e. the crosslinking system is broken down by heating in air.

Limitations and Possible Errors.

a) The Dilatometer Method for measuring the Non-stationary State of a Polymerisation Reaction.

Temperature Variations.

The temperature variation of the contents of a dilatometer enclosed in a vacuum jacket can be controlled to ± 0.001 C^o in the thermostat used. Thus, accurate measurements of change in volume can be made.

Factors Governing Breakdown of Adiabatic Conditions.

The factors influencing the length of period over which the contents of these dilatometers remain adiabatic have been discussed earlier (page 94). It was determined that in a dilatometer of about 20ml capacity without a surrounding vacuum jacket, this period was approximately 8 sec., and with a vacuum jacket, about 30 sec.. The estimated error introduced by conduction of heat through the mercury in the dilatometer is about -5%.

Errors in Recording Measurements.

In the dilatometer method, measurements have been recorded by three different means[31], by stopwatch, by penrecorder and by photography. The first two methods involve an observer's error although with most operators this does not exceed ± 0.1 sec., whereas no such personal error occurs with the photographic method.

However, it was found that the pen-recording method was the most convenient to use; the stopwatch method of recording involved further errors since each experimental point in the rate curve would have to be obtained from a separate non-stationary state reaction; the photographic method is more difficult to operate and a considerable lapse of time occurs between carrying out the experiment and the calculation of results, since a length of film has to be developed and meniscus movement measured from this film.

b) The Thermocouple Method for measuring the Non-stationary State of a Polymerisation Reaction.

Temperature Variations.

Again, the maximum temperature error from bath fluctuations is of the order of ± 0.001 C°.

Instrument Limitations.

The value of the noise level in the amplifier used corresponds to a fluctuation of 0.00014 C°; and so, even with a much improved thermostatically controlled system, the minimum possible temperature fluctuation measurable would be 0.00014 C° using the Tinsley D.C. amplifier.

The relationship between voltage and temperature for a constantan/copper thermocouple was obtained from The International Critical Tables, since the difficulty of calibrating the thermocouples for small temperature differences in the reaction vessel would be great. Avoiding this difficulty and using the standard tables appears to be justified, however, since it is reported[14] that good agreement is obtained between temperature measurements and dilatometer measurements made similtaneously on the same vessel.

For an accurate measure of lifetimes of the kinetic chain it is critical that the response time of the instrument as a whole is known. The response time of the amplifier is 0.04 sec. whereas that of the thermocouples is rather less. The Elliot pen recorder has a half life of response of 0.5 sec. which results in a considerable delay in the recording of the full signal. The lag in response of the total set-up was measured and found to be approximately 1.3sec. (page 78).

Overall Instrument Lag.

The overall instrument lag in response can be obtained[14] by plotting the reciprocal of the rate of polymerisation against measured intercept; the rates are varied by inserting screens of known transmission between the ultra violet light source and the reaction vessel.

From the kinetics of polymerisation,

$$\tau = (k_p/k_t) x 1/\text{rate} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; 18$$

Also, the intercept on the time axis of the extrapolation of the straight line portion of the fractional conversion against time curve is $\tau \ln 2$; therefore, the measured intercept, X, is given by

$$X = C + (k_p/k_t)(1/\text{rate})\ln 2 \quad \text{. . . . . 19.}$$

where C is the lag response of the circuit (in seconds). Hence, by plotting X, the measured intercept against reciprocal of rate, a straight line is obtained which cuts the time axis at C, the response lag. The slope of this plot $= (k_p/k_t)\ln 2$ and is independent of the response lag of the instrument.

Instrument lag is affected slightly by the amount of ink in the bucket pen and also by how accurately the pen is balanced. Thus, there will be small variations in response lag from one measurement to another.

Inaccuracies may also arise in the extrapolation of the stationary state temperature/time line back to the time axis and occasionally difficulties occur due to circuit noise from external sources.

Adiabatic Requirements.

In the early stages of the reaction prior to a gel state, the adiabatic period at the centre of the reaction vessel is of the order of 30 sec. which means that values of τ of up to 6 sec. can be measured accurately. When, however, heat transfer is cut down due to a large increase in viscosity (gelling), then the adiabatic period at the centre of the vessel is increased, although a limit is reached when measuring values of τ around 10 sec..

c) Possible Errors Common to Both Methods.

In order to have reproducibility from one experiment to another, it is important that the reaction vessel and light source are in constantly fixed positions. It is not sufficient to have the distances between the two constant, for an alteration of actual position means that the activating light has an altered depth of thermostat water to penetrate i.e. absorbtion of light by the water will change. These errors can be overcome by simply having fixed positions for both lamp and reaction vessel.

The thermostat water had to be changed frequently because of cloudiness due to atmospheric dirt and micro-organisms in the water. Again, light penetration would be affected by such polution.

Catalyst concentration was finely controlled by using dilute solutions of catalyst and by accurate measurement of monomer. In the dilatometer method, the monomer was distilled into the reaction vessel from a graduated section in the vacuum distillation line. An error in measurement of 0.1 ml. would result in a volume error of 0.7%. With the thermocouple reaction vessel, the volume of the vessel is measured directly (see experimental) and the likelyhood of error is even smaller.

Reproducibility may be affected by traces of oxygen in the monomer. Oxygen retards methyl acrylate polymerisation to begin with and then the reaction rate accelerates finally reaching values much in excess of those normally encountered with pure monomer due possibly to formation of peroxides.

Comparison of the Dilatometer and Thermocouple Methods of Measuring the Non-stationary State of the Polymerisation of Methyl Acrylate.

a) The Early Stages of the Reaction.

On examination of the intensity exponents derived through results from both methods, it can be seen that there are the same characteristics at the same stages i.e. at very early stages there are erratic results and the order of the termination reaction approaches one, probably due to the presence of trace impurities; later, after about 2% conversion, there is better reproducibility with both methods and a second order termination reaction is apparent; after gelling, both methods show a deviation from second order termination possibly as a result of high values of τ preventing the straight section of the reaction curve being reached before bfeakdown of adiabatic conditions.

Table XIX.

Methyl acrylate polymerisation: comparison of values of τ and rate of reaction measured by thermocouple and dilatometer methods.

Method	Rate %/h.	τ (sec.)
Dilatometer	13	2.5
Thermocouple	21	3.2

Although values of τ are of the same order of magnitude (table XIX) and reproducibility between the two methods in this respect is good, there is a large difference in measured rates. The lower rates with the dilatometer method were expected, for despite precautions taken to reproduce experimental conditions exactly, there was no accurate way of compensating for light absorbed by the additional thickness of the glass jacket; moreover, light will be reflected by the two surfaces of this jacket. Also, reaction vessels for the dilatometer method are made from Pyrex glass whereas the thermocouple ones are soda glass, resulting in different absorbtion of light according to which reaction vessel is used.

It will be seen on examination of the results given in table VI for the dilatometer method at 25°C that both the rate of polymerisation and τ are reproducible to within about ±10% but at 35°C the spread is rather greater. The cause of the poorer reproducibility at the higher temperatures is not known but it may be associated with the thermal rate of polymerisation which according to Ross[19], varies with extent of reaction. It will be noticed that, although there is a ±10% error in both rate and τ at 25°C, the reproducibility of the product of the rate and lifetime (i.e. k_p/k_t) is about ±5%. This would be expected if the major error in the determination of rates and values of τ was due to variability of the rate of initiation, for reasons discussed earlier. It will be noticed from the results at 25°C in table VI (page 51) that the reproducibility for reactions carried out in the same dilatometer is better than for those performed in different dilatometers which again fits with the above postulate that part of the variation is due to variations in the rate of initiation.

Again, examination of the results in tableXII (page 80) for the thermocouple method shows that values for rate of polymerisation and τ at 25°C are both reproducible to about ±15%, although values of k_p/k_t are reproducible only to about ±25%. Also, results from one reaction vessel vary just as widely as results obtained from different ones. This suggests that physical conditions within the reaction vessel are changing e.g. early gelling may occur.

Comparison of Results with those of Other Workers.

Table XX.

Method.	T°C.	k_p/k_t x10^5	k_p	k_tx10^{-6}	Reference
Dilatometer	25	8.9	580	6.5	This work.
Thermocouple	25	18.4	590	3.3	This work.
Sector	30	17.4	720	4.3	17
Sector	25	2.8	245	9	19
		2.8	1580	55	19
Sector	50	28	1000	3.6	18
Dielectric constant	15	1.1	-	-	10
Interferometer	15	1.5	-	-	11

In table XX values of k_p and k_t obtained by the dilatometer and thermocouple methods are compared with those obtained by other workers using different methods. It can be seen that there is a tenfold variation in the value of k_p/k_t obtained by different workers using the rotating-sector method.

The simplest explanation for such a variation is differences in the purity of the monomer, for methyl acrylate peculiarities such as "popcorn" polymer and the unusually high thermal rates have also been found by these other workers. The presence of traces of retarding impurities might explain the lower values of k_p/k_t, but if such impurities were present, the intensity exponent should have been greater than 0.5. Values of around 0.5, however, were reported by these workers.[10,11,19]

Another possible explanation is that the lower values of k_p/k_t were obtained for direct photopolymerisations of methyl acrylate in which no sensitizer was used, whereas the higher values were obtained from photosensitized reactions. This explanation, however, does not seem to hold, as dilatometer experiments using no photosensitizer gave values of k_p/k_t almost identical to values from photosensitized experiments using the same method (page 64, fig.24).

The values of the individual velocity coefficients, k_p and k_t, have been determined from the ratio k_p/k_t and the value of the ratio $k_p{}^2/k_t$ obtained from measurements of the rate of initiation. In view of the differences in values of k_p and k_t obtained by Ross[19] using the inhibitor and molecular weight methods of measuring rates of initiation, it is surprising that the values obtained by Matheson[17] agree so well with the values obtained by this present work, for Matheson calculated rates of initiation from molecular weight data. Furthermore, partly owing to the early "gel" effect in methyl acrylate polymerisation, the scatter of experimental points in the rate against flash-time plot was considerable in Matheson's experiments, and large errors in the values of the velocity coefficients are possible.

Overall activation energies, E_o, and the activation energies for the termination reaction, E_t, derived from various methods are shown in table XXI.

Table XXI.

Activation energies for the initial stages of the polymerisation of methyl acrylate.

Method	E_o $(=E_p-\frac{1}{2}E_t)$ k.cal./mole	E_t k.cal./mole	Reference.
Dilatometer	6.2	0-7.8	This work
Thermocouple	5.1-6.8	0-3	This work
Sector	3.5	5	17
Sector	3.7	0	19
Sector	4.7	0	18

It will be seen from table XXI that the value of the overall energy of activation obtained in this work is rather greater than the values found by other experimenters. This may be because our measurements were carried out a little earlier on in the polymerisation, and because, at slightly later stages, the overall activation energy may fall as has been observed[32,36] in the "gel" stages of the polymerisation of vinyl acetate and methyl methacrylate.

The wide scatter in the possible value of E_t is due to the rather large variation in the value of τ at 35°C. Unfortunately, experiments could not be carried out at higher temperatures owing to the presence of an appreciable dark rate at these temperatures. From the experimental data of Matheson[17] the value of 5 k.cal./mole suggested by him for E_t is also doubtful, again because of the wide variation in his values of τ.

<u>b) The Later Stages of the Reaction.</u>

The effect of conversion on values of polymerisation rates, τ and velocity coefficients were compared for the two methods.

With polymerisation rate, curves for both methods were of the same shape although the thermocouple results were higher (fig. 20 and 38). After a sharp initial rise, however, both curves start falling at the same extent conversion. The reasons for the higher rates with the thermocouple method have been discussed previously.

Values for τ (fig. 21 and 39) also follow similar shapes for the two methods although again the thermocouple results are higher. Early termination of the thermocouple experiments was the result of "popcorn" formation.

With the velocity coefficient k_p, both sets of results again follow a similar patern with a drop in value as extent conversion increases. There is, however, considerable scatter of values from the thermocouple method (fig. 22 and 40).

Also, values of k_t (fig. 22 and 41) assume similar curves for both methods with dilatometer results in the higher position.

The Effect of Transfer Agent on Later Stages of the Reaction.

The effect of addition of CCl_3Br was to cut down average molecular weights by introducing chain transfer. This resulted in delaying gelling to a later stage of the reaction. It was found that because of this delay in gelling, there was very little change in rates of reaction or in lifetimes of the kinetic chain.

When changes in temperature were introduced to examine energies of activation, some erratic results were obtained. A similar effect was found at conversions over 30%. It is suspected that the thermocouple metals are attacked by the CCl_3Br at elevated temperatures or over long periods at 25°C.

In general, therefore, it can be seen that with CCl_3Br present, the kinetics of polymerisation of methyl acrylate over the first 30% conversion correspond to the early pregel state of normal experiments.

Both types of reaction vessel are easily replaced compared to those used in other methods, such as the refractive index method. Also, in the dilatometer method, all the apparatus required is simple and inexpensive, whereas the thermocouple method requires an amplifier and recorder. However, the simpler the apparatus for the former method, the greater the personal error e.g. the replacement of the chart recorder by a stopclock steps up the personal error considerably. Even with a recorder, the lag between the operator's observation and his recording of it will be <u>ca</u>. 0.1 sec.. In the thermocouple experiments all the recording is done automatically by instruments, the total lag of the system being known. The only personal error here is in the measuring of the recorder charts; this may be further complicated by external circuit noise.

The greatest difficulty with the dilatometer experiments was experienced in the filling section, for difficulties (such as sealing, measuring monomer volumes accurately and frozen seals causing breakages) were numerous. The simpler method used in filling thermocouple vessels was much preferred.

"Popcorn" Formation.

It was noticed that "popcorn" formation was much more frequent with the contents of the thermocouple vessels. Both methods were therefore examined closely to determine any differences in conditions of reaction. Two differences are apparent:

a) Experiments with dilatometers are run under atmospheric pressure together with the pressure

from the short mercury column, whereas the thermocouple vessels are only under the vapour pressure of the monomer which is considerably less than atmospheric at the temperatures of the experiments.
b) The thermocouple method vessels have a monomer vapour pocket in the filling stem whereas there is only one phase present in the dilatometers.

It has been noticed, too, that "popcorn" seems to form in the vapour phase - formation has been observed at various points in the vacuum line where only monomer vapour was present - and so would form more readily in thermocouple vessels as was observed. It is thought that the effect of the different pressures with the different methods is small.

The dilatometer and thermocouple non-stationary state measurements on separate experiments have been compared. Differences between the two methods have been found but it is not known whether these differences are the result of a fundamental error in one of the methods or whether they are due to experimental error arising from separate reaction mixtures. A more direct method of comparison would be to take measurements by both methods simultaneously on the one reaction mixture. Some preliminary work along these lines has been carried out the results of which are given in appendix III.

Appendix I.

Calculation of Reaction Rates.

Molecular weight = 86

Specific heat = 0.47 cal./g.

Heat of polymerisation = 18.7 k.cal./mole[39]

At 0% extent conversion,

Coefficient of expansion = 0.126 %/C°

Let W be weight of monomer,

Then moles of monomer = W/86.

Heat supplied by 100% polymerisation

$= (Wx18.7x10^{3})/86$ cal.

Therefore, temperature rise

$= (Wx18.7x10^{3})86xWx0.47$ C°.

Thence, expansion from this temperature rise

$= (18.7x10^{3}x0.126)/86x0.47$

= 58.2%.

Now at 25°C,

density of monomer = 0.9423 g./ml.

density of polymer[37] = 1.218 g./ml.

Whence,

specific volume monomer = 1.0612 ml/g.
specific volume polymer = 0.8211 ml/g.
Therefore, contraction due to 100% polymerisation
= 0.2401/1.0612
= 22.6%.

For adiabatic conditions, therefore, actual expansion for 100% polymerisation = 35.6%.

If percentage expansion is plotted against time and the gradient m%/sec., measured, then the rate of polymerisation is given by

(mx3600x100)/35.6 %/h..

Appendix II.

Coefficients of Expansion of Monomer/Polymer Mixtures.

Before rates could be measured for later stages, it was found that there was a change in coefficient of expansion of the monomer/polymer mixture as the extent of polymerisation changed. Since the calculation for determining rates depends on knowing the coefficient of expansion, this was measured for various mixtures.

A graph was constructed of expansion against temperature (e.g. fig.7 for 25% conversion) and from the slope, the combined coefficient of expansion of mercury, monomer and polymer was measured.

Sample Calculation.

Volume polymer = 0.6239 ml.
Volume monomer = 2.4061 ml.
Volume mercury = 2.1553 ml.
Total volume = 5.1853 ml.

$$\left.\begin{array}{ll}\text{Volume fraction of polymer} & = 0.1203 \\ \text{Volume fraction of monomer} & = 0.4640\end{array}\right\} = 0.5843$$

Volume fraction of mercury = 0.4157

Coefficient of expansion of mercury = $1.82\text{x}10^{-4}$ /C° 38

Temperature in °C was plotted against height of mercury column in cm. - fig.7.

Gradient of curve = 2.250/10 cm./C°.

Diameter of capillary = 1.5 mm. (Veridia tubing).

Combined (polymer/monomer/mercury) coefficient of expansion

$$= \frac{\pi \text{x} 0.075^2 \text{x} 2.250}{10\text{x}5.1853}$$

$$= 7.668\text{x}10^{-4} \ /\text{C}^\circ.$$

If α is the coefficient of expansion of polymer/monomer mixture, then

$$0.5843\alpha = 7.668\text{x}10^{-4} - 0.4157\text{x}1.82\text{x}10^{-4}$$

$$\text{i.e. } \alpha = 1.183\text{x}10^{-3} \ /\text{C}^\circ$$

Now, weight of polymer = 0.7599 g.

Volume of monomer from this = 0.7599/0.9423

= 0.8064 ml.

Therefore, total original volume

= 2.4061 + 0.8064

= 3.2125 ml.

Therefore, extent conversion

= (0.8064x100)/3.2125

= 25.10%.

The results obtained and calculated in this manner were plotted (fig. 17) and compared to the theoretical values on the same graph. The points for the theoretical curve were compiled from the following calculation.

Calculation of "Theoretical" Coefficients of Expansion for various Monomer/Polymer Mixtures.

Example.

Extent conversion = 50%.
Therefore, weight fraction of polymer
= 0.5
Specific volume monomer = 1.0612 ml/g.
Specific volume polymer = 0.8211 ml/g.
Therefore, volume polymer relative to 0.5 weight fraction = 0.5x0.8211/1.0612
= 0.3882
i.e. total volume mixture = 0.3882 + 0.5
= 0.8882
Hence, volume fraction polymer = 0.3882/0.8882
= 0.4370
and volume fraction monomer = 0.5000/0.8882
= 0.5630

From density measurements at different temperatures[17,37]

Coefficient of expansion polymer $= 0.6607\text{x}10^{-3}$ /C°.

Coefficient of expansion monomer $= 1.281\text{x}10^{-3}$ /C°.

Therefore, coefficient of expansion of mixture

$$= (0.4370\text{x}0.6607 + 0.5630\text{x}1.281)\text{x}10^{-3}$$
$$= 1.0099\text{x}10^{-3} \text{ /C}^{\circ}.$$

Appendix III.

Combined Dilatometer and Thermocouple Method for Measuring the Non-stationary State of the Polymerisation of Methyl Acrylate.

Introduction.

Some preliminary work has been done on the design of a reaction vessel wherein both the dilatometer and the thermocouple methods of measuring the non-stationary state can be carried out similtaneously. The design of the reaction vessel has been changed only slightly from the thermocouple vessel. However, since the reaction vessel should be surrounded by a vacuum jacket, some difficulty has been encountered; for thermocouple leads have to be led from the vessel to an outside circuit. Moreover, side arms joined to the vessel increase its size and therefore the use of a larger vacuum jacket is entailed.

However, this preliminary work will show the effect of early breakdown of adiabatic conditions with the dilatometer method and rates under these

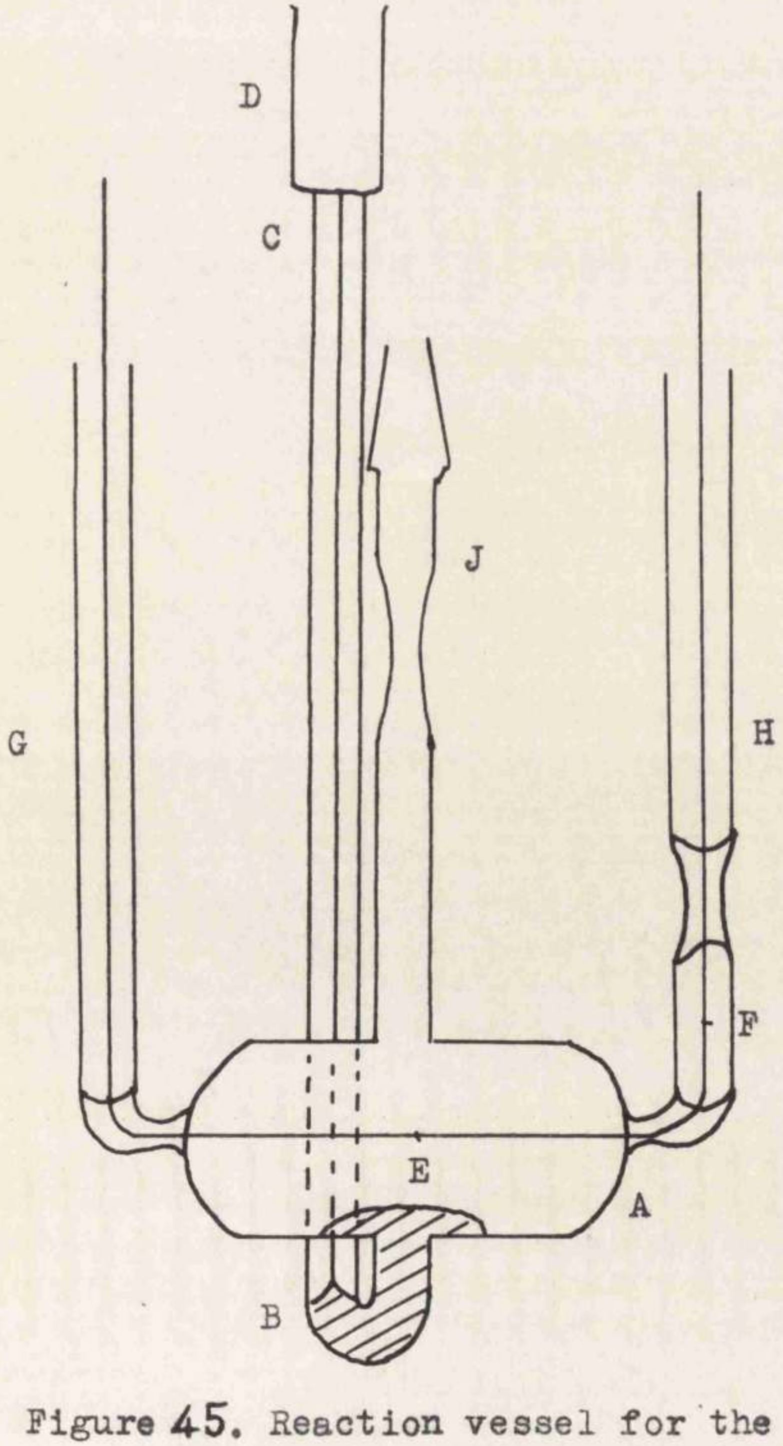


Figure 45. Reaction vessel for the combined thermocouple/dilatometer method.

conditions can be compared to the true rates measured by the thermocouple method.

Experimental.

a) Apparatus.

The reaction vessel arrangement is shown in fig.45. A is the reaction vessel which has a calibrated capillary, BC, joined to the base. This capillary has a cupped extension to facilitate the filling of mercury. The thermocouple junctions, E and F, are sealed onto the side arms, G and H, of the vessel as described in the thermocouple method. J is a Quickfit B.10 soda glass joint which is used as a connection to the vacuum line. The apparatus is made in soda glass.

b) Filling of Reaction Vessels.

The volume of the reaction vessel was measured by sealing the base outlet with mercury and running in acetone from a burette. After drying the apparatus the requisite amount of catalyst solution was run into the vessel and the chloroform distilled off.

Mercury was run into the capillary till its level reached the reaction vessel proper. The mercury was frozen in this position thus sealing this outlet. The apparatus was pumped to high vacuum via the Quickfit joint; monomer was distilled in and the vessel sealed at the constriction. When the mercury is unfrozen, the monomer fills the whole stem volume i.e. there is no vapour pocket.

Note: care must be taken to prevent mercury from contacting the thermocouple wires for an amalgam would be formed affecting subsequent temperature measurements.

c) Measurements on the Reaction.

With the reaction vessel set in position in the thermostat, the contents were allowed to settle to the set temperature. The shutter to the lamp was opened by pressing a push-button switch and the polymerisation reaction started. The rate of reaction was recorded by the thermocouple method i.e. the course of the reaction was traced automatically. Similtaneously, the mercury level in the capillary was followed using a cathetometer with a graduated film in the eyepiece. At each division an impulse

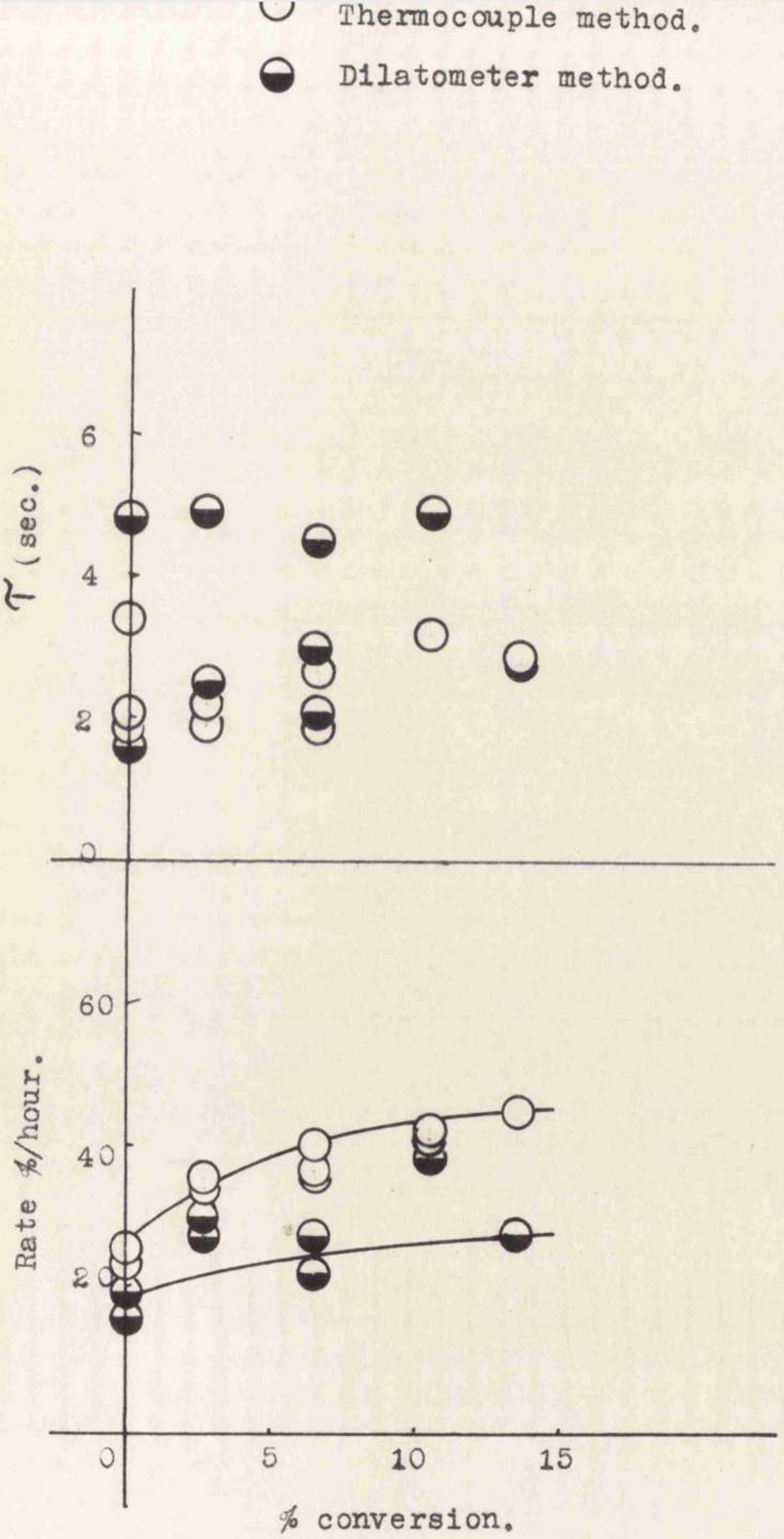


Figure 46. Rate and τ for the polymerisation of methyl acrylate measured by the combined thermocouple/dilatometer method.

was relayed to the recorder by depressing a push-button switch. This impulse was recorded on the thermocouple time/temperature curve. Thus the two different measurements have a common time axis. From the measurements, rates and values of τ can be evaluated for both methods.

Results.

Calculation of rates of polymerisation and lifetimes of the kinetic chain is based on the method used in the dilatometer and thermocouple experiments. Rates of reaction at different extents of reaction have been graphed for the two methods (fig.46). It can be seen that in both methods there is a slight increase in rate with extent conversion. However, results by the dilatometer method are lower than the thermocouple results.

Also, the lifetimes of the kinetic chain measured on the same experiments gave higher results for the dilatometer method (fig.46).

Since there was no vacuum jacket surrounding the system, it can be safely assumed that the adiabatic conditions, necessary for dilatometer type measurements, have broken down before time $= 3\tau$. Thus, rates measured by this method would be low. However, if the time/expansion curve does fall away before 3τ, the resultant effect would be to lower measured values of τ. As can be seen in fig.46, this does not happen. Again, on examination of the log cosh t/τ against t/τ curve, (fig.43) i.e. the theoretical rate curve, it can be seen that the error involved when measuring rates up to the section of the curve, time $= 2\tau$ is only of the order of 10%. therefore, if adiabatic conditions broke down after 2τ, there would be very little difference from the true measurement of rate or τ.

The main disadvantage in attempting to make comparisons between the two methods using this reaction vessel is the error involved in the use of soda glass capillary, for precision bore tubing was not available in soda glass. The diameter of the capillary varies conciderably over its length and very little variation is required to affect kinetic measurements.

Even taking into account the two errors discussed, it is apparent that rate measurements by the thermocouple method are higher and measured values of τ are lower than the corresponding measurements by the dilatometer method. This seems to indicate that some factor or factors upon which the calculation of one of the methods depends is not strictly accurate. Table XXII shows the factors involved in the calculation of results for both methods.

Table XXII.

The factors involved in the calculation of results for the dilatometer and thermocouple methods.

Dilatometer	Thermocouple
Molecular weight	molecular weight
Specific heat	Specific heat
Heat of polymerisation	Heat of polymerisation
Coefficient of expansion	
Personal error	
	Instrument lag
	Thermocouple constant

It can be seen that the first three factors are common to both methods. In the dilatometer method there are two additional factors, coefficient of expansion and personal error. The coefficient of expansion measurements made on the monomer correspond to those of Matheson[17].

The personal error will be the variable lag between observation and recording of meniscus height. Because of the different type of push-button switch used in the combined methods experiments, it is probable that this error will be larger than that normally recorded in dilatometer experiments. Also, very early breakdown of adiabatic conditions would give low rate measurements although the correspondingly low measurements of τ would be much increased by a positive personal error.

In the thermocouple method, there are two additional factors. The instrument lag, if not determined accurately, would only affect measured values of τ. However, the basis of the method for the determination of this lag is quite sound. The thermocouple constant was obtained from the literature and seems to be accurate, since results obtained for vinyl acetate correspond favorably with results from other methods.

This type of reaction vessel is still in the early stages of development and although the method of recording measurements is reasonably satisfactory there is still room for improvement; for recording pips from the dilatometer method superimposed on the heating curve tend to distort the latter and obscure final rate and τ measurements. A 2-pen recorder would be more suitable, but one was not available for these experiments.

A vacuum jacket for the system has still to be designed although it is probable that an air jacket would be satisfactory for kinetic measurements involving lifetimes of up to 6 seconds.

The primary purpose of the combined set up is to compare the two methods of measuring kinetic constants rather than an accurate determination of these constants; such accurate determinations should be examined preferably through a single method to keep the system as simple as possible although with the apparatus described the experimental conditions could be simplified sufficiently to give accurate results.

Appendix IV.

Heat of Polymerisation.

Introduction.

In appendix III, the dilatometer and thermocouple methods for following the non-stationary phase of the polymerisation have been combined in the one reaction vessel. If, however, two methods, one of which depends on heat of polymerisation, the other independent, can be incorporated in the same reaction vessel, then comparison of the results should yield a value for heat of polymerisation.

Contraction measurements, using a simple dilatometer, are independent of heat of polymerisation and a thermocouple vessel can easily be adapted for such measurements by replacing the filling stem by a calibrated length of wide bore capillary (2 mm.). Thus, both rates of reaction and temperature rise can be recorded on the same reaction mixture.

Experimental.

With the thermocouple reaction vessel filled and set in position in the usual manner, temperature measurements were made by the non-stationary method described in the thermocouple method. Without changing the position of the reaction vessel, the rate of reactiom was followed from contraction measurements using a cathetometer focused on the stem; 30 second readings were taken over a period of 15 minutes. After this time, the contents of the reaction vessel were allowed to settle to the bath temperature and were again measured by the thermocouple method i.e. non-stationary state measurements have been made both before and after dilatometer measurements.

Results.

From contraction measurements,

Rate of reaction = 26.7 %/h.

From the thermocouple measurements the average of the gradients of the recorder traces taken before and after dilatometer measurements

= 0.525/3

i.e. $\mu v/h$ = 0.525x3600/15x0.327

where 0.327 is the factor for converting scale deflection to μv.

This is equivalent to a temperature rise of

$$\frac{0.525\text{x}3600}{15\text{x}0.327\text{x}40} \quad \text{C}^{\text{o}}/\text{h.}$$

where 40μv are equivalent to 1 C$^{\text{o}}$.

Now, rate of reaction = temperature rise per unit time / temperature rise from total conversion

= (temp. rise/h.)x0.47/H

where specific heat = 0.47 cal./g.

and H = heat of polymerisation.

Whence,

H = 0.47x0.525x3600/15x0.327x40x0.267

= 16.95 k.cal./mole.

The value obtained by Tong and Kenyon[39] for the polymerisation of methyl acrylate is 18.7 ±0.2 k.cal./mole and this latter value has been chosen for calculations on the two non-stationary state methods.

Appendix V.

Calculation of the Effect of Heat Losses to Mercury in a Dilatometer.

In a typical example,

Volume of methyl acrylate = 16 ml.

Volume of mercury = 4 ml.

	Mercury	methyl acrylate
Specific gravity	13.6	0.9533
Specific heat	0.033	0.47
Coefficient of expansion	$1.83\text{x}10^{-4}$	$1.26\text{x}10^{-3}$

Initially, for a heat input of X cal., if no heat is transferred to the mercury,

$$\text{Expansion} = \text{X}\text{x}1.26\text{x}10^{-3}/0.47\text{x}0.9533$$

$$= 2.81\text{x}10^{-3}\text{X ml.}$$

If, for the same heat input, the mercury attains the same temperature as the monomer:

Weight fraction methyl acrylate = 15.25/69.7

Weight fraction mercury = 54.4/69.7

Coefficient of expansion of mixture

$$= \frac{16\text{x}1.26\text{x}10^{-3} + 4\text{x}1.83\text{x}10^{-4}}{20}$$

$$= \frac{20.9\text{x}10^{-3}}{20} \quad /\text{C}^{\circ}$$

Specific heat of mixture $= \frac{0.47\text{x}15.25 + 0.033\text{x}54.4}{69.7}$

$$= \frac{8.95}{69.7}$$

Density of mixture $= \frac{4\text{x}13.6 + 16\text{x}0.9533}{20}$

$$= \frac{69.7}{20} \quad \text{g./ml.}$$

If the mixture assumes the same temperature throughout, then expansion

$$= \frac{\text{Xx}20\text{x}20.9\text{x}10^{-3}\text{x}69.7\text{x}20}{20\text{x}8.95\text{x}20\text{x}69.7}$$

$$= 2.34\text{x}10^{-3}\text{X} \quad \text{ml.}$$

% difference $= \frac{(2.81 - 2.34)\text{x}100}{2.81}$

$$= 17\%.$$

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