THE EFFECTS OF ALTERNATING ELECTRICAL FIELDS ON THE POLYMERIZATION OF STYRENE

A Thesis

by

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GENERAL INTRODUCTION

Review of Electrostatics, Magnetism and Electromagnetic Theory (1,2,3,4,5)

The region around an electrically charged object is considered to be pervaded by an electrostatic field, the idea of a field being adopted to explain the "action at a distance" of the charge.

The field strength at any point is measured by the work required to move a unit charge to this point against the repulsion of the field. The field strength, or potential gradient, is commonly expressed in volts/cm. and the potential difference across the field is measured in volts.

Capacity is defined by the equation $Q=CE$ where Q is the quantity of the charge in coulombs, E is the field potential in volts and C is the capacity in farads. A common unit of capacity is the micro micro farad, i.e., 10^{-12} farad.

The concept of a field is also used to explain the force exerted by a magnet. The unit of intensity of a magnetic field is the gauss (oersted) which is defined as the intensity of a magnetic field in which a unit magnet pole experiences a force of one dyne.

A uni-directional electromagnetic field pervades the region around a conductor through which a direct current is passing. If the current in such a conductor is alternating the conductor has associated with it an oscillatory electromagnetic field. The intensity of an electromagnetic field is customarily measured in volts/cm.

Radiation arising from electromagnetic pulsations in a vibrating system is represented by waves. These waves cover a large spectrum of wave lengths, e.g., radio, infra-red, visible light, ultra-violet, X-rays, etc., and range from a wave length of one thousand meters to one of 10^{-11} cm.

In a radio transmitter electrons are surging back and forth in the aerial circuit, and this to and fro movement causes pulses of electricity to travel away from the aerial as electromagnetic waves. The velocity of propagation of these waves is 3×10^{10} cm./sec., the same as the velocity of light. Hence frequency is related to wave length by

$$\nu\lambda = C$$

where ν is the frequency in vibrations per second (cycles per second), λ is the wave length in cm., and C, the velocity of light, is in cm./sec.

The energy of an electromagnetic field is related to frequency by the equation

$$E = h\nu$$

where E is energy in ergs, ν is frequency in cycles per second and h is Planck's constant, i.e., 6.63×10^{-27} erg.-sec.

An electromagnetic wave is considered to have electrostatic and magnetic components equal in magnitude.

Molecules are often regarded as containing net positive and negative charges resulting from interactions among constituent atoms. When the charges are coincident, the molecule has no resultant electrical dipole, but, when the charges are displaced from one another, a dipole exists.

In an electrical field a dipolar molecule tends to be turned so that the charged ends of the dipole point toward the oppositely charged poles of the external field. Such molecules oscillate in an alternating field, the arc of rotation decreasing as the frequency of the field increases.

Electrical dissymmetry, i.e., a dipole, is produced in molecules as a result of interaction between the charges in the molecule and the field which is associated with electromagnetic waves. Hence all molecules are regarded as polar in the presence of electromagnetic waves. This is called polarization and is expressed as

$$P = q\ l$$

where P is the polarization, q is the charge on the dipole and l is the length of the dipole. The total polarization is the sum of P_E, the electronic, P_A, the atomic, and P_M, the permanent polarizations.

Ferro-, para-, and diamagnetism have been recognized as three magnetic properties of matter.

A material is considered diamagnetic if, when placed in a magnetic field, the magnetic lines of force prefer to pass through a vacuum as compared to this material. That is, the magnetic permeability is less than unity.

For a ferro- or paramagnetic material, the lines of force of a magnetic field prefer to pass through the material rather than through a vacuum. That is, the magnetic permeability is greater than unity. The preference is more marked in ferro- than in paramagnetic materials.

The magnetic susceptibility of a material is defined by the equation

$$\mu = 1 + 4\pi\rho\chi$$

where μ is the magnetic permeability, ρ is the density and χ is the specific magnetic susceptibility. χ is positive for ferro- or paramagnetic materials and it is negative for diamagnetic materials.

Paramagnetism is observed in molecules containing an odd number of electrons, and hence free radicals are paramagnetic. The oxygen molecule is also paramagnetic.

Electrical Fields and Chemical Reactions

Changes in the interatomic binding forces of molecules, and the relation of these changes to temperature, are of prime interest in chemical kinetics. Theories have been developed to explain chemical change and its dependence on temperature by means of various generalized mechanisms. One of these theories is the electronic theory.

This is based on the conception of organic molecules as groups of atoms bound together by bonds consisting of pairs of electrons. The electronic theory attempts to explain chemical change by proposing that positive and negative poles in a molecule may be formed by an intramolecular transmission of electrical charge. Subsequent chemical reaction is visualized as a result of attraction between these unlike poles, either in the same molecule or in different molecules.

Proponents of the electronic theory of chemical reaction have suggested that the reactivity of molecules may be altered as a result of an electrostatic disturbance such as that which may occur in an electrical condenser (6). Interest in this suggestion prompted the present investigation.

There are several reports in the literature that describe systematic surveys of the influence of electrical fields on chemical reactions. There are also a number of shorter studies described which are incidental to other research. These reports may be grouped according to whether an alternating or a uni-directional field was used.

In a number of studies an alternating field was used to supply thermal energy to the chemical system. However, this thesis is concerned only with athermal effects of an electrical field; hence it is important to distinguish between thermal and athermal effects in the literature survey.

The phenomena of anomalous absorption observed during the passage of electromagnetic waves (decimeter and centimeter waves) through a dielectric material are related to deformation of dipole molecules (7). Not only thermal effects, but also athermal effects connected with excitation, are possible. It is suggested in the reference cited that resonance phenomena should be observed in the region of anomalous dispersion; but this has not been shown experimentally.

Studies have been made by Liechti on the polymerization of styrene in bulk and in toluene solution in the presence of a 50-cycle electrical field (8). Homogeneous fields were used at first, but hyperbolic fields were introduced later to obtain a higher voltage gradient across the reaction mixture. The samples were activated in the field and then polymerized thermally at 80°C. The progress of reaction was followed by refractive index measurements and percent conversion analyses.

In these studies one of the electrodes in the reaction cell was in direct contact with the reaction mixture. Also, no mention is made of any means of measuring temperatures in the reaction cells.

For the polymerization occurring in solution no effect of the field was found, but, for the reaction with pure styrene, it was found that the largest increase in rate of formation of active nuclei occurred at a definite critical voltage of about 43.5 kilovolts/mm. The rate of formation of nuclei suddenly increased at this voltage but decreased again with a further increase in potential gradient.

It was found that the effect of the field, that is, production of nuclei, was maintained without loss for periods up to one week after removal of the field. The number of nuclei formed by the field apparently was a maximum after twelve hours' treatment. Re-application of the field during the heat treatment at 80°C. had a retarding effect.

A high frequency field of 26 megacycles showed an influence on the polymerization, but, as it was found impossible to separate the influence of the field from that due to temperature rise resulting from dielectric loss, the results were not published.

The application of a high frequency electrical field (10 and 100 cm. waves) as a method of heating styrene to accelerate the polymerization has been studied (9). The yield of polymer was three to four times greater in the presence of the field than in its absence.

It was found that oxygen inhibits the polymerization only with the ten cm. waves. In the presence of air, the average molecular weight of the polymer was decreased ten percent by the field while, in an atmosphere of carbon dioxide, the molecular weight was increased twenty percent by the applied field.

It is suggested by the investigators that the 10 cm. waves activated the oxygen so that it took part in the polymerization reaction and caused inhibition. Only a thermal effect was found with the 100 cm. waves.

The polymerization of chloroprene under the influence of an ultra-high frequency field (37.5×10^6 cycles per second) has been studied (10). A higher rate of polymerization occurred in the field reaction than under equivalent heating periods on a water bath.

An X-ray analysis indicated that only the degree of polymerization was affected, the structure and particle size remaining unchanged.

The evidence was used to show the presence of an extra-thermal component in the ultra-high frequency field.

Oils used as insulation in high voltage cables and condensers show a polymerization product called X-wax (11). To elucidate the mechanism of this reaction, polymerization studies were made on such simple compounds as styrole, indene, and paraffin. Three stages were distinguished: first, production of a nucleus by excitation of the molecules; second, chain formation; and third, saturation of the free valences or ring formation. The velocity of polymerization was found to depend upon the field distribution and the field frequency.

It was considered that nuclei could be produced without polymerization occurring, after which polymerization could be induced by heating. Substances which have otherwise resisted polymerization have been polymerized in an alternating field.

The rate of vulcanization of rubber in benzene solution and in sheets was increased in an ultra high frequency field; the percentage of sulfur combining with the rubber increased with time of exposure to the field (12). Obviously the high frequency electrical field here was being used as a source of heat.

An oscillatory electric circuit of wave length equal to 1.256 metres increased the rate of esterification of ethanol by acetic acid and also decreased the acidity of olive oil, wine and vinegar (13). Later investigation on the esterification reaction suggested that the increase in rate was due to an increase in temperature caused by the field (14).

When a high frequency electrical field was applied to aniline black, a chemical effect was indicated by a change in colour of the reaction product (15).

The rates of hydrolysis of starch and of bleaching by hypochlorite in the textile industry are accelerated by the heating produced in a high frequency field (15). An optimum wave length was found for each reaction studied; for hydrolysis of starch the wave length was 6.8 meters, and, for decolourizing copper blue with hypochlorite, it was 41.7 meters.

Petroleum and aromatic compounds gave tars, and primary alcohols were oxidized to aldehydes, in the presence of air and of a high frequency field. Ethylenic compounds reacted with hydrogen when a high frequency field was applied (16).

The rate of combusion of a mixture of 25 percent acetylene and 75 percent air has been reported to be reduced in an electrical field of frequency ranging from 10^5 to 0.8 x 10^7 Hertz units (cycles per second) (17). The reduction amounted to 6.7 percent at 10^5 and 0.6 percent at 10^7 Hertz units.

A further study on this reaction showed that the rate of combusion of acetylene-air mixtures was not affected by a field of frequency 1.8 x 10^7 cycles per second, but the rate was increased twenty percent at a frequency of 3.4 x 10^7 cycles per second (18). Furthermore, it was shown that the rate of combusion was decreased nine percent in a "constant" (presumably uni-directional electrostatic) field of 670-700 volts/cm.

The last two reports indicate that the effect of the applied field is closely connected with its frequency. In the frequency range used it was found that an inhibiting field effect a lower frequencies changed to an accelerating effect at higher frequencies.

There are a number of patents which describe methods of accelerating chemical reactions by application of alternating electrical fields.

The reaction of a gas with a dielectric liquid is promoted by discharging the gas into the liquid in an electrical field formed by undamped, high frequency oscillations (19).

The oxidation of H_2S and CO_2 to H_2SO_4, the reaction of NH_3 and CO_2 on $CaSO_4$ to produce $(NH_4)_2SO_4$, and the production of NH_3 from N_2 and H_2 on BaC_2 are accelerated by the application of an alternating field of high tension and low intensity (20).

Another patent describes the production of acetaldehyde from a mixture of CH_4 and CO_2 with CH_4 in excess concentration in a field of frequency greater than 10,000 cycles per second at voltages greater than 20,000 volts. Also formaldehyde may be produced by passing CH_4 and CO_2, with the concentration of CO_2 at least equal to that of CH_4, through electrical fields generated by high frequency and voltage (a voltage of 80,000 volts and a frequency of 1.5 megacycles are mentioned) (21).

A fourth patent is described for the promotion of the gas reaction between distilled products from solid fuels and a mixture of CO and H_2 by subjecting the gases simultaneously to an electrostatic field and to ultra -violet rays (22).

A magnetic field of 15,000 gauss and a constant electrostatic field of 10,000 volts/cm. failed to produce any noticeable effect on the addition of hydrogen bromide to the two electromers of 2-pentene to form 2 and 3-bromopentanes (23). The solvent in this study was one of the reactants, 2-pentene.

No effect greater than experimental error was noted when benzoic acid was nitrated in a magnetic field of 23,000 gauss per $\frac{\pi}{4}$ cm.^{2}. Neither was an effect noted when a constant electrostatic field of 10,000 volts/cm. was used (24). The solvent for the reaction was concentrated nitric acid.

A large influence was found by Clark and Gray (25) when a magnetic field of 14,300 gauss was applied to the addition reaction of hydrogen bromide and allyl bromide in glacial acetic acid. The products formed in the reaction are trimethylene dibromide and propylene dibromide.

The following results were obtained in two experiments with and without the magnetic field:

	I	II
Yield of trimethylene bromide without field	54.5%	58.7%
Yield of trimethylene bromide with field	19.4%	22.3%

While the effect indicated in these data may be the result of the magnetic field influencing the reactivity of one or both of the reactants, the writer suggests that it is possible to explain the effect by means other than an effect on the reactants themselves.

Kharasch has since shown (26) that the normal product in the addition of hydrogen bromide to allyl bromide is propylene dibromide. This product is obtained when oxygen and peroxides are absent. In the abnormal reaction, where oxygen or peroxides are present, a different mechanism occurs and the product obtained is predominantly trimethylene dibromide. It is not clear whether the experimental procedure used by Clark and Gray was such that oxygen or peroxides could affect the control more than the field experiment. Even though the procedure was exactly the same in both experiments, the action of oxygen, if present in the field sample, might be altered, since the oxygen molecule is paramagnetic and might be influenced by a strong magnetic field.

The influence of a magnetic field on solvation effects may also be offered as an explanation. In two of the three investigations polar solvents were used. In the study where a magnetic field was found to have a definite effect, the solvent used was glacial acetic acid. This compound is known to be highly associated and this association is explainable on the basis of dipole-dipole coupling (27,28). The possibility of an influence by the magnetic field on the association of either solvent-solvent or solvent-reactant molecules is apparent for such compounds as allyl bromide and glacial acetic acid.

Experiments with magnetic fields of 20,000 gauss on the gas reaction

$$2NO + Cl_2 = 2NOCl$$

showed no variation in rate compared with the rate when no field was applied (29).

The kinetics of the reaction

$$2NO + O_2 = 2NO_2$$

were investigated at low pressures with and without strong magnetic fields. The influence of a field could not be determined (30).

From a study of a number of inorganic and organic reactions it is concluded that the rate of reaction is accelerated, retarded or uninfluenced by a magnetic field according as the sum of the molecular susceptibilities of the final products is greater than, less than, or equal to those of the initial reactants (31). This conclusion is further substantiated by studies of the rate of solution of ferro-, para-, and diamagnetic metals in acid (32), and by the formation of ferric chloride from an ether solution of ferric thiocyanate and hydrochloric acid (33).

The preceding survey suggests that a chemical reaction is more likely to be influenced by an alternating electrical field than by a uni-directional electrostatic or magnetic field. In every study where an oscillatory field was used, a definite change in reactivity was found. Obviously the effects were mainly thermal, but in several studies an athermal component was claimed. Only one definite result was obtained with uni-directional fields to show that chemical reactivity might be notably changed by such fields; and in this particular study the reaction chosen (allyl bromide plus hydrogen bromide) is now known to produce anomalous results, the degree of anomaly depending upon experimental conditions.

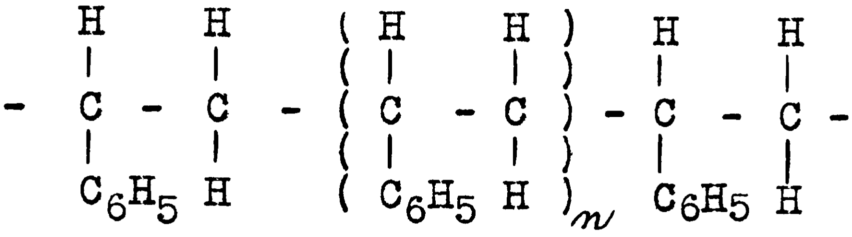
An oscillatory electrical field has been used in the present study, the reaction chosen being the polymerization of styrene in the liquid phase. This reaction was selected for two reasons: the kinetics of the reaction have been more thoroughly investigated than for other polymerizations; also two reports of studies have been published where claims are made that an electrical field has produced a significant change in the reaction. However it must be remembered that both of these studies were made with little or no emphasis placed on temperature control, so that the results may have been due to thermal effects only.

The program for the present investigation included a study of the effects of radio frequency electrical fields on the polymerization of styrene in the liquid phase, which is often termed "bulk phase". It will be shown that particular care was taken to equalize the temperatures of the field and control samples. Hence, any field effect found should presumably be the result of athermal, rather than thermal effects, of the applied field.

In addition to control over the temperature of reaction, the present study differs from others in that radio frequencies have been used in contrast to the very low and very high frequencies reported in the literature. The field strengths used were much lower than those used by Liechti (8) in his work on styrene polymerization.

Polymerization of Styrene

According to Staudinger (34) polystyrene consists of long chain macromolecules which are formed as a result of styrene molecules being joined by primary valences through their vinyl groups.



$$\begin{array}{ccccccccccc} & H & & H & & \big(H & & H \big) & & H & & H & \\ & | & & | & & \big(| & & | \big) & & | & & | & \\ - & C & - & C & - & \big(C & - & C \big) & - & C & - & C & - \\ & | & & | & & \big(| & & | \big) & & | & & | & \\ & C_6H_5 & & H & & \big(C_6H_5 & & H \big)_n & & C_6H_5 & & H & \end{array}$$

Recent investigations emphasize the fact that polystyrene is a mixture of macromolecules of different molecular weights, different chain lengths, different internal structures and even different terminal groups.

Polymerization occurs with and without the use of a catalyst, but the temperature required for a reasonable reaction rate is lower when catalyst is used. Use of a catalyst decreases the average molecular weight as also does an increase in temperature of reaction (34). The uncatalyzed reaction at lower temperatures is characterized by an induction period. The overall temperature coefficient for photochemical activation has been found to be approximately 1.3 per 10° C. (35).

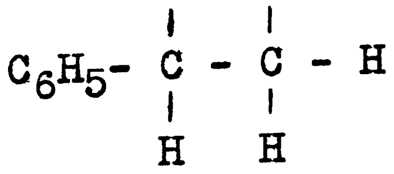
Although the literature on styrene polymerization and on similar reactions is voluminous, there is much not yet understood in regard to the mechanism of the reaction. However, it is generally conceded that the reaction occurs by a chain mechanism consisting of three essential steps. Other steps may or may not occur depending upon experimental conditions. The three essential steps in the formation of polystyrene chains are considered to be: a) activation, or production of nuclei; b) propagation, or chain growth; and c) termination, or cessation of chains. Other possible steps are: chain branching, ring closure and chain transfer (36).

It is thought probable that the activation process of certain monomer styrene molecules can result from thermal collisions, irradiation with light, or with the aid of a catalyst (36). This initiation step may be represented by the equation

$$M_1 \longrightarrow M_1^*$$

where M_1 is a styrene molecule and M_1^* is an activated monomer molecule.

The activation energy for this step is believed to be about 24,000 cal. per mol (37). This corresponds in order of magnitude to the activation energy required to open a double bond between two carbon atoms. Therefore, the activation step may be considered as the formation of radicals or biradicals with free valences on the vinyl group carbon atoms, (38), thus



$$C_6H_5-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}-H$$

Alternatively, the active nuclei may be regarded as styrene molecules containing vinyl group double bonds in an excited electronic state (39).

According to theory the fruitful collision of an active center with a monomer molecule, results in a dimer. This is the first stage of the propagation reaction. The dimer is still a free radical and it continues to grow by successive collisions with monomer molecules. This is represented by the equation

$$M_1^* + M \rightarrow M_2^* \longrightarrow \longrightarrow \longrightarrow \rightarrow M_n^*$$

The activation energy for the propagation step is considered to be much lower than that for initiation. Calculated values for propagation vary from 5,000 to 8,000 cal. per mol (40), and hence, the propagation step is much faster than initiation. It is estimated that the lifetime of a growing chain is less than one-hundredth of a second (40).

Experiment shows that a chain does not continue to grow indefinitely; hence mechanisms have been suggested to account for cessation of chains (41). Among these are: 1) collision of two free radicals to give a neutral chain; 2) chain transfer, by which a hydrogen atom from a monomer molecule is transferred to the chain, leaving the remainder of the monomer as a new active center; 3) ring formation, where a biradical chain free to grow at both ends forms a polymembered ring by the two ends coming together; 4) addition of inhibitor molecules to the chain at its free valences; 5) migration of a hydrogen atom from one end of the chain to the other end resulting in a double bond on the atom originally bonded to the hydrogen atom.

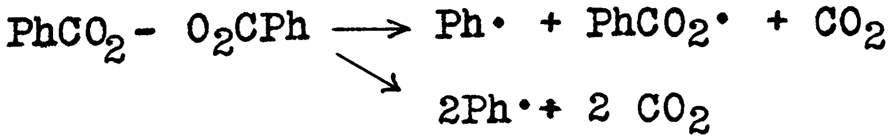
In general the termination step may be represented by

$$M_n^* \longrightarrow M_n$$

There are two general types of catalysts used for accelerating the rate of styrene polymerization, namely, those giving rise to a radical mechanism - peroxides, ozonides and free radicals, and those which are thought to polarize the vinyl double bond and to cause polymerization by an ionic mechanism; in the latter class are compounds such as BF_3, $AlCl_3$, etc.

The standard rate equation, $k = PZe^{-E/RT}$, may be used in comparing the two types of catalytic action with the uncatalyzed reaction. For the peroxide type, E, the activation energy, remains the same - approximately 24,000 cal. per mol. The accelerated rate occurs as a result of an increase in the frequency factor, PZ, from approximately 10^5 to about 10^{11} (42). On the other hand polar catalysts lower the activation e[illegible]y but produce little change in the frequency factor (49).

It is now generally accepted that the decomposition of a [illegible]oxide, such as benzoyl peroxide, yields free radicals as [illegible]own below (43).



$$PhCO_2-O_2CPh \longrightarrow Ph\cdot + PhCO_2\cdot + CO_2$$
$$\searrow 2Ph\cdot + 2\ CO_2$$

In a solvent, such as benzene, recombination of the radicals may occur or they may react with the solvent. In such solvents the half-life of benzoyl peroxide is 55-75 hours at 60°C. and 35-45 minutes at 100°C. (44). In styrene the rate of decomposition is increased several times (45).

As shown in the above equation one molecule of benzoyl peroxide would produce two free radicals capable of initiating a chain. This is substantiated by experimental data which show that the rate of polymerization is proportional to the square root of the catalyst concentration (46). It is also supported by data collected by Price (47) for twenty samples of polystyrene prepared with various peroxide-type catalysts containing atoms such as bromine or nitrogen. He found that on the average there was one catalyst fragment per polymer chain for the low molecular weight polymers used. Similar evidence for ester groups in polystyrene has been found (48).

The simplest propagation reaction is the normal chain growth by which an active center grows very rapidly into a long chain molecule by successive additions of styrene units. When this type of chain is terminated by reaction with a free radical from either catalyst or inhibitor, by reaction with another growing chain, by ring closure, or by migration of a hydrogen atom, one active center is destroyed. If polymerization occurred entirely in this manner, the average molecular weight of the polymer could be calculated by equations derived from formal kinetics. However, a complicating mechanism is usually present, since calculated molecular weights seldom agree with experimental values.

An explanation for this was proposed by Flory (49) and involves a chain transfer mechanism. A simple illustration of this is given in the equation

$$M_j^* + M_1 \longrightarrow M_j + M_1^*$$

where M_j^*, a growing chain of j units, collides with a monomer, M_1, and abstracts a hydrogen atom. Hence M_j is terminated but its reactivity is transferred rather than destroyed. The monomer molecule receiving the radical character then grows into another chain. In this way, one initial active center ultimately may be responsible for the production of several chains. Such chains may contain a smaller number of styrene units per chain than where only one chain results from one active center. Hence, chain transfer may have the effect of decreasing the average molecular weight of the polymer. The experimental conditions that aid chain transfer are not clearly defined, but it is probable that its influence is increased at higher temperatures and at lower catalyst concentrations.

It has been shown that samples of polystyrene prepared at different temperatures have an intrinsically different internal chain structure (49). This difference is explained on the basis of chain branching; the latter occurs where a special step in the formation of a chain creates two or more free valences on one chain end, thus making it possible for the chain to grow in two independent branches. It is found experimentally that branching occurs more frequently as the temperature of polymerization increases (50).

A number of methods are available for the evaluation of molecular weights from physical measurements. Osmotic pressure measurement is considered to give a reasonably accurate value for the number average molecular weight (51). This number average is defined as

$$M_n = \frac{\sum M_i N_i}{N_i}$$

where M_n is the molecular weight averaged over the number of particles, M_i is the molecular weight of particles of chain length i and N_i is the number of particles of chain length i.

The use of osmotic pressure measurements is not suitable where molecular weights must be evaluated for a large number of polymer samples. Hence, viscosity measurements are often used and the molecular weight is evaluated by means of Staudinger's equation (52),

$$M = \frac{N_{sp}}{c\ K_m} , \qquad N_{sp} = \frac{t_p - t_s}{t_s}$$

where M is the molecular weight, N_{sp} is the specific viscosity, t_p and t_s are the flow times for the polymer solution and solvent respectively, c is the concentration of the solution in base mols of styrene per liter, and K_m is a constant.

The viscosity molecular weight multiplied by K_m is approximately equal to the osmotic pressure molecular weight (52). Hence M from Staudinger's equation is considered to give a reasonably accurate measure of the number average molecular weight.

The physical significance of the constant K_m is connected with branching of chains. One would expect on an equal weight basis that straight chain molecules would hinder flow of liquids more than branched chain molecules. Since chain branching becomes more noticeable as temperature of polymerization increases, K_m should decrease with a temperature increase. This is observed experimentally; K_m varies non-linearly from 1.5×10^{-4} at 20° C. to 0.48×10^{-4} at 140°C. (53).

EXPERIMENTAL

AND

RESULTS

Equipment

The main components of the apparatus used in this investigation are shown schematically in Fig. 1. The source of the alternating electrical field, a radio transmitter, is shown on the left side of the diagram. The voltage of the signal from this source is amplified and the amplified voltage is applied across the electrodes of the reaction cell. The magnitude of the potential drop across the latter is measured on a voltmeter.

The Transmitter

The availability of equipment suitable for use as a source of an electrical field of variable frequency and voltage necessarily was a limiting factor in the scope of this investigation. A suitable instrument, which was readily obtainable, was a 60-watt T.W.12 Marconi transmitter. It emits on three discontinuous wave bands from 10 megacycles (30 meters) to 375 kilocycles (800 meters). It requires two sources of direct current: 1500 volts, with a maximum current of 200 milliamperes, for the plate of the power amplifier tube, and 10 volts for the tube heaters. The wiring diagram of this transmitter is shown in Fig. 2.

The plate voltage for the amplifier tube ordinarily is supplied by a 1500 volt motor generator which operates on an input of either 110 or 220 volts D.C. However, these generators were designed for intermittent transmitter operation and

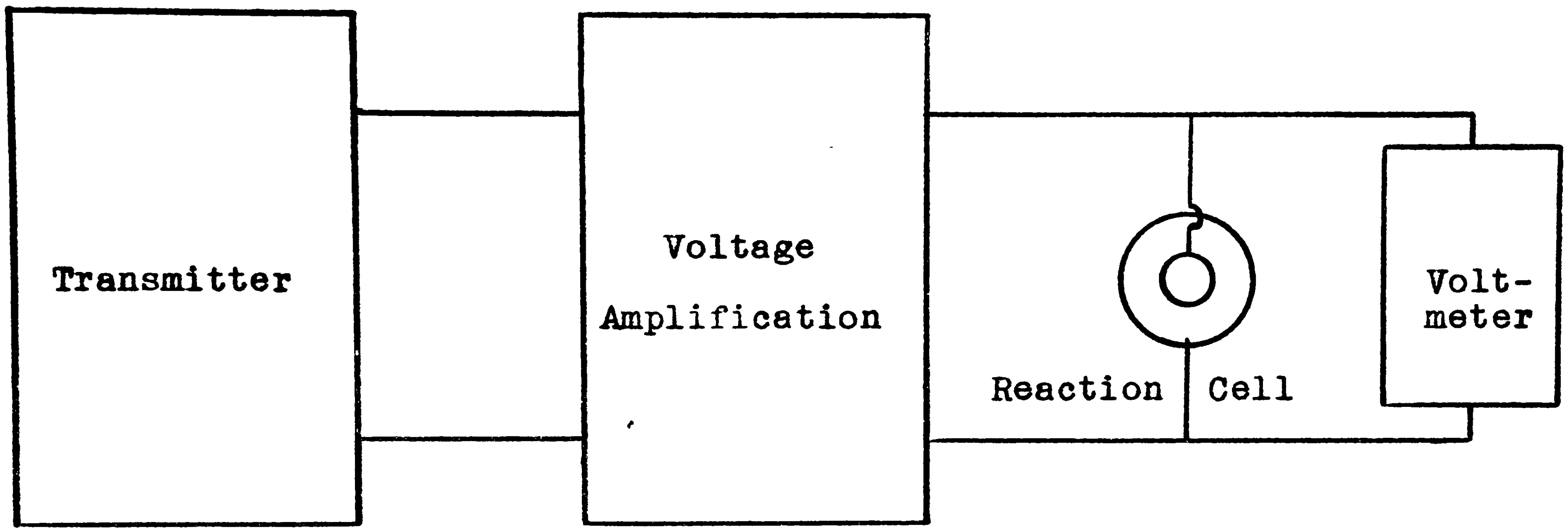
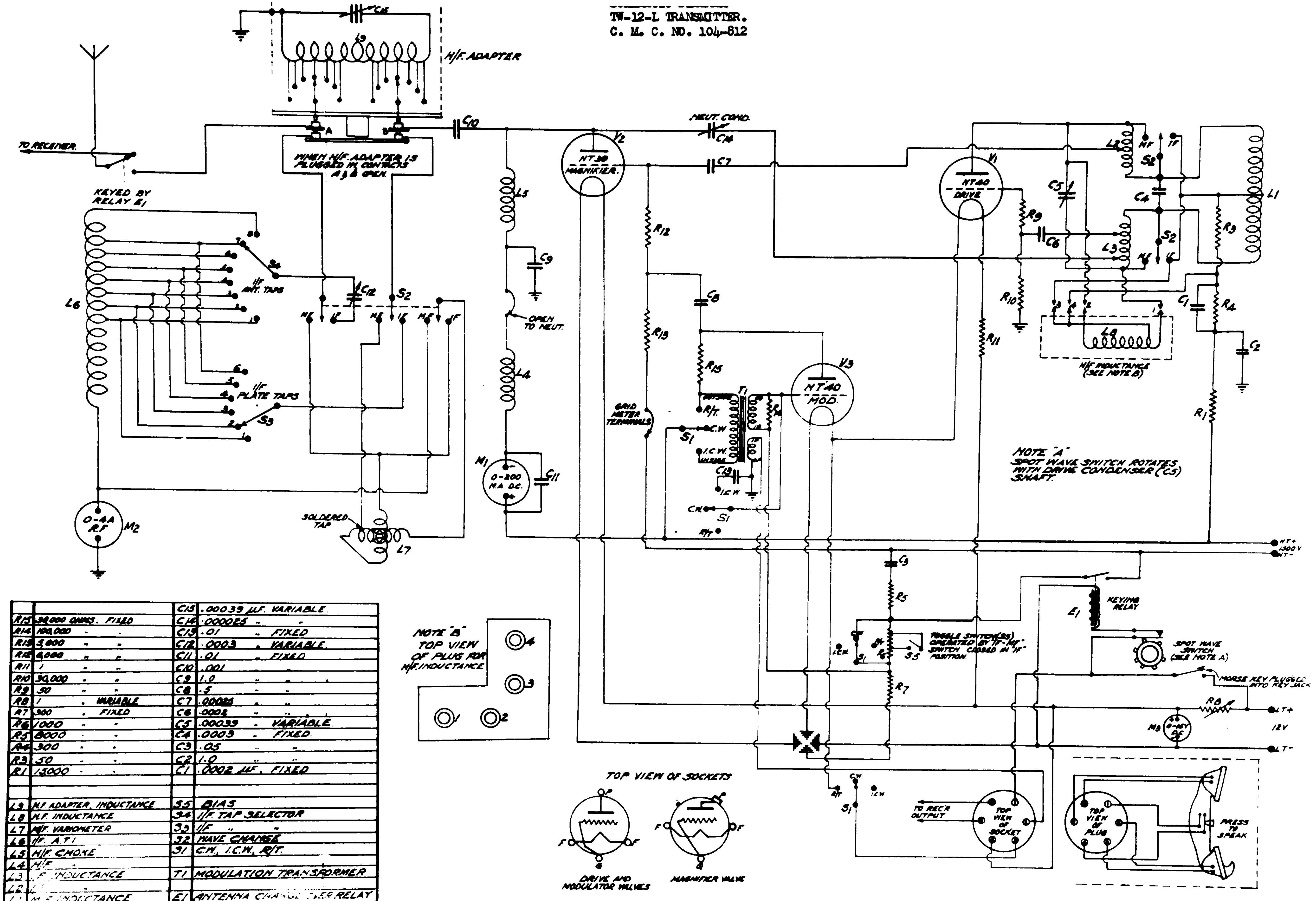


Fig. 1 : Schematic diagram of the components of the apparatus.

TW-12-L TRANSMITTER.
C. M. C. NO. 104-812



NOTE "A"
SPOT WAVE SWITCH ROTATES WITH DRIVE CONDENSER (C5) SHAFT.

NOTE "B"
TOP VIEW OF PLUG FOR H/F. INDUCTANCE

TOP VIEW OF SOCKETS

DRIVE AND MODULATOR VALVES

MAGNIFIER VALVE

		C15	.00039 µF. VARIABLE.
R15	30,000 OHMS. FIXED	C14	.000025 " "
R14	100,000 " "	C13	.01 " FIXED
R13	5,000 " "	C12	.0003 " VARIABLE.
R12	6,000 " "	C11	.01 " FIXED
R11	1 " "	C10	.001 " "
R10	30,000 " "	C9	1.0 " "
R9	50 " "	C8	.5 " "
R8	1 " VARIABLE	C7	.00025 " "
R7	300 " FIXED	C6	.0002 " "
R6	1000 " "	C5	.00039 " VARIABLE.
R5	8000 " "	C4	.0003 " FIXED.
R4	300 " "	C3	.05 " "
R3	50 " "	C2	1.0 " "
R1	15000 " "	C1	.0002 µF. FIXED
L9	H.F. ADAPTER. INDUCTANCE	S5	BIAS
L8	H.F. INDUCTANCE	S4	I/F. TAP SELECTOR
L7	M/F. VARIOMETER	S3	I/F " "
L6	I/F. A.T.I	S2	WAVE CHANGE
L5	H/F. CHOKE	S1	C.W., I.C.W., R/T.
L4	H/F "		
L3	[illegible] INDUCTANCE	T1	MODULATION TRANSFORMER
L2	[illegible] "		
L1	M.F. INDUCTANCE	E1	ANTENNA CHANGE-OVER RELAY

LIST OF PARTS

were found to be of too light construction for continuous operation. During the investigation the motor generator was replaced by a 110 volt A.C. power pack.* An added advantage in using this power pack was that it permitted a more stable output from the transmitter.

The frequency of the signal emitted by the transmitter may be altered on any one frequency band by adjustment of the drive tuning condenser (C_5 in Fig. 2). The dial on this condenser is graduated from zero to 180°. A change is made from the medium frequency band (375-500 k.c.) to the intermediate band (1.1-3.2 m.c.) by adjusting the wave change switch (S_2 in Fig. 2). To use the high frequency band (3.8-10.0 m.c.) the H.F. adapter and plug-in inductance must be installed in the transmitter assembly.

The medium frequency band (375-500 k.c.) was not used in this investigation owing to difficulties in suitably adapting this part of the transmitter circuit. The I.F. and H.F. bands were used.

The transmitter is constructed so that the signal output may be changed from code wave to intermittent code wave by adjusting the switch S_1 (Fig. 2). In the I.C.W. position a one thousand cycle modulated wave is superimposed on the carrier wave. In the C.W. position only the carrier wave is emitted.

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*Borrowed from the Department of Electrical Engineering, McGill University, by courtesy of Dr. F. S. Howes.

Originally it was planned to make use of the one thousand cycle modulated wave in measuring and checking the frequency of the field being applied to the reaction cell. This was to be done with a detector-oscilloscope combination.

A battery-operated detector was constructed with a vernier dial on its condenser. With the transmitter operating on intermittent code wave, the detector was tuned until the maximum size of the one thousand cycle wave was visible on the screen of the oscilloscope. The frequency of the signal could then be obtained from the setting of the calibrated vernier dial of the detector. The latter calibration was to be made with an accurate signal generator. However, no signal generator of sufficient output strength was readily obtainable, and therefore this method of measuring the frequency of the field in the reaction cell was not used.

Each of the I.F. and H.F. bands of the transmitter was calibrated directly with a sensitive wave meter*. Hence the frequency corresponding to a setting of the drive tuning condenser was known.

This method of calibration provides no means of checking the frequency of the field in the reaction cell during the course of a chemical reaction. However, the frequency emitted by the transmitter may be considered very nearly constant; it

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*Borrowed from the Department of Electrical Engineering, McGill University.

is governed by the physical constants of the oscillator in the transmitter assembly and not by changes in the circuits external to the transmitter, such as a change in dielectric constant in the reaction cell as the reaction progresses from reactants to products.

In Table I are given calibration data for the I.F. and H.F. bands of the transmitter. Measurements on the wave meter were made for seven positions spaced over the 180° range of the drive tuning condenser of the transmitter (C_5 in Fig. 2).

TABLE I

FREQUENCY CALIBRATION FOR I.F. AND H.F. BANDS OF T.W. 12 MARCONI TRANSMITTER # 337

H. F. Adapter # 344   Plug-in Inductance # 362

Setting on Drive Tuning Condenser	Frequency (I.F. Band)	Frequency (H.F. Band)
180°	1.15 m.c.	3.75 m.c.
150	1.21	4.05
120	1.37	4.47
90	1.55	5.08
60	1.84	6.01
30	2.39	7.72
0	3.21	10.0

A considerable portion of the frequency range of the ransmitter is in the standard broadcast band. To prevent nterference with radio reception in the neighborhood of the aboratory the transmitter with its assemblage of external ircuits and connections was enclosed in a cage of bronze creening connected to ground.

he Reaction Cell

A reaction cell in the form of a condenser is suitable or the application of an electrical field to a chemical eaction.

The capacity of a condenser depends directly on the areas f the electrodes and varies inversely with the distance beween them. The capacity is also directly proportional to the ielectric constant of the insulator between the electrodes.

The potential difference that appears across a condenser n a circuit with set operating conditions is inversely proortional to the capacity of the condenser. Hence, for a paricular applied voltage the field strength in a condenser-type eaction cell is governed by the dielectric constant of the rection medium.

Part of the work done by the field in displacing the elecrical centers of the molecules of the dielectric appears as eat. This heat, called dielectric heating, is related directly o the frequency of the applied field.

In the following approximate formula (54)

$$P = 1.4\ fE^2e'' \text{ watts per cu. in.}$$

P is the heat power, f is the frequency in megacycles per second, E is the voltage gradient in kilovolts r.m.s. per inch, and e" is the loss factor. A change in e", the product of the dielectric constant and the power factor, involves an accompanying change in voltage and current.

It is apparent that the application of a radio frequency field to a chemical reaction will result in a temperature rise in the reaction mixture. The inability to maintain constant temperature is of course undesirable for a kinetic study. However, this difficulty was resolved by constructing a cell with maximum cooling surface, and then developing a suitable experimental procedure, which is described later, whereby the temperature rise that did occur was effectively eliminated as a significant source of error in the data obtained.

A number of conflicting factors must be balanced in constructing a suitable reaction cell. On the one hand, the cell must have the largest cooling surface possible and its volume must be large enough to permit sampling as the reaction proceeds without the amount withdrawn being a significant portion of the total volume. On the other hand, for reasons to be described later, the capacity (as a condenser) must be as small as possible.

A number of designs for a reaction cell were tried; the final model, which was used throughout the investigation is shown in Fig. 3. It is externally and internally cooled and it presents only a glass surface to the reaction mixture.

The cell consists of a two-sectional pyrex glass envelope which is joined by a 50/50 ground glass joint. The lower section of the cell has a hemispherical bottom, and this hemisphere, together with the bottom part of the cylindrical cell wall, is covered with silver foil; this constitutes the grounded electrode of the cell. The inner electrode is a thin layer of mercury contained in the space between the outer two glass walls of the cooling finger. The latter is held in place in the center of the cell by being sealed into the top section of the ground glass joint. Through this top section also are sealed thermometer and stirrer wells. Electrical connections to the two electrodes of the cell are made by clipping leads to the two wires shown in the diagram. In constructing this cell particular care was taken that the inner electrode was exactly centered and that the thickness of the annular space between the two electrodes was symmetrical.

The volume of the cell between the two electrodes is 40.5 ml. Its capacity as a condenser is 7.9 micro micro farads with pure styrene as the dielectric.*

This reaction cell has been found satisfactory in that it has withstood voltages up to the maximum obtainable from the

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* This measurement was made on a capacity bridge by courtesy of Mr. H. J. Johnson.

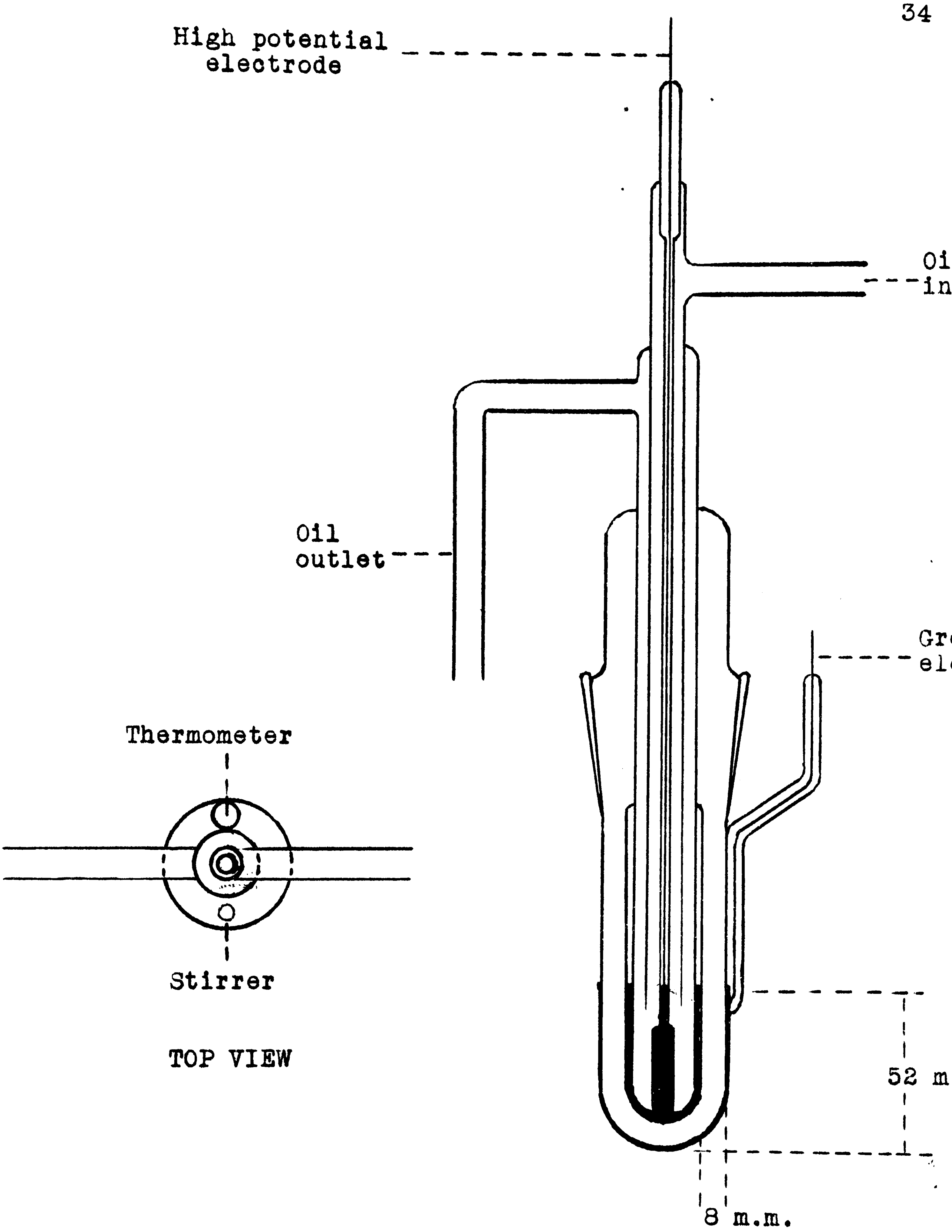

Fig. 3 : Reaction cell

transmitter and it is likely that the cell would give no difficulty in using considerably higher voltages. Dissipation of the heat due to dielectric loss was reasonably good, and the rise in temperature of the reaction cell gave no undue trouble.

Calculation of the Field in the Reaction Cell

It is apparent from Fig. 3 that the voltage gradient between the inner electrode (mercury layer) and the outer electrode (silver foil) is applied across a series of three dielectrics: pyrex glass, reaction mixture, and pyrex glass. Hence the applied potential is not the potential across the reaction mixture. However, a correction factor may be calculated to obtain this potential.*

These calculations apply when styrene is used as the dielectric and employ the dimensions of the part of the cell where the chemical reaction occurs; these dimensions are shown in Fig. 4.

The field strength at any point in the hemispherical part of the cell will be different from that at a similar point in the cylindrical part. Consequently the correction factors are calculated separately, that for the cylindrical part being given first.

Near an infinitely long cylindrical conductor the field

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* The suggestions of Mr. R. L. Clark in the formulation of these calculations is gratefully acknowledged.

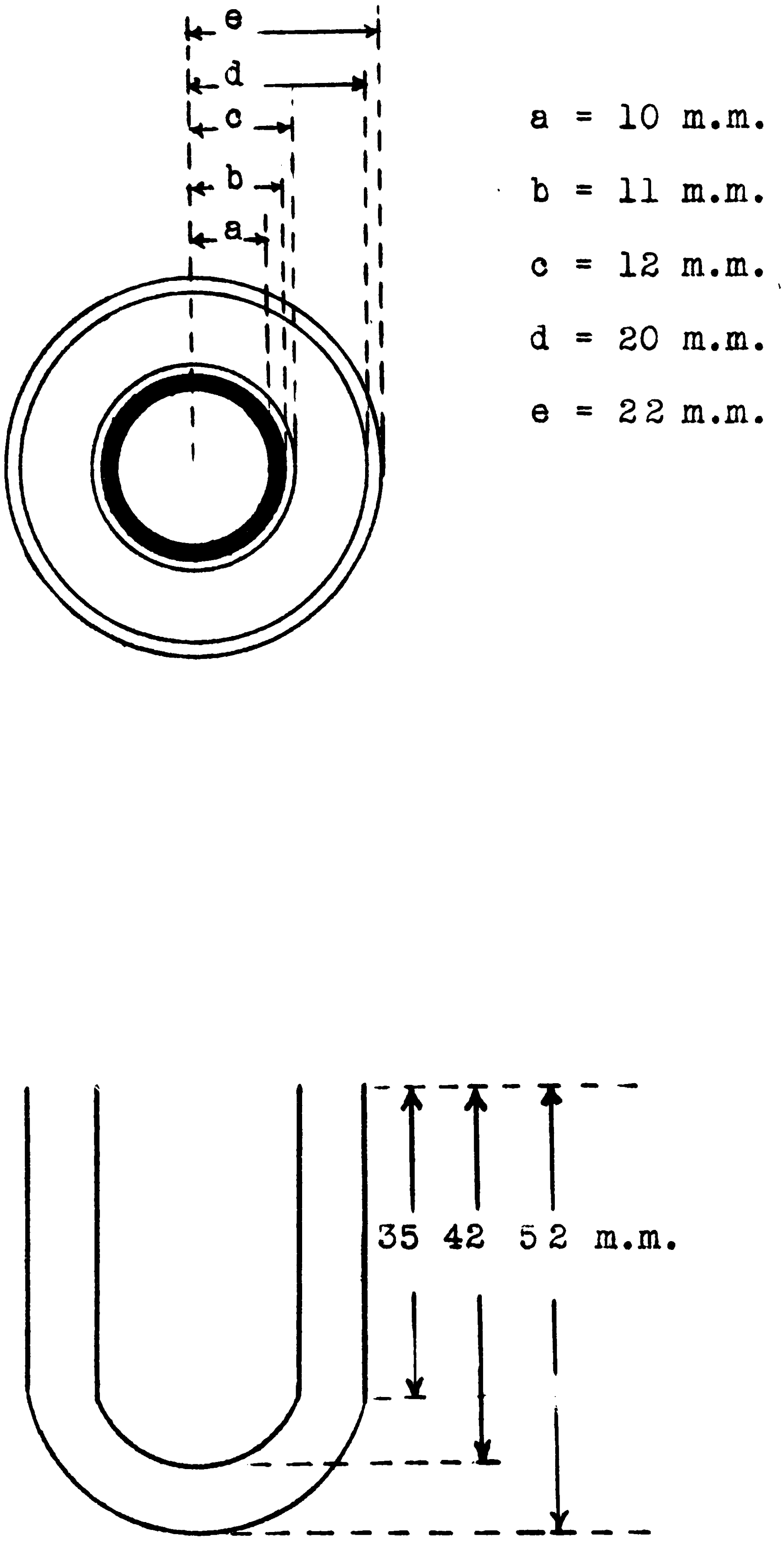

Fig. 4 : Dimensions of condenser portion of reaction cell.

is given by (55)

$$E = \frac{2\sigma}{Dr}$$

where σ = charge per unit length

D = dielectric constant

r = distance from the axis of the cylinder

If the potential difference between the inner and outer electrode is P, then work = P must be done in carrying a unit charge against the repulsion of the field, F.

$$\text{i.e., } P = \int_b^e F(r)dr$$

where b represents the outside of the mercury layer and e the inside of the silver foil.

This integral may be represented by three parts, one for each of the three layers between the electrodes of the cell.

$$\text{i.e, } P = \int_b^c \frac{2\sigma}{D_1 r}\,dr + \int_c^d \frac{2\sigma}{D_2 r}\,dr + \int_d^e \frac{2\sigma}{D_3 r}\,dr$$

where $D_1 = D_3 =$ dielectric constant for pyrex glass

and $D_2 =$ dielectric constant for styrene

Solution of the above gives

$$P = 2\sigma\left(\frac{1}{D_1}\ln\frac{c}{b} + \frac{1}{D_2}\ln\frac{d}{c} + \frac{1}{D_3}\ln\frac{e}{d}\right)$$

On the assumption that D_2 may be taken as constant, then the fraction of P across the region c-d is independent of P; if f_1 is this fraction, then

$$f_1 = \frac{\frac{1}{D_2} \log \frac{d}{c}}{\frac{1}{D_1} \left(\log \frac{ce}{bd} \right) \frac{1}{D_2} \log \frac{d}{c}}$$

for a spherical condenser (56)

$$E = \frac{q}{Dr^2}$$

where q = charge per unit area

and D and r are dielectric constant and

distance from the spherical conductor

$$P = \int_b^c \frac{q}{D_1 r^2}\,dr + \int_c^d \frac{q}{D_2 r^2}\,dr + \int_d^e \frac{q}{D_3 r^2}\,dr$$

$$= q \left(\frac{1}{D_1} \left(\frac{1}{b} - \frac{1}{c} \right) + \frac{1}{D_2} \left(\frac{1}{c} - \frac{1}{d} \right) + \frac{1}{D_3} \left(\frac{1}{d} - \frac{1}{e} \right) \right)$$

Assuming that D_2 may be taken as constant then the fraction of P across the region c-d is again independent of P, and

$$f_2 = \frac{\frac{1}{D_2} \left(\frac{1}{c} - \frac{1}{d} \right)}{\frac{1}{D_1} \left(\left(\frac{1}{b} - \frac{1}{c} \right) + \left(\frac{1}{d} - \frac{1}{e} \right) \right) + \frac{1}{D_2} \left(\frac{1}{c} - \frac{1}{d} \right)}$$

A number of values were found for the dielectric constant of pyrex glass ranging from 4.2 to 4.9. The value used for $D_1 = D_3$ (57) was 4.83 and was supplied by the Corning Glass Company, the manufacturers of the pyrex glass used in the reaction cell. The dielectric constant for styrene, D_2, was taken as 2.48 (58). These values were the best obtainable but were both measured at 25°C. and one thousand cycles per second; hence they can only be regarded as approximate for higher temperatures and frequencies.

Using the dimensions given in Fig. 4 and $D_1 = 4.83$, $D_2 = 2.48$, the following values for f_1 and f_2 were obtained:

$$f_1 = 0.85 \text{ and } f_2 = 0.85$$

It is apparent that an average correction factor of 0.85 may be used; hence the applied voltage multiplied by 0.85 gives the potential difference across the styrene layer on the assumption that the potential decreases as a linear function of distance.

Since the thickness of reaction mixture is uniformly 8 mm., the voltage gradient across the styrene may be expressed in volts/cm. by

$$\frac{P_M \times 0.85}{0.8} \text{ volts/cm.}$$

where P_M is the applied voltage measured on the voltmeter.

It will be noted that the correction factor is approximately unity. By taking into account errors in using low frequency and low temperature dielectric constants at higher frequencies and temperatures, errors in measuring the various dimensions of the cell, and also remembering that the dielectric is not always pure styrene, it is apparent that the applied voltage in volts/cm. may be used as the potential gradient (field strength) in the styrene layer.

Henceforth, except where specifically stated, all potential gradients will be corrected gradients as above and will

The Control Cell*

The control cell is shown in Fig. 5. It contains a 50/50 ground glass joint and is constructed so that its dimensions are similar to those of the reaction cell. Hence the surface to volume ratio is very nearly the same in both cells. Although the "inner electrode" of the control cell is of the same diameter as the inner electrode of the reaction cell, it is not constructed so that oil is circulated through it as is done in the reaction cell. Wells for the thermometer and stirrer were sealed into the top section of the control cell, as in the reaction cell.

Measurement of Temperature

Ordinarily a thermometer bulb and the liquid in which it is immersed are in thermal equilibrium, and heat exchange between the liquid in the bulb and the liquid in the bath occurs rapidly through the thin glass interface.

However, in an alternating electrical field both the bulb and the bath liquid are heated; hence the volume change in the stem records the change in temperature of both liquids. If the recorded temperature is taken as the temperature of the bath liquid, a slight error is introduced. The magnitude of this error depends upon the electrical properties of the liquid used

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*The term "reaction cell" is used henceforth as pertaining to the cell where the chemical reaction is subjected to the applied electrical field. The "control cell" pertains to the control reaction where no field is applied.

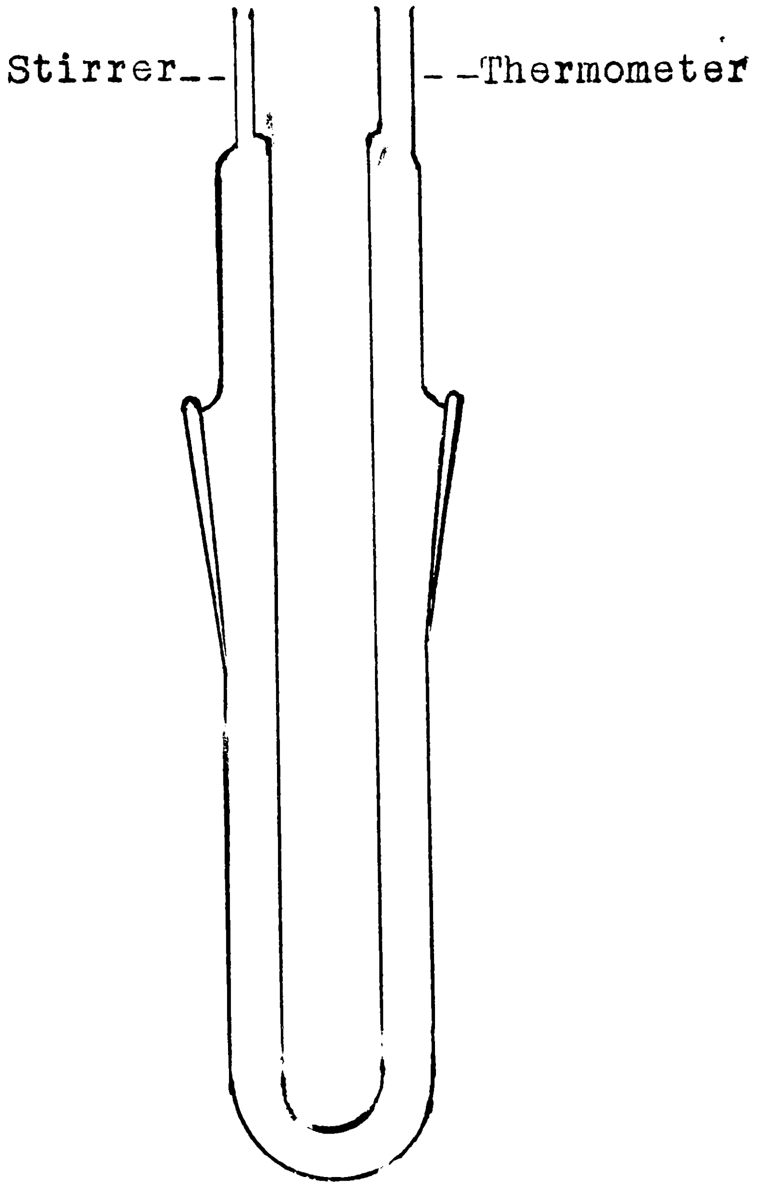

Fig. 5 : Control cell

in the bulb of the thermometer.

Therefore a suitable choice for a thermometer for measuring temperature in the reaction cell was one using a liquid not appreciably affected by the field. The one selected was a 0-110°C. alcohol thermometer, since an error of not more than 0.01°C is introduced in using this type of thermometer in a radio frequency field (59).

Two tests were made in a 3000 volts/cm. field at 1.55 megacycles with styrene in the reaction cell using an alcohol and a mercury thermometer. The latter recorded a temperature rise 0.2°C. higher than the former. It is apparent that even though a mercury thermometer were used the error would not be significant in a study such as the present one.

A 0-110°C. mercury thermometer of length similar to the alcohol one was used in the control cell. The upper ranges of the two thermometers (above 70°C) were found to agree exactly within the limit of error in reading them (± 0.05°).

Only the bulbs of the thermometers were immersed in the reaction mixtures in the cells. However, a stem correction was not considered necessary since the exposed stems were subjected to nearly identical conditions.

The Voltmeter

The potential difference, at radio frequencies, between the two electrodes of the reaction cell must necessarily be measured by a vacuum tube voltmeter. A Barber instrument was used in this investigation; it was equipped with a specially built probe capable of measuring potentials up to 10,000 volts r.f. with an error not exceeding five percent for all frequencies above 100 k.c. but not exceeding 100 m.c.

Voltage Amplification Circuit

Since the project required a study of the effect of voltage variation on reaction rates, etc., it was desirable to be able to obtain across the cell the maximum voltage that could be produced by the transmitter. The average circulating r.f. voltage in the aerial tank circuit of the transmitter is approximately 1200 volts at 1.55 megacycles, but it was found impossible to tap off more than a third of this voltage into the reaction cell circuit without upsetting the tuning capability of the transmitter. Hence, a means was required for amplifying voltage from about 400 volts to whatever maximum could be obtained.

A number of amplification circuits were constructed before the one used at present was developed.* It utilizes a Tesla type auto-transformer coil and is shown in Fig. 6. In this circuit maximum voltage was obtained by tuning the various parts to resonance.

The coil in the aerial tank circuit of the transmitter, i.e., L_1, was originally inside the transmitter assembly, but

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* The writer acknowledges the suggestions and help rendered by Dr. F. S. Howes and Mr. L. A. Geddes in the design of the voltage amplification system.

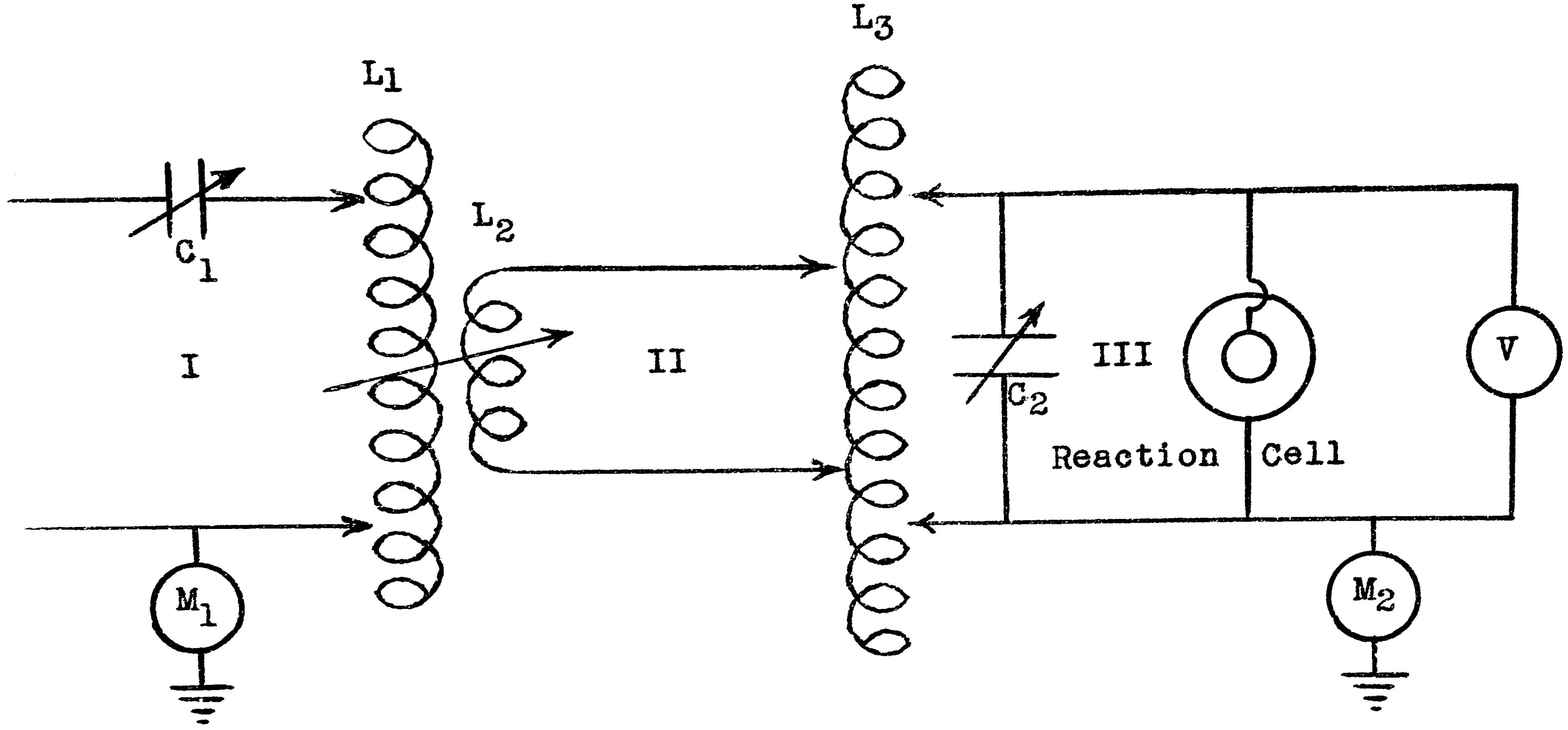

Fig. 6 : Circuit diagram for voltage amplification, showing transmitter stage (I), link circuit (II), and reaction cell circuit (III).

it was removed and mounted in a more convenient position. Circuit I was tuned to resonance at the selected frequency by means of variable taps on L_1, and by the tuning condenser, C_1, using the r.f. ammeter, M_1, as resonance indicator. Circuit II was an untuned link circuit between I and III. Variability in the coupling between L_1 and L_2 was secured by having L_2 mounted on a glass rod along which it could slide. At approximately critical coupling between L_1 and L_2 the maximum transfer of energy occurred.

L_2 was a fixed inductance wound on a porcelain form. The impedance of L_2 was matched with that of the part of L_3 in II to obtain maximum efficiency of energy transfer. That is, about one third of the voltage in L_1, approximately 1200 volts, appeared in circuit II about evenly divided between the two series inductances. The number of turns of L_3, included in II had to be a minimum in order that the turns ratio in L_3 be a maximum. This latter consideration naturally had to be compatible with other characteristics required in circuit II; for example, the fact mentioned above, that the inductance of the part of L_3 in the circuit II had to match approximately the inductance of L_2. But the inductance of L_2 had to be within relatively narrow limits since it had to be capable of being approximately critically coupled with L_1.

The number of turns on L_3 tapped into circuit II was necessarily as large as possible since the turns ratio in L_3

largely determined the maximum voltage across the reaction cell. However the number of turns of L_3 that could be used in III was limited by the minimum capacitance included in the circuit owing to the capacitances of the cell (C_3), tuning condenser (C_2), Voltmeter (V), leads, etc. This capacitance was approximately 25 micro micro farads, and hence, at 1.55 megacycles, the largest inductance that could be tuned in circuit III was approximately 450 micro henries.

At 1.55 megacycles the maximum voltage obtainable across the reaction cell was approximately 5000 volts/cm. with styrene as the dielectric. At this frequency, only one easy means of further increasing the cell voltage was possible and that was to decrease the capacitance of the cell. This could have been done by decreasing the height of the electrodes and hence diminishing the volume of the reaction mixture. Obviously a limit would soon be reached here, since it was necessary to put sufficient liquid in the cell originally to permit sampling as the reaction proceeded, and also to permit immersion of the thermometer bulb in the liquid at the conclusion of an experiment. This suggestion probably would have allowed the cell voltage to be raised to about 6000 volts/cm. However, at voltages in this neighborhood, difficulties in operating the apparatus appeared, e.g., sparking occurred across tuning condensers and between various parts of the transmitter assembly.

The previous discussion has been concerned with describing how the maximum cell voltage was obtained. Lower voltages were achieved readily be manipulating C_2 so that circuit III (Fig. 6) was not tuned to resonance and also by operating with L_1 and L_2 at less than approximately critical coupling.

The total capacitance in the voltage amplification circuit remained practically constant for a given dielectric in the reaction cell, and hence, as the frequency increased, the inductance of the circuit had to decrease following the law

$$f = \frac{1}{2\pi\sqrt{LC}}$$

where f is frequency in cycles per second, L is inductance in henries, and C is capacitance in farads. But a decrease in L meant a decrease in the turns ratio of L_3 and hence a decrease in maximum voltage unless another coil at L_3 with a smaller inductance was used. To a certain extent, this decrease in voltage could be minimized by having a series of coils for L_3 whose inductances gradually decreased to match frequency increases. However, it was found that smaller L_3 coils were not as effective voltage amplifiers as were larger coils giving approximately the same turns ratio.

The maximum voltage across the cell at 10.0 megacycles was about 900 volts/cm. as compared with 5000 volts/cm. at 1.55 megacycles. While the increasing ineffectiveness of a small coil at L_3 probably explains part of the decrease in voltage, the more important reason was undoubtedly the greater inefficiency of the transmitter at higher frequencies, and hence a lower circulating voltage in the aerial tank circuit; such a transmitter as the one used in this investigation was designed for a range of frequencies but was necessarily more efficient in the lower part of the range.

In the circuit shown in Fig. 6 the tuning condenser and reaction cell are connected in parallel. In this way the total voltage across the coil, L_3, is applied across the cell, as well as across the tuning condenser. The sum of the currents through the two condensers is equal to the current in the coil, the size of each condenser current being dependent on the relative capacities of the two. The meter, M_2, in Fig. 6 was used for recording the cell current; this latter was proportional to the potential applied to the cell and at any one voltage the current increased with an increase in frequency.

The Thermostatting System

Experience showed that the heating coils, rheostats, and electrical circuits necessary for maintaining an oil bath at constant temperature could not be placed inside the grounded screened cage, since electrical fields associated with these circuits increased the capacity of the reaction cell so much that the desired voltage could not be obtained. Also, vibrations from stirrer motors, etc. were not desirable in the cage where there were numerous electrical connections carrying high voltages. Accordingly, a small oil bath, in which the reaction cell was immersed, was placed inside the cage and a large thermostatted oil reservoir was built outside of the cage at a level higher than the small bath. Oil flowed from the large bath through a valve and thence through the inner electrode of the cell into the small bath; from the latter it was pumped back to the large one again by means of a small one-twentieth H.P. centrifugal pump.

A device shown in Fig. 7 was designed to keep the oil level constant in the small bath. It consisted of a cylindrical glass float inside a glass tube of slightly larger diameter; the latter was clamped in a perpendicular position in the small oil bath. To the top of the float was attached a wire which dipped into a mercury well. When contact was made through the mercury, i.e., by the float falling, the magnetic circuit of a relay was closed, cutting off the full line voltage to the pump, and the pump operated at slow speed, i.e., with a variable resistance in series with its motor. This resistance was adjusted so that the return flow of oil through the pump to the large bath was slightly less than the gravity flow out of the bath. As the oil level in the small bath passed the desired height, the float rose and the magnetic circuit of the relay was broken; the pump then operated on the full line voltage until the oil level dropped again.

This oil circulation system proved satisfactory and temperatures in the small bath remained constant within ± 0.1°C.

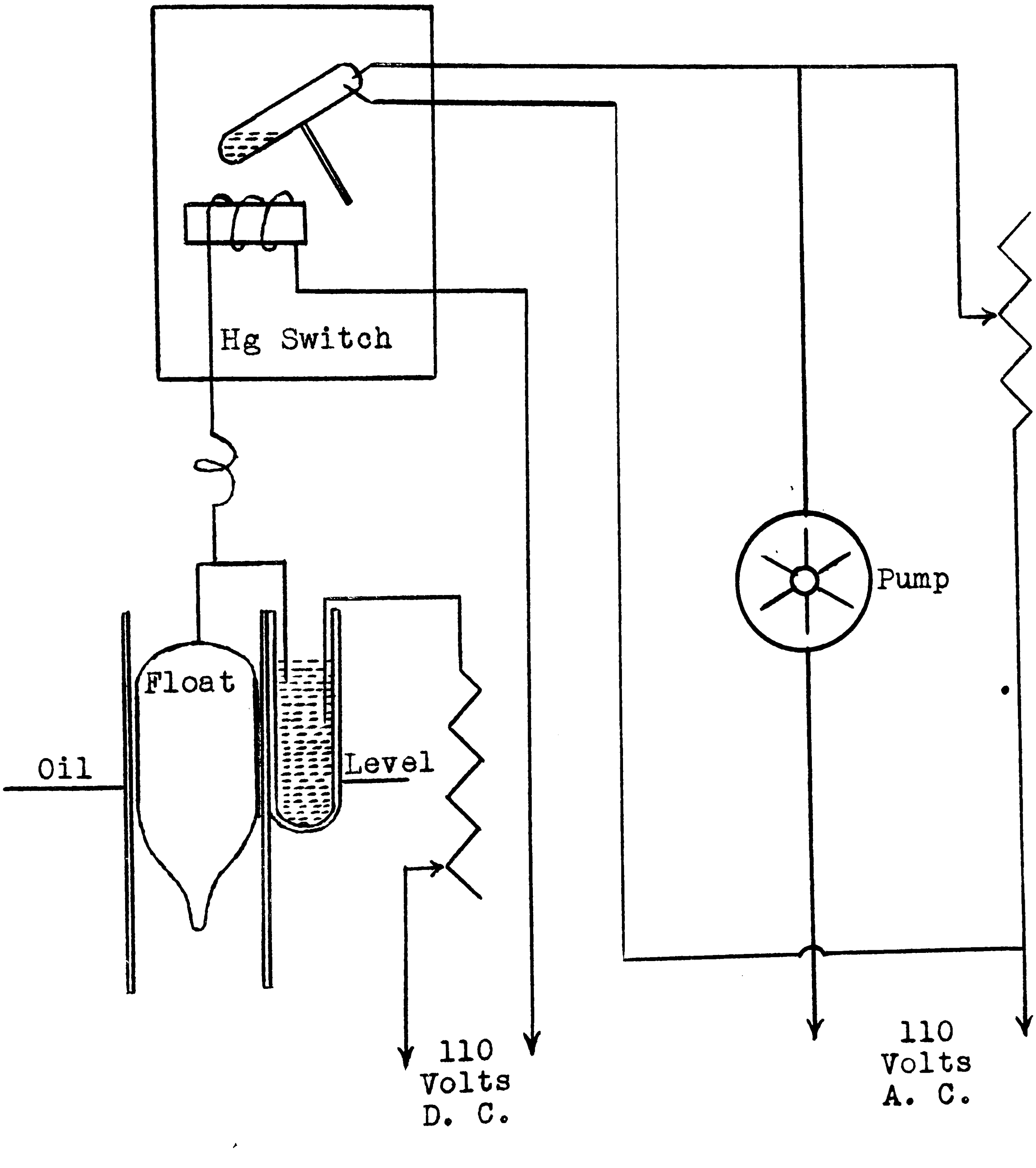

Fig. 7 : Circuit diagram for automatic regulation of oil flow in thermostat.

A small oil bath placed outside of the grounded cage served as a thermostat for the control cell. This thermostat was equipped with a mercury thermoregulator which could be rapidly adjusted to allow the temperature of the control bath to be changed quickly.

Most of the apparatus as described in the foregoing is shown in the photograph in Fig. 8. In the bottom right corner, the front panel of the transmitter may be seen. Above the transmitter is the instrument panel showing condenser dials and radio frequency ammeters. This panel was modified after the photograph was taken. The meters, etc., are part of the voltage amplification circuit. The latter is not shown but is located behind the instrument panel and above the transmitter assembly. The vacuum tube voltmeter is shown through the open doorway in the top center of the cage. Behind the voltmeter is located the small oil bath in which the reaction cell is immersed while the field is being applied. Only the bottom part of the case of this oil bath is visible through the open door in the lower left of the cage. This bath is shown on top of the detector. To the left of the detector the front panel of the oscilloscope may be seen. The large thermostatted oil bath is shown in the upper left corner of the photograph.

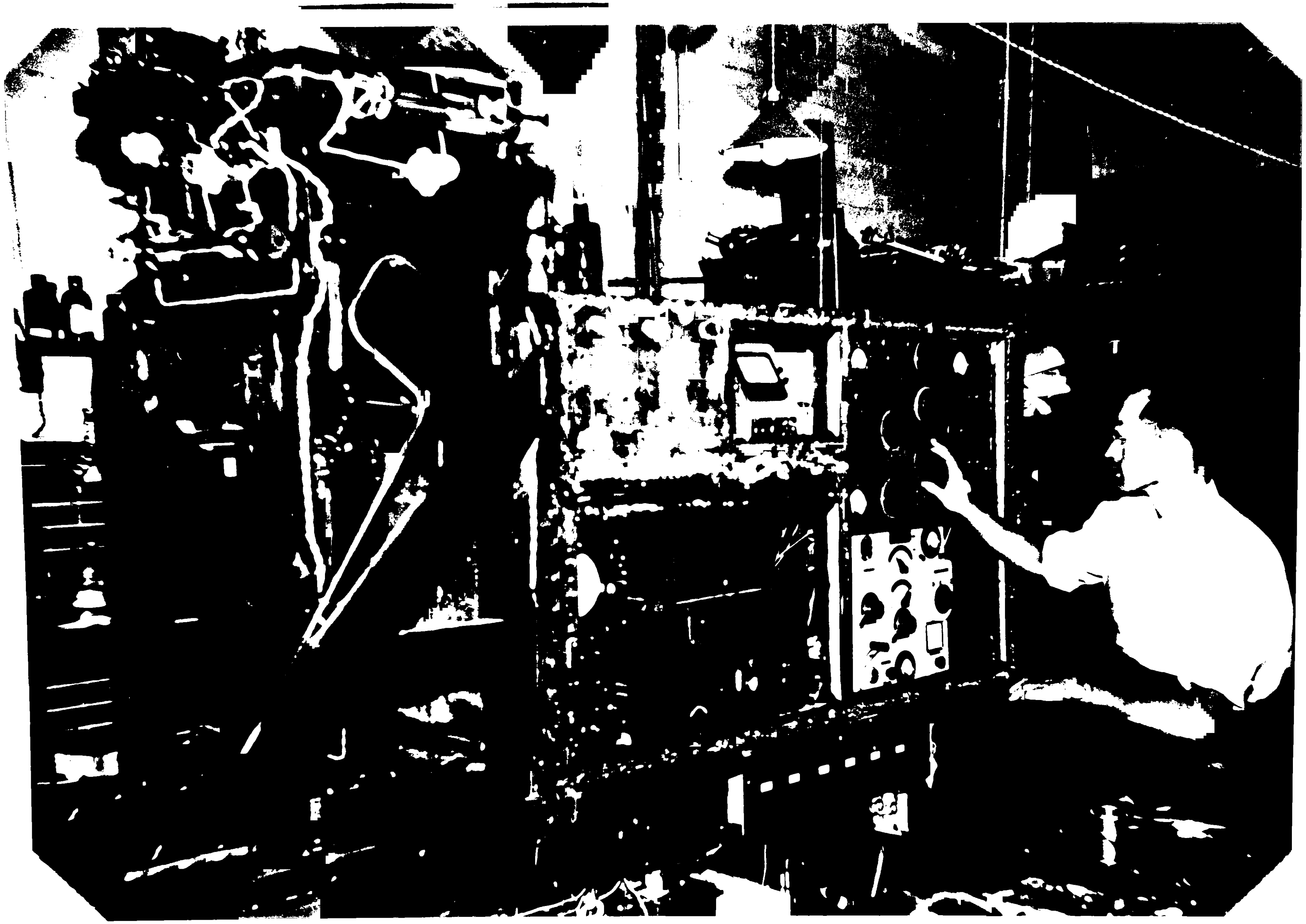

Fig. 8 : Photograph of the apparatus

Reagents

The styrene was obtained by vacuum distillation (b.p.= 28-30°C. at 4-6 mm.) of styrene procured from Polymer Corporation, Sarnia, Ontario. The styrene was usually distilled 15-18 hours before an experiment was started and was stored in a tightly stoppered brown bottle during this time.

The benzoyl peroxide was of analytical grade purchased from Eastman-Kodak Co., Rochester, N.Y.

The toluene used in the study of the decomposition of benzoyl peroxide was a distilled product (b.p.= 110°C. at 760 mm.) of U.S.P. toluene.

The benzene used was Merck's thiophene-free Benzol and the methanol was U.S.P.

Analytical Methods

Percent Conversion

A weighed sample of styrene plus polystyrene (1.0-1.5 grams) was dissolved in 10 ml. of benzene (containing a trace of hydroquinone) in a weighed 100 ml. beaker. The polystyrene was precipitated by addition of 50 ml. of methanol. The liquid was evaporated in a vacuum oven at 65°C. and the polymer dried to constant weight.

This method of dissolving the polystyrene and then precipitating it produced an amorphous polystyrene that was easily dried to constant weight. Drying of polystyrene plus styrene without added benzene and methanol was found unsatisfactory in that a gum formed before all the styrene was evaporated, this gum being difficult to dry.

Refractive Index

The results of the percent conversion analyses were not known until the second day following an experiment; but an approximate measure of the percent conversion was obtained during an experiment by refractive index measurements. These did give a relative measure of the differences between control and field reactions, but were unreliable past 30-35 percent conversion.

The refractive index - percent conversion relation is shown in Fig. 9, where the increased degree of scattering of the points is apparent for conversions greater than 30 percent.

Molecular Weights of Polystyrene

The viscosity method was used, and employed an Ostwald-type

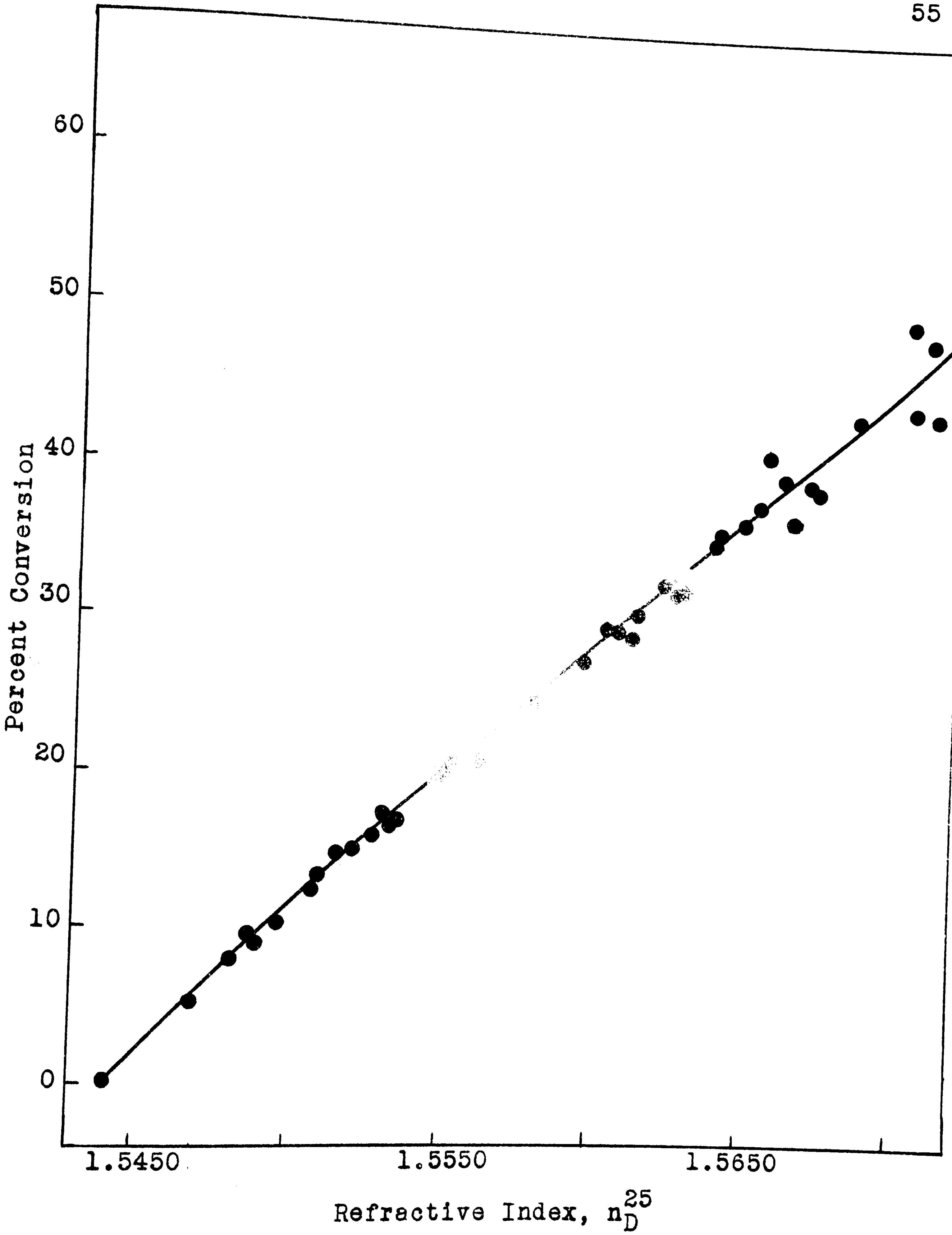

Fig. 9 : Relationship between percent conversion and refractive index for polymerization of styrene using benzoyl peroxide as catalyst.

viscosimeter with a flow-time for benzene of approximately 180 seconds.

The dried polymer samples from the percent conversion analyses were dissolved in benzene and the flow-times determined relative to that for benzene. The concentrations of the polymer solutions were determined by evaporating 50 ml. of the solutions to constant weight in weighed 100 ml. beakers.

Molecular weights were calculated by means of the Staudinger equation (52). The values of K_M for the three polymerization temperatures used were 0.75×10^{-6}, 0.64×10^{-6}, and 0.54×10^{-6}.

Procedure

In general, the procedure involved two simultaneous experiments, one being subjected to the oscillatory r.f. field of a selected voltage and frequency and the other one acting as a control. Every effort was made to have all details exactly the same in the two experiments except for application of the field to the reaction cell.

Before an experiment was begun at a selected frequency the transmitter and voltage amplification system were adjusted with the reaction cell in the latter circuit (Fig. 6) so that the proper taps on the coils could be chosen to give tuned circuits. This involved tuning the transmitter by proper selection of the taps on L_1 and adjustment of C_1 to give a feed current in the range 50-80 milliamperes on M_1. The coupling between L_1 and L_2 was set approximately for the voltage desired; then suitable taps on L_3 were chosen so that the reaction cell circuit could be tuned by means of the variable condenser, C_2. It was necessary to re-tune each of the circuits I and III by making minor adjustments whenever a slight change was made in any one circuit.

A change in frequency or a change in the reaction mixture in the cell required the above adjustments; but a change in field strength from one experiment to another using the same dielectric material could usually be made by slight adjustments on C_1 and C_3 to obtain the desired voltage.

Very little control was possible over the cell current as measured on the thermal ammeter, M_2, This current was proportional to the frequency at any one voltage and to the voltage for a set frequency. Usually the taps selected to obtain maximum voltage gave a minimum cell current in any one experiment.

In the study on the polymerization of styrene the effect of the applied field was measured by a comparison of the reaction rates in the control and field reactions. However, for some experimental conditions, the reaction is subject to an induction period which is not always re-producible.

To avoid differences in the rates which might be due to factors extraneous to the field effect, the field was not applied until reaction in both cells had progressed to approximately 5-10 percent conversion.

Several hours before an experiment was to be started, the reaction and control cells with thermometers, etc., in place were immersed to more than half their depth in a thermostatted oil bath set for the selected temperature. A quantity of oil, similar in amount to that remaining in the inner electrode of the reaction cell, was put into the "inner electrode" of the control cell and the open end of the latter electrode was stoppered. The cells were usually left in the thermostat overnight so that ample time was allowed for attaining thermal equilibrium.

The experiment was started by adding 40.5 ml. of pure styrene plus the selected amount of catalyst to the reaction cell. Fifteen minutes later a similar volume of the same reaction mixture was added to the control cell. The reactants were not stirred during this thermal treatment. The approximate percent conversion was ascertained at intervals of time by measuring the refractive index of small samples of the reaction mixture withdrawn through the thermometer wells.

Experience showed that the time required in most experiments for the conversion to reach or exceed 5-10 percent was three hours at 70°C., two hours at 80°C. and half an hour at 100°C. These were the usual periods of time used, but for small or no catalyst concentrations periods of up to seventeen hours were used.

At the end of the thermal treatment for the reaction cell a sample was withdrawn for a gravimetric percent conversion analysis. Then the cell was removed from the control thermal bath and was transferred to the small oil bath inside the cage. The temperature of this bath was similar to that of the control thermostat. The oil flow and the stirrer were started and the cell was connected to the voltage amplification circuit. The transmitter was switched on and any slight adjustments necessary were made on C_2 (Fig. 6) to obtain the desired voltage. Approximately one and one half minutes were required to transfer the cell and apply the field.

Reaction cell temperatures were recorded every minute for approximately the first eight minutes and then less frequently until the maximum temperature rise was reached. This was usually attained within fifteen minutes of the field being applied; after this time the cell temperature was recorded at fifteen minute intervals.

The fifteen minute difference in starting times was arranged so that the maximum temperature rise was attained in the reaction cell before the preliminary thermal treatment time for the control cell had elapsed. At this time a sample of reactants was withdrawn from the control cell for gravimetric determination of percent conversion. The thermoregulator of the control bath was then adjusted so that the temperature in the control cell rose in a manner analogous to that in the reaction cell. This temperature change was facilitated by use of an adjustable rheostat in series with the control bath heater and also by use of a supplementary heater when required.

The temperature of the reactants in the control cell was recorded in a manner similar to that for the reaction cell. Once the two temperatures were equalized, which usually required less than fifteen-twenty minutes, only slight adjustments were required to keep them equal.

During the remainder of the experiment samples for percent conversion analyses were withdrawn from each of the two cells at regular intervals.

Fig. 10 depicts a typical temperature rise due to dielectric heating, and is also a typical illustration of the degree of success in duplicating the field cell temperature in the control cell.

It is clear from Fig. 10 that the temperatures recorded by the calibrated thermometers in the two cells may be considered essentially equal during an experiment. However the temperatures in the two cells were only equal if the thermometer exposed to the field recorded the true temperature of the reactants in the field cell.

It has been stated that an alcohol thermometer was used because of the very slight effect of the field on this type of thermometer; the error in the temperature recorded in a radio frequency field is reported to be considerably less than the error in reading the 0-110°C. thermometer used.

Further proof that there was no appreciable error in the reaction cell temperature was obtained in tests made in this investigation. As previously described, thermometers, using such widely different materials as alcohol and mercury, recorded approximately the same amount of dielectric heating with styrene as the dielectric at a potential gradient of 3000 volts/cm. and at 1.55 megacycles. Also it was noted during several experiments that no drop in reaction cell temperature was noticeable for a few seconds after switching off the transmitter. The fall in temperature that did occur shortly after the field was stopped naturally was due to cooling by the thermostat.

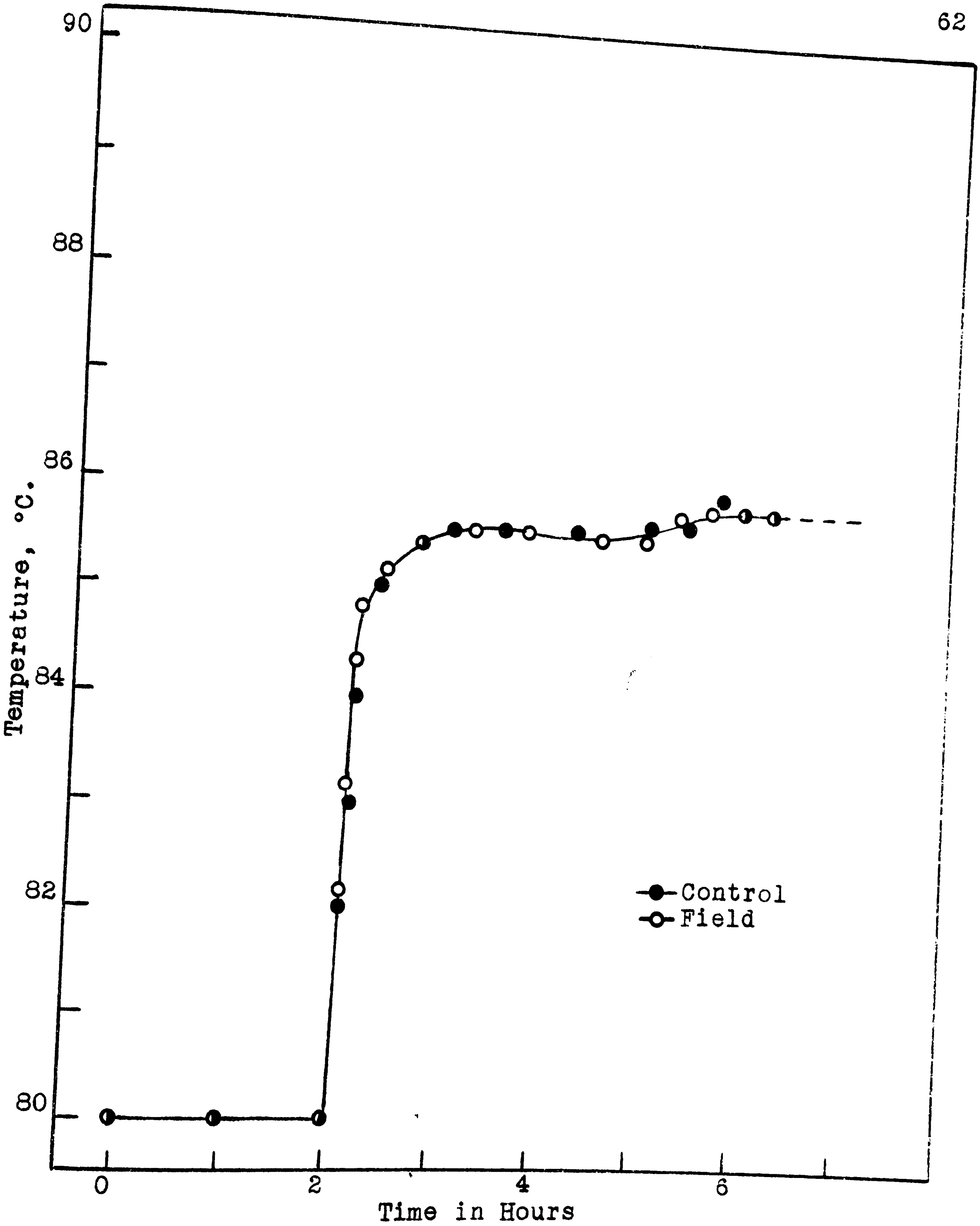

Fig. 10 : Example of temperature rise caused by dielectric heating, and of typical duplication of field cell temperature in control cell; 3000 volts/cm.; 1.55 megacycles; 2.182 gms. of benzoyl peroxide per liter of styrene; average temperature = 85.6°C

It is of interest to note at this point that a similar method of measuring the temperature rise due to dielectric heating was used in a study of the effect of an ultra-high frequency field on the polymerization of chloroprene (10).

It is evident that the alcohol thermometer was not appreciably influenced by the applied field, and, hence, it recorded the true temperature of the reactants in the reaction cell.

It is clear that in this investigation the temperatures may be considered as essentially equal during an experiment.

In addition to the fact that the field was applied only to the reaction cell, one other known difference did exist between control and field reactions. This arose because of the necessity to thermostat the reaction cell in order to dissipate the heat due to dielectric loss.

In the reaction cell the outer and inner walls were cooler than the reactants in the annular space. However, the oil in the inner electrode was approximately one degree hotter than the oil around the outer electrode.

In contrast to the temperature gradients indicated for the reaction cell, where both walls were cooler than the reactants in the annular space, in the control cell the outer wall was approximately the same temperature as the reactants, while the inner wall was a few degrees cooler than the reactants.

This difference in treatment of control and field samples admittedly may account for a slight difference in reaction rate, but this was minimized by stirring the reactants. This stirring was regarded as reasonably efficient up to 40-50 percent conversion.

The following presentation of experimental data includes one table in which temperatures typical to experiments at 4500 volts/cm. are given. It will be shown that the temperature gradients can account for only a small part of the field effect found.

Results

Preliminary Experiments

Three experiments were made in a study of the effect of a radio frequency field on the polymerization of pure styrene in bulk-phase. In these, the reaction and control cells were immersed in a thermostat at 80.0°C. for approximately sixteen hours before a field of 3000 volts/cm. at 1.55 megacycles was applied to the reaction cell. The progress of the reaction was followed by refractive index measurements.

The results of these three experiments indicated a probable lower rate in the field, than in the control reaction but duplication of results was unsatisfactory. On the supposition that the inexact duplication was due to the unpredictable effects of atmospheric oxygen, one experiment was made in which the two cells were swept out with nitrogen before beginning the experiment and after each sample was withdrawn. However, no special precautions were taken to exclude oxygen from the styrene during its purification by distillation.

Since the results were still not satisfactory, the use of a catalyst was introduced to increase the rate of reaction to such an extent that the effects of oxygen were insignificant.

A catalyst also was advantageous in that a thermal treatment of two hours was sufficient instead of a fifteen hour treatment as in the uncatalyzed polymerization.

Two experiments were made using 0.934 grams of benzoyl peroxide per liter of styrene at 3000 volts/cm. and 1.55 megacycles and reasonably good duplication of the percent conversion data was obtained.

In Table II are shown the percent conversion and temperature control data for these two experiments.

The temperature control between sampling times was regarded as satisfactory, and the duplication of results was such that the rate of polymerization in the field reaction was definitely lower than in the control reaction.

This field effect may be the result of the applied field affecting the mechanism of the catalyzed polymerization, or, more simply, an inhibition in the decomposition of the catalyst into free radicals with a consequent lower rate of polymerization of the styrene. If the latter be the cause of the field effect, the field should influence the decomposition of benzoyl peroxide in other solvents.

Decomposition of Benzoyl Peroxide

The latter possibility was tested by applying a field of 3000 volts/cm.* at 1.55 megacycles to the decomposition of benzoyl peroxide in toluene.

Two duplicate experiments were made using a 0.1 M peroxide solution. A thermal treatment of two hours at 80.0°C., as in the polymerization of styrene, was used before the field was applied to the reaction cell. The average temperature for the two experiments was 83.0°C.

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* This voltage gradient is only approximate

TABLE II

POLYMERIZATION OF STYRENE

0.934 grams of benzoyl peroxide per liter

3000 volts/cm.; 1.55 megacycles

Aver. Temp.= average temperature of control and field reactions after field was applied

Time after field applied (Hours)	Experiment A			Experiment B		
	Aver. Temp.	Hourly Average Temp.	% Conv.	Aver. Temp.	Hourly Average Temp.	% Conv.
0	84.3	*80.0 80.0	11.9 13.1	83.7	*80.0 80.0	12.9 13.0
2		84.1 84.2	22.0 25.2		83.4 83.3	22.5 25.7
4		84.3 84.3	32.0 37.2		83.0 83.2	31.6 35.6
6		84.8 84.6	40.6 48.0		84.0 83.9	39.2 47.6
8		84.7 84.6	52.8 61.3		84.3 84.0	49.5 61.9

---

* The first row pertains to the field reaction and the second row to the control.

Samples of reaction mixture (approximately 3 ml. of solution) were withdrawn, cooled to room temperature in glass-stoppered weighing bottles, and 2.0 ml. of this cooled solution transferred to an Erlenmeyer flask from which the toluene was evaporated rapidly by directing a stream of nitrogen over the surface of the liquid. The solid residue was dissolved in acetone and an excess of potassium iodide added. The iodine liberated according to the equation

$$(PhCOO)_2 + 2KI = 2\ PhCOOK + I_2$$

was titrated with $Na_2S_2O_3$;

$$I_2 + Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

Starch indicator was added just before the end point was reached.

Subtraction of the titer for the sample from the initial titer gave the amount of benzoyl peroxide decomposed.

The experimental data for the decomposition of benzoyl peroxide are given in Table III.

In experiment C, the rate of decomposition was consistently faster in the control than in the field reaction; in experiment D, the opposite was generally true. Hence, the results for C and D were averaged and these averages are shown in Fig. 11.

On the basis of these results it is apparent that an applied field of approximately 3000 volts/cm. at 1.55 megacycles has little or no influence on the rate of decomposition of benzoyl peroxide in toluene.

Hence the decreased rate of polymerization in the field reaction, cannot be explained by inhibition in the rate of

TABLE III

DECOMPOSITION OF BENZOYL PEROXIDE

0.1 M solution in toluene

3000 volts/cm.; 1.55 megacycles

Time after exp. started in thermostat (Hours)	Experiment C		Experiment D		
	Hourly Aver. Temp.	% Decomp.	Hourly Aver. Temp.	% Decomp.	Aver. % Decomp.
1	*80.0	8.4	*80.0	9.7	9.1
	80.0	11.1	80.0	8.9	10.0
x 2	80.0	20.7	80.0	22.8	21.8
	80.0	22.0	80.0	19.1	20.6
3	82.9	32.7	82.8	31.6	32.2
	82.9	35.3	82.8	29.2	32.3
4	82.9	44.6	83.0	42.2	43.4
	83.0	44.8	83.0	41.2	43.0
5	83.2	49.2	82.9	50.8	50.0
	83.3	51.6	83.0	51.5	51.6
6	83.6	54.9	83.3	56.8	55.9
	83.7	57.9	83.3	57.2	57.6
7	84.5	58.9	83.3	62.3	60.6
	84.2	-	83.2	61.2	61.2

x - field applied after two hours in thermostat.

* - the first row pertains to the field reaction and the second row to the control.

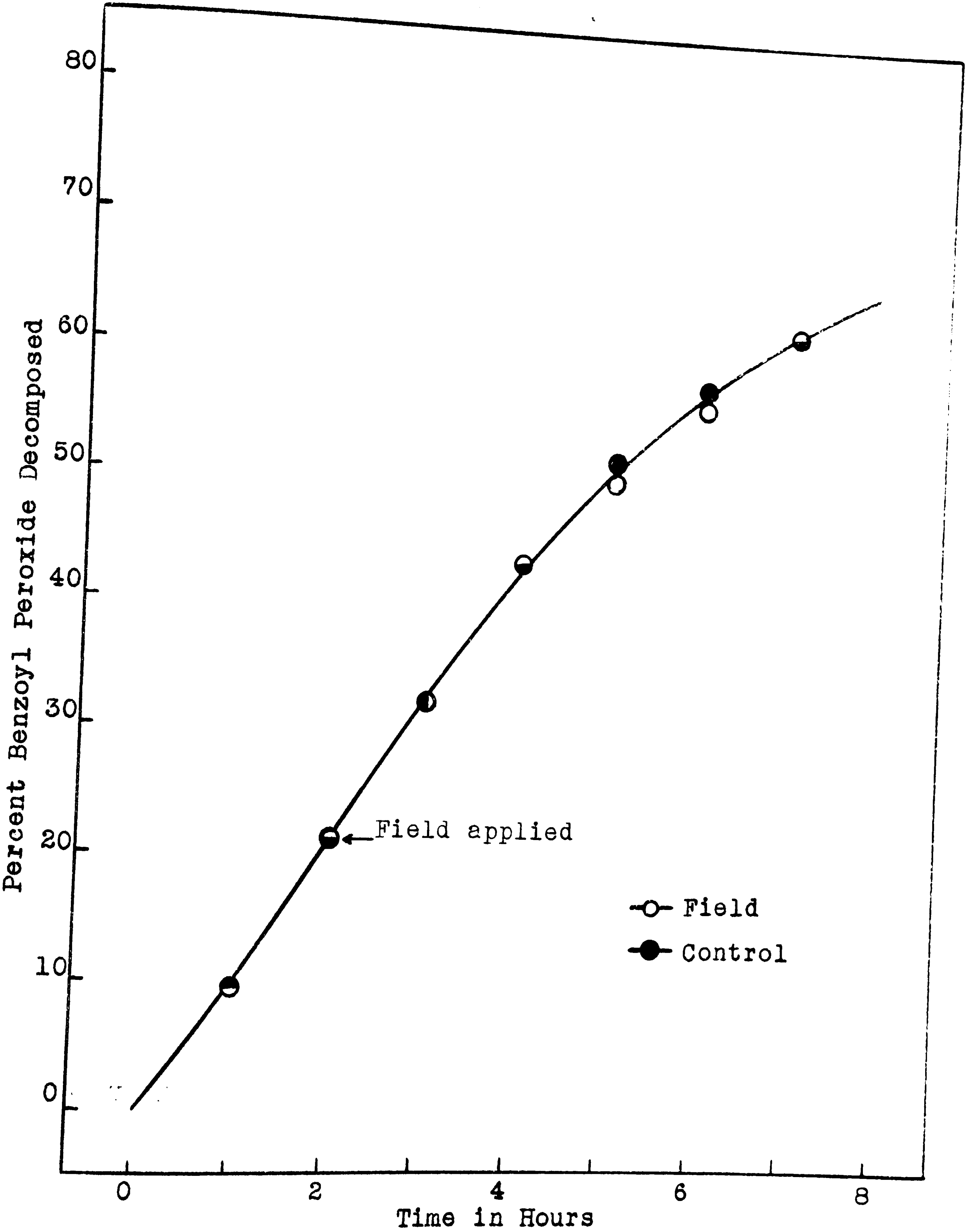

Fig. 11 : Rate curves for field and control samples for decomposition of benzoyl peroxide in toluene; 3000 volts/cm.; 1.55 megacycles; 24.33 gms. of benzoyl peroxide per liter of toluene; average temperature = 83.0°C.

decomposition of the catalyst. The explanation may involve a modification in one or more steps in the mechanism of the polymerization reaction itself.

Further information about the inhibiting effect was obtained in studies relating the field effect with the catalyst concentration, with the potential gradient and frequency of the applied field, and with the temperature of polymerization.

The percent conversion and the average molecular weights were determined with a view to correlating the field effect with one of the three steps essential in the chain mechanism, i.e., with initiation, propagation, or termination of chains.

Dependence of the Field Effect on the Catalyst Concentration and on the Voltage Gradient

Experimental Data

In this combined study voltage gradients of 4500, 3000, and 1500 volts/cm. at 1.55 megacycles, and concentrations of benzoyl peroxide ranging from zero to 2.600 grams per liter, were used.

The data obtained in experiments one to thirteen at 3000 volts/cm. are shown in Table IV. Experiments A and B described previously, are shown as numbers 8 and 9 in this table.

The data for 14-23 at 4500 volts/cm., and for experiments 24-26 at 1500 volts/cm. are given in Table V.

In experiments one and 14 the time of thermal treatment before application of the field was seventeen hours, and for two and 15 it was six hours. In each of the other twenty-two

TABLE IV

POLYMERIZATION OF STYRENE

Compilation of Percent Conversion and Molecular Weight Data

3000 volts/cm.; 1.55 megacycles;

temperature before field applied = 80°C.

Bz_2O_2 Conc. = gm. of benzoyl peroxide per liter of styrene;

Aver. Temp.= average temperature after field was applied;

T.= time in hours after field was applied;

H.A.T. = hourly average temperature;

%C.= percent conversion to polystyrene;

M.W.= average molecular weight of polymer.

Sample III				Sample IV				Sample V			
T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.
3½	86.1	6.5	-	5	86.2	8.4	-	7	86.0	10.6	-
	86.0	10.8	-		86.0	13.9	-		86.0	17.0	-
2	86.4	11.5	-	3	86.0	13.0	-	4	85.1	14.7	-
	86.1	12.6	-		86.1	14.4	-		85.3	17.7	-
2	84.9	9.4	-	3	84.9	11.8	-	4	85.2	14.0	-
	84.8	10.3	-		84.9	12.6	-		85.0	15.3	-
6	84.2	24.8	24100	10	83.5	35.3	-	14	84.3	43.8	29000
	84.0	27.7	26600		83.5	39.6	29200		84.3	48.5	36600
4	86.9	26.0	17700	6	87.6	31.7	16100	8	88.6	39.2	26300
	86.9	29.9	16800		87.7	37.3	17200		88.6	46.3	20000
2	86.2	18.4	-	3	86.9	22.0	-	4	86.4	25.7	-
	86.0	19.3	-		86.7	24.2	-		86.6	28.4	-
4	86.6	29.8	16700	6	86.8	35.2	17500	8	86.4	43.4	18800
	86.6	31.8	16700		86.8	37.6	15900		86.6	47.3	21200
4	84.3	32.0	17900	6	84.8	40.6	18400	8	84.7	52.8	21700
	84.3	37.2	21000		84.6	48.0	18900		84.6	61.3	22200
4	83.0	31.6	18300	6	84.0	39.2	19300	8	84.3	49.5	18800
	83.2	35.6	27400		83.9	47.6	21600		84.0	61.9	15500
4	86.3	36.8	13400	6	86.2	50.0	14100	-	-	-	-
	86.5	44.4	13100		86.3	63.4	16300		-	-	-
2	86.7	29.2	13500	3	87.1	35.0	12500	4	87.6	41.6	12200
	86.7	31.8	10100		86.9	39.5	11700		87.5	48.0	13400
4	84.2	48.8	13100	6	84.5	65.0	14600	-	-	-	-
	84.3	53.6	12400		84.4	77.1	16800		-	-	-
2	85.6	32.5	11000	3	85.5	40.4	12000	4	85.8	48.5	11400
	85.6	35.2	11000		85.6	45.1	11400		85.8	55.2	12900

TABLE V

POLYMERIZATION OF STYRENE

Compilation of Percent Conversion and Molecular
Weight Data

4500 and 1500 volts/cm.;1.55 megacycles
temperature before field applied= 80°C.

Bz_2O_2 Conc.= gm. of benzoyl peroxide per liter of styrene;
Aver. Temp.= average temperature after field was applied;
T.= time in hours after field was applied;
H.A.T. = hourly average temperature;
%C.= percent conversion to polystyrene;
M.W.= average molecular weight of polymer.

	Sample III				Sample IV				Sample V		
T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.
4	86.9	18.8	-	6	87.4	21.9	-	7½	87.0	24.8	-
	87.0	21.2	-		87.3	25.6	-		87.1	29.8	-
2	86.3	8.7	-	3	86.5	10.1	-	4	87.4	11.6	-
	86.0	11.3	-		86.7	13.2	-		87.4	16.6	-
2	83.1	10.8	-	3	84.9	13.2	-	4	84.5	15.6	--
	83.5	11.8	-		84.8	15.4	-		84.8	17.5	-
3	86.1	20.5	15700	4	86.5	22.4	14900	6	86.5	30.7	17800
	86.2	25.6	15700		86.5	31.0	16400		86.3	43.2	18100
2	86.2	25.3	12300	3	86.2	30.7	13300	4	86.1	36.3	16500
	86.0	29.9	12200		86.4	37.3	14000		85.9	45.3	15500
3	87.2	29.0	11700	4	87.5	33.5	11900	5	87.5	40.5	12300
	87.0	37.8	11700		87.4	45.5	12000		87.5	58.2	13100
2	85.3	31.0	11700	3	85.2	37.5	11600	4	85.1	46.5	12300
	85.2	37.3	11700		85.2	46.4	10700		85.1	58.6	13100
2	86.2	29.8	-	3	87.8	35.7	-	4	88.0	39.2	-
	86.0	39.2	-		87.6	44.8	-		88.0	63.0	-
2	86.5	32.2	-	3	85.1	40.7	-	4	85.0	47.0	-
	86.4	42.2	-		85.3	54.3	-		85.1	67.9	-
2	84.0	34.7	10800	3	83.3	43.5	11100	4	83.4	52.9	11700
	84.1	42.2	10100		83.6	53.7	11200		83.3	69.8	11500
3	85.0	25.6	16300	4	85.0	29.6	16800	6	84.9	37.8	17700
	85.1	26.4	16200		85.0	31.0	16500		84.9	39.0	17600
3	85.5	33.6	12800	4	85.6	39.2	16100	5	85.5	46.9	14400
	85.6	-	-		85.4	42.1	14000		85.5	48.7	14400
2	85.0	34.4	10700	3	85.0	42.2	10900	4	85.0	51.1	11800
	85.1	35.3	9600		84.9	43.3	9200		85.0	51.7	11700

experiments a routine two hour thermal treatment was used.

In an experiment, five samples were usually withdrawn from the field cell and from the control cell. The data for each of these five samples are shown in a vertical column which is sub-divided into four columns for the time of sampling, the hourly average temperature, the percent conversion, and the molecular weight. For each experiment the first row contains data for field samples and the second row, data for the control.

An examination of the hourly average temperatures demonstrates the success with which the field cell temperature was duplicated in the control cell. Where the temperatures were slightly different during the interval between the two sampling times, the difference was often reversed between the next two sampling times.

The average temperature reported for each experiment in column three of Table IV and column four of Table V is an average of the hourly average temperatures for both the field and the control reactions. In the twenty-six experiments in this study the lowest average temperature was 83.7°C. and the highest was 87.5°C. The average for the group is 85.5°C.

It was difficult at first to make suitable adjustments on the thermoregulator in the circulating oil system so that the temperature rise due to dielectric heating could be controlled to give an average temperature of approximately 85°C. With experience better control was found possible, but it is obvious from the preceding tables that the average temperature of polymerization from one experiment to another fluctuated considerably.

The temperature rise due to dielectric heating increased with an increase in potential gradient. No significant trend was noted between dielectric heating and catalyst concentration; hence, the temperature rise reported for each voltage gradient is an average value. For the thirteen experiments at 3000 volts/cm., the average temperature rise in the reaction cell was 4.6°C. This value was obtained by averaging the individual values of $T_F - T_{AB}$, where T_F is the average temperature of reactants in the reaction cell after the field was applied and T_{AB} is the average of the temperatures of the oil in the inner electrode and of the oil in the bath around the outer electrode of the reaction cell.

For the ten experiments at 4500 volts/cm. the average rise in temperature calculated by the above method was 6.7°C. and, for the three experiments at 1500 volts/cm., the average temperature rise was 1.7°C.

Influence of the Field on Reaction Rates

All rate curves in this study of the polymerization of styrene start at the time the field is applied.

Rates for the field and control reactions in each of the twenty-six experiments in this group were calculated from the slopes of these curves. An example, experiment eighteen, is given in Fig. 12.

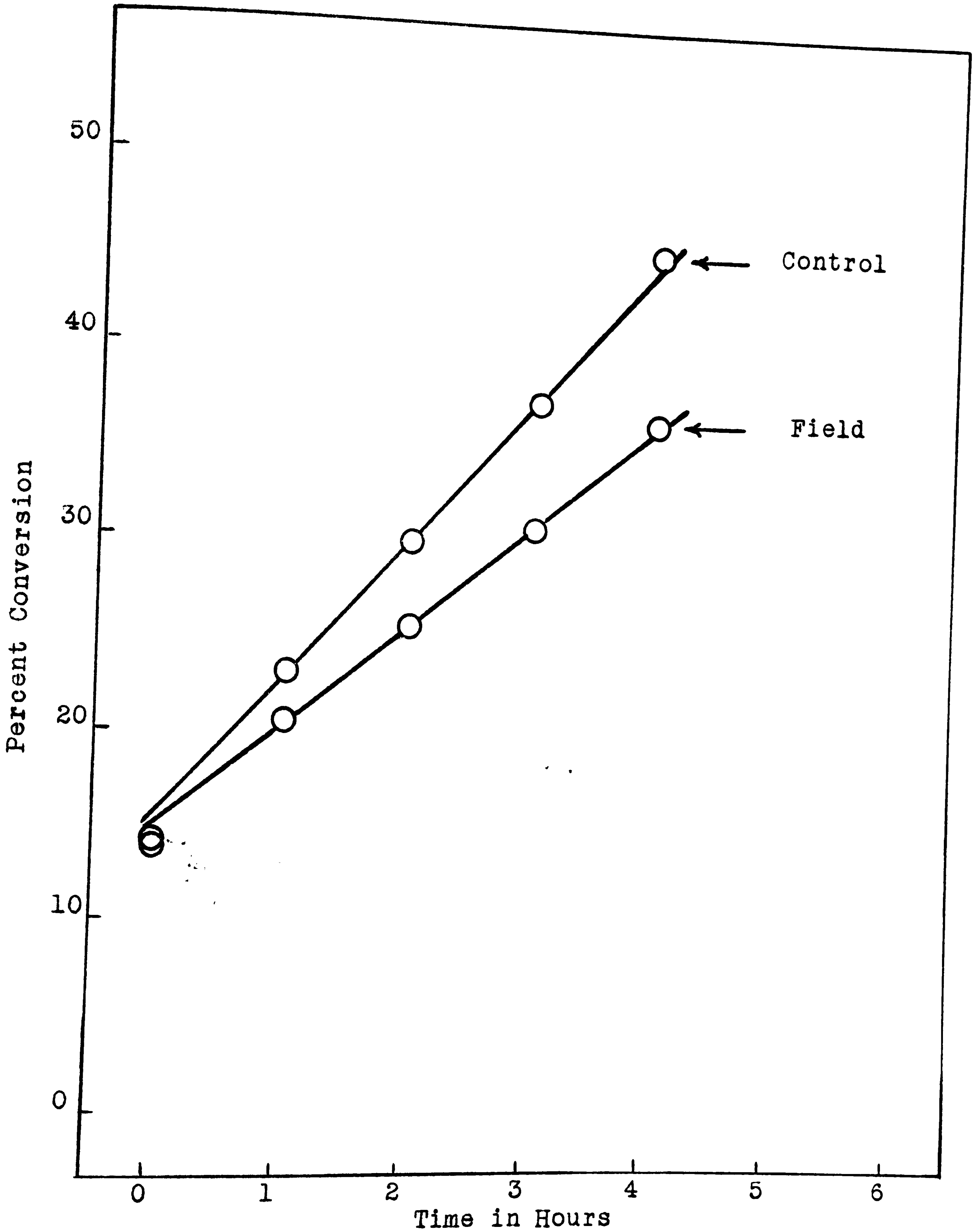

Fig. 12 : Rate curves for field and control samples for polymerization of styrene; 4500 volts/cm., 1.55 megacycles, 1.244 grams of benzoyl peroxide per liter of styrene, average temperature = 85.6 °C.

An increase in rate of reaction might be expected between the first two points on a rate curve because of the change in temperature of the reactants after the percent conversion samples were removed at zero hours and the field was applied. For this reason, the first point was considered low and was not emphasized in drawing the curve.

It was found that a rate curve was best represented by a straight line up to 40-50 percent conversion for the experiments where benzoyl peroxide was added.

This straight line relation between percent conversion and time in hours, indicates that the catalyzed reaction is zero order over the range investigated.

The data for experiments where no benzoyl peroxide was added to the reaction mixture, i.e., experiments one and 14, gave rate curves convex to the time axis. For these two experiments the reaction rates were obtained from the slopes of initial tangents, although the first points on the curves were considered inexact.

The rates for the control and field reactions in experiments one to twenty-six are listed in Tables, VI, VII and VIII.

The expression for the specific rate constant of a zero order reaction

$$- \frac{dc}{dt} = k$$

relates slope, i.e., reaction rate, with the specific rate constant. In what follows, the constant reaction rate has

TABLE VI

RATES FOR CONTROL AND FIELD REACTIONS

3000 volts/cm.; 1.55 megacycles

Aver. Temp.= average temp. after field was applied

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene

k_c = control rate; k_F = field rate

Exp. No.	Aver. Temp.	Bz_2O_2 Conc.	$\sqrt{Bz_2O_2 \text{ Conc.}}$	k_c	k_F
1	85.8°C.	Nil	Nil	1.71	1.20
2	85.8	0.0408	0.20	1.83	1.55
3	84.6	0.156	0.40	2.53	2.24
4	83.8	0.311	0.56	3.10	2.55
5	87.5	0.622	0.79	4.87	3.87
6	85.9	0.623	0.79	4.87	3.93
7	86.5	0.723	0.85	4.67	4.10
8	84.3	0.934	0.97	5.77	4.77
9	83.7	0.934	0.97	5.97	4.60
10	86.7	1.244	1.12	8.30	6.00
11	86.8	1.554	1.23	8.10	6.44
12	84.5	1.866	1.37	9.27	8.10
13	84.6	2.182	1.48	9.95	8.20

TABLE VII

RATES FOR CONTROL AND FIELD REACTIONS

4500 volts/cm.; 1.55 megacycles

Aver. Temp.= average temp. after field was applied

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene

k_c = control rate; k_F = field rate

Exp. No.	Aver. Temp.	Bz_2O_2 Conc.	$\sqrt{Bz_2O_2 \text{ Conc.}}$	k_c	k_F
14	87.1°C.	Nil	Nil	1.66	1.04
15	86.5	0.0408	0.20	2.45	1.43
16	84.2	0.156	0.40	2.88	2.56
17	85.9	0.723	0.85	5.32	3.60
18	86.0	1.244	1.12	7.50	5.15
19	87.0	1.554	1.23	7.60	4.67
20	85.2	1.866	1.37	10.0	6.73
*21	86.9	2.182	1.48	8.80	5.00
*22	85.6	2.182	1.48	10.9	7.00
23	83.8	2.600	1.61	11.3	7.33

* Averages of 21 and 22 used in Fig. 13.

TABLE VIII

RATES FOR CONTROL AND FIELD REACTIONS

1500 volts/cm.; 1.55 megacycles

Aver. Temp.= average temp. after field was applied

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene

k_c= control rate constant; k_F= field rate constant

Exp. No.	Aver. Temp.	Bz_2O_2 Conc.	$\sqrt{Bz_2O_2 \text{ Conc.}}$	k_c	k_F	k_c/k_F
24	84.9°C.	0.723	0.85	4.27	4.07	1.05
25	85.4	1.244	1.12	7.15	6.65	1.08
26	85.0	2.182	1.48	8.40	8.00	1.05

been termed a rate constant, though strictly speaking, the specific rate constant should be obtained by dividing the measured rate by the concentration.

For experiments one and 14 the order of the reaction is unknown and the specific rate constant cannot be determined from the slope of the initial tangent, i.e., from the reaction rate, by dividing by an appropriate concentration term.

The temperature gradients in the reaction and control cells for experiment 18 may be estimated from the temperatures given in Table IX. It is evident that these temperature gradients can account for only a small part of the 31 percent difference found in the reaction rates for experiment 18 from the curves in Fig. 12.

TABLE IX

TEMPERATURE GRADIENTS FOR EXPERIMENT 18

1.244 grams of benzoyl peroxide per liter

4500 volts/cm.; 1.55 megacycles

	Reaction Cell °C.	Control Cell °C.
Temperature in inner electrode	80.4	* 75
Temperature of thermostat	79.0	86.2
Average temperature of reactants after field was applied	86.0	85.9

* Approximate only

There are theoretical and experimental reasons for believing that each molecule of benzoyl peroxide furnishes two free radicals which may act as catalysts in the initiation of polymer chains. Hence, it is to be expected that the rate of polymerization in the catalyzed reaction is proportional to the square root of the catalyst concentration.

The dependence of the rates for the control and field reactions on the square root of the catalyst concentration is shown in Fig. 13.

A number of points in this figure represent averages where two or more similar experiments were made. This is particularly so in the curve for the controls; often two or more experiments were made at the same catalyst concentration, but at different voltages, and, in such cases, the rates for the corresponding controls were averaged.

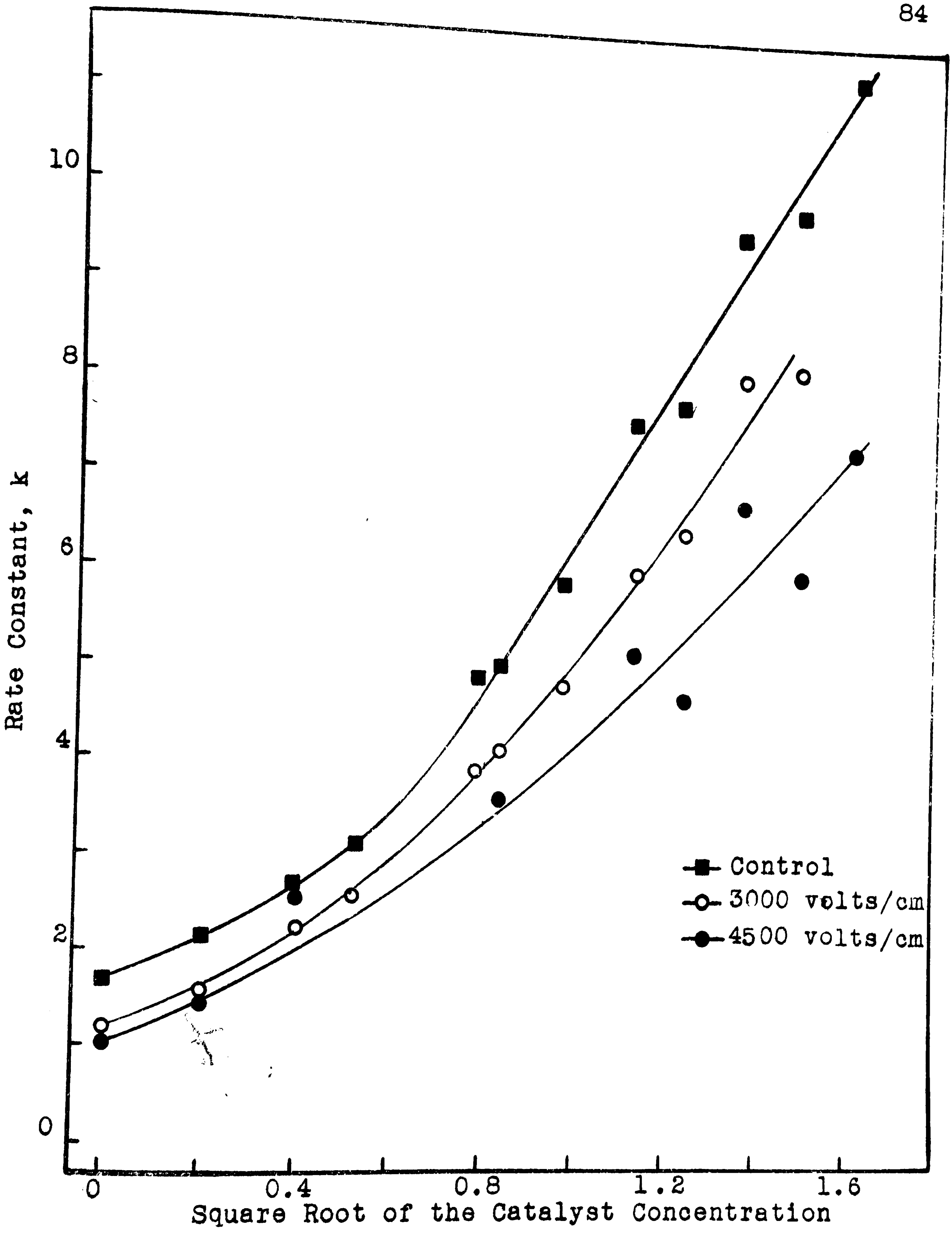

Fig. 13 : Dependence of the rate constants on the square root of the catalyst concentration (gms. of benzoyl peroxide per liter of styrene); 1.55 megacycles; average temperature = 85.5°C.

The plot of the control rate constants versus the square root of the catalyst concentration consists of two portions, both essentially linear but of different slopes. The change of slope occurs at a concentration of approximately 0.36 grams of benzoyl peroxide per liter.

This difference at lower catalyst concentrations may be explained by the "oxygen effect". A strictly thermal polymerization of styrene is not regarded as possible at temperatures less than 180°C. However, "pure" liquid styrene with no added catalyst is known to polymerize at temperatures as low as 60°C. when oxygen is present (60). It is postulated that this latter polymerization occurs as a result of the formation of styrene peroxides formed by oxidation of the styrene (61,62). This assumption has been supported by measurements of difference in the change of diamagnetic susceptibility during styrene polymerization in vacuum and in oxygen (63).

At other times oxygen appears to inhibit the polymerization of styrene, or at least, to counteract the influence of other catalysts on the polymerization reaction.

The scattering of points around the curve for the control reactions was regarded as reasonable. In addition to the usual deviations which occur when styrene is polymerized at constant temperature, other deviations must be expected in the present work because of the variation in temperature during each experiment. A further reason for the scattering of points is that the average temperatures in this group of experiments cover a range of four degrees.

For the 3000 volts/cm. data, the "best-fitting" line for the field rate constants appeared to be a curve. A similar line was drawn for the 4500 volts/cm. data.

The scattering of points around the 3000 volts/cm. curve is approximately the same as for the control reaction rates, and was regarded as reasonable. For the 4500 volts/cm. data, the points are more widely scattered, but this difference cannot be explained by any known change in experimental procedure. Greater difficulty was experienced in duplicating results at the highest potential gradient used.

The deviations in values of the rate constants for an applied field of 4500 volts/cm. is apparent in experiments 21 and 22 in Table VII. For these experiments the average of the two k_c values is 9.85 and for the two k_F values it is 6.00. These average values were used since they appeared to be reasonably close to the curves established from the other experiments.

Only three points were obtained at 1500 volts/cm., and the data are not plotted in Fig. 13.

The amount by which the reaction rate in the field is lower than in the control may be related to both the catalyst concentration and the voltage gradient of the applied field. This is shown in Fig. 14 where values of k_c/k_F are plotted for the three potential gradients, 1500, 3000 and 4500 volts/cm., and for a range of catalyst concentrations. The values of k_c and k_F for the latter two voltage gradients were obtained from the smooth curves of Fig. 13; the three values of k_c/k_F for the 1500 volts/cm. data are experimental and are listed in Table VIII

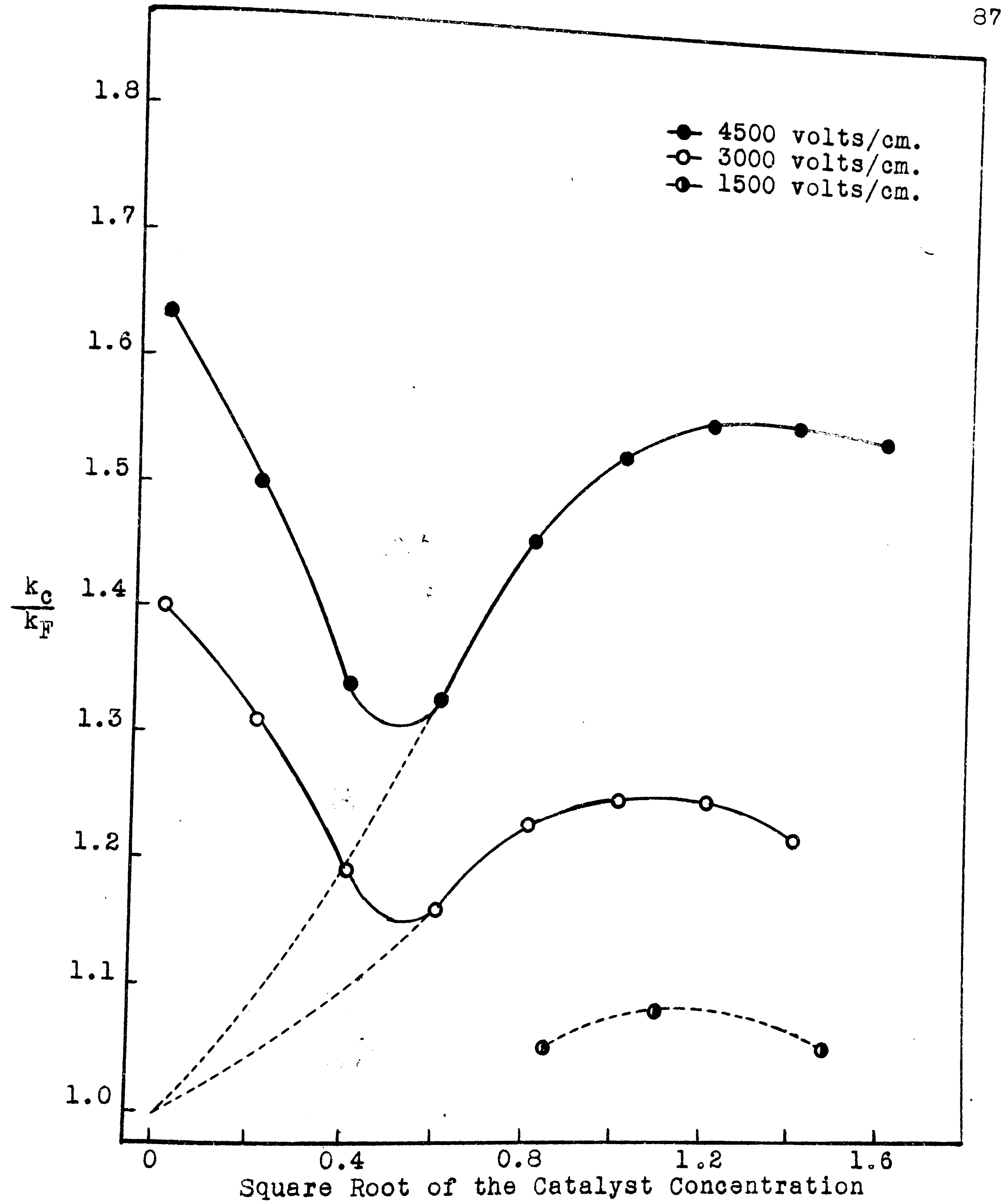

Fig. 14 : Relation of the ratio of the rate constants for control and field samples to the square root of the catalyst concentration (gms. of benzoyl peroxide per liter of styrene); 1.55 megacycles; average temperature = 85.5°C.

There is a pronounced minimum field effect for the two higher potential gradients. This minimum occurs at a catalyst concentration of approximately 0.36 grams of benzoyl peroxide per liter.

The increase in field effect at low catalyst concentrations may be explained by the "oxygen effect" already discussed.

At catalyst concentrations greater than that corresponding to the minimum, the field effect increases rapidly at first as the benzoyl peroxide concentration increases, but appears to attain an optimum value.

An estimate of the increase in the field effect due to increasing the potential gradient may be made from Fig. 14. The relation between the field effect and the potential gradient is shown in Fig. 15, where the field effect is shown as the percent reduction of the reaction rate, i.e.,

$$\frac{k_c - k_F}{k_c} \times 100$$

The value of the percent reduction of rate for each of three potential gradients is an average as shown in Table X.

The equation for the extrapolated curve is

$$R = aE^{1.73}$$

where R is the percent reduction of reaction rate, E is the potential gradient of the applied field in volts/cm., and $a = 1.85 \times 10^{-5}$.

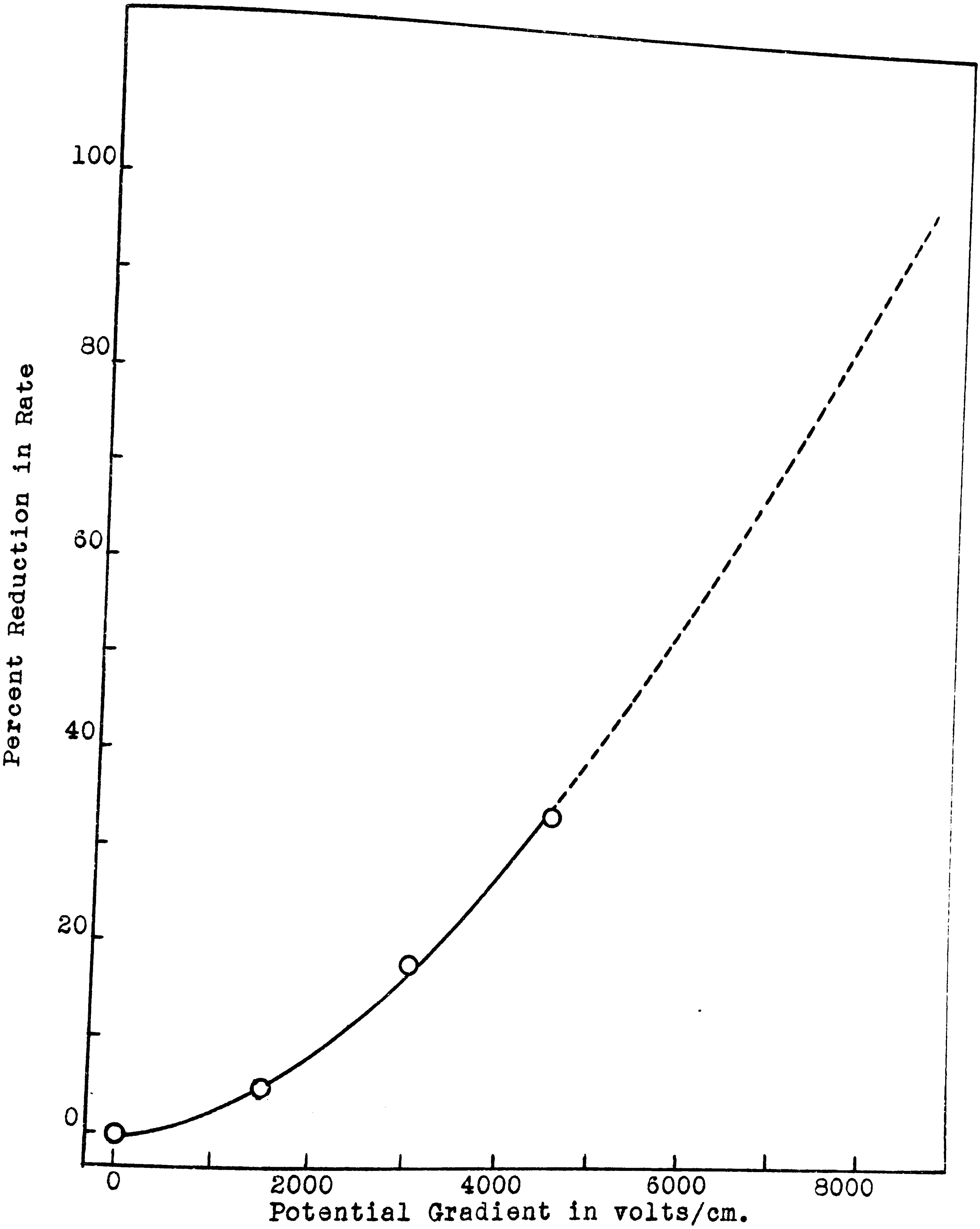

Fig. 15 : Dependence of percent reduction in reaction rate on field strength; points are average values for benzoyl peroxide concentrations of 0.723, 1.244, and 2.182 grams per liter of styrene; frequency = 1.55 megacycles; average temperature = 85.5 °C.

TABLE X

DEPENDENCE OF FIELD EFFECT ON POTENTIAL GRADIENT

1.55 megacycles; average temperature=85.5°C.

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene

Aver. Temp.= average temp. after field was applied

k_c = control rate; k_F = field rate

Bz_2O_2 Conc.	Aver. Temp.	Pot. Grad.	k_c	k_F	Reduction in Rate %	Aver. Reduction in Rate %
0.723	84.9	1500	4.27	4.07	4.7	
1.244	85.4	1500	7.15	6.65	5.6	5.0
2.182	85.0	1500	8.40	8.00	4.8	
*0.723	85.5	3000	5.05	4.12	18.4	
1.244	85.5	3000	7.37	5.93	19.5	18.0
2.182	85.5	3000	10.3	8.63	16.2	
0.723	85.5	4500	5.05	3.47	31.3	
1.244	85.5	4500	7.37	4.76	35.4	33.8
2.182	85.5	4500	10.3	6.70	34.6	

* k_c and k_F values for applied fields of 3000 and 4500 volts/cm. were obtained from smooth curves in Fig. 13.

However, it may be that the approximate square relation is not applicable at higher voltages, and the curve may become a flattened S-shape. Further experiments at voltages considerably higher than 4500 volts/cm. are indicated as a desirable extension of this present study.

Influence of the Field on Molecular Weights

The percent conversion analyses in experiments one to 26 have been used to show that the rate of the field reaction is lower than that of the control. However, the percent conversion is evaluated from a weight of polymer, and does not indicate whether the lower reaction rate in the field occurs as a result of lower rates of initiation or of propagation, or whether it occurs from a higher rate of termination.

Each activated styrene molecule has, on the average, approximately the same chance of growing into a chain of given length before being terminated; the relative rates of propagation and termination determine the average molecular weight of the polymer. Hence, the average molecular weights for the control and field reactions may be used to determine whether the applied field is modifying the relation between the rates of propagation and termination. However, this measurement cannot be used to indicate which rate is changed or whether both rates are changed.

The average molecular weights listed in Tables IV and V are reproduced in Table XI.

TABLE XI

REPRODUCTION OF MOLECULAR WEIGHTS FROM TABLES IV AND V

1500, 3000, 4500 volts/cm.; 1.55 megacycles; average temperature = 85.5°C.
Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene
Aver. Temp.= average temperature after field was applied

Exp. No.	Bz_2O_2 Conc.	Aver. Temp.	Pot.Grad. (volts/cm.)	Sample I	Sample II	Sample III	Sample IV	Sample V
*24	0.723	84.9	1500	15600 16200	15500 15100	16300 16200	16800 16500	17700 17600
25	1.244	85.4	1500	12700 12100	11500 14000	12800 -	16100 14000	14400 14400
26	2.182	85.0	1500	9700 9800	10000 10100	10700 9600	10900 9200	11800 11700
4	0.311	83.8	3000	- -	20200 21600	24100 26600	- 29200	29000 36600
5	0.622	87.5	3000	14900 15600	15400 16000	17700 16800	16100 17200	26300 20000
7	0.723	86.5	3000	16700 15500	15900 13900	16700 16700	17500 15900	18800 21200
8	0.934	84.3	3000	- -	- -	17900 21000	18400 18900	21700 22200
9	0.934	83.7	3000	- -	- -	18300 27400	19300 21600	18800 15500

TABLE XI (cont'd.)

Exp. No.	Bz_2O_2 Conc.	Aver. Temp.	Pot.Grad. (volts/cm.)	Sample I	Sample II	Sample III	Sample IV	Sample V
10	1.244	86.7	3000	11800	12000	13400	14100	-
				11200	11200	13100	16300	-
11	1.554	86.8	3000	14300	13000	13500	12500	12200
				12500	12400	10100	11700	13400
12	1.866	84.5	3000	10600	11800	13100	14600	-
				11200	12200	12400	16800	-
13	2.182	85.6	3000	11200	11100	11000	12000	11400
				11400	12300	11000	11400	12900
17	0.723	85.9	4500	13600	14300	15700	14900	17800
				14700	15200	15700	16400	18100
#18	1.244	86.0	4500	11700	11200	12300	13300	16500
				10700	11800	11200	14000	15500
19	1.554	87.0	4500	9800	11400	11700	11900	12300
				9900	10900	11700	12000	13100
#20	1.866	85.2	4500	11500	11900	11700	11600	12300
				10800	11900	11700	10700	13100
#23	2.600	83.8	4500	10500	9800	10800	11100	11700
				9700	9700	10100	11200	11500

* In each experiment the first row pertains to the field reaction and the second row to the control reaction.

\# Molecular weights in these experiments were obtained in other similar experiments not recorded here.

It is evident that the deviations among these molecular weights are large; also, although the molecular weights in each one of the reactions usually do increase as the reaction proceeds to higher conversions, this increase is often irregular. Occasionally the latter irregularity may be explained by temperature changes (see Tables IV and V), but more often it appears to be due to other causes.

The average deviation in molecular weights between field and control reactions at any one time is at least ten percent. It is clear from the figures in Table XI that, within this ten percent deviation, there is no definite trend to indicate that the average molecular weights in the control reaction are consistently higher or lower than in the field reaction. Hence, it is concluded that the lower rate in the field reaction is not explainable as the result of a modification of either or both of the rates of propagation and termination.

Influence of the Field on the Average Number of Active Centers

The average number of active centers per mol of styrene may be calculated to obtain an estimate of the effect of the applied field on the initiation step in the polymerization of styrene.

The percent conversion and average molecular weight data for the field reaction in Sample I of experiment 24 (Table V) are used in the following sample calculation:

Percent conversion = 10.7

Average molecular weight = 15600

On the basis of one mol of styrene = 104 gm. = 6.06×10^{23} molecules, the number of styrene molecules in the polymer at 10.7% conversion = $0.107 \times 6.06 \times 10^{23}$. The number of styrene molecules per average chain = $\frac{15600}{104}$. Since one active center is required for each chain, therefore, the number of active centers per mol of styrene = $\frac{0.107 \times 104 \times 6.06 \times 10^{23}}{15600}$ = $\frac{0.107 \times}{15600} 6.30 \times 10^{25} = 4.32 \times 10^{20}$.

In Table XII are given the calculated average numbers of active centers per mol of styrene for three experiments at 1.55 megacycles, 0.723 grams of benzoyl peroxide per liter of styrene, and at 1500, 3000, and 4500 volts/cm.

These results are plotted in Fig. 16, where the black squares represent averages for the three control reactions.

Although experimental and other errors in the percent conversion and average molecular weight determinations do cause considerable scattering of the points, particularly for the 3000 volts/cm. experiment, the four curves clearly indicate the relation between a lower over-all rate and a lower rate of initiation in the field reaction. The dependence of the number of active centers on the potential gradient of the applied field is also apparent.

TABLE XII

AVERAGE NUMBER OF ACTIVE CENTERS PER MOL OF STYRENE

1.55 megacycles; 0.723 grams of benzoyl peroxide per liter of styrene
Time of sampling - hours after the thermal treatment was started
Aver. Temp.= average temperature after the field was applied

Exp. No.	Pot. Grad. Volts/cm.	Aver. Temp.	Time of Sampling (Hours)	% Conv.		Aver.Mol. Wt.		Aver. No. Active Centers	
				Field	Control	Field	Control	Field	Control
24	1500	84.9	2	10.7	10.5	15600	16200	4.32×10^{20}	4.08×10^{20}
			4	21.6	22.4	15500	15100	8.78	9.34
			5	25.6	26.4	16300	16200	9.99	10.3
			6	29.6	31.0	16800	16500	11.1	11.8
			8	37.8	39.0	17700	17600	13.5	13.9
7	3000	86.5	2	10.3	9.5	16700	15500	3.89	3.86
			4	18.9	21.7	15900	13900	7.48	10.0
			6	29.8	31.8	16700	16700	11.3	12.0
			8	35.2	37.6	17500	15900	12.7	14.9
17	4500	85.9	2	9.2	8.9	13600	14700	4.26	3.81
			4	15.8	20.6	14300	15200	6.96	8.54
			5	20.5	25.6	15700	15700	8.22	10.3
			6	22.4	31.0	14900	16400	9.47	11.9
			8	30.7	43.2	17800	18100	10.8	15.0

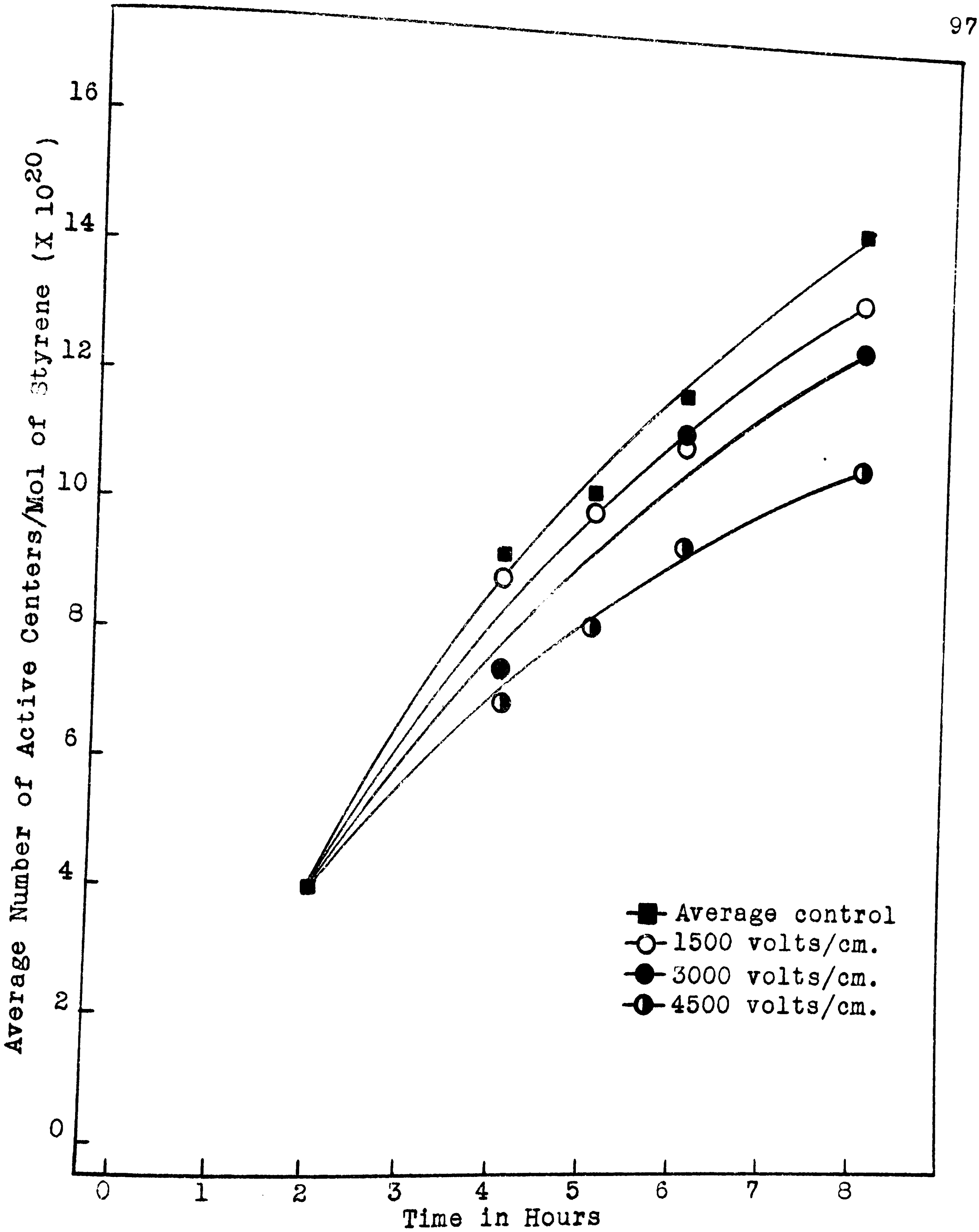

Fig.16 : Effect of applied voltage on the average number of active centers formed per mol of styrene; 1.55 megacycles; 0.723 gms. of benzoyl peroxide per liter of styrene; average temperature = 85.8°C.

Dependence of the Field Effect on the Temperature of Polymerization

Experimental Data

It has been shown (Fig. 13) that the effect of the applied field may be related to the square root of the catalyst concentration, i.e., to the free radical concentration, where the temperature is regarded as approximately constant. But, at one catalyst concentration, the free radical concentration in the styrene is largely dependent upon the temperature of polymerization, and therefore the field effect may also be dependent upon the temperature.

In an examination of the dependence of the field effect on temperature two potential gradients, 3000 and 4500 volts/cm., and three catalyst concentrations, 0.723, 1.244, and 1.866 grams of benzoyl peroxide per liter of styrene, were used. The experimental data obtained at approximately 70°C. are given in Table XIII, and at approximately 100°C. in Table XIV. Hereafter the data at these two temperatures and those obtained at approximately 80°C. will be referred to as the 70°, 80° and 100° data.

In the experiments at 70°C. a three hour thermal treatment was used before the field was applied. At 100°C. a period of half of an hour was used.

In the 70° data the average rise in temperature of the reactants in the reaction cell owing to dielectric heating after the field was applied was 1.9°C. for the 3000 volts/cm., and 4.5°C. for the 4500 volts/cm. data.

TABLE XIII

POLYMERIZATION OF STYRENE

Compilation of Percent Conversion and Molecular Weight Data

3000 and 4500 volts/cm.;

1.55 megacycles;

temperature before field applied = 70.0°C.

Bz_2O_2 Conc. = gm. of benzoyl peroxide per liter of styrene;

Aver. Temp.= average temperature after field was applied;

T. = time in hours after field was applied;

H.A.T. = hourly average temperature;

%C.= percent conversion to polystyrene;

M.W.= average molecular weight of polymer.

Sample III				Sample IV				Sample V			
T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.
2	72.0	11.7	17800	3	72.0	14.2	19800	-	-	-	-
	72.1	12.3	17300		72.1	15.0	16800		-	-	-
2	72.8	14.8	14700	3	72.8	16.8	15000	4	72.6	19.8	15500
	72.9	17.4	14300		72.8	19.6	14700		72.6	23.3	15000
2	73.0	18.4	-	3	72.7	21.3	16300	4	72.9	24.7	16100
	73.2	18.3	15000		72.9	23.4	15800		72.9	26.4	15700
2	75.3	11.6	20000	3	75.5	13.9	20000	4	75.6	17.5	19600
	75.2	13.2	19200		75.5	15.9	18400		75.6	19.3	18700
2	74.0	15.6	14400	3	74.4	18.9	14500	4	74.6	21.6	14700
	74.3	16.6	14700		74.4	19.9	14700		74.7	22.5	14500
3	73.7	21.4	13700	4	73.6	24.0	12800	5	73.6	27.2	13800
	73.7	24.8	12200		73.5	28.2	12300		73.6	32.4	13100

TABLE XIV

POLYMERIZATION OF STYRENE

Compilation of Percent Conversion and Molecular Weight Data

4500 and 3000 volts/cm.; 1.55 megacycles;

temperature before field applied = 100.0°C.

Bz_2O_2 Conc. = gm. of benzoyl peroxide per liter of styrene;

Aver. Temp. = average temperature after field was applied;

T. = time in hours after field was applied;

H.A.T. = hourly average temperature;

%C. = percent conversion to polystyrene;

M.W. = average molecular weight of polymer

Sample III				Sample IV				Sample V			
T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.
2	101.2	34.4	15300	3	101.2	40.7	18600	4	101.4	47.6	20700
	100.8	37.1	16400		101.2	40.9	18900		101.4	49.1	21800
2	103.8	37.1	-	3	103.5	43.7	-	-	-	-	-
	103.5	36.6	-		103.5	42.5	-		-	-	-
2	100.6	44.4	12800	3	102.0	55.5	15300	-	-	-	-
	100.4	46.0	13700		100.4	55.5	14300		-	-	-
2	103.8	49.1	-	3	104.8	57.6	-	-	-	-	-
	103.9	47.5	-		103.8	57.3	-		-	-	-
2	106.0	57.8	12300	3	106.0	67.1	15000	-	-	-	-
	106.1	58.4	12800		105.9	72.0	16000		-	-	-
1	103.9	40.7	-	2	102.2	54.3	-	3	102.1	64.3	-
	103.8	44.8	-		102.7	56.2	-		102.1	68.7	-
2	103.4	34.4	15300	3	103.1	40.7	18600	4	103.6	47.6	20700
	103.4	37.1	16400		103.2	40.9	18900		103.6	49.1	21800
2	104.6	43.7	12600	3	104.0	52.2	14700	-	-	-	-
	104.2	47.8	14000		103.8	56.7	16500		-	-	-
2	102.4	49.6	12200	3	102.6	62.1	13500	-	-	-	-
	102.5	56.4	12800		102.6	70.0	16600		-	-	-

For the 100° data, the average rise in temperature was 2.6°C. for the six experiments at 3000 volts/cm. and it was 6.6°C. for the three experiments at 4500 volts/cm.

Influence of the Field on Reaction Rates

Reaction rates for the 70° data were evaluated in a manner similar to that used for the 80° data. No difficulty was experienced in drawing a "best-fitting" straight line through the points for percent conversion versus time in hours, when the points for zero time were given little emphasis. An example of a 70° rate curve, experiment 29, is shown in Fig. 17.

Again the straight line was taken as an indication of a zero order reaction in the conversion range studied. Hence the reaction rate obtained from the slope of the line in percent conversion per hour gave the "rate constant".

The reaction rates for the 70° data are given in Table XV. From the values of k_c/k_F, it is clear that there is no significant difference in field effect when the applied field is 3000 or 4500 volts/cm. This differs from the results obtained in the 80° data, where a pronounced increase in field effect was found for an increase in the potential gradient (see Fig. 15).

When the 100° data, percent conversion and time in hours, were plotted, curves concave to the time axis were obtained instead of straight lines as at 70° and 80°C. The change from straight lines at 70° and 80°C. to curves at 100°C. is probably the result of the very rapid disappearance of the catalyst at 100°C.; thus the reaction rates measured are likely a combination of rates for the thermal polymerization reaction and for

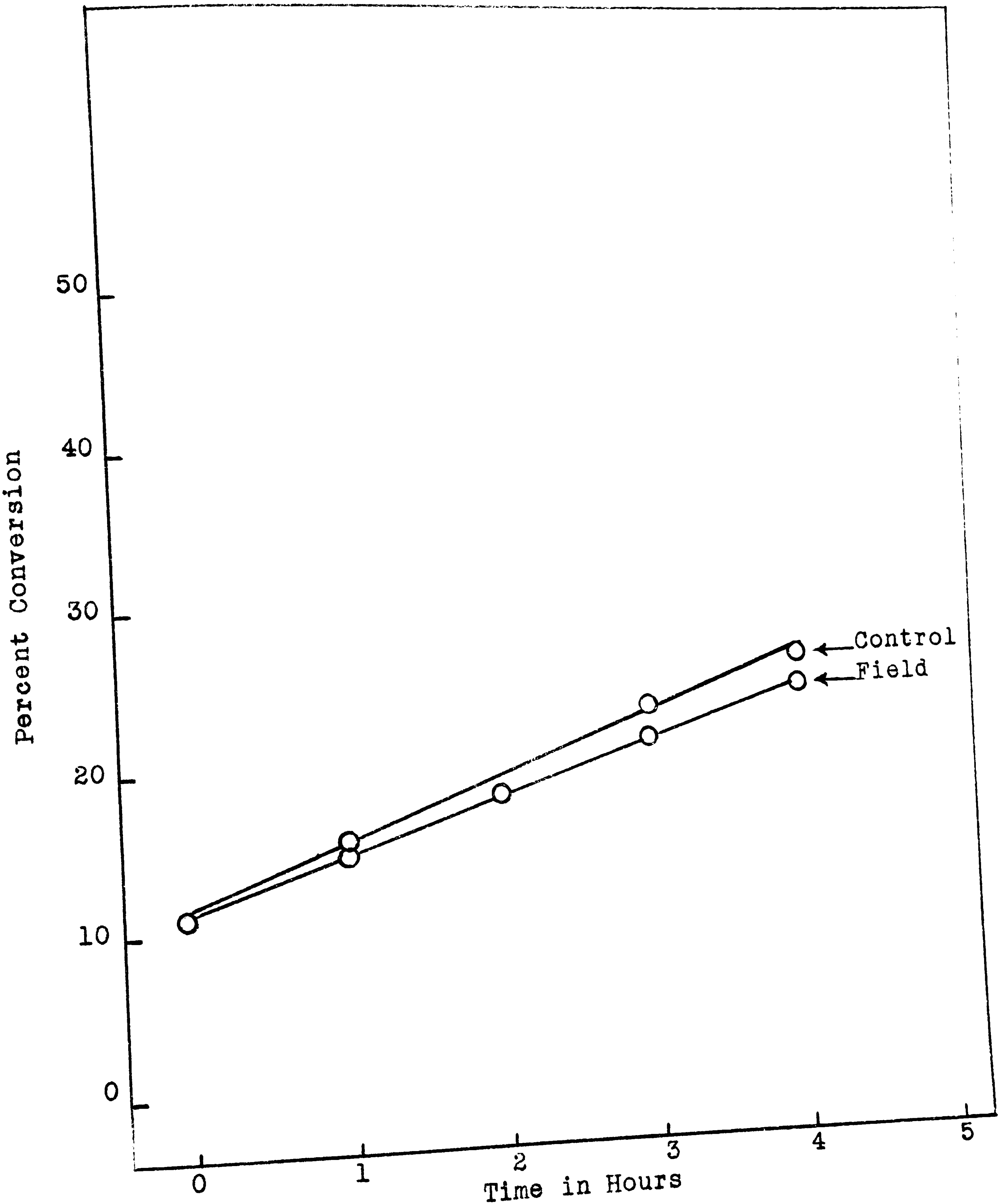

Fig. 17 : Rate curves for field and control samples for the polymerization of styrene; 3000 volts/cm.; 1.55 megacycles; 1.866 gms. of benzoyl peroxide per liter of styrene; average temperature = 72.6 °C.

TABLE XV

RATES FOR CONTROL AND FIELD REACTIONS

1.55 megacycles

Aver. Temp. = average temp. after field was applied

Bz_2O_2 Conc. = grams of benzoyl peroxide per liter of styrene

k_c= control rate; k_F= field rate

Exp. No.	Pot. Grad. (volts/cm.)	Aver. Temp.	Bz_2O_2 Conc.	$\sqrt{Bz_2O_2 \text{ Conc.}}$	k_c	k_F	k_c/k_F
27	3000	72.1°C.	0.723	0.85	2.70	2.45	1.10
28	3000	72.6	1.244	1.12	3.13	2.57	1.22
29	3000	72.6	1.866	1.37	3.87	3.33	1.16
30	4500	75.3	0.723	0.85	3.03	2.63	1.15
31	4500	74.5	1.244	1.12	3.50	3.13	1.12
32	4500	73.6	1.866	1.37	3.89	3.23	1.20

the polymerization at a rapidly changing catalyst concentration.

It was attempted to overcome this difficulty by drawing initial tangents to the curve at the time when the field was applied. However, this zero time point was considered to be consistently low owing to the rise in temperature after application of the field; hence initial tangents can only be expected to give approximate values for the rates of the reaction during the field treatment.

In Fig. 18 are shown curves for experiment 38. In this one experiment the usual procedure of sampling was changed slightly, in that samples were withdrawn from each cell halfway through the thermal treatment in the thermostat. This change in procedure was made in an attempt to obtain better placement of the initial parts of the reaction curves.

Hence in Fig. 18 the time axis is different from previous graphs in that zero time is the beginning of the half hour thermal treatment instead of the time when the field was applied. The percent conversion values for these two additional samples are shown in Fig. 18 but are not included in Table XIV.

The shape of the curves in Fig. 18 suggests that a first order plot, i.e., logarithm of the percent conversion versus time in hours, might be used. The 100° data were plotted in this manner, but they were found not to fit a straight line logarithm plot.

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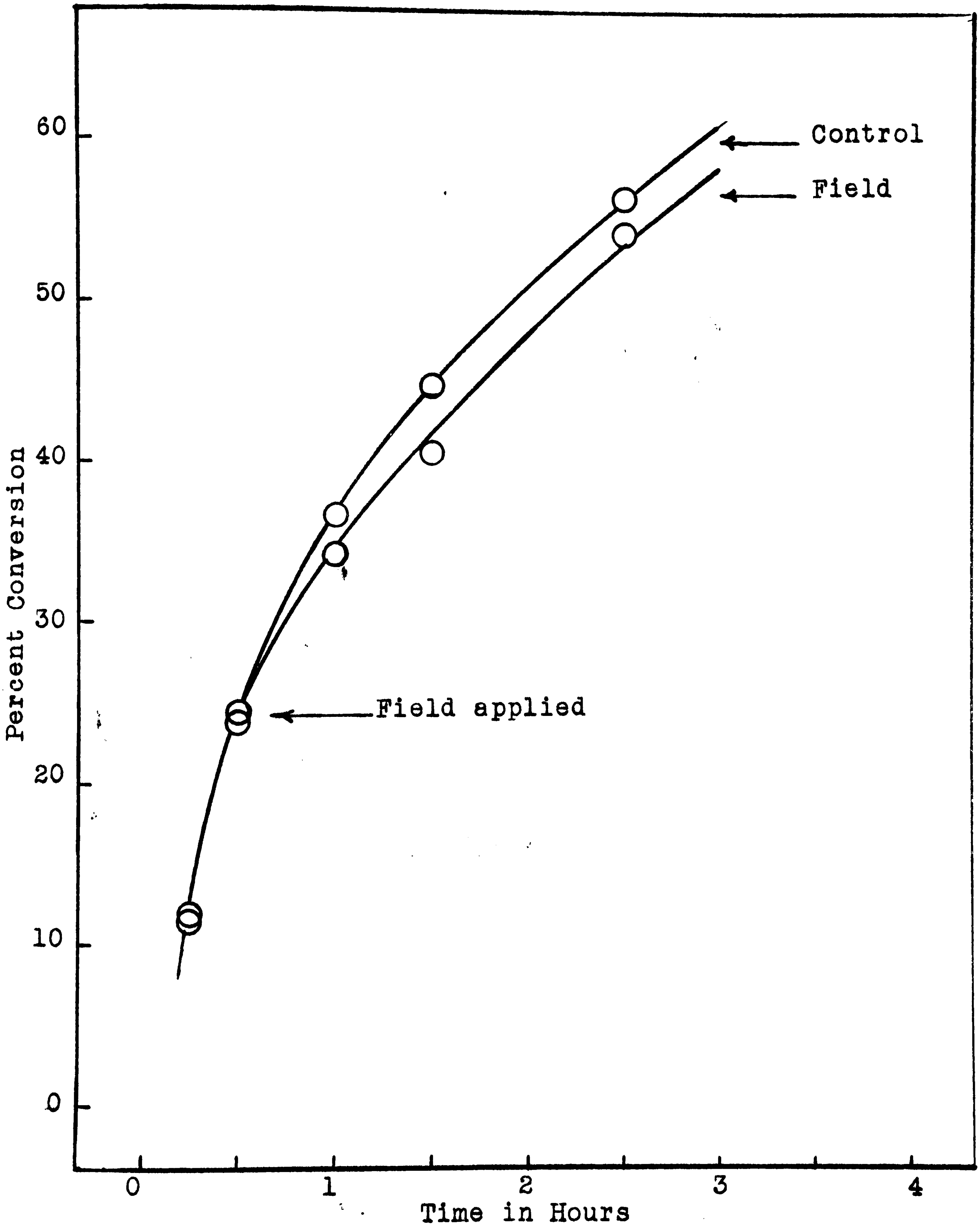


Fig. 18 : Rate curves for field and control samples for polymerization of styrene; 3000 volts/cm.; 1.55 megacycles; 1.866 gms. of benzoyl peroxide per liter of styrene; average temperature = 103.1°C.

The reaction rates for the 100° data are given in Table XVI and are calculated from slopes of tangents drawn to the curve at the time of application of the field. Large differences in the k_c and k_F values were produced by slight differences in the placement of the curves and tangents. The magnitude of these errors is apparent from the k_c and k_F values for the duplicate experiments, 37 and 38, in Table XVI. The errors due to placement of the curves and tangents, in conjunction with the errors due to a change in temperature in the initial part of the curves, preclude any quantitative use being made of the reaction rates for the 100° data.

Four of the six values for k_c/k_F in Table XVI, in the experiments using applied fields of 3000 volts/cm., show a lower rate of reaction in the field, while one of the other two values indicates a considerably faster rate. The k_c/k_F values for the data where an applied field of 4500 volts/cm. was used indicate an appreciably lower reaction rate in the field.

Probably it can be stated, although only qualitatively, that the field effect at 100°C. is still a lower reaction rate, and also that the difference in rates between control and field reactions increases with an increase in the applied voltage gradient.

TABLE XVI

RATES FOR CONTROL AND FIELD REACTIONS

1.55 megacycles

Aver. Temp.= average temp. after field was applied

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene

k_c= control rate; k_F= field rate

Exp. No.	Pot. Grad. (volts/cm.)	Aver. Temp.	Bz_2O_2 Conc.	$\sqrt{Bz_2O_2 \text{ Conc.}}$	k_c	k_F	k_c/k_F
33	3000	101.3	0.723	0.85	22.0	20.7	1.06
34	3000	104.0	0.723	0.85	26.8	27.0	0.99
35	3000	100.8	1.244	1.12	19.5	16.5	1.18
36	3000	103.9	1.244	1.12	23.5	20.6	1.14
37	3000	105.6	1.866	1.37	30.4	33.2	0.92
38	3000	103.1	1.866	1.37	90.8	81.6	1.11
39	4500	103.5	0.723	0.85	24.0	22.0	1.09
40	4500	104.3	1.244	1.12	34.6	22.2	1.56
41	4500	103.0	1.866	1.37	16.7	9.9	1.69

Temperature Coefficients of Reaction Rate

From the rates for the 70° and 80° data a tempe coefficient may be evaluated for each of three catal centrations. These are overall values for the polym tion, and give no information as to individual steps reaction.

Temperature coefficients per 10°C. are given in XVII. The k_C and k_F values, and the average tempera for the 80° data were obtained from the curves in Fi while the values for the 70° data are experimental. may account in part for the discrepancies among the vidual temperature coefficients, but another reason the temperatures are only average values.

In general the temperature coefficients for bot field and control reactions increase slightly with a crease in catalyst concentration. This increase may apparent in that it may result from errors. The wri found no report in the literature suggesting, that th temperature coefficient for the bulk-phase catalyzed ization of styrene is dependent upon the catalyst co tion.

An estimate of the field effect may be obtained paring the average temperature coefficient for the c

TABLE XVII

TEMPERATURE COEFFICIENTS FOR CONTROL AND FIELD REACTIONS

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of styrene
Aver. Temp.= average temperature after field was applied
k_c= control rate constant; k_F= field rate constant

Exp. No.	Pot. Grad. (volts/cm.)	Aver. Temp.	Bz_2O_2 Conc.	k_c	Control Temp. Coeff./10°C.	Control Aver. Temp. Coeff.	k_F	Field Temp. Coeff./10°C.	Field Aver. Temp. Coeff.
27	3000	72.1	0.723	2.70	1.45		2.45	1.27	
*	3000	85.5	0.723	5.25			4.16		
28	3000	72.6	1.244	3.13	1.83		2.57	1.75	
*	3000	85.5	1.244	7.38			5.80		
29	3000	72.6	1.866	3.87	1.86		3.33	1.78	
*	3000	85.5	1.866	9.30			7.65		1.60
30	4500	75.3	0.723	3.03	1.70		2.63	1.25	
*	4500	85.5	0.723	5.25			3.36		
31	4500	74.5	1.244	3.50	1.92		3.13	1.31	
*	4500	85.5	1.244	7.38			4.48		
32	4500	73.6	1.866	3.89	2.01		3.23	1.51	
*	4500	85.5	1.866	9.30		1.80	5.80		1.36

* These values were obtained from the smooth curves in Fig. 11.

accompanying an increase in potential gradient is similar to a decrease in temperature of polymerization.

The activation energies corresponding to the temperature coefficients are shown in Table XVIII. These E values were calculated from the equation (64)

$$\log \frac{k_2}{k_1} = \frac{E}{2.303\ R} \frac{(T_2 - T_1)}{T_2 T_1}$$

The individual values of the activation energies are subject to considerable fluctuation as would be expected on recognition that a combination of experimental data and data from smooth curves are used and also from the fact that the temperatures used are only averages. In general there appears to be only a slight difference between the activation energies for the control and field reactions in the 3000 volts/cm. data. However, the difference in activation energies for the 4500 volts/cm. data is startling. In the latter, the average value of E for the controls is 16,000 cal/mol. as compared with an average of 8700 cal. per mol. for the field samples.

Since the field effect is a lower rate in the field reaction, it might be expected that the activation energy for the field reaction should be larger than that for the control; instead, the activation energy for the field reaction appears to be only half that for the control. Possible explanations for such a decrease in activation energy are discussed later.

TABLE XVIII

ACTIVATION ENERGIES FOR CONTROL AND FIELD REACT

1.55 megacycles

Aver. Temp.= average temp. after field was app

Bz_2O_2 Conc.= grams of benzoyl peroxide per liter of

k_c= control rate; k_F= field rate

E_c= control activation energy; E_F= field activation

Exp. No.	Pot. Grad. (volts/cm.)	Aver. Temp.	Bz_2O_2 Conc.	k_c	E_c	k_F
27	3000	72.1	0.723	2.70	12200	2.45
*	3000	85.5	0.723	5.25		4.16
28	3000	72.6	1.244	3.13	16400	2.57
*	3000	85.5	1.244	7.38		5.80
29	3000	72.6	1.866	3.87	16700	3.33
*	3000	85.5	1.866	9.42		7.65
30	4500	75.3	0.723	3.03	13400	2.63
*	4500	85.5	0.723	5.25		3.36
31	4500	74.5	1.244	3.50	16800	3.13
*	4500	85.5	1.244	7.38		4.48
32	4500	73.6	1.866	3.89	18000	3.23
*	4500	85.5	1.866	9.30		5.80

* These values were obtained from the smooth curves Fig. 13.

Influence of the Field on Molecular Weights and on the Average Number of Active Centers

The average molecular weights for the 70° and 100° data are given in Tables XIII and XIV.

When molecular weights are compared in experiments where similar catalyst concentrations are used, it is evident that, at comparable percent conversions, the average molecular weight decreases with increase in temperature. Also, in the 70° and 100° data, the molecular weight usually decreases with an increase in catalyst concentration.

The average deviation in molecular weights evaluated in the experiments at 70° and at 100° C. may again be taken as at least ten percent. Within this average deviation, there appears to be no significant trend to indicate that the applied field influenced either the rate of propagation or of termination.

A calculation of the average number of active centers per mol of styrene indicates that the field influenced the initiation step of the reaction in the 70° data in a manner similar to that in the 80° data. However, in the experiments at 70° there is a smaller difference between the average number of active centers for applied fields of 3000 and 4500 volts/cm. than there is in the 80° data. As already mentioned this decreased difference is also shown in the reaction rates for the experiments at 70°C.

Dependence of the Field Effect on the Frequency of the Applied Field

Experimental Data

A study of the relation between frequency of the applied field and the field effect was made at temperatures comparable to the 80° data. One catalyst concentration was used, i.e., 1.244 grams of benzoyl peroxide per liter of styrene, and two voltage gradients were used: 3000 and 1500 volts/cm. The frequency range in the group of experiments at 3000 volts/cm. was limited by the apparatus to 1.15-2.39 megacycles, and that for the 1500 volts/cm. to 1.15-7.72 megacycles.

The experimental data obtained are given in Table XIX.

In each experiment the reaction and control cells were thermostatted at 80°C. for two hours before the field was applied to the reaction cell.

The change in temperature rise accompanying a change in the frequency of the applied field required slight adjustments of the temperature of the circulating oil to maintain the average temperature of the reactants at approximately 85°C.

Influence of the Field on Reaction Rates

In Table XX are shown the rates for the control and field reactions in this group of experiments.

No significant change in the field effect was noted for the eight experiments made. The values of k_c/k_F given in the latter table do fluctuate, but there is no definite trend whereby the frequency of the applied field may be said to modify the field effect found for applied fields of 1.55 megacycles.

TABLE XIX

POLYMERIZATION OF STYRENE

Compilation of Percent Conversion and Weight
3000 and 1500 volts/cm.;
1.244 grams of benzoyl peroxide per liter of st
temperature before field applied = 80°C.

Bz_2O_2 Conc. = gm. of benzoyl peroxide per liter of s
Freq.=frequency in megacycles;
Aver. Temp.= average temperature after field was a
T.= time in hours after field was appl
H.A.T. = hourly average temperature;
%C.= percent conversion to polystyrene;
M.W. = average molecular weight of polymer

Sample III				Sample IV				Sampl		
T.	H.A.T.	%C.	M.W.	T.	H.A.T.	%C.	M.W.	T.	H.A.T.	
2	83.0	27.0	16600	3	83.5	32.3	14200	4	83.4	3
	82.9	30.4	13600		83.4	36.9	13600		83.4	4
4	86.3	36.8	13400	6	86.2	50.0	14100	-	-	
	86.5	44.4	13100		86.3	63.4	16300		-	
2	83.1	27.4	16100	3	83.1	32.7	14200	4	83.4	3
	83.2	29.3	15300		83.0	35.2	14600		83.4	4
3	85.5	33.6	12800	4	85.6	39.2	16100	5	85.5	4
	85.6	-	-		85.4	42.1	14000		85.5	4
2	83.3	27.8	12600	$3\frac{1}{4}$	84.3	36.0	13400	4	84.3	4
	83.1	28.5	13100	$2\frac{3}{4}$	84.5	34.7	13700		84.3	4
2	83.8	27.6	10500	3	83.9	33.7	13900	4	83.6	4
	83.7	29.9	14200		83.8	37.3	14300		83.7	4
2	83.7	28.6	13800	3	83.8	35.5	14400	4	83.8	4
	84.0	30.5	13300		83.6	38.8	14200		83.5	4
2	84.5	26.9	13600	3	84.6	33.5	14300	4	84.4	4
	84.0	29.6	13600		84.6	37.0	14200		84.5	4

TABLE XX

RATES FOR CONTROL AND FIELD REACTIONS

1.244 grams of benzoyl peroxide per liter of st

Aver. Temp.= average temperature after field was

k_c= control rate; k_F= field rate

Exp. No.	Pot. Grad. (Volts/cm.)	Freq. Megacycles	Aver. Temp.	k_c	k_F
42	3000	1.15	8.34	7.80	6.0
10	3000	1.55	86.7	8.30	6.0
43	3000	2.39	83.3	7.07	6.0
25	1500	1.55	85.4	7.15	6.6
44	1500	3.75	83.8	7.37	6.1
45	1500	4.47	83.8	7.80	6.4
46	1500	6.01	83.8	7.43	6.6
47	1500	7.72	84.5	8.13	6.6

Influence of the Field on Molecular Weights

It is apparent from Table XIX that there is no real difference in the average molecular weights of the control and field reactions, and therefore, the frequency of the applied field presumably has no significant effect on the average molecular weight in the range of frequencies studied.

DISCUSSION

The main interest in these studies has been placed on the influence of the field, but many data have been obtained for the ordinary polymerization of styrene in bulk-phase; it is of some interest to compare these with the results of previous work.

The linear relation between reaction rates and the square roots of the catalyst concentrations for the control experiments in the present work is in general agreement with the results reported by other investigators (65,66). The existence of an "oxygen effect" at low concentrations of added catalyst has also been reported previously (60,61,62,63).

There is considerable divergence of opinion in the literature as to the order of the over-all rate of reaction for the catalyzed and non-catalyzed polymerization of styrene in bulk-phase. The simple kinetics which appear to be consistent for polymerization in solution, break down for concentrated solutions or for bulk-phase polymerization.

The zero order rates for low percent conversions found in this investigation for the catalyzed reactions agree with those by Staudinger and Frost (67). Recently it has been shown, however, that a straight line is obtained when the cube of the monomer concentration divided by the square of the initial rate is plotted against the monomer concentration (68). This indicates that the order is more complex than that suggested by the zero order plots used here.

The order for the non-catalyzed reactions, however, is not evident from the plots obtained; according to other workers, the order for this reaction is first, three-halves, second, etc. (69). The disagreement appears to be due to the fact that no one order can be used up to high percent conversions.

The average temperature coefficient of the control reaction rates, 1.80 per 10°C., was peculiar to this investigation in that the value was found by comparing rates at the same initial catalyst concentrations, instead of comparing rates at "constant catalyst" concentration. A value of 1.45 per 10°C. was obtained by Cohen (70) using the latter standard of comparison. In his study, suitable amounts of catalyst were used so that the rates of decomposition of the catalyst at different temperatures were similar. A value of 1.34 per 10°C. is reported (71) for the non-catalyzed photochemical polymerization.

The observed increase of average molecular weights with time of polymerization is in qualitative agreement with the observations of Houtz and Adkins (72), while the observed decrease in average molecular weight with an increase in either catalyst concentration or temperature is in agreement with the results of several previous investigators (73,74,75,76).

The consistent retardation of the reaction rate in the applied field found in the present investigation may be compared with the results of Shorygima and Petrova (9) and of Liechti (8).

The studies by Shorygima and Petrova (9) used ultrahigh frequency fields (10 and 100 cm. waves) on the non-catalyzed polymerization of styrene in bulk-phase. This study is not, however, comparable to the present one, since the purpose of the experimenters was to use the field for heating the reaction system. In the control experiments, the temperature was approximately that of the environment and not that of the reactants exposed to the field. The observed acceleration in rate of reaction was regarded as a result of the heat energy supplied by the field. The present study appears to be the only one yet made in which the control experiments were made at temperatures similar to those of the field reactions.

Liechti (8) applied low frequency, high voltage fields (50 cycles, 40-50 kilovolts/mm.) to the non-catalyzed polymerization of styrene and found that the field accelerated the rate of reaction. This acceleration occurred only after the field was removed and the experiment continued in a thermostat at 80°C. It was reported that re-application of the field to the reaction after it had been in the thermostat caused a retardation of polymerization.

The results were interpreted by Liechti as an "actication" of centers of polymerization by the applied field with a consequent accelerated rate after the field was removed. He suggested that the field could activate styrene molecules, but at the same time could prevent growth of the active centers into polymer chains.

His reaction cell was immersed in a thermostat, but no mention is made of whether the temperature in the cell rose owing to dielectric heating. The percent conversion analyses were only made at the end of the heating period in the thermostat and hence, no rate curves for the polymerization during the field treatment are available.

Regardless of the differences in the procedures and types of fields used in the two studies, the present results are in agreement with Liechti's work in that retardation of reaction rate was found in the presence of the applied field.

The above comparison applies only to the few experiments where no catalyst was used. For the large bulk of the present work, i.e., for the catalyzed reactions, no comparison can be made with previous work.

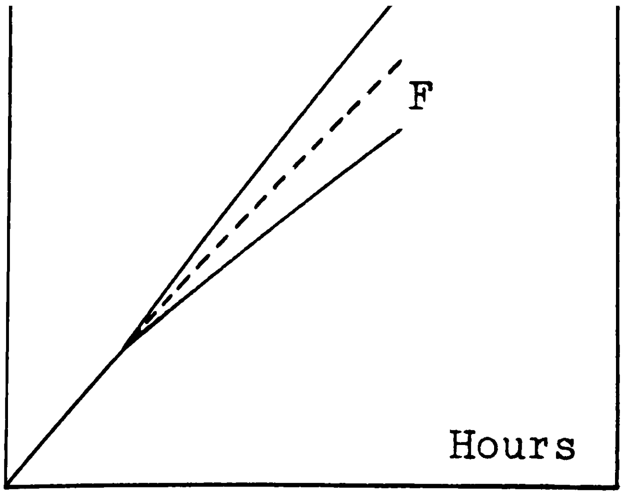
In the present studies, the temperature rise resulting from dielectric heating was a feature of the experimental work which demanded much attention; the precautions taken to be sure that the cell thermometer recorded the real temperature of the reactants have been described in detail.

There would seem to be no reason to doubt that the observed retardation of the over-all rate of polymerization is a net athermal effect of the applied field. Examination of certain features of the rate curves will serve to demonstrate that any accelerating effect due to increased temperature resulting from dielectric loss has been essentially compensated for by the procedure of comparing the field reaction with a control reaction at a similar temperature.

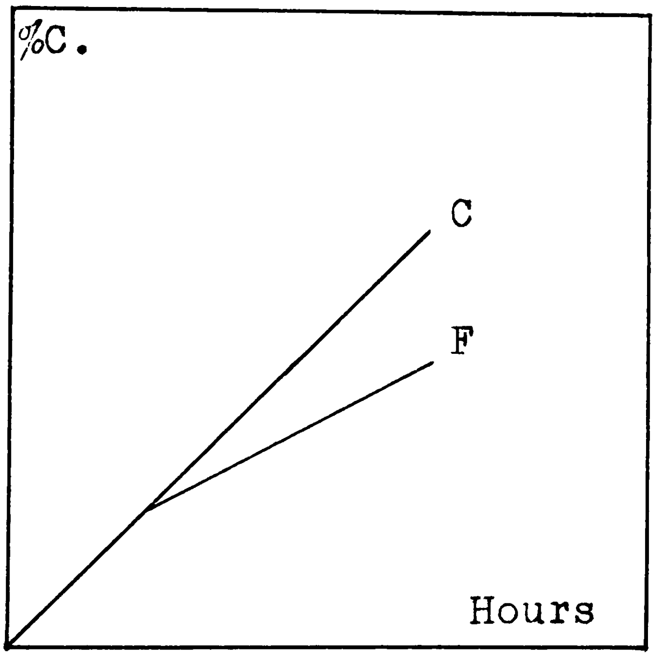
Typical rate curves are illustrated in Sketch A of Fig. 19, where it is notable that the control rate curve breaks upward and the field rate curve breaks downward at the time the field is applied.

The increase in slope of the control rate curve is to be expected because of the increased temperature. The decreased slope of the field rate curve shows that the influence of the applied field decreases the rate of reaction in spite of the increased temperature in the field reaction corresponding to the increased temperature of the control. Apparently, then, the slope of this typical experimental field rate curve is the result of two conflicting influences: an increased rate owing to the increase in temperature, and a decreased rate because of retardation by the applied field. The relative positions of the field and control curves depends on the potential gradient, as well as on the efficiency of the reaction cell thermostat.

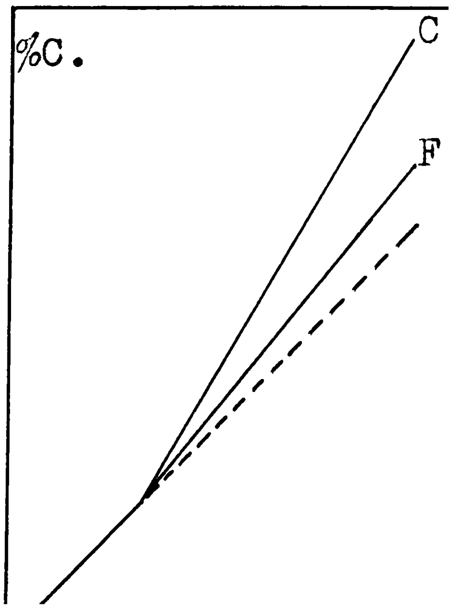
If the heat resulting from dielectric loss were dissipated as fast as it was produced, the control reaction temperature would be the same as the temperature during the preliminary thermal treatment. Then, on the basis of a zero order reaction, the control rate curve would be a straight line as represented in Sketch B. With no dielectric heating in the reaction cell, the position of the field rate curve would again be below the control. However, the ratio of k_c/k_F should be the same as it was when both reaction rates



Sketch A



Sketch B



were increased by the same temperature rise after the field was applied.

Sketch C illustrates theoretical control and field curves where the increased temperature in the reaction cell is sufficiently large that the break in the field curve is upward instead of downward. Again, however, the field effect, k_C/k_F, should remain unchanged because the slope of each of the two curves is multiplied by the same temperature coefficient.

Obviously, then, the efficiency of thermostatting has no effect on the influence of the field, measured relative to a control at the same temperature, although the relative positions of the control and field rate curves is dependent on the temperature rise.

Actually the field effect has been found to be somewhat different at 75° than at 85°C. Presumably, therefore, the field effect, k_C/k_F, might be slightly different in two similar experiments made at temperatures differing by a degree or two.

It is apparent from Sketch A that the applied field prevented the field rate from taking the value it would have taken at the increased temperature, and that the retardation of the field rate may be expressed as a difference of x°C. for a particular voltage gradient. For the 1500, 3000 and 4500 volts/cm. fields, x is approximately equal to 1, 3, and 7°C. respectively as shown in Table XXI. The catalyst

TABLE XXI

RETARDATION BY THE FIELD AS EQUIVALENT TO A DECREASE IN TEMPERATURE

Average temperature = 85.5°C.; 1.55 megacycl

Bz_2O_2 Conc. = grams of benzoyl peroxide per liter o

Bz_2O_2 Conc.	Pot. Grad.	Temp. Equiv. of Field Retardation	k_c	k_F	k_F
0.723	1500	1°C.	4.27	4.07	
1.244	-		7.15	6.65	
1.866	-		8.40	8.00	
*0.723	3000	3	5.05	4.12	
1.244	-		7.37	5.93	
1.866	-		10.3	8.63	1
*0.723	4500	7	5.05	3.47	
1.244	-		7.37	4.76	
1.866	-		10.3	6.70	1

* k_c and k_F values for applied fields of 3000 and 4 volts/cm. were obtained from smooth curves in Fig

concentrations used in this table correspond to the broad optimum in Fig. 14 where the retarding influence of the field is approximately constant for one particular voltage gradient.

The k_c and k_F values in this table for the 1500 volts/cm. data are experimental, but, for the 3000 and 4500 volts/cm. data, the values are taken from the smooth curves in Fig. 13. In correcting k_F for these temperature equivalents of the retarding influence of the field, the temperature coefficient used was 1.80 per 10°C.

Corrected values of k_F at lower catalyst concentrations could not be expected to agree with the values of k_c as well, if the same temperature equivalents as in Table XXI were used, because the retarding influence of the field has been shown to be somewhat dependent on the catalyst concentration.

One might naturally wonder whether there is a relation between the temperature equivalents of the retarding influence of the field and the temperature rise resulting from dielectric heating. The observed average temperature rises for the experiments using fields of 1500, 3000, and 4500 volts/cm. at 1.55 megacycles and at an average temperature of 85.5°C. were 1.7, 4.6, and 6.7°C. respectively.

The magnitude of these observed average temperature rises obviously must have been governed by the efficiency of the thermostat which may be considered as essentially constant in these studies. These values might well have been proportionately decreased by better thermostatting or proportionately increased by poorer thermostatting, but their ratios would have remained approximately the same. By coincidence they are approximately of the same order of magnitude as the values of 1,3, and 7°C. calculated for the temperature changes equivalent to retardation of rate by the field. However, even if the thermostatting had been poorer or better, it is clear that the observed temperature rises due to dielectric heating at different voltages would have been in the same ratios as the temperature equivalents of retardation at these same voltages.

The relation between potential gradient, E, and percent retardation in rate, R, as given in equation (1) is similar in form to equation (2) which relates the energy of a charged condenser, W, to the potential gradient, E, (77).

$$R = aE^{1.73} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$W = \tfrac{1}{2}CE^{2} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In (2), W is energy in joules, C is capacitance in farads and E is potential gradient in volts/cm.

It is evident, that to a first approximation, both the percent reduction in rate and the energy of a condenser are directly proportional to the square of the impressed voltage gradient.

Since both the inhibiting influence of the field and temperature rise due to dielectric heating are approximately proportional to the square of the voltage gradient, a relation between them, such as discussed previously, might well be expected. Hence, it is possible that the field acts on the reactant molecules to give retardation by a mechanism similar to, perhaps the same as, the mechanism by which it acts to produce dielectric heating.

Dielectric heating presumably results from the oscillatory rotation of molecules in an electrical field. The energy supplied to the molecules by the field is transformed into translational energy by molecular collisions and a rise in temperature results.

A physical basis may exist for the relation between the rise in temperature and the effect of the field on the rate of reaction, for a given field strength, if the observed field effect on rate is also the result of oscillatory motion of the molecules. Such a physical basis might account for the apparent differences in field effect on the oxygen catalyzed and benzoyl peroxide catalyzed reactions. Fig. 14 indicates that at concentrations from 0.3 to zero grams of benzoyl peroxide per liter of styrene, the field effect increased rapidly. It might be that the difference in field effect is due to a greater effect on activated complexes resulting from 'styrene peroxide' than from benzoyl peroxide. If, on the other hand, oxygen itself is regarded as the catalyst, the activated complex with it might be smaller so that an increase in field effect might be due to the greater ability of the field to cause oscillatory rotation of this smaller complex. It is difficult, however, to see how such an oscillatory mechanism could explain the increase of field effect to a broad optimum value at higher concentrations of benzoyl peroxide.

The observed increase in k_c/k_F accompanying an increase in added catalyst concentration may well be related to the increase in the field effect with an increase in temperature. The real concentration of catalyst is presumably the concentration of free radicals and this is increased by increase of temperature of polymerization as well as by increase in amount of benzoyl peroxide.

It is interesting to inquire whether the field influences the over-all rate of polymerization by reducing the concentration of free radicals or whether it reduces one or more rates of the reaction steps in the polymerization process.

The first suggestion presumably may be disregarded since no field effect was observed for the decomposition of benzoyl peroxide in toluene, and it seems unlikely, therefore, that the field should influence the rate of production of free radicals in styrene.

The propagation and termination steps of the polymerization seem also to have been uninfluenced by the field, since no effect of the field on average molecular weight of the polymer was observed, at least within the limits of error in evaluating average molecular weights by the viscosity method.

On the assumption that chain transfer and other secondary reactions are not different between control and field experiments, the effect of the field may be regarded as a retardation of the initiation of polymer chains.

Evidently then,any explanation of the observed retardation of rate must account for the apparent inhibition in forming active centers of polymerization. This explanation would probably be considerably easier if more were known about the mechanism by which such active centers are formed. The following two theories do attempt to account for initiation, but, at the present time, they are largely speculative.

One of the current ideas regarding initiation is based on quantum mechanical considerations of the ethylenic double bond and is extended only qualitatively to a system of conjugated double bonds as in styrene (78).

In the ground state of the ethylene molecule, both of the unsaturation electrons occupy the same bonding orbital. By the Pauli Principle, they must have anti-parallel spins, and, therefore, the ground state is a singlet. However, if one electron is promoted to a higher orbital, two states are possible, a singlet, in which spins are paired, and a triplet, with unpaired spins. Since the ground state of oxygen, which is isoelectronic with ethylene, is a triplet state, it might be expected that the triplet in ethylene is very little higher than the ground state.

Transition to the triplet state involves uncoupling of the spins of the unsaturation electrons, and this uncoupling can occur in a magnetic field. In the presence of free radicals, the uncoupling becomes more probable and may be expected to occur readily whenever the particle carrying a free electron comes within kinetic theory radius of the ethylene molecule (78).

When this theory is extended to the case where a styrene molecule is supposedly activated by a free radical, it is no longer quantitative, but still gives a qualitative description of a process whereby a styrene molecule might become an active center. According to this view, a peroxide-type catalyst accelerates the initiation reaction, not by decreasing the activation energy, but by facilitating the singlet-triplet transition by magnetic perturbation. The activation energy for initiation, when a peroxide catalyst is used, is similar to that for the thermal reaction, i.e., approximately 24000 cal. per mol. The frequency factor is increased by a peroxide catalyst from 10^5 for the thermal polymerization of styrene to about 10^{11} for the catalyzed reaction.

Another recent theory explains polymer formation by supposing that initiation occurs as a result of an equilibrium reaction in which the product formed is a catalyst-monomer molecular complex. This complex supposedly undergoes unimolecular decomposition and the products from this decomposition are the active centers which initiate polymerization (68). In the following, C represents molecules of a peroxide-type catalyst, M, monomer styrene molecules, and A•, active centers.

$$C + M \underset{}{\overset{K}{\rightleftharpoons}} C{\cdot}M \xrightarrow{k_a} A{\cdot}$$

The rate of initiation would be proportional to the concentration of the complex, which would be related to the catalyst and monomer concentrations by the equilibrium constant, K.

The above theories are interesting possibilities for a real explanation of the mechanism of initiation, but it is evident that knowledge of this part of the polymerization reaction is still elementary. However, in the light of these theories several possible mechanisms are suggested in the following to account for the influence of the field. It is emphasized of course that these possibilities are mainly speculation, and, at present, cannot be tested experimentally.

The rate of a chemical reaction is given by the Arrhenius equation,

$$k = PZe^{-E/RT}$$

where the specific rate constant, k, is expressed as a function of probability, P, collision number, Z, energy of activation, E,, and absolute temperature, T. The collision number, Z, may be taken as constant and T as approximately constant, since the main concern here is an explanation of the data obtained at an average temperature of 85.5°C. Hence, any changes in k may be ascribed to changes in P or in E brought about by the applied field.

The data in Table XVIII indicate that E is decreased by the applied field and also that the field retards the rate of reaction. For the 4500 volts/cm. field the decrease in E is about fifty percent, and, since E is an exponent in the rate equation, such a decrease must be accompanied by a very large decrease in P for a net reduction in rate to be observed.

A consideration of P and E may allow suggestions to be made as to ways by which the field could change the value of P and E so that a lower value of k would result.

P, the probability factor, was introduced into the Arrhenius equation to account for rates greater or less than 'normal'; for the latter, P is approximately unity. That is, P measures the probability that activated collisions will result in products. Hence P is a measure of all the necessary conditions, except activation energy, which must be fulfilled for reaction to occur.

For example, large molecules must be suitably orientated at the moment of collision so that the reactive parts of the molecules concerned may come into contact with one another. Suitable orientation may involve not only the molecules as entities, but also appropriate collisions in respect of oscillation and vibration phase of groups and bonds within the molecule.

If the probability of suitable orientation in the normal reaction were decreased in the field reaction, then a lower value of P might result, with a consequent decrease in rate. This lower P value might result from a restrictive influence by the field on the random orientation of the reactant molecules.

may arise from non ization of the activated complex; the formation of s plex has been postulated by the transition state the 80). If the field were to decrease the probability activation energy would be distributed among the new of freedom in the complex, then the complex would be liable to become stable and there would be less prob of formation of products. According to the theory t ability of suitable distribution of energy decreases increasing complexity of the reactant molecules; thi well be an important factor in molecules such as sty

If the applied field interfered with this distr of energy by such means as polarization, rotational tion, or oscillatory vibrations, etc., there might b tendency for the complexes to return along the path tants.

It is of interest to note that Eyring (81) has that the specific rate constant for the combination methyl free radicals would be decreased by a factor if free rotation of the radicals were restricted.

Moreover, Zener (82) has calculated that electr fields of 20,000 volts/cm. should show a marked diss effect on excited states of diatomic molecules whicl crossed by appropriate repulsive states. Assuming t and a free radical, it might be expected that a 'dis of complexes might occur for the voltage gradients u these studies.

The electronic theory (83) of organic reactions in rather different terms, mechanisms by which the r of organic molecules may be altered; this theory is the assumption that different atomic groups are elec tracting or repelling. In a molecule, a center of e electrons may occur as a result of electron-repellin in this molecule or in adjacent molecules. This ele rich point would be reactive toward an electron-seek in an attacking molecule.

According to the postulates of this theory thes displacements may result from inductive or tautomeri The former refer to the tendency for electrons from atoms to be attracted by a more electrophilic atom.

This inductive mechanism may be static or dynam it is static, the molecule is permanently polarized, if it is dynamic, the electron displacement occurs o porarily as a result of the approach of another mole the latter, the inductomeric effect, the molecule lo polar character when equilibrium is re-attained in i vironment.

The tautomeric mechanism is also regarded as ei as a number of resonating forms which result from rapid to and fro movement of electrons through multiple bond molecules.

The dynamic tautomeric effect is called electromerism. As in the mesomeric effect, it is postulated that actual movement of electrons may occur toward or away from a focal point in a molecule as a result of the approach of an attacking molecule. As in the inductomeric, the electromeric effect vanishes as soon as equilibrium between the fields of the two molecules is re-established.

The inductomeric and electromeric effects are of particular interest here in that it has been postulated that an electrical field might induce electronic shifts in reactant molecules similar to those thought necessary before reaction may occur (4). These suggested electron displacements might either increase or diminish the reactivity of the reactants, and, therefore, a change in rate of the chemical reaction might be expected.

A further change in reactivity might be anticipated if the applied field were strong enough to induce appreciable changes in the permanent effects, i.e., the inductive and mesomeric mechanisms.

The Stark effect (84) furnishes evidence that electrical fields of strengths similar to those used in this investigation might affect the polar nature of reactants. It is of interest to note that this effect, made apparent in an electrical field by the splitting of spectral lines corresponding to a splitting of energy levels, is dependent on th of the voltage gradient.

Wheland (85) has pointed out that organic mole such as hexaphenylethane, in solution decompose to f icals because the radicals are stabilized by resona the dissociation of styrene-free radical is conside ogous to dissociation of a molecule into free radic dissociation of the complex would result in resonan ilized products. If, now, the field increased the of the styrene-free radical complex to resonance st monomer and radical, reduction in rate would follow. corresponds to a decrease in P factor of collision theories, and would have the same result as a decre ability of singlet-triplet transition in the unsatu electrons to which the effect of catalyst has been

A field effect on polarization might result in creased activation energy, tending to increase the However, a lower rate might still result from a pro ately larger decrease in P factor. The situation is cated by the fact that the observed decrease in acti energy may occur in one of the activation-complex st zation-reaction steps, whereas, a proportionately la crease in the P factor might occur in another of the and this might still result in a lower rate.

for the observed inhibition of reaction rate. It is difficult, however, to suggest reasons for the increase in the inhibiting effect of the field through an optimum value as the benzoyl peroxide concentration was increased. Whatever the explanation for this may be, it is possible that the same explanation may account for the lower retardation of rate at 75°C. than at 85°C., since a decreased temperature corresponds to a decreased catalyst concentration.

As previously stated, these suggested possible explanations for the influence of the field found in this investigation are based on too few experimental data. Extensions of the present work might well eliminate some of the suggestions made here, and perhaps might lead to a better understanding of the retarding influence of the field.

The following are a few suggestions for suitable studies to supplement the present investigation:

1) The effect of voltage gradients higher than 4500 volts/cm.
2) The influence of a radio frequency field on polymerization in solution in several different solvents.
3) The relation between the field effect and the type of catalyst used, e.g., a heavier peroxide-type catalyst, or a polar type of catalyst, such as $SnCl_4$.
4) The temperature dependence of the field effect at "constant catalyst concentration" (see reference 69).

5) The field effect in other polymerizations, e.g., chloroprene, etc.

6) The field effect in other types of reactions, e.g., addition of methyl iodide to pyridine, etc.

SUMMARY

AND

CLAIMS TO ORIGINAL WORK

1) An apparatus has been built for the application of alternating electrical fields to chemical reactions; frequencies of 1.15 to 7.72 megacycles per second and applied voltages up to 4500 volts/cm. have been used.

2) The reaction studied was the catalyzed and non-catalyzed polymerization of styrene in bulk-phase. The catalyst used was benzoyl peroxide.

3) The over-all rate of polymerization was found to be approximately zero order and the rate of reaction was dependent on the square root of the catalyst concentration.

4) The procedure used permitted separation of the athermal effects of the applied field from the thermal effects by comparing the reaction subjected to the applied field with a control experiment made at similar temperature.

5) The athermal effect of the applied field was found to be a retardation of the rate the reaction would have attained at the same temperature in the absence of the field.

6) The field effect was found to be dependent on the catalyst concentration.

7) For applied fields of 3000 and 4500 volts/cm. at 1.55 megacycles and at an approximate temperature of 85.5°C., the field effect was a maximum for initial concentrations of approximately 1.2 to 1.7 grams of benzoyl peroxide per liter of styrene.

8) For these last conditions, a minimum field effect was found at an initial catalyst concentration of approximately 0.3 grams of benzoyl peroxide per liter of styrene.

9) At concentrations lower than 0.3 grams of catalyst per liter, the field effect increased down to zero concentration of added catalyst.

10) The average retarding influence of the field on the rate of reaction was found to be proportional to the voltage gradient according to the following equation

$$R = aE^{1.73}$$

where R is the percent reduction in rate, E is the voltage gradient in volts/cm. and $a = 1.85 \times 10^{-5}$.

11) The field effect was found to increase with an increase in temperature of polymerization from approximately 75° C. to approximately 85°C.

12) Variation in the frequency of the applied field between 1.15 and 7.72 megacycles per second produced no perceptible difference in the retarding influence of the applied field.

13) An applied field of approximately 3000 volts/cm. at 1.55 megacycles and at a temperature of approximately 83.0°C. produced no perceptible reduction in rate of decomposition of benzoyl peroxide in toluene.

14) Applied fields in the range of potential gradients and frequencies employed had no effect on the average molecular weight of the polymer within the estimated error of

ten percent in this determination from viscosity measurements.

15) The data show that the applied field retarded the initiation of polymer chains, but was without influence on the propagation and termination of chains.

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