PHYSICO-CHEMICAL EFFECTS OF RADIO FREQUENCY FIELDS

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By

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TABLE OF CONTENTS

Page

TABLE OF CONTENTS

Page

Recent investigations into the nature of matter place emphasis not so much upon the actual constitution of the ultimate particles, as upon the short range force fields which characterize their interaction within the nucleus. In a similar manner, the modern conception of the atom is based upon the interaction of nuclear and electronic force fields of longer range, and the development of this concept describes quite successfully the reactions of some atomic groups. Even for the more complex systems of organic chemistry, the qualitative behaviour is derived with limited success by a consideration of the interactions of force fields set up by the various component groups within the molecules.

These considerations have led experimentalists to investigate the possibility of affecting such reactions by the application of external force fields of several types, including electric, magnetic, and electromagnetic fields. Indeed, the great variety of fields and reactions studied makes it difficult to generalize the results, which are often quite different, and in some instances even contradictory. This is not altogether surprising because most communications report an effect on the reaction kinetics, but very few mention the measurement and control of temperature. Certainly these factors should receive special attention in systems where field energy may be transferred not only to the reacting materials, but to the temperature measuring

device itself - and especially since the rate of energy transfer depends upon the nature of the substances involved.

The present investigation represents an attempt to determine what effect high frequency electric fields have on the kinetics of various systems when every effort is made to measure and control the temperature.

INTRODUCTION

The first application of an electric field to a chemical reaction was probably made by Nicholson and Carlisle in 1801, when they decomposed water by an electric current. However, such a process requires not only the application of the field, but conduction of an electric current by the reacting medium. This type of phenomenon is not a simple field effect, and will not be considered here. But numerous investigations have claimed a variety of effects produced in chemical systems simply by the application of a field. Both one and two phase systems were used, including inorganic as well as organic materials.

In 1925, Ruben (1) claimed the promotion of gas-liquid reactions by discharging the gas into the liquid in an electric field formed by undamped high frequency oscillations. This method required liquids of higher dielectric constant than the gas, and the reaction between hydrogen and cottonseed oil was mentioned. A later report (2) claimed gas-liquid and gas-solid reactions to be effected by projecting particles of the liquid or solid into the gas in an electric field. Examples given include the formation of hydrogen peroxide from water and oxygen and of sulfuric

acid from water, sulfur dioxide and oxygen. Stimulation of reaction by propelling solid or liquid auxiliary particles at high velocity between electrodes at right angles to the path of a reacting gas mixture or emulsion has been claimed (3). It has also been stated that rutile or brookite dispersions promote the polymerization of organic liquids of high dielectric value in electric fields of 100 to 100,000 kilocycles (4).

The reaction time for such processes as evaporation, crystallization, saponification, etc. was found to be shortened in an earthen vessel placed between two plates with 1,000 volts applied. An isolated electrode was dipped into the liquid (5).

Numerous inorganic reactions have been subjected to a variety of fields, and several different explanations were offered for the results obtained. Among these, the gaseous reaction between nitric oxide and chlorine to form nitrosyl chloride was found to be unaffected by magnetic fields up to 20,000 gauss (6). Parker and Armes (7), however, reported the rate of reduction of potassium permanganate by metallic iron in sulfuric acid to be increased by a magnetic field of 10,000 gauss, with similar results for the reduction of ferric chloride by metallic iron or aluminum in hydrochloric acid. A concentration of reagents in certain parts of the system by the field was suggested when stirring was found to reduce the effect.

In a more extensive investigation (8), Bhatnagar et al studied the following reactions in a magnetic field:

(a) The reduction of ferric chloride in hydrochloric acid by iron, aluminum, and zinc.

(b) The oxidation of oxalic acid by potassium permanganate.

(c) The reduction of chromic acid by phosphoric acid.

(d) The oxidation of potassium iodide by chromic acid.

(e) The reduction of potassium permanganate by chloral hydrate.

(f) The oxidation of hydrogen iodide by hydrogen peroxide.

(g) The esterification of acetic acid by ethanol.

Their results led to the conclusion that the rate of a reaction is increased, decreased, or unaffected by a magnetic field according as the sum of the molecular susceptibilities of the final products is greater than, less than, or equal to that of the initial reactants.

Tocco (9) has claimed the use of a.c. fields of high tension and low intensity to accelerate the rate of oxidation of sulfur dioxide and hydrogen sulfide to sulfuric acid, the rate of formation of ammonium sulfate by the action of ammonia and carbon dioxide on calcium sulfate, and the formation of

of ammonia from the elements in the presence of barium carbide.

Activation of a nickel catalyst by waves from a 4 watt radio transmitter or a large induction coil has been claimed to give 14 to 38 percent improvement in yield in the decomposition of nitrous oxide (10). On the other hand, intense exposure of platinum sols to electric fields of ultra high frequency was found to decrease the catalytic action of the platinum for hydrogen peroxide decomposition (11). Moderate exposure to the same fields gave the opposite effect.

Also claimed are the liberation of iodine from aqueous sodium iodide (12), and the formation of water and ammonia from the elements (13) by high frequency fields. There is some indication that reverse and/or harmful side reactions may be avoided when ozone, nitric oxide, and sulfur dioxide are prepared in a 10 megacycle field modulated at 40 kilocycles (14).

Many organic reactions have been studied in various types of fields, and it is here particularly, that the results are inconsistent and often in direct contradiction. The addition of hydrogen bromide to 2-pentene was unaffected by a magnetic field of 15,000 gauss (15), and also by an electrostatic field of unspecified strength (16). The nitration of benzoic acid remained unaltered in a magnetic field of 23,000 gauss, and in an electrostatic field of approximately 10,000 volts per cm. (16). However,

the extent of reaction between hydrogen bromide and allyl bromide in glacial acetic acid was reduced by 65 percent in a magnetic field of 14,000 gauss (17).

The gas phase reaction between carbon monoxide, hydrogen, and solid fuel distillation products was promoted by a high potential electrostatic field in conjunction with ultraviolet radiation (1), and Moens et al decomposed ethyl alcohol, amyl alcohol, and diethyl ether in high frequency fields (13).

The esterification of acetic acid and ethanol was accelerated by an oscillating field of 1.256 meters wave length, which was also claimed to reduce the acidity of wine, olive oil, and vinegar (18).

The reaction between carbon dioxide and methane (the latter in excess) to form acetaldehyde in fields of 10 kilocycles and 20 kilovolts was described in a patent (19), which also claimed that with equal concentrations of the reactants, formaldehyde could be formed.

The combustion rate of acetylene-air mixtures was reduced by 9 percent in electrostatic fields of 670 to 700 volts per cm. and to a lesser extent by high frequency fields of about one megacycle (20). At 8 megacycles the reduction was negligible (21), and an increase beginning at 18 megacycles amounted to

20 percent at 34 megacycles. The authors explained the decrease in rate by a removal of ions and electrons from the combustion zone, and the increase in rate by a "sort of resonance energy exchange between the electrons and molecules of the reacting system".

Belenki (22) reported optimum wave lengths for the transformation of analine black, starch hydrolysis, and the decoloration of analine copper blue with hypochlorite. Thermal effects were also noted. The catalyzed reactions of ethylene and hydrogen to form ethane, and of hydrogen bromide and allyl bromide to form dibromopropane were retarded in a magnetic field (23).

The oxidation of primary alcohols to aldehydes was accomplished by placing the reaction vessel between condenser plates forming part of a tuned circuit (24). In the same manner, tars were produced from aromatic compounds or petroleum products in the presence of air at reduced pressures, and hydrogen was reacted with ethylenic compounds.

The majority of recent investigations into the field effect have dealt with polymerization reactions, and here also results of a most controversial type have been obtained. Yakubovitch and Evdokimova (25) studied the polymerization of chloroprene in a high frequency electric field by sealing chloroprene, with air,

in small ampoules which were placed between the plates of a con-
denser. A field of 37.5 megacyoles was found to increase the rate
of polymerization over that found for equivalent heating in a
water bath. X-ray analysis indicated the structure and particle
size to be unaffected, which was offered as evidence for an
athermal effect.

In 1937 Liechti and Scherrer (26) tried to find the
cause of X-wax formation in the insulation oils used in high vol-
tage cables and transformers. Simple oompounds like styrene,
indene, and paraffin were polymerized in electric fields, and the
rates were found to depend on the field distribution and the
frequency. Also, substances that previously resisted polymeriza-
tion were polymerized in the fields used. Liechti (27), continuing
the investigation, studied the polymerization of styrene in bulk
and in toluene solution under the action of 50 cycle fields of
various types. To duplicate the conditions found in cables and
transformers, one electrode was in contact with the reaction
mixture. No mention is made of the measurement or control of
temperature. The rate of the bulk polymerization, which was
unaffected at low field strengths, increased markedly at 43.5
kilovolts per mm. and then decreased again with still stronger
fields. Preliminary treatment with these stronger fields increased
the purely thermal reaction; the pre-activation persisted for as

long as one week. Reapplication of the field during the thermal polymerization of the activated styrene caused retardation. At 26 megacycles, dielectric heating was sufficient to account for the observed effects. The polymerization in toluene solution was not affected by any of the fields used.

The polymerization of styrene was further investigated by Shorygina and Petrova (28) using fields of 10 cm. and 100 cm. wave length. In an inert atmosphere the 10 cm. field increased the rate of polymerization and caused a 20 percent increase in the molecular weight of the polymer. The inhibiting action of oxygen was intensified in the field and there was a decrease of 10 percent in the molecular weight of the polymer formed. The 100 cm. field was claimed to have only a thermal effect, but no further mention is made of possible temperature effects.

An early patent (19) claimed the polymerization of ethylene to oily products in 1,500 kilocycle fields of high potential, and Moens and Julliard found that benzene and acetylene could be polymerized in high frequency electromagnetic fields of unspecified strength (13). Berraz and Davie obtained complete polymerization of acetylene fed, at constant pressure in the range 0.01 to 1.5 mm. of Hg., through a reaction tube in a 15 megacycle field (29).

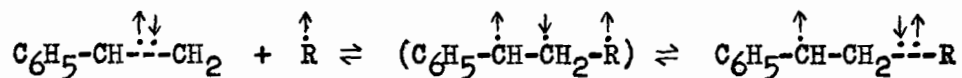In 1950, Bryce et al (30, 42) reported an extensive

study of the bulk polymerization of styrene in electric fields,
in which particular attention was given to the measurement and
control of the reaction temperature. Following regular commercial
practise, the temperature of the styrene in the field was measured
with a calibrated alcohol thermometer, although it was noted that
a similar mercury thermometer gave essentially the same reading in
the field. Only the bulb of the thermometer was immersed in the
liquid. The effect of dielectric heating was minimized by flowing
oil from a constant temperature bath against the electrodes. Under
these conditions the temperature of the styrene in the field was
found to be as much as 6°C. above that of the surrounding oil, the
actual extent of the temperature rise depending on the field
strength used. This was compensated by an equivalent increase in
the temperature of the control reaction at the time the field was
turned on.

The effect of catalyst concentration (benzoyl peroxide),
frequency, field strength, and temperature were studied, and the
results were summarized as follows:

The field caused an inhibition which was roughly pro-
portional to the square of the field strength in the range from zero
to 4500 volts per cm. The effect was greater at 80°C. than at 70
or 100°C., although the data at 100°C. were considered rather doubt-
ful for quantitative comparison. Several frequencies in the range
1150 to 7720 kilocycles were used, with no measurable difference in
the inhibition obtained. Catalyst concentrations from zero to 2.6 g.

per l. were used, and the inhibition, which was greatest for the
uncatalyzed reaction, decreased to a fairly sharp minimum at a
concentration of 0.25 g. per l. Beyond this point the effect
increased to a broad maximum in the region of 1 g. per l. None
of the variables studied showed any effect on the viscosity
average molecular weight of the polymer, which was offered as evi-
dence that only the initiation stage of the reaction was affected
by the field. This was further supported by calculations showing
a decrease in the rate of formation of active centers caused by
the field. The decomposition of benzoyl peroxide in toluene was
shown to be unaffected by the field in a concentration of about
24 g. per l. (approximately 10 times that used in the polymeriza-
tion experiments).

Schmid et al (31) found the rate of styrene polymeri-
zation to methanol insoluble polymer to be decreased in a magnetic
field. This was explained on the basis of a restricted mobility
of the reacting molecules due to orientation by the field. Details
of the investigation have not been obtained, but in a recent note
on this study Leffler and Sienko (32) state that calculations show
such a mechanism to be rather unlikely for the type of field used.
They propose that chain propagation in field free space occurs by
a preliminary uncoupling of the pi-electrons; the process to be
represented as follows:

$$C_6H_5-\overset{\uparrow\downarrow}{CH}\text{---}CH_2 + \overset{\uparrow}{\dot{R}} \rightleftharpoons (C_6H_5-\overset{\uparrow}{\dot{C}H}-\overset{\downarrow}{\dot{C}H_2}-\overset{\uparrow}{R}) \rightleftharpoons C_6H_5-\overset{\uparrow}{\dot{C}H}-CH_2\overset{\downarrow\uparrow}{\text{---}}R$$

It is suggested that in the presence of a strong magnetic field
the three uncoupled electrons of the transition state all become
oriented with respect to the external field, and lead to the
following configuration:

$$(C_6H_5-\overset{\uparrow}{\overset{\centerdot}{C}}H-\overset{\uparrow}{\overset{\centerdot}{C}}H_2-\overset{\uparrow}{\overset{\centerdot}{R}})$$
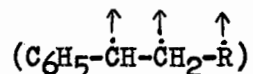
This arrangement would not readily result in bond formation in
either direction, a condition which would reduce the rate of chain
propagation and also, therefore, the rate of formation of methanol
insoluble polymer.

In contrast to the work of Schmid et al, Breitenbach
and Richter (33) found the rate of styrene polymerization in
sealed glass tubes at 80 and 100 $^{\circ}$C. to be unaffected (within 1 per-
cent) by magnetic fields of 8,000 to 40,000 gauss. Also, Collins
and Bryce (34) report no change in the rate for both the catalyzed
and uncatalyzed reactions in a magnetic field of 12,000 gauss at
80°C. The rates of decomposition of benzoyl peroxide and hydrogen
peroxide were found to be equally unaltered, confirming a previous
report (35) that a magnetic field of 7,518 gauss did not affect the
decomposition rate of benzoyl peroxide.

In an attempt to extend the results obtained by Bryce
et al, Russel and Winkler (36) studied the decomposition of benzoyl
peroxide in the same apparatus. Both alcohol and mercury thermo-
meters suspended in the vapors of a boiling liquid gave higher

readings in the presence of the field than those obtained normally,
and a better method of determining the field reaction temperature
was sought. The method finally chosen gave a comparison of the
reaction temperature in the field cell with that in the control
cell, the latter being measured with a calibrated mercury thermo-
meter. The comparison was made using a potentiometer and two
copper-constanin thermocouples of naked 28 B. & S. gage wire, as
follows (see fig. 5).

The potentiometer was maintained in balance with one
thermocouple placed in the control cell. The second thermocouple
was "stored" close to reaction temperature in a test-tube located
in the field bath near the field cell. To make a determination,
the field thermocouple was removed from "storage" just as the field
was turned off. It was immediately placed in the cell and connected
to the potentiometer. The temperature of the thermocouple, as
indicated by galvanometer deflection, rose several degrees to the
reaction temperature in about 3 seconds, remained steady for about
5 to 8 seconds, and then began to drop as the heat supplied by the
field was dissipated. By careful choice of the field bath tempera-
ture, the steady galvanometer reading was adjusted to be zero indi-
cating the same reaction temperature in the field and control cells.
The system was calibrated in the absence of the field to determine
the temperature equivalence of non-zero readings.

Using this procedure the effect of electric fields on

the decomposition of benzoyl peroxide in toluene solution was investigated. Fields and concentrations similar to those used by Bryce et al were studied, both in a normal atmosphere and in a nitrogen atmosphere. An inhibition corresponding to that obtained in the styrene polymerization experiments was indicated, although analytical difficulties at these low concentrations appeared to be a source of considerable error. However, one observation is particularly worthy of note. Although the benzoyl peroxide decomposition seemed to be inhibited, the appearance of a red color occurred about an hour earlier in the field when an air atmosphere was used. The red color did not occur in a nitrogen atmosphere, and other evidence was obtained which suggested an oxygen effect. This behaviour will be further considered in a later section.

The results obtained by Russel and Winkler were sufficiently interesting to encourage further study of a similar reaction in the presence of a high frequency electric field. The decomposition of benzene-diazo-acetate, described in detail by Waters and others (37-40), was finally chosen for the purpose. This reaction is similar to the decomposition of benzoyl peroxide in that both are first order processes involving free radical mechanisms and attack of the solvent by the free radicals formed. Moreover, the two compounds themselves have certain structural similarities, viz.,

$$C_6H_5 - N = N - O - CO - CH_3 \qquad C_6H_5 - CO - O - O - CO - C_6H_5$$

and it was felt that the action of an electric field on the acetate decomposition might well be similar to its effect on the peroxide decomposition.

A practical advantage in the choice of benzene-diazo-acetate as a subject for investigation lay in the fact that the kinetics of its decomposition may be studied by measuring the evolution of nitrogen which accompanies the reaction. This permits a wide range of concentrations to be used, and eliminates the necessity for sampling the reaction mixture, with the attendant readjustments to the electrical system.

The Out-gassing of Liquids

Some of the results obtained in the experiments with the decomposition of benzene-diazo-acetate indicated that it would be necessary to include some work on the evolution of gas from super-saturated gas-liquid solutions. Much of the information on this topic is scattered through the literature in the form of observations made in broader investigations. However, the following review will serve to bring out the points of major interest to this investigation.

Kenrick et. al. (41) noted in 1924 that in a properly cleaned capillary tube various liquids, including water, could be superheated from 50 to 170°C. above the boiling point without bubbling.

It was later (42) reported that the cavitation of water caused by high frequency sound waves did not occur when precautions were taken to remove gas nuclei from the liquid before application of the waves.

Harvey et. al. (43), in 1946, found that when soda water was poured into an ordinary glass container, degassing occurred rapidly with the formation of many bubbles at the glass walls; but when soda water was poured into a carefully cleaned and wet container, no bubbles formed and the supersaturation remained. Bubbles did not form on a clean wet quartz rod dipped into the soda, but when the rod was drawn across the container wall, bubbles did form at the point of contact and at certain points along the scratch. However, a scratch made on the clean wet surface prior to addition of the soda water caused no bubbles. Scratching the outside walls did not give rise to bubble formation, so that sound waves were not the basic cause.

Pease and Blinks (44) investigated the formation of bubbles in supersaturated gas-liquid solutions caused by a sharp blow on the container bottom. They found that bubbles formed readily using water and glass without special precautions. However, when the glass was cleaned carefully and the system subjected to high pressures, subsequent evacuation and sharp blows failed to produce bubbles. A cast latex container gave similar results which were not so critical to cleaning. Organic liquids with glass did not

produce bubbles, even when dirty. The presence of a few organic crystals caused easy cavitation, whereas many ionic crystals were necessary. Cavitation occurred readily at the surface of paraffin crystallized from the melt while pressurized under water, but did not occur during the solidification or melting processes. They concluded that water does not cavitate, when free of the gas phase (nuclei), nor does it tear away from wetted glass except under considerable tension. They also concluded that a surface of fixed molecules is essential for cavitation.

Harvey et. al. (45) photographed the trailing end of a blunt 5 mm. glass rod moving at high velocity in a liquid contained in a 16 mm. tube. They reported that the presence of gas nuclei in the liquid, or hydrophobic patches on the rod, caused cavitation at the rear end of the rod at velocities less than 3 m. per sec. On the other hand, a completely hydrophilic rod in a nucleus free liquid did not give rise to cavitation at velocities up to 37 m. per sec. The addition of a detergent did not prevent cavitation at low velocities. Coating the rod with paraffin wax or General Electric repellant varnish caused cavitation at less than 3 m. per sec. leaving a misty trail and fine bubbles scattered throughout the liquid.

The kinetics of the solution and evolution of air by distilled water, and petroleum fuels and oils was studied in some detail by Schweitzer and Szebehely (46). By assuming that the solutions

obeyed Henry's Law and that the rate of evolution (solution) was
proportional to the amount of supersaturation (undersaturation)
they derived the expression

$$2.303 \log \frac{S}{r} \cdot \frac{Pe - Pe'}{Pe' - P} = kt$$

for the variation of pressure P with time t in a constant volume
system. In this expression S is the solubility constant, r the
gas-liquid volume ratio, Pe the equilibrium pressure equivalent to
the initial solution, Pe the equilibrium pressure finally obtained,
and k the rate constant. Graphs of $\log \frac{S}{r} \cdot \frac{Pe - Pe'}{Pe' - P}$ against t
were found to be straight lines showing the above assumptions to be
essentially valid. The half life T_E for the process was found to
depend upon r according to the expression

$$T_E = (T_E)_{r \to \infty} \cdot 1/(1 - e^{-cr})$$

where C is a constant. For a given value of r and a fixed agita-
tion, T_E was found to depend upon the solubility constant, and such
liquid properties as viscosity, density, surface tension, etc.

Containers of steel and lucite were used in this work,
and water always led to bubble formation. Petroleum products, on
the other hand, were easy to supersaturate without bubble formation,
and it is noted that these latter materials wet both steel and lucite,
whereas water wets neither.

Distinguishing carefully between dissolved gas and gas entrained in the form of microbubbles, they concluded that the cavitation (formation of visible bubbles) occurring at reduced pressure is a false cavitation depending on pre-existing flaws in the liquid, such as microscopic or sub-microscopic bubbles (nuclei) into which dissolved gas can escape. True cavitation, claimed to be failure of the liquid proper, requires much greater tensions than those produced by merely lowering the pressure.

EXPERIMENTAL AND RESULTS

In early experiments two reaction vessels were used, one with the field applied (designated the field cell), and the other without (designated the control cell). Attempts to measure the volume of nitrogen evolved at constant pressure failed owing to poor sensitivity of the pressure regulators, and the measurement of pressure at constant volume was finally adopted.

Apparatus

The apparatus used in this investigation was made up of two distinct parts: the electrical and the chemical. The electrical equipment, which was essentially the same as that used by Bryce, et. al. and by Russel and Winkler, served to generate the desired field and to apply it to the reacting system. The chemical equipment was composed of reaction cells, pressure measuring apparatus, and equipment for measuring and controlling reaction temperature.

The electrical equipment

A schematic diagram of the electrical equipment is shown in fig. 1. The generator was a Marconi Transmitter Type 98347 with

Figure 1.

Schematic Diagram of the Electrical Equipment
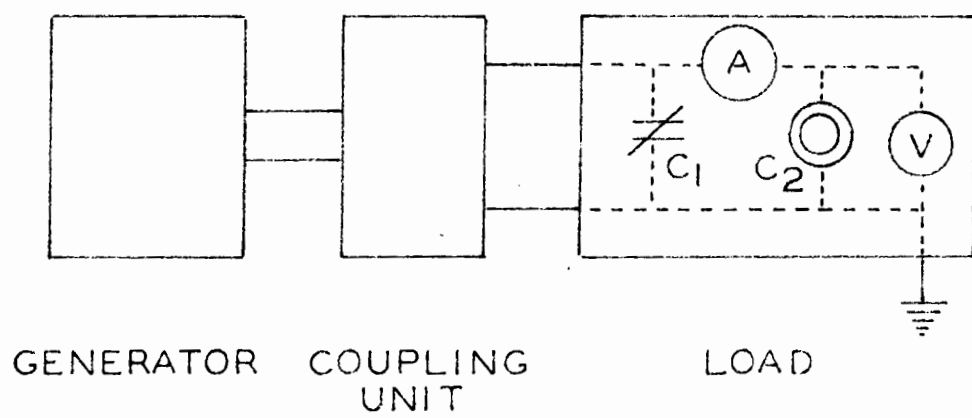
Generator   -   Marconi Transmitter Type 98347

Coupling Unit -   1:100 variable step-up auto-
transformer (air cored).

Load   - C_1 - tuning capacitor

                 A   - thermo-ammeter

                 V   - vacuum tube voltmeter

                 C_2 - capacitance of field cell

GENERATOR   COUPLING   LOAD
             UNIT

H.F. adaptor (fig. 2), modified in the out put circuit by grounding the antenna lead through a small resistor and capacitor in series. Power was supplied to the transmitter from a standard type power pack delivering up to 200 ma. at 1500 volts. Filament voltage was obtained from a 110 volt D.C. line using a resistance voltage divider.

The coupling unit, which also served as a voltage amplifier, was an air core step-up autotransformer, of which the one turn primary was inductively coupled to L_6 of figure 2. The variable secondary (usually about 100 turns) was connected to the load made up of a tuning capacitor C_1, a radio frequency thermo-ammeter A, a vacuum tube voltmeter V, and the capacitance C_2 of the reaction vessel which will be described shortly.

When properly adjusted at 1.5 megacycles, this arrangement was capable of supplying up to 4000 volts across the reaction vessel for slightly polar solvents such as toluene, xylene, etc. Somewhat lower voltages were obtained with more polar materials such as the halogenated benzenes and certain esters and acids.

The field strength corresponding to any given voltage may be calculated in a manner similar to that used by Bryce (48). Toluene, used in most of this work, has a dielectric constant of 2.3, and results in a field strength (volts per cm.) roughly equivalent to the voltage applied. An increase in the dielectric constant of the liquid will cause a decrease in the field strength relative to the applied voltage.

Figure 2.

Circuit Diagram for the Marconi Transmitter

Type 98347

Fig. 2   Circuit Diagram For Transmitter.

·The frequency was adjusted with a calibrated Hallicrafter receiver using a small pick-up coil near the air-core autotransformer. Interference with broadcast signals was prevented by a grounded copper screen completely enclosing the electrical system.

The chemical apparatus

A diagram of the field cell is given in fig. 3. It was essentially a pyrex glass cylindrical annulus about 1 cm. thick, 6 cm. in outside diameter, and 10 cm. high. One outlet, fitted with a ball and socket glass joint, connected to the nitrogen measuring system. The cell was filled through a second outlet, fitted with a 10/30 ground glass joint and stopper. A thermocouple well extending about 8 centimeters into the cell, was spaced symmetrically relative to the two outlets as shown. Three lugs at the top of the cell served to hold it in a loosely fitted mounting ring. Thin copper electrodes extending from the lugs to the bottom of the cell were fixed to the external walls with liquid solder. The control cell was as nearly like the field cell as possible except that electrodes were not mounted on the control cell. Also, the ground glass stopper was replaced by a calibrated mercury thermometer incorporating a 10/30 ground glass joint so located that the thermometer bulb was situated mid-way in the reacting liquid. The volume of each cell was about 105 ml. and a 90 ml. sample in the field cell just covered the

Figure 3.

Diagram of the Field Cell

E - electrodes

L_1 - liquid level

L_2 - depth of thermocouple well

M - mounting lugs

O_1 - outlet to pressure system

O_2 - filling outlet

W - thermocouple well
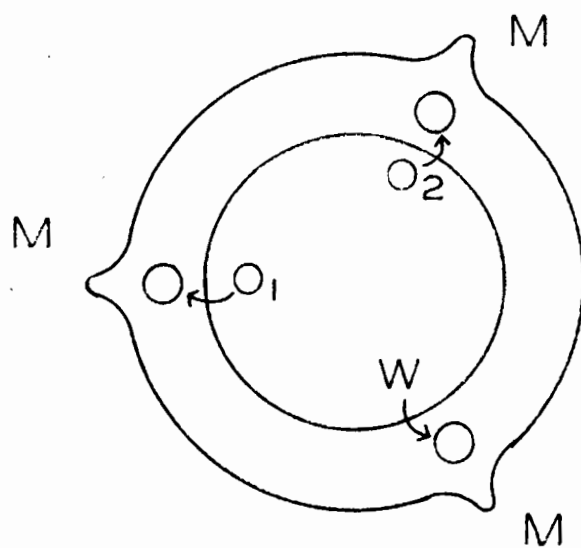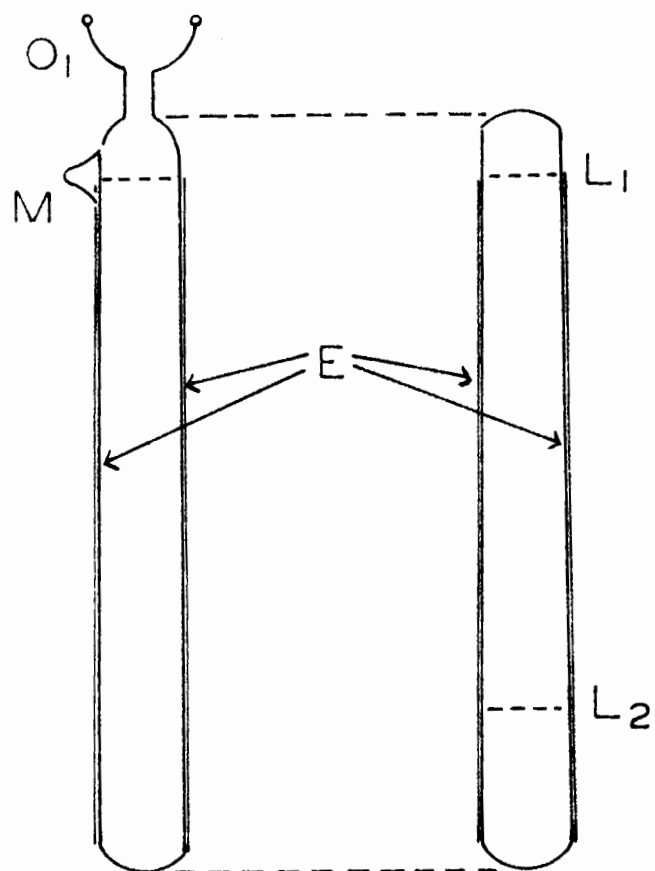
electrodes completely.

The pressure measuring system is shown in fig. 4. The outlets C_1 and C_2 connected to the ball and socket joints of the control and field cells respectively, through flexible coils of 3 mm. glass tubing. M_1 was a mercury manometer of 12 mm. glass tubing to measure the pressure in the control system. It was set up initially by closing S_3, raising the mercury level above S_6, and then closing S_6 and lowering the mercury level to the desired position (see later). M_2 was a differential mercury manometer of capillary tubing to measure the pressure difference between the control and field systems without seriously altering their volumes. The control system included the control cell, the connecting tubing up to stop-cock S_1 and the variable volume over the mercury of the manometer M_1. The field system was similar, with the small volume v replacing the manometer volume.

The volumes V_1 and V_2 of the two systems were measured and equalized using the known volume V, as follows. Volume V was filled with air to some given pressure Po measured on M_1, and stop-cock S_5 closed. With stop-cock S_1 closed, the field system and network N were evacuated and stop-cock S_7 was closed. Stop-cock S_5 was opened, and when the pressure indicated on the differential mano-meter M_2 was steady, stop-cock S_2 was closed. This procedure was repeated with the control system, using exactly the same initial

Figure 4.

Diagram of the Pressure Measuring System

Used in Conjunction with Two Cells

C   - connections to cells

M_1 - manometer

M_2 - differential manometer

S   - stop-cocks

V   - calibrating volume

v   - compensating volume

L   - mercury levelling bulbs

S6

V

S5

TO GAS CYL. OR ATMS.

TO VACUUM PUMP

N   S7.

C1   S1   S2   C2

V

L1   M1   M2

S3

L2

S4
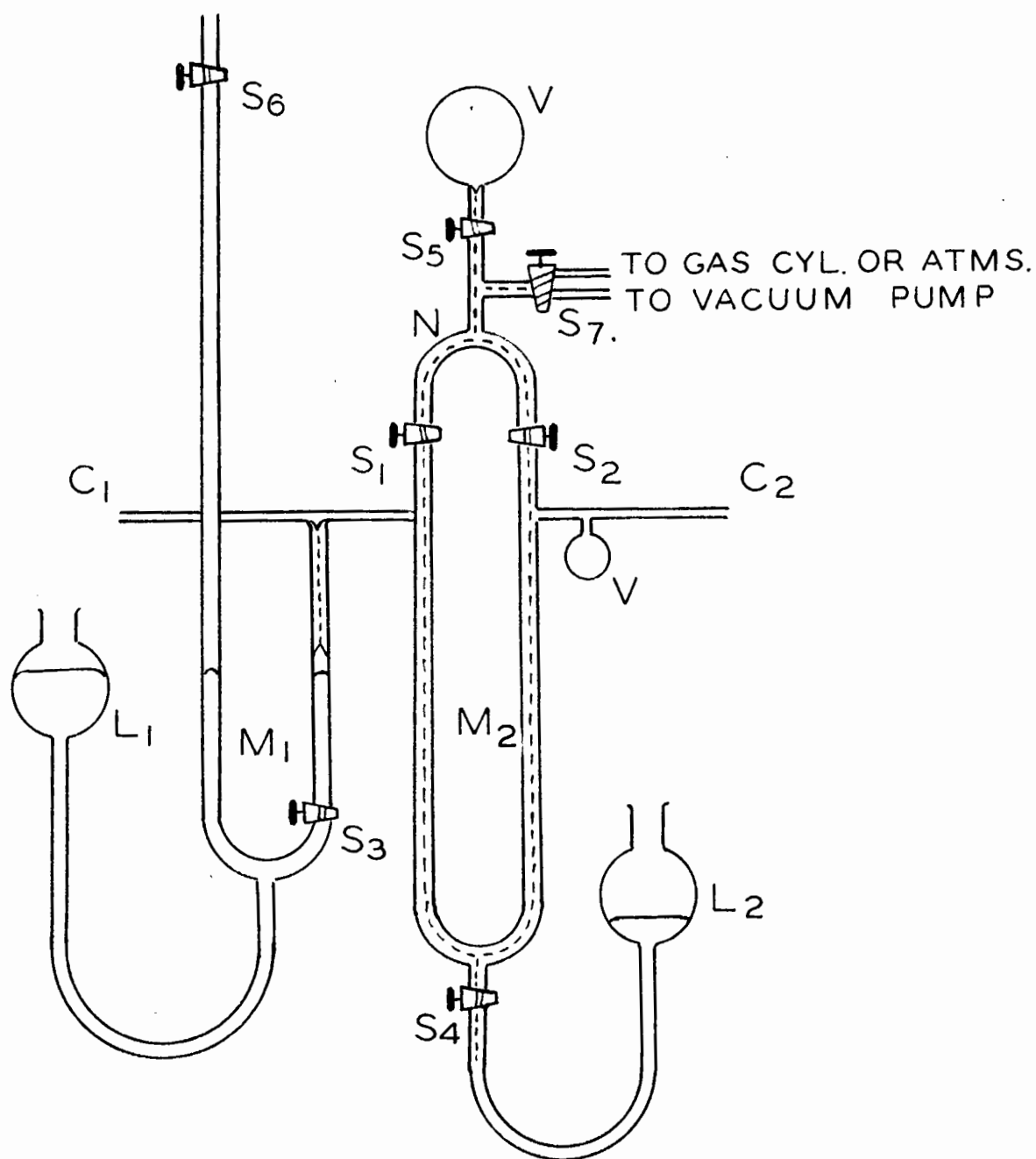
pressure. The differential manometer was then balanced by adjusting the mercury level in the right hand arm of M_1, and the pressure $P_1(=P_2)$ was read. The position of the mercury level was carefully marked, and this position was used for all subsequent readings. The small volume of the network N was then determined by evacuating both systems and connecting volume V, at the same initial pressure Po, to the combined system. The resulting pressure P_{12} was read, and the volumes V_1, V_2 and N were then calculated from the relations

$$\text{Po } V \;=\; P_2 \,(V_2 + N) \;=\; P_1 \,(V_1 + N) \;=\; P_{12} \,(V_1 + V_2 + N)$$

$$P_1 \;=\; P_2$$

The volume of the control system was maintained constant between readings by keeping stop-cock S_3 closed. To take a pressure reading, the mercury level was adjusted approximately, and stop-cock S_3 was opened. The final adjustments were made to bring the mercury level back to the marker and S_3 was closed. The reading was then taken at the operator's convenience.

The control cell was placed in a constant temperature bath filled with a low viscosity mineral oil and maintained at the desired reaction temperature. The oil completely covered the cell proper, leaving the outlets about $3/4$ inches exposed. The temperature of the reaction mixture was measured with a calibrated mercury thermometer placed in the outlet fitted with the 10/30 ground joint, as stated previously.

The field cell was placed in a similar bath maintained at a temperature sufficiently below the reaction temperature to compensate for field heating. Adequate flow of oil around the cell was ensured by a propeller type stirrer fitted to a glass shaft extending down the core of the cell. The reaction temperature in this cell was compared with that in the control cell using a potentiometer-thermocouple arrangement similar to that used by Russel and Winkler. This is shown in fig. 5. The copper-constantin thermocouples were made from 28 B. & S. gage wire. To make a temperature comparison the potentiometer was balanced against the thermocouple located in the well of the control cell (reaction mixture was placed in the wells at the same time that the cells were filled). The field thermocouple, "stored" in a test-tube in the field bath, was removed from "storage" just as the field was turned off. It was immediately placed in the well of the field cell and connected to the potentiometer. As noted by Russel and Winkler, the temperature of the thermocouple rose quickly to a plateau where it remained steady for about 5 seconds, and then dropped slowly to the bath temperature as field heating was dissipated. A proper choice of the field bath temperature adjusted the field reaction temperature to that of the control reaction as indicated by a zero galvanometer deflection for the plateau. The procedure required that the field be turned off for about 15 to 20 seconds.

During the latter part of the investigation the general

Figure 5.

Diagram of the Temperature Measuring Apparatus

B -   dry cell

R_1, R_2 -   resistance decade boxes

G -   galvanometer (minor type)

C_1 -   control cell thermocouple well

C_2 -   field cell thermocouple well

J -   cold junctions

S -   storage test tube
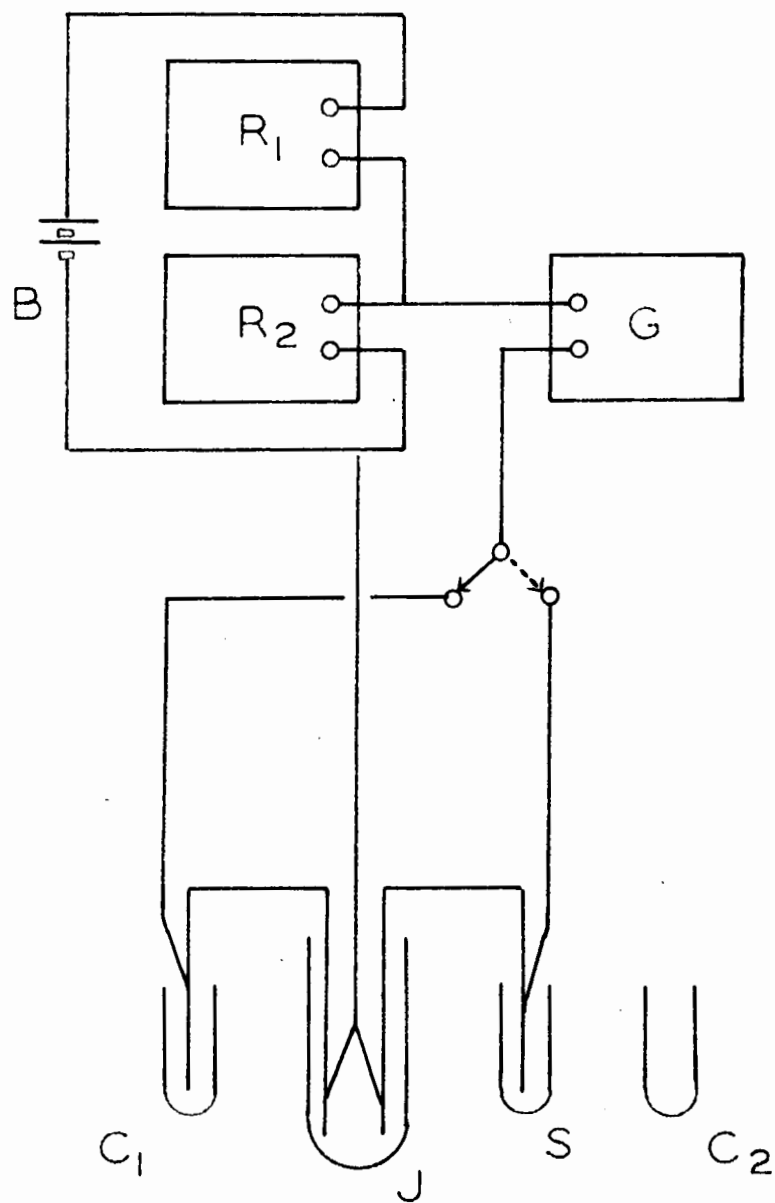
approach was modified in such a way that only one cell was used. A diagram of the pressure measuring apparatus for this phase of the work is given in fig. 6. Its calibration was accomplished by the same method as for the previous system.

Other smaller modifications made to various parts of the apparatus from time to time will be described in the appropriate parts of the next section.

Figure 6.

Diagram of the Pressure Measuring System
Used in Conjunction with One Cell

C - Connection to cell

M - manometer

S - stop-cocks

V - calibrating and pressure reducing volume

L - mercury levelling bulb

S_6

V

S_5

TO GAS CYL. OR ATMS.
TO VACUUM PUMP

S_7

C

M

L

S_3
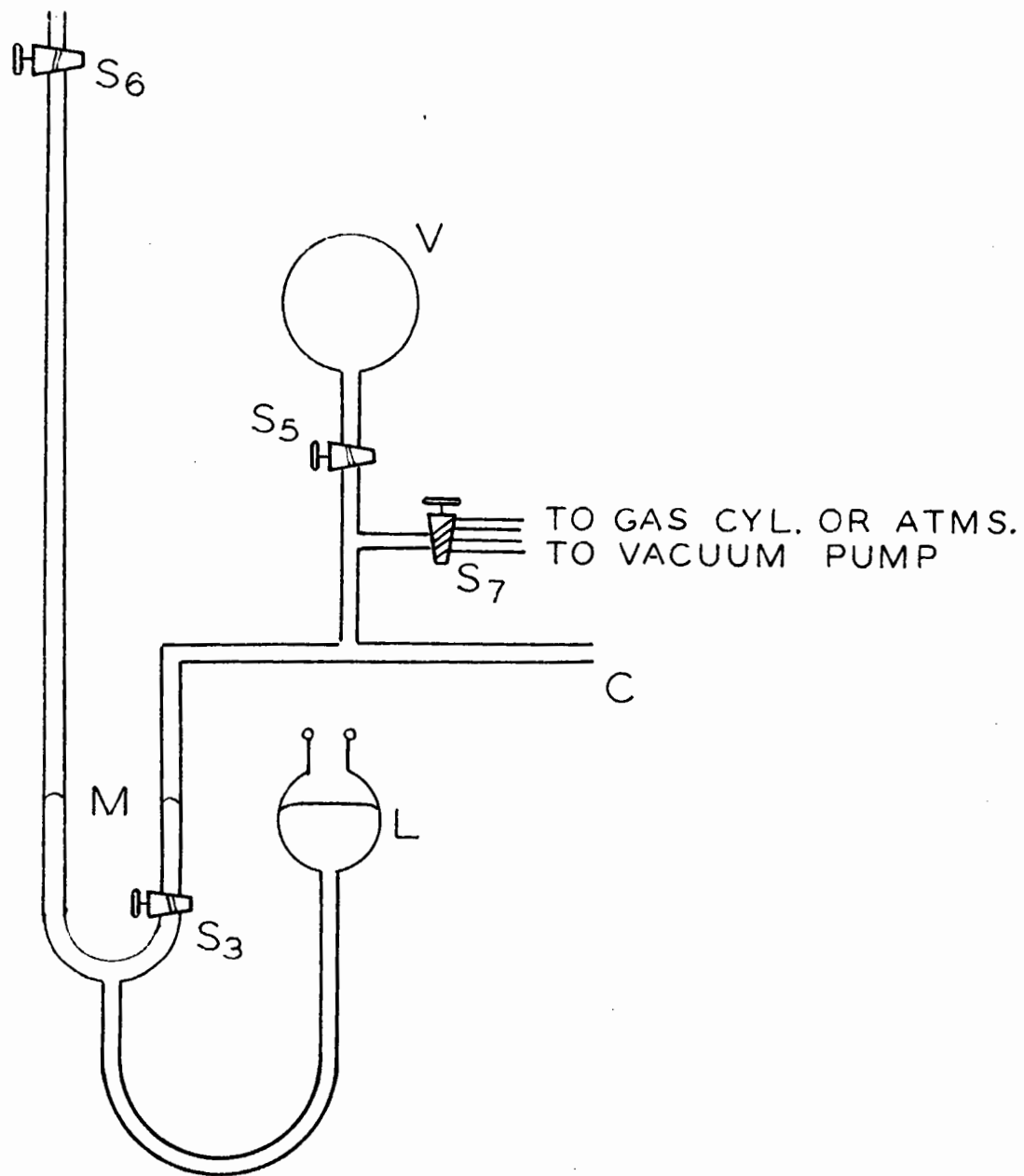
Methods and Results

The decomposition of benzene-diazo-acetate initially chosen for this investigation was studied under a variety of conditions, with results that led, in turn, to a number of experiments involving the out-gassing of liquids in electric fields. Several different procedures were used in each set of experiments, and it is expedient to consider together the details of each method and the results obtained.

The decomposition of benzene-diazo-acetate

Benzene-diazo-acetate was prepared indirectly (47) by bubbling nitrous fumes, produced by the action of dilute sulfuric acid on solid sodium nitrite, through a solution of acetanilide in a 9 to 1 mixture of acetic acid and acetic anhydride until the solution turned dark green (usually 3 to 4 hours). The product of this reaction was a solution of nitroso-acetanilide, which rearranged on precipitation in cold water to form benzene-diazo-acetate as follows:

$$C_6H_5 - N - CO - CH_3 \qquad C_6H_5-N = N - O - CO - CH_3$$
$$\overset{|}{N}O$$
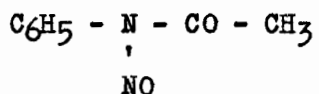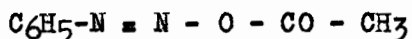
nitroso-acetanilide   benzene-diazo-acetate

The nitroso-acetanilide solution was poured slowly into well stirred

ice water to prevent the occurrence of large lumps. The fine yellow crystals thus formed were filtered with suction and washed with ice water to remove all traces of acetic acid odor. With occasional stirring to prevent caking of the moist crystals, clean dry air was drawn through the product for about 2 hours. After further drying for 48 hours in a vacuum dessicator maintained at $0^{\circ}C$. the fine powdery crystals were found to keep indefinitely in a glass stoppered bottle at the temperature of dry ice. The acetate thus formed melted fairly sharply at 49 to $50^{\circ}C$. and then exploded giving off copious white fumes and leaving a black tarry residue.

The decomposition of benzene-diazo-acetate in toluene at room temperature was reported by Bamberger (37) who isolated toluene, acetaldehyde, acetic acid and methyl diphenyls from the reaction products, together with a high boiling black residue. More recently Grieve and Hey (38) obtained first order curves for the volume of nitrogen evolved in a constant pressure system, and separated the same compounds from the products. Good equivalence between the amount of acetate decomposed and the nitrogen evolved was obtained only when the acetate was dried until a slight amount of discoloration had occurred. This was felt to be impractical for the present investigation because the discolored acetate could not be stored without further decomposition. The only serious difficulty involved in using the less pure product was the necessity for an experimental determination of the final nitrogen pressure.

The toluene used in this work was of C.P. grade, supplied by Merck and Company, Inc.

The same general procedure was used in all of the acetate decomposition experiments. The cells were cleaned, rinsed with water and then with alcohol, and finally dried in an oven. Each was then placed in its thermostate and connected through the ball and socket joint to the pressure measuring system with stop-cocks S_1, S_2 and S_7 open. The desired solution was then prepared from a weighed amount of the acetate using a 250 ml. volumetric flask. Measured samples were transferred to the cells through the 10/20 ground glass joints which were immediately cleaned with a Kleenex swab moistened with benzene. The mercury thermometer was then placed in the control cell and the ground glass stopper in the field cell. The systems (still connected through stop-cocks S_1 and S_2) were partially evacuated, and S_7 was closed. Stop-cock S_3 was opened and the mercury level of manometer M_1 was brought to and maintained at the special marker. The experiment was then "begun" by starting the clock, closing stop-cocks S_1, S_2, and S_3, and immediately reading the differential manometer. The field, if used, was then turned on and adjusted, and the manometer M_1 was read. Subsequent readings were made by opening stop-cock S_3 and levelling the mercury at the marker. At the desired time, the stop-cock was closed, and the manometers were read in the same order noted above. The pressure attained in 20 to 24 hours was taken as the final pres-

sure, since an extended experiment indicated that the change after this period of time was negligible. Following each pressure reading, the reaction temperatures were determined in the manner indicated previously.

Partial evacuation of the system at the start of an experiment was found necessary because the apparatus was designed initially to operate at constant (atmospheric) pressure, and experiments started at atmospheric pressure invariably developed leaks before they were completed.

Preliminary experiments were made without the field to ensure satisfactory reproducibility between the two cells. The best results were obtained when the cells were washed with a hot concentrated sodium hydroxide solution, and this procedure was adopted for most of the later work. Even under these conditions an unpredictable difference was found, but it was sufficiently small that a field effect of the magnitude reported by earlier workers would be readily detected.

The differential manometer used in the initial experiments was made of 10 mm. diameter tubing. It's operation caused a significant change in the volume of the system for which correction was applied in the following manner.

It was assumed that the reaction was sufficiently slow and the nitrogen evolution sufficiently fast that gas in solution was in equilibrium with gas in the free volume at

all times. It was also assumed that the solubility of
nitrogen in toluene obeyed Henry's Law. Then the number
of moles of gas in the system at a given time would be
given by

$$P' k \quad + \quad \frac{P' (V + \Delta V)}{R T}$$

where P' is the pressure, k is the solubility constant
based on the 90 ml. sample and the experimental tempera-
ture, V is the initial free volume, ΔV is the change in
free volume caused by operation of the differential mano-
meter, T is the temperature of the free volume and R is
the gas constant. If the volume had remained constant,
this same number of moles would be given by

$$P k \quad + \quad \frac{P V}{R T}$$

where P is the pressure which would have resulted with
no change in volume. Be equating these expressions the
corrected pressure P was shown to be

$$P = P' \quad + \quad \frac{\Delta V}{k R T + V} \quad P'$$

The cross-sectional area of the differential manometer
tubing was determined by measuring the length, at various
positions, of a mercury thread of known weight. It was
found to be 0.51 and 0.48 cm. in the field and control
arms respectively. Whence

$$\Delta V \text{ (field)} \quad = \quad 0.051 \quad x \text{ mm. displacement}$$

$$\Delta V \text{ (control)} = \quad 0.048 \quad x \text{ mm. displacement}$$

The factor (kRT + V) was determined experimentally by
obtaining, for a given system, the equilibrium pressures
for several readings of the differential manometer, inclu-
ding the zero position. The average of three determinations
for each system was 44.8 ml.

No attempt was made to flush oxygen from the system before intro-
ducing the acetate solution. The two samples were measured in
graduates and transferred to the cells using special long neck
funnels. Partial evacuation of the system was accomplished by
connecting it carefully to the vacuum pump through stop-cock S_7.
The initial pressure was adjusted so that complete decomposition
would give a pressure approaching, but not exceeding, the atmos-
pheric value. The reaction temperature was $30.0^{\circ}C$.; the field,
when used, was 3000 volts.

Initially, concentrations of about 3.5 g. per l. were
used with quite inconclusive results. However, a very small
acceleration of the reaction by the field was indicated, and
since earlier workers had obtained the greatest effect with very
low concentrations, solutions ranging in concentration from 0.4
to 1.6 g. per l. were decomposed. The data for a concentration
of 0.4040 g. per l. are given in table I, as representative of
decompositions with the field applied. Figs. 7, 8, and 9 show
the variation of pressure (corrected) with time for concentrations
of 0.4040, 0.8028 and 1.6016 g. per l. with 3000 volts applied to
the field cell. Fig. 10 gives the same information for a concen-
tration of 0.8020 g. per l. with no field applied.

These results indicated a remarkable acceleration of the
rate by the field. At a concentration of 0.4040 g. per l., the rate

TABLE I

DATA FOR THE PRESSURE INCREASE OVER A TOLUENE SOLUTION OF BENZENE-DIAZO-ACETATE
(0.4040 g. per l.) AT 30°C. WITHIN AND WITHOUT AN ELECTRIC FIELD OF 3000 VOLTS PER Cm.

P' - uncorrected pressure P - corrected pressure
C - correction for volume change ΔP - pressure increase

TIME	MANOMETER READINGS			CONTROL DATA				FIELD DATA			
Mins.	M_1	M_2		P_1'	C_1	P_1	ΔP_1	P_2'	C_2	P_2	ΔP_2
	R_1	R_2	R_3	$R_1-236.0$	$-0.480 R_2 P_1'$	$P_1'+C_1$	$P_1-P_1^0$	$P_1'+R_2-R_3$	$-0.511 R_3 P_2'$	$P_2'+C_2$	$P_2-P_2^0$
					44.8				44.8		
0	780.2	0.0	0.0	544.2	0.0	544.2	0.0	544.2	0.0	544.2	0.0
5	787.8	6.3	-6.5	551.8	-3.7	548.1	3.9	564.6	4.2	568.8	24.6
10	792.8	9.3	-9.1	556.8	-5.5	551.3	7.1	575.2	6.0	581.2	37.0
20	799.8	12.5	-12.0	563.8	-7.6	556.2	12.0	588.3	8.0	596.3	52.1
30	805.0	13.9	-13.5	569.0	-8.5	560.5	16.3	596.4	9.2	605.6	61.4
45	809.5	13.8	-13.4	573.5	-8.5	565.0	21.8	600.7	9.3	610.0	65.8
60	813.5	13.2	-12.9	577.5	-8.2	569.3	25.1	603.6	8.9	612.5	68.3
80	818.0	12.1	-11.8	582.0	-7.6	574.4	30.2	605.9	8.2	614.1	69.9
100	822.0	11.0	-10.6	586.0	-6.9	579.1	34.9	607.6	7.3	614.9	70.7
120	824.8	10.1	-9.9	588.8	-6.4	582.4	38.2	608.8	6.9	615.7	71.5
150	827.8	8.8	-8.7	591.8	-5.6	586.2	42.0	609.3	6.0	615.3	71.1
180	831.8	7.5	-7.5	595.8	-4.8	591.0	46.8	610.8	5.2	616.0	71.8
210	834.5	6.4	-6.4	598.5	-4.1	594.4	50.2	611.3	4.4	615.7	71.5
240	836.5	5.0	-4.9	600.5	-3.2	597.3	53.1	610.4	3.4	613.8	69.6
1320	843.0	0.2	-0.2	607.8	-0.1	606.9	62.7	607.4	0.1	607.5	63.3

Manometer readings are in mm.
Pressures are in mm. of Hg.

Figure 7.

Variation of ΔP with Time for a Toluene Solution of
Benzene-diazo-acetate (0.4040 g. per l.) at 30ºC.

       O   no field

       ●   3000 volts

Figure 8.

Variation of Δ P with Time for a Toluene Solution of
Benzene-diazo-acetate (0.8028 g. per l.) at 30°C.
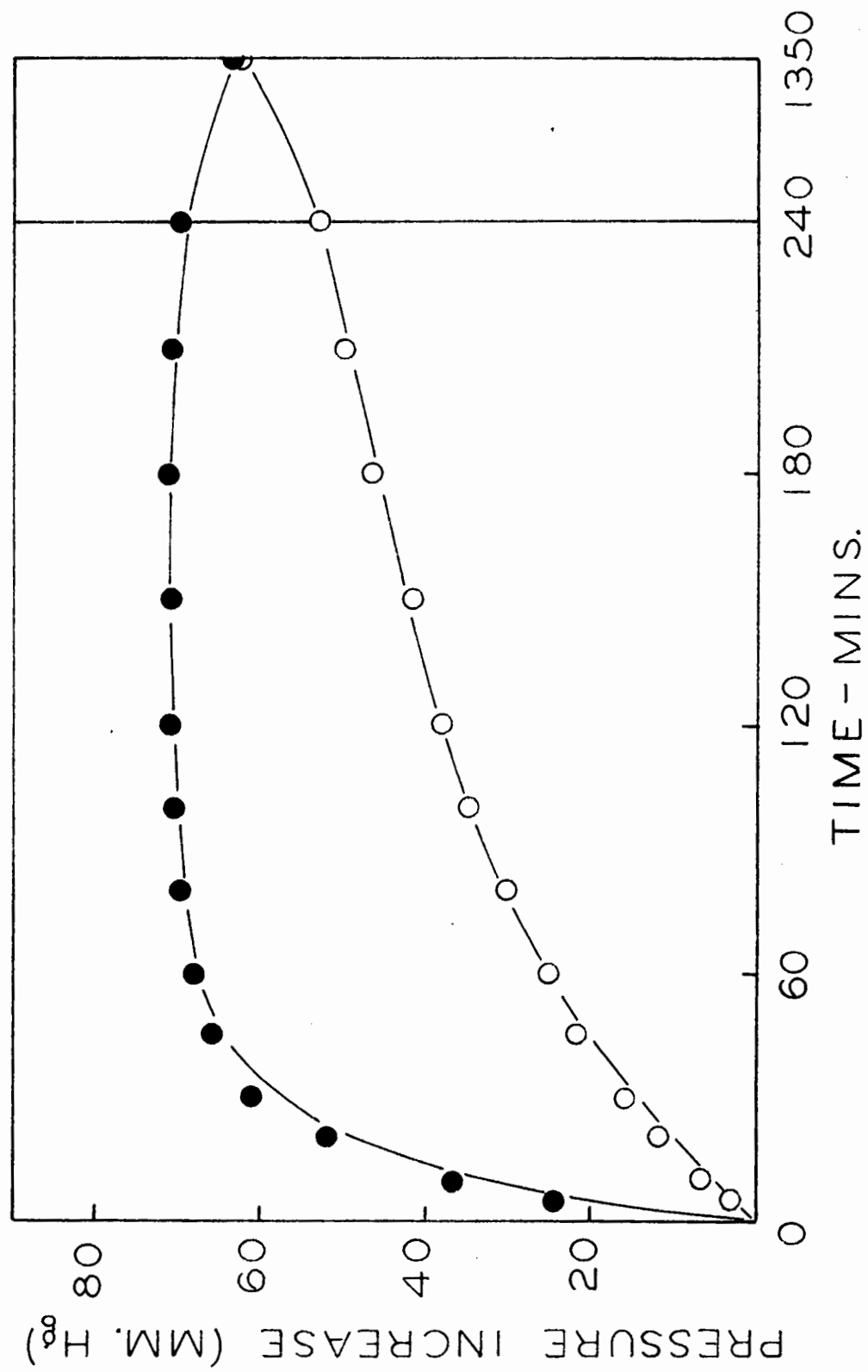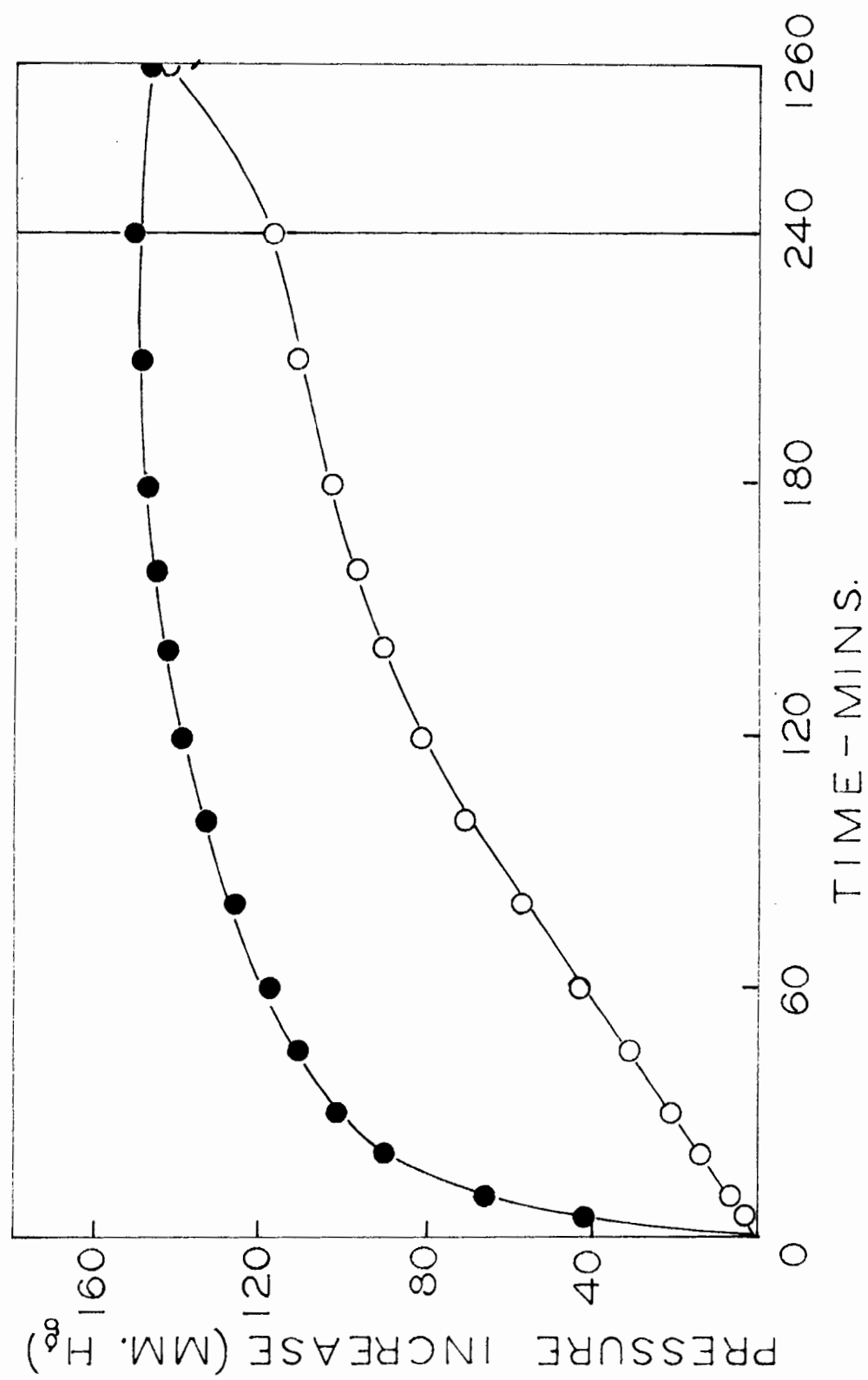
O   no field

●   3000 volts

Figure 9.

Variation of Δ P with Time for a Toluene Solution of Benzene-diazo-acetate (1.6016 g. per l.) at 30°C.
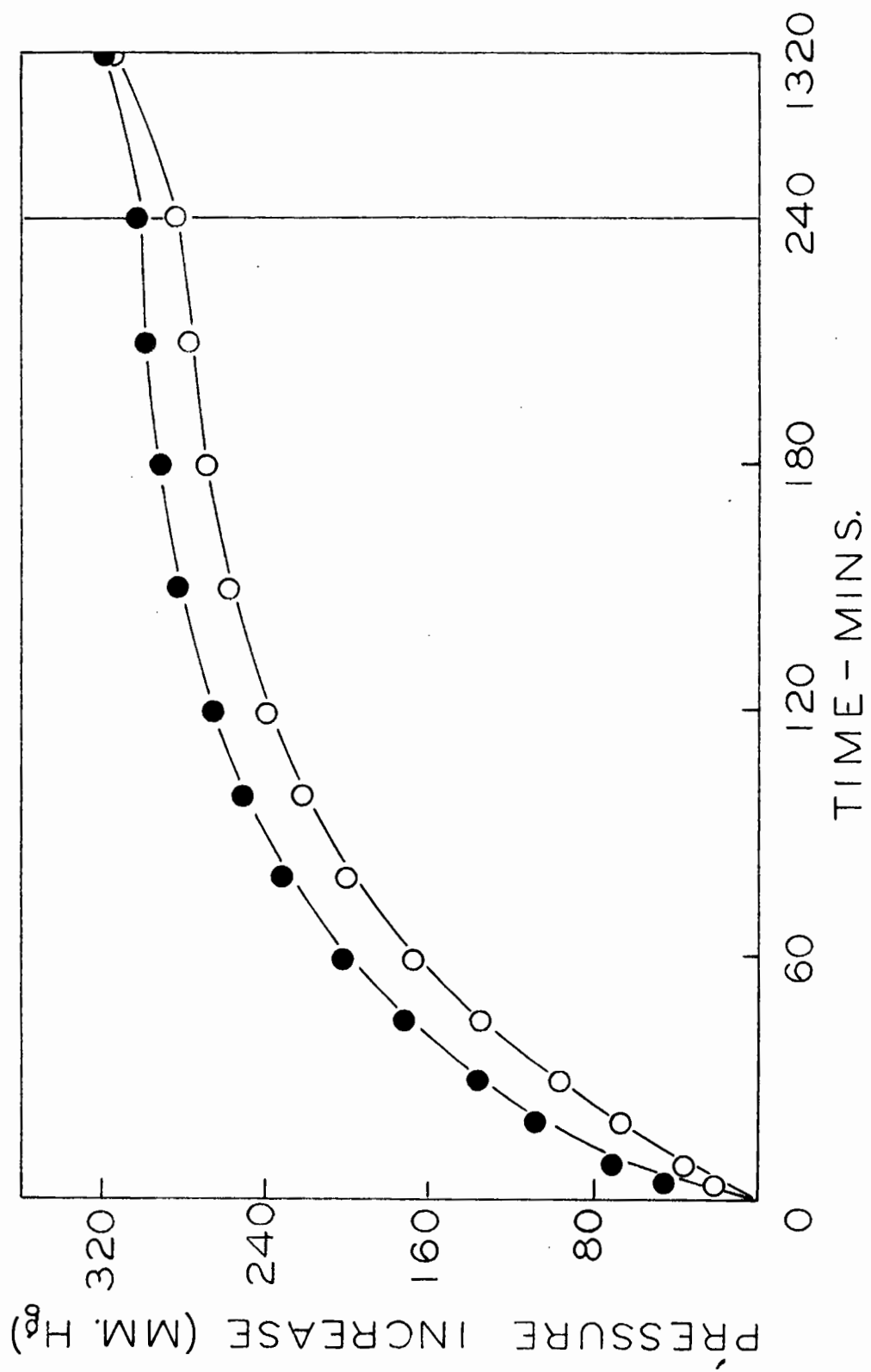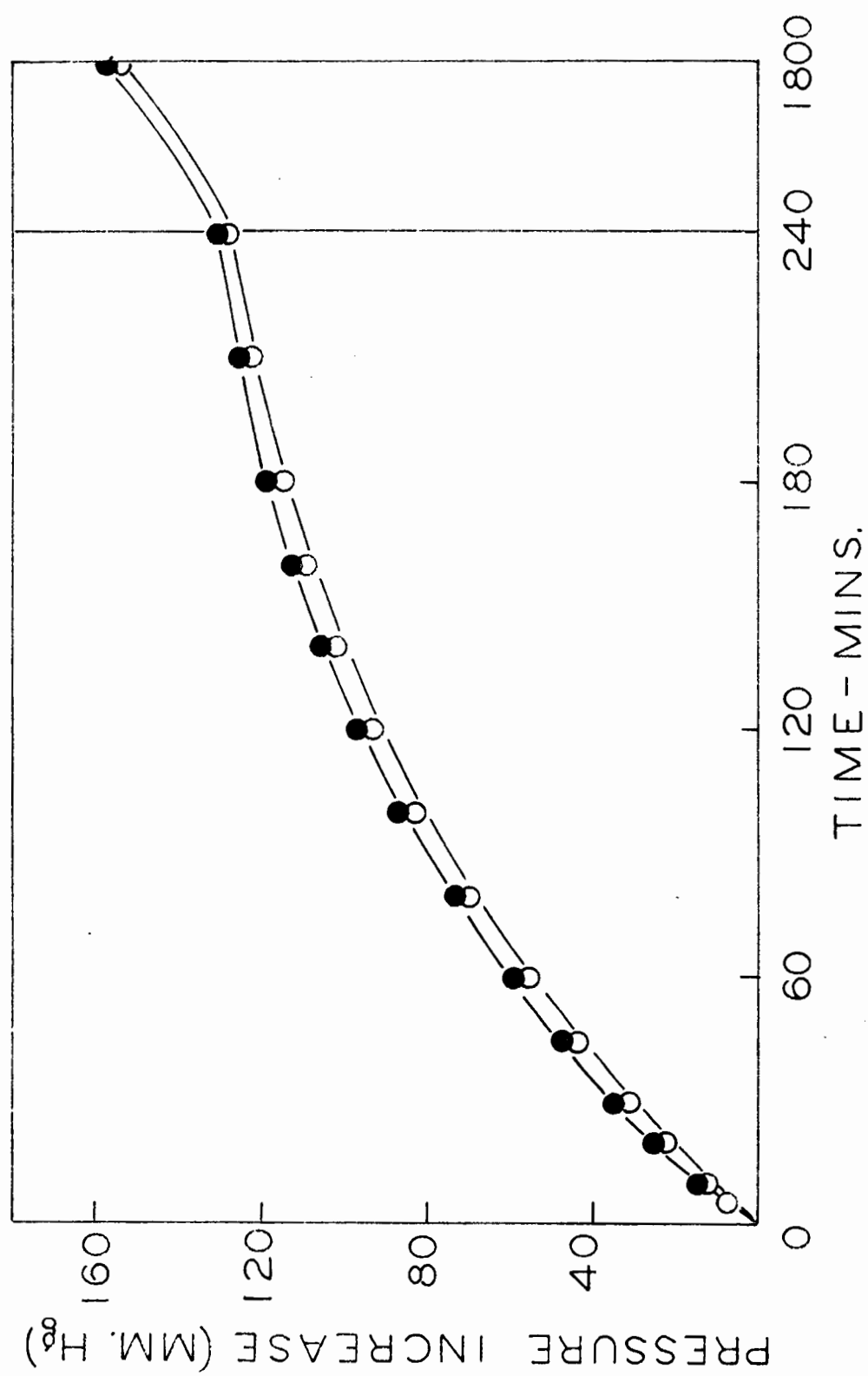
O   no field

●   3000 volts

Figure 10.

Variation of ΔP with Time for a Toluene Solution of
Benzene-diazo-acetate (0.8020 g. per l.) at 30°C.

O   control cell - no field

● field cell - no field

of pressure increase was 10 to 15 times greater in the field than it was for the purely thermal system. The effect decreased rapidly as the concentration was increased; at a concentration of 1.6010 g. per l. the rate in the field was about twice that of the control reaction.

Fig. 7 shows an unexpected decrease in pressure in the field system towards the end of the decomposition. This was only noticeable for low concentrations, where the relatively great field effect caused extensive changes in the volumes due to changes in the mercury levels in the differential manometer.

This drop in pressure was shown to result from such a volume change by decomposing a solution of the same concentration in the field, with the two arms of the differential manometer maintained at the same level. This was done by adjusting the pressure in the control system, which for this experiment was not connected to the control cell. The results were very similar to those shown in fig. 7 for decomposition in the field, but no drop in pressure occurred. The substitution of capillary tubing for the differential manometer eliminated this difficulty for all practical purposes, and subsequent experiments showed no drop in pressure even when the field effect was very great.

Experiments with the re-designed apparatus indicated

the desirability of still better reproducibility for a detailed
investigation of the effect of the field, which was large only
at very low concentrations. Table II lists the results of a
number of experiments at a concentration of about 0.4 g. per l.
The pressure increase was roughly first order, and the slopes

$$\frac{d \, \log \Delta P_{\infty} / \, (\Delta P_{\infty} - \Delta P)}{d \, t}$$

were determined graphically from the best straight line drawn
through the points on a $\log \Delta P_{\infty} / \, (\Delta P_{\infty} - \Delta P)$ – time plot.
Fig. 11 shows this graph for a typical experiment with the field
applied. The rates obtained in the two cells for a given solution
agreed within 10 percent, but the rates in the control cell for the
different solutions ranged from 0.0031 to 0.0052 with an average
deviation from the mean of 13 percent. The final pressure increases
showed the same tendencies, and several possibilities were considered
in an attempt to minimize these differences.

The method of evacuating the system at the start of
an experiment made it extremely difficult to obtain the same rate
or degree of evacuation for each experiment. This could cause
deviations in two ways: both the time lapse before starting the
readings, and the degree of supersaturation of the nitrogen in the
solution at the beginning of an experiment might vary. The difficulty
was eliminated by using the volume V to evacuate the system when

TABLE II

VARIATIONS IN THE RATE AND FINAL AMOUNT OF PRESSURE INCREASE OVER TOLUENE SOLUTIONS OF BENZENE-DIAZO-ACETATE (ABOUT 0.4 g. per l.) at 30°C

Concentration grams/liter	$\dfrac{d \log \Delta P_\infty/(\Delta P_\infty - \Delta P)}{dt}$		Final Pressure Increase mm Hg	
	Control Cell	Field Cell	Control	Field
0.4076	0.0031	0.0028*	141.4	131.8
0.3648	0.0039	0.0040*	123.4	117.0
0.4048	0.0052	0.0056*	165.1	161.5
0.3968	0.0036	0.0327	136.4	141.1
0.4076	0.0036	0.0298	170.4	169.5

* - no field applied.

Figure 11.

Variation of Log $\dfrac{\Delta P_{\infty}}{\Delta P_{\infty} - \Delta P}$ with Time for a Toluene

Solution of Benzene-diazo-acetate (0.4086 g. per l.) at 30° C.

○   no field

●   3000 volts
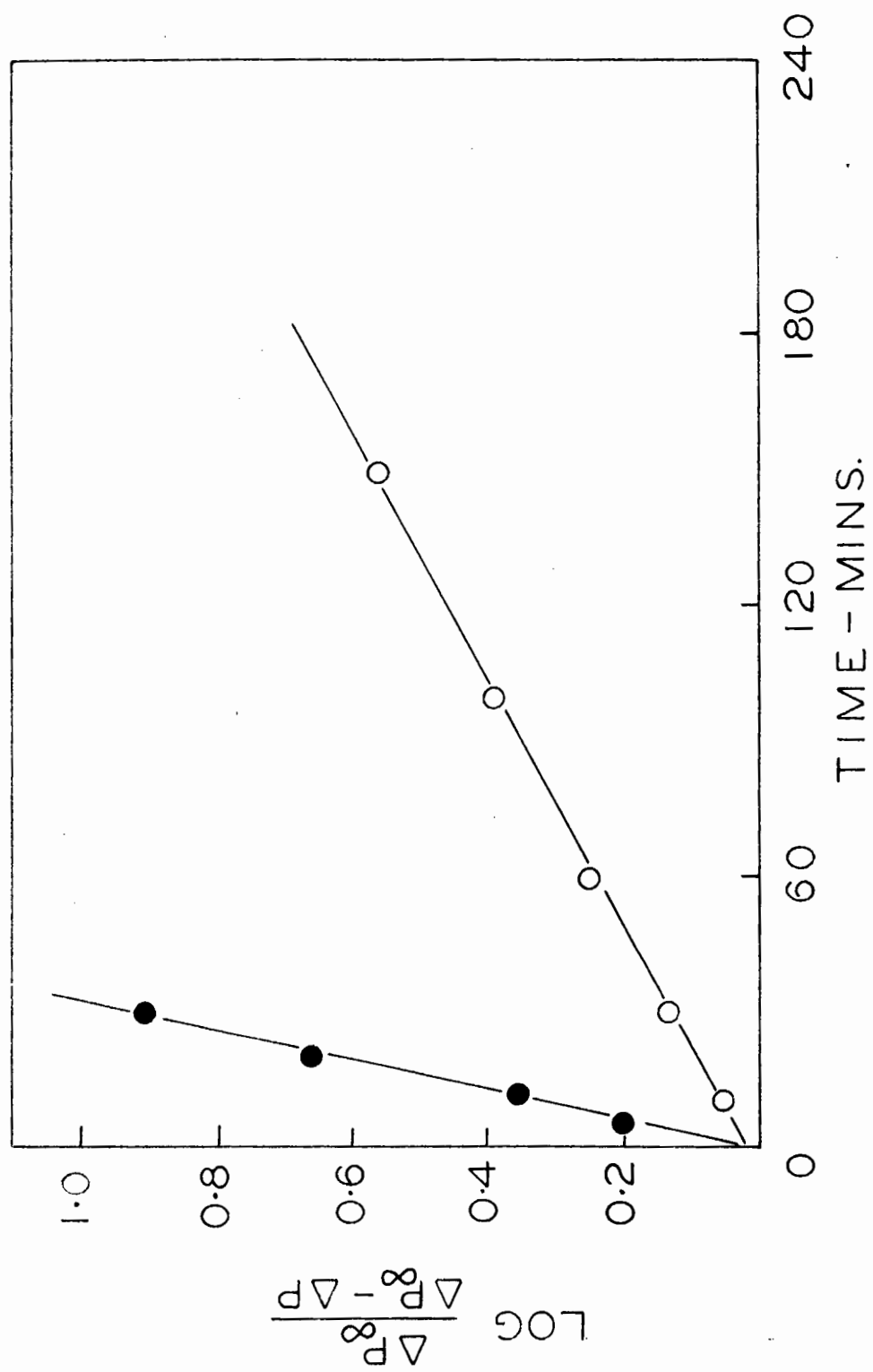
starting an experiment. The desired degree of evacuation was obtained by making V the correct size. The evacuation was accomplished simply by connecting the volume V (previously evacuated) to the system by opening stop-cock S_5.

Manipulations of the solution were also scrutinized, because of the unpredictable behaviour of oxygen in free radical systems. Two 90 ml. pipettes were made and calibrated for transferring the samples from the volumetric flask to the cells. All apparatus was flushed with nitrogen prior to contact with the solution, which was run into the cells against a counter-current of nitrogen introduced through stop-cock S_7.

The reproducibility was improved somewhat by these changes, and the degree of evacuation at the start of an experiment was increased to reduce further the oxygen content of the solution. The volume V of fig. 4 was adjusted so that the pressure of the system was decreased to about 120 mm. of Hg. when stop-cock S_5 was opened. Also, after being saturated with nitrogen, the toluene was partially degassed before the acetate solution was made.

The results of two experiments, in which the modified procedure was used, were similar to those obtained previously, as shown in figs. 12 and 13. However, the final pressure increase for a concentration of 0.4 g. per 1. was 235 mm., as compared with an increase of 140 mm. obtained previously (see fig. 7). A concentration

Figure 12.

Variation of ΔP with Time for a Toluene Solution of
Benzene-diazo-acetate (0.3964 g. per 1.) at 30° C.

O   no field

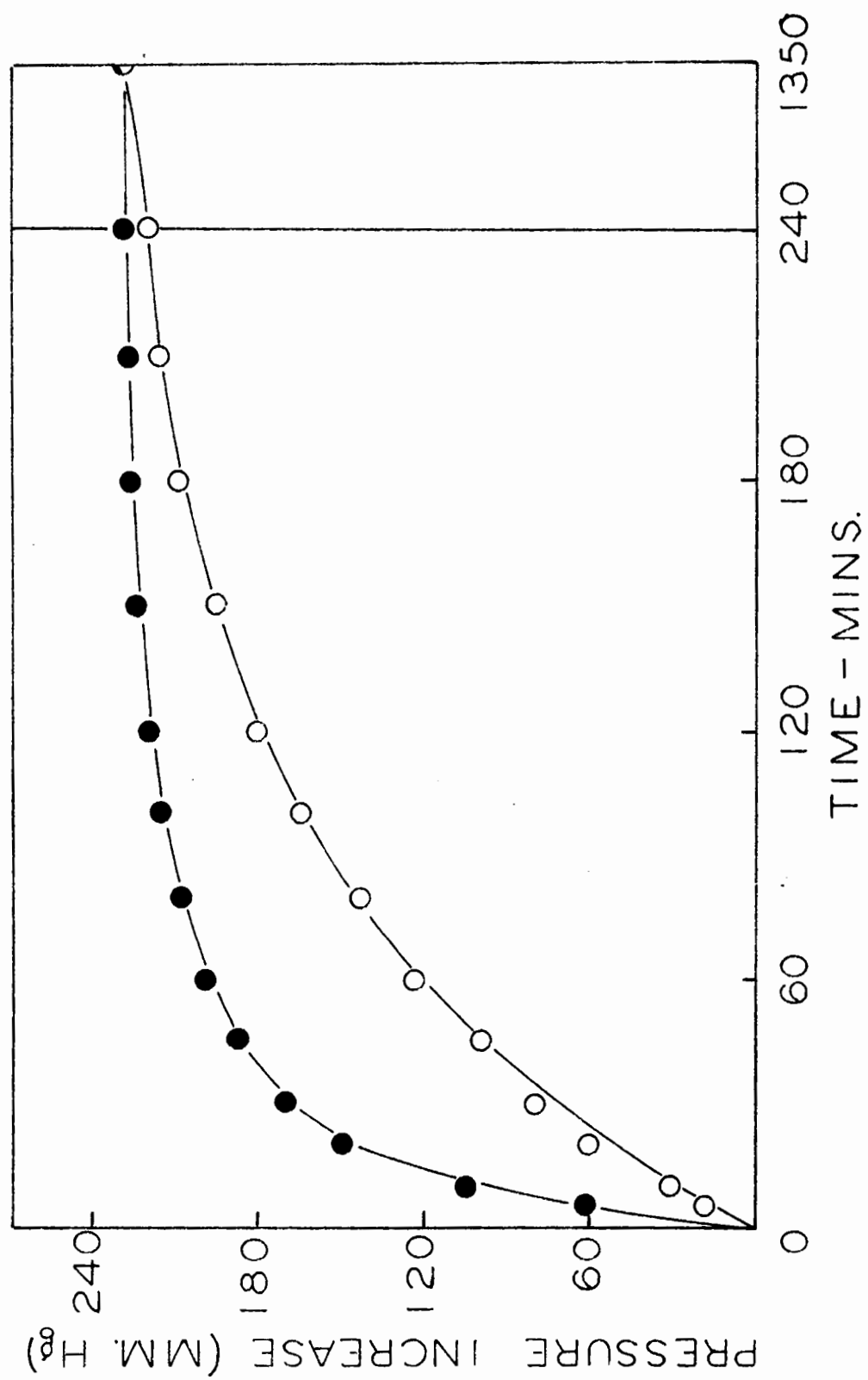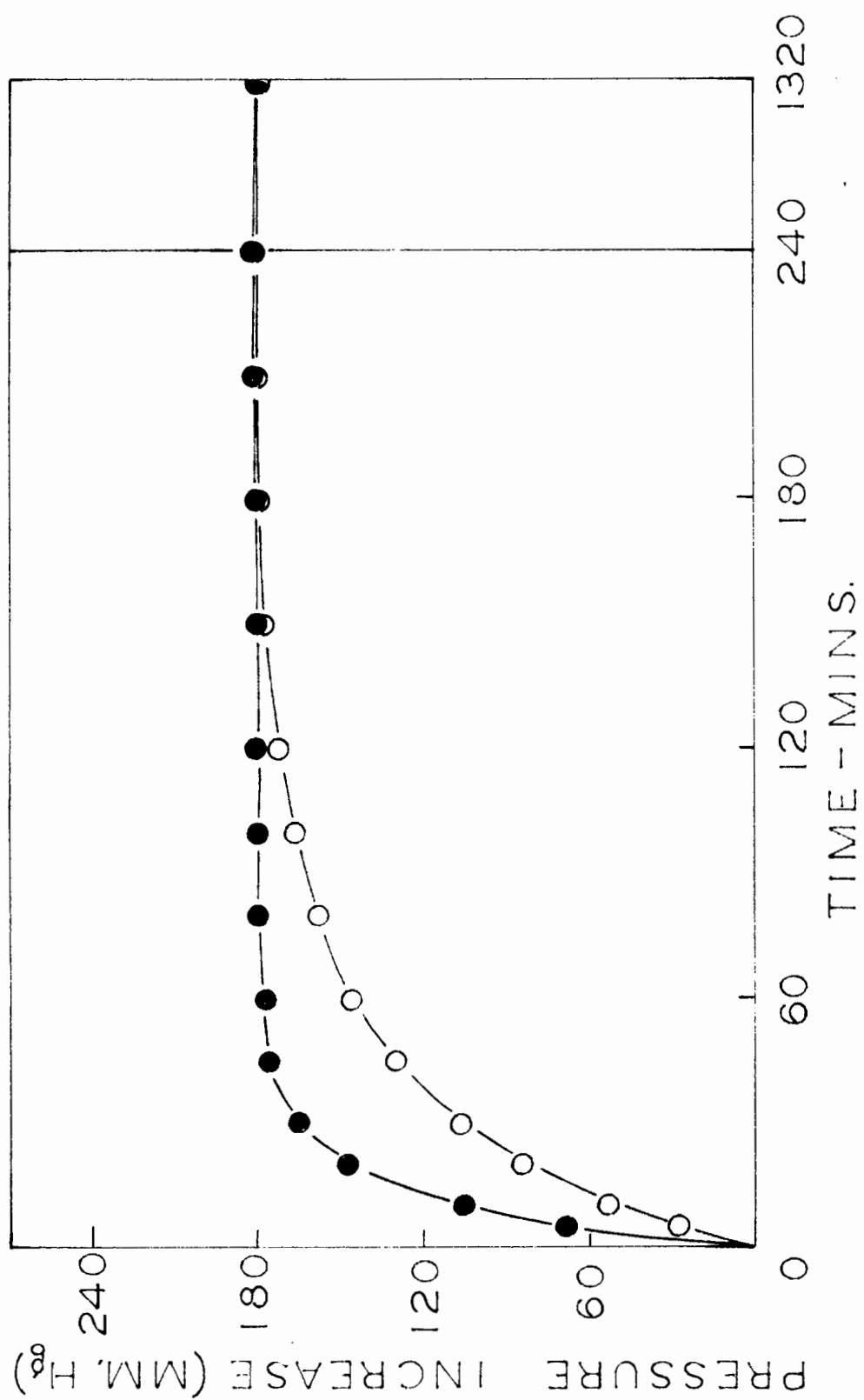●   3000 volts

Figure 13.

Variation of ΔP with Time for a Toluene Solution of
Benzene-diazo-acetate (0.2000 g. per l.) at 30° C.

        ○   no field

        ●   3000 volts

of 0.2 g. per l. gave a final pressure increase of 180 mm. instead
of 117 mm. expected on the basis of the concentration ratio.

It seemed fairly obvious that part of the pressure
increase in these experiments was due to the evolution of nitrogen
from the supersaturated solution, as a result of the sudden large
initial reduction of pressure. To determine how much of the pressure
increase was brought about in this way, a blank experiment was made.
Toluene was treated in the same manner as for a decomposition experi-
ment, except that no acetate was added to the volumetric flask.
Samples were transferred to the cells, and the experiment was "started"
in the usual way.

The results (fig. 14) demonstrate very clearly that,
using the starting procedure indicated at these low concentrations,
most of the pressure increase obtained was a consequence of super-
saturation of the solution; only a small part was due to decompo-
sition of the acetate. Also, the effect of the field was just as
pronounced for this out-gassing experiment as it was for the
decomposition reactions.

A consideration of all the results obtained up to this
point showed very clearly that

1. At high concentrations, where the pressure increase
   was due mainly to decomposition, the field effect
   was negligible.

2. At low concentrations, where out-gassing of the solu-
   tion accounted for most of the pressure increase, the
   field effect was very great.

Figure 14.

Variation of Δ P with Time for a Supersaturated
Toluene-Nitrogen Solution at 30°C.

○   no field

●   3000 volts

PRESSURE INCREASE (MM. H$_2$)

240

180

120

60

0   60   120   180   240   1380

TIME - MINS.
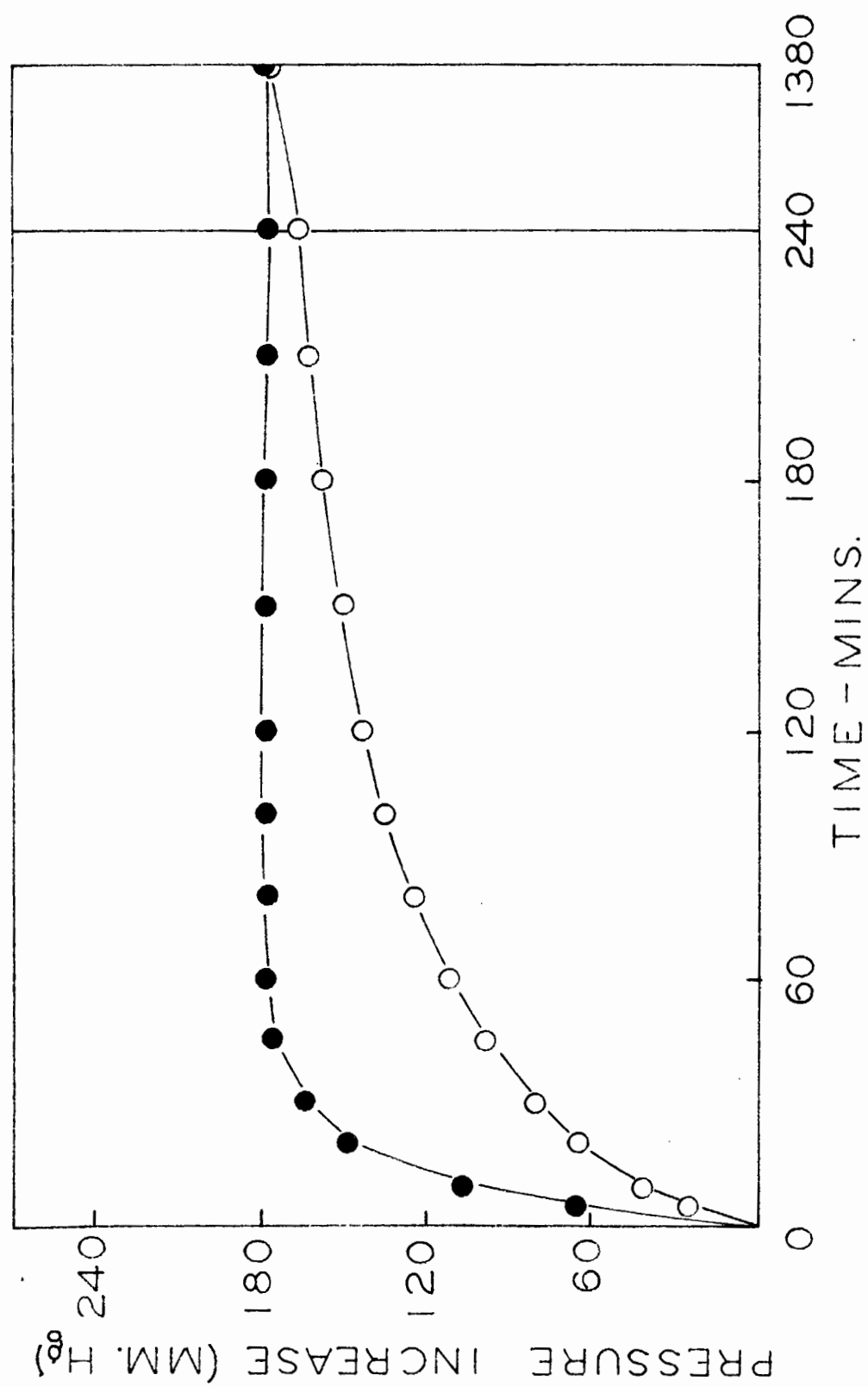
It was therefore decided to study more thoroughly the action of the field on the out-gassing phenomenon.

The out-gassing of gas-liquid solutions

Most of the out-gassing experiments were made with the same apparatus used in the decomposition experiments. The starting procedure was changed slightly to take advantage of the fact that the reaction did not have to be started as soon as possible after the solution was introduced into the cells. The apparatus was cleaned as before, and flushed with the gas used in the solution. The liquid was saturated with the gas at the experimental temperature and atmospheric pressure. Samples were transferred to the cells against a counter-current of the gas, and the stopper and thermometer were placed in the cleaned outlets. At this point, the two systems were separated and the field was turned on. When the temperature in the field cell remained steady at the correct value, the systems were joined, the field was turned off, and the reaction was started immediately in the manner described in the previous section. This procedure eliminated initial temperature differences between the two solutions.

It was assumed, following Schweitzer and Szebehely (46) that the rate of evolution would be proportional to the supersatura-

tion. For the present system, this may be represented

$$\frac{d\,(\Delta P)}{dt} \;=\; k\;\;(\Delta P_{\infty} - \Delta P)$$

where ΔP is the pressure increase at time t, ΔP_{∞} is the final
pressure increase and k the rate constant. On integration this
becomes

$$\log\;\;\frac{\Delta P_{\infty}}{\Delta P_{\infty} - \Delta P}\;\;=\;\;k't$$

where $2.303\; k' = k$. This expression is equivalent to that derived
by Schweitzer and Szebehely (see page 18), since ΔP_{∞} is equiva-
lent to $\frac{S}{r}\,.\,(Pe - Pe')$ and $(\Delta P_{\infty} - \Delta P)$ is equivalent to $(Pe' - P)$.

A number of gas-liquid pairs were studied, and generally
speaking, the graphs of $\log \dfrac{\Delta P_{\infty}}{\Delta P_{\infty} - \Delta P}$ against time were straight
lines. Typical of such graphs is that shown in fig. 15 for the
system nitrogen-methyl benzoate. Rate constants k' were determined
as the slopes of such straight lines. Occasionally, a slight
downward curvature was found for the control reaction, particularly
with halogenated benzenes. In such instances the best straight line
was drawn through the points for the first 60 to 80 minutes, as
illustrated in fig. 16 for the system nitrogen-ortho dichlorobenzene.

The results of experiments using toluene with nitrogen,

Figure 15.

Variation of Log $\dfrac{\Delta P_{\infty}}{\Delta P_{\infty} - \Delta P}$ with Time for the System

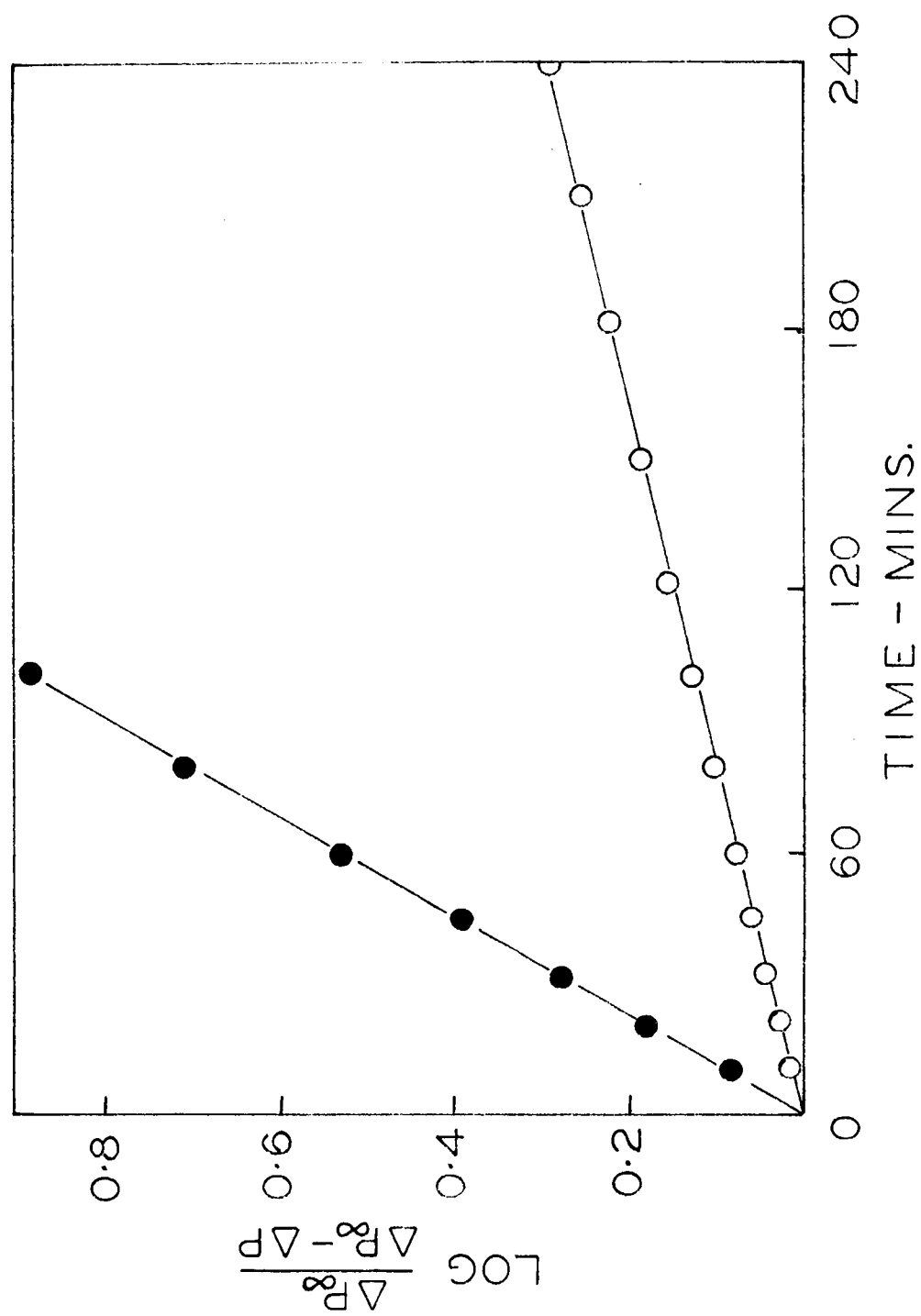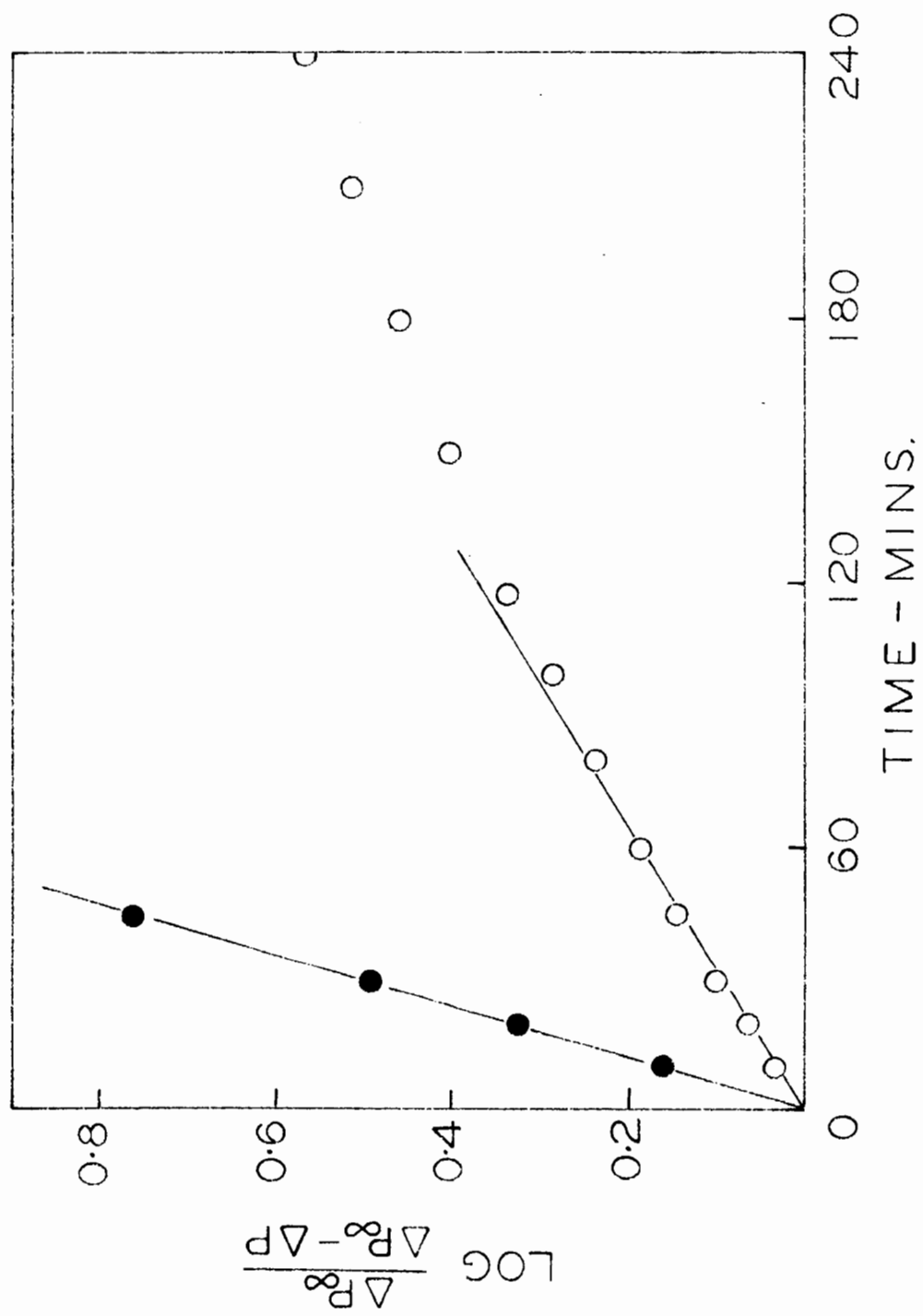Nitrogen-Methyl Benzoate at 30° C.

O   no field

●   2000 volts

Figure 16.

Variation of Log $\dfrac{\Delta P_{\infty}}{\Delta P_{\infty} - \Delta P}$ with Time for the System

Nitrogen-Ortho dichlorobenzene at 30° C.

        O   no field

        ●   2000 volts

oxygen and hydrogen are given in table III. The final pressure
increases attained are listed, and the rate constants k' are
compared for the out-gassing reactions in the presence and absence
of a field (3000 volts). The final pressure increases were of
the order expected from the solubilities of the three gases in
toluene, and were not noticeably affected by the field. The ratio
of k' (field) to k' (control) was about 5 for hydrogen and nitrogen,
and somewhat higher for oxygen. Carbon dioxide and nitric oxide in
toluene caused much greater initial rates of change of pressure, so
that accurate measurements of pressure were impossible. Also, the
difference in pressure between the two systems soon exceeded the
limit of the differential manometer, and the experiments had to be
discontinued.

Table IV lists the results obtained with a field of
2000 volts using nitrogen in a number of different liquids. In all
cases the field caused an acceleration of the gas evolution which,
as a general rule, was greater for liquids having higher dielectric
constants. This is indicated in fig. 17, in which the ratio of the
rate constant in the field cell to that in the control cell is
plotted against the dielectric constant of the liquid. The straight
line of best fit was determined using the "Method of Least Squares"
outlined by C. H. Richardson (49) in which the slope is given by

$$m = \frac{n \, \Sigma X Y - \Sigma X \, \Sigma Y}{n \, \Sigma X^2 - (\Sigma X)^2}$$

TABLE III

A COMPARISON OF THE RATE CONSTANT k' FOR THE
OUT-GASSING OF VARIOUS TOLUENE-GAS SOLUTIONS
AT 30°C., WITH AND WITHOUT AN ELECTRIC FIELD
(3000 Volts., 1.5 Megacycles)

GAS	CONTROL REACTION		FIELD REACTION		RATIO
	ΔP_{∞}(mm.)	k_c' (sec.$^{-1}$)	ΔP_{∞}(mm.)	k_f' (sec.$^{-1}$)	k_f'/k_c'
Nitrogen	206.9	$.0065_1$	206.6	$.033_7$	5.1_8
Oxygen	270.6	$.0057_0$	279.2	$.038_4$	6.7_4
Hydrogen	141.1	$.0052_3$	143.7	$.025_7$	4.9_1

TABLE IV

A COMPARISON OF THE RATE CONSTANT k' FOR THE OUT-GASSING OF VARIOUS NITROGEN-LIQUID SOLUTIONS AT 30°C. WITH AND WITHOUT AN ELECTRIC FIELD (2000 Volts, 1.5 Megacycles)

Liquid	Viscosity*	Dielectric Constant*	Control Reaction		Field Reaction		Ratio
			ΔP_∞ (mm.)	k_c'(sec⁻¹)	ΔP_∞(mm.)	k_f'(sec⁻¹)	k_f'/k_c'
M-Butyl phthalate	-	-	118.8	0.00032	117.9	0.00165	5.15
O-Dichloro benzene	-	7.5 (20)	147.0	0.00304	147.4	0.0166	5.45
Ethyl benzoate	0.02	6.2 (20)	158.4	0.00145	158.7	0.00727	5.01
p-Xylene	0.0056	2.3 (17)	212.0	0.00730	207.5	0.0206	2.82
Chlorobenzene	0.008	5.9 (20)	183.4	0.00491	175.1	0.0250	5.09
n-Valeric acid	0.02	2.6 (18)	239.4	0.00592	233.4	0.0125	2.12
o-Xylene	0.0074	2.6 (17)	183.5	0.00312	180.3	0.00500	1.60
Bromobenzene	0.012	5.4 (20)	148.6	0.00538	144.5	0.0187	3.48
Methyl benzoate	0.02	6.9 (20)	144.8	0.00123	145.2	0.00867	7.05
Toluene	0.0058	2.3 (24)	217.7	0.00917	211.4	0.0131	1.43
Bromobenzene	0.012	5.4 (20)	138.2	0.00427	130.3	0.00257**	0.602
Methyl benzoate	0.02	6.9 (20)	142.8	0.00252	136.4	0.00207**	0.822

* Values taken from International Critical Tables. Parentheses enclose temperatures, °C.

** The field was not turned on in these experiments, but the field cell was used.

Figure 17.

Variation of the Ratio k_f'/k_c' with Dielectric

Constant of the Liquid Used
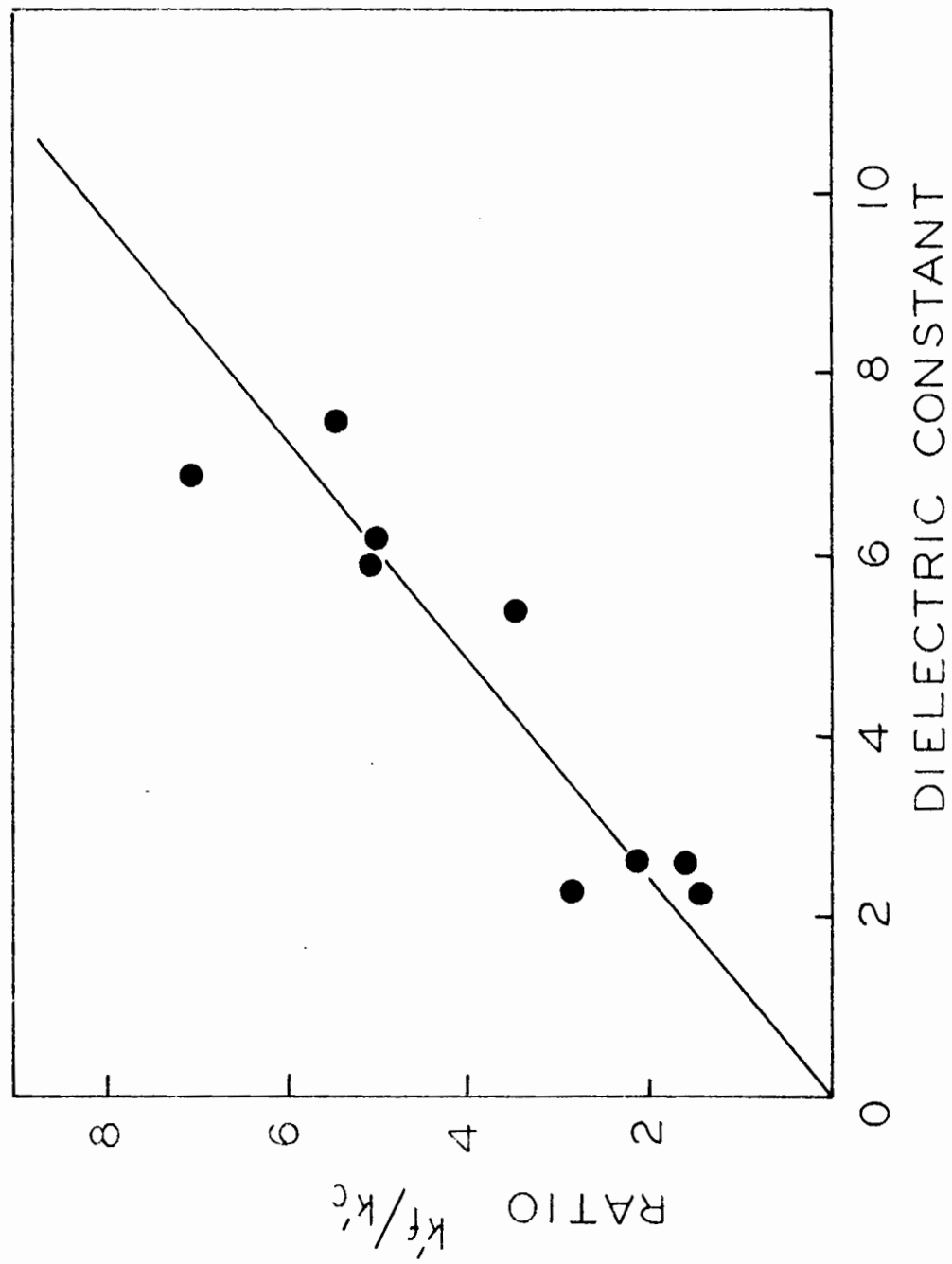
and the intercept by

$$b = \frac{\sum X^2 \sum Y - \sum X \sum X Y}{n \sum X^2 - (\sum X)^2}$$

where X and Y are corresponding values of the dielectric constant and the ratio k_f'/k_c', and n is the number of values used in the calculation. The equation for the line was found to be

$$k_f'/k_c' = 0.84\ e' - 0.09$$

in which e' is the dielectric constant of the liquid.

The rate constant in the control cell was generally greater for liquids of lower viscosity, but the relation here was much less certain.

Satisfactory temperature coefficients of dielectric constant and viscosity were not available for the liquids studied, and the necessity of using values of these properties obtained at different temperatures undoubtedly introduced considerable error into both relations. However, some of the uncertainty was probably caused by poor reproducibility of results in the control cell for repeated experiments. The first indication of this was obtained when the nitrogen-toluene system was out-gassed in a field of 2000 volts. The rate in the control cell during this experiment (table IV) was 1.41 times the rate for the same system in the same cell during the 3000 volt experiment (table III).

As a further check on the reproducibility, the nitrogen-bromo benzene system was again out-gassed, this time without application of the field. The results are listed in the second last line of table IV. The control rate was 0.93 times the value obtained previously with this liquid, but much worse, the ratio k_f'/k_c', which should have been approximately 1 in the absence of the field, was 0.602.

The critical nature of the container surface in out-gassing experiments had been pointed out by earlier workers (43-45), and a careful examination of the system during an experiment brought to light a small scratch on the thermometer, which was acting as a nucleus for bubble formation in the control cell. The thermometer was replaced, and the nitrogen-methyl benzoate system was out-gassed without application of the field. The results are given in the last line of table IV. Although some improvement was noted, the repro-ducibility was still believed to be inadequate for a detailed study of the field effect.

Continued attempts to improve the reproducibility failed, and the decision was made to use only one cell. The out-gassing could then be allowed to proceed thermally in the field cell for a given time, and after the necessary adjustment of the bath temperature, the field could be turned on. A plot of $\log \Delta P_\infty / (\Delta P_\infty - \Delta P)$ against time under these conditions should give two intersecting straight lines, provided both parts of the out-gassing remained first

order. The ratio of the slopes of these lines should measure the
effect of the field. The apparatus used for these "one cell"
experiments is shown in fig. 6.

The same general procedure was used to "start" these
experiments as in experiments with the two cells. Details were
altered to take advantage of the simplified apparatus, but the same
quantities were determined under essentially the same conditions.
The temperature was determined after each reading, in the manner
described previously; the control cell and thermostat were main-
tained for this purpose.

The results of such an experiment using nitrogen and
methyl benzoate and a field of 2000 volts are given in figs. 18 and
19, which show the variation of pressure increase and $\log \Delta P_\infty / (\Delta P_\infty - \Delta P)$
respectively with time. The out-gassing was allowed to proceed thermally
for the first 50 mins. At this time the bath temperature was lowered
from 30.0 to 27.5°C. and the bath regulator was set to maintain this
temperature. At 60 mins. the field was turned on and left on until
the reaction was practically completed. The field was then turned
off and the bath temperature reset at 30.0°C. The two rate constants
k_c' and k_f' were determined as the slopes of the straight lines in
fig. 19, and are listed, together with the final pressure increase
and the ratio k_f'/k_c', under experiment No. 1 in table V. Although the
ratio of the two rates was in fair agreement with that obtained in the

Figure 18.

Variation of $\triangle P$ with time for the System
Nitrogen-methyl benzoate at 30°C., with and
without an Electric Field (30°C.)

0 - 50 mins.   no field

50 - 60 mins.   bath temp. lowered

60 - 210 mins.   2000 volts
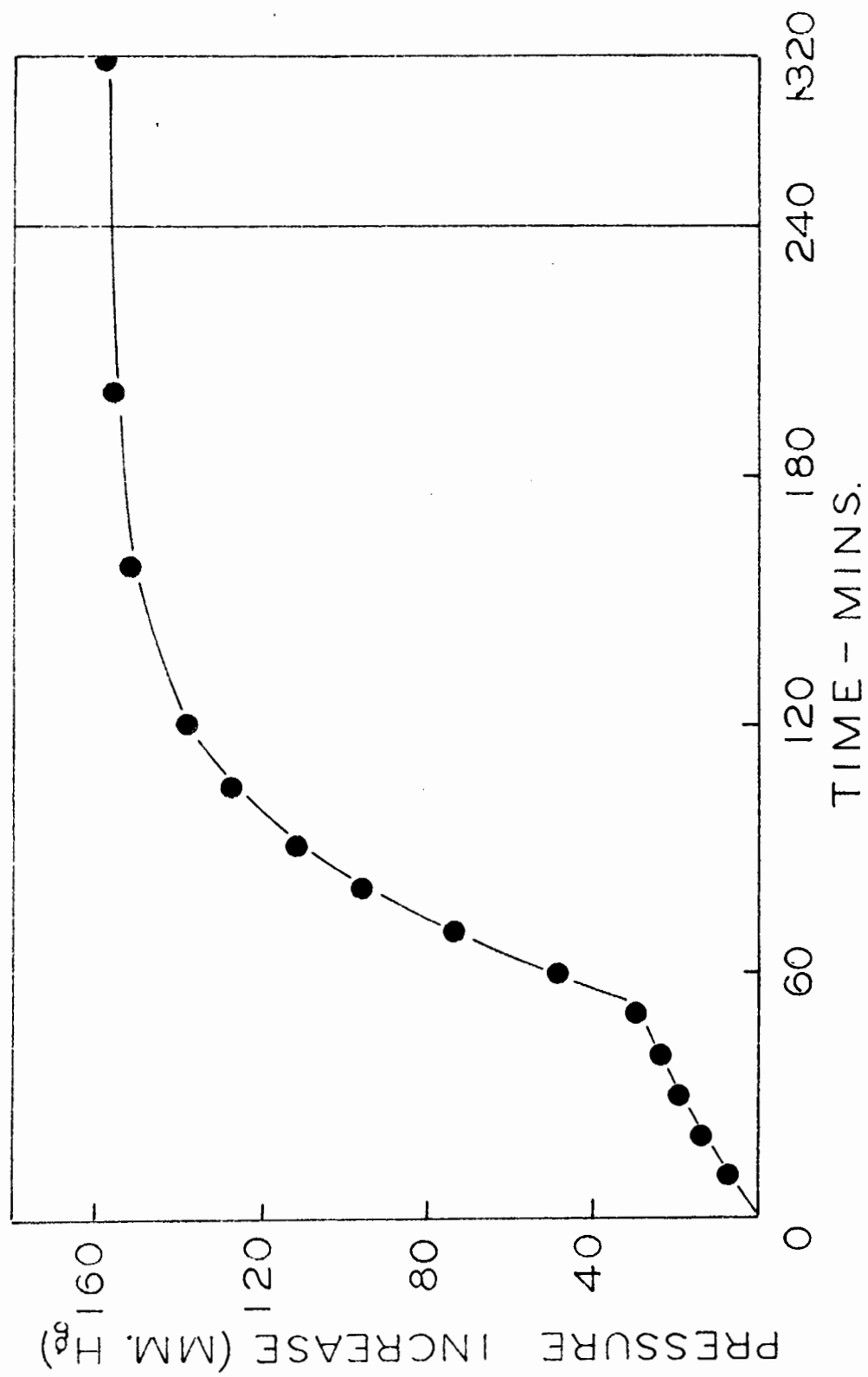
Figure 19.

Variation of Log. $\Delta P_{\infty}/(\Delta P_{\infty} - \Delta P)$ with Time for the
System Nitrogen-Methyl Benzoate at 30°C.
With and Without an Electric Field (30°C.)

            0 - 50 mins.   no field

           50 - 60 mins.   bath temp. lowered

           60 - 210 mins.   2000 volts
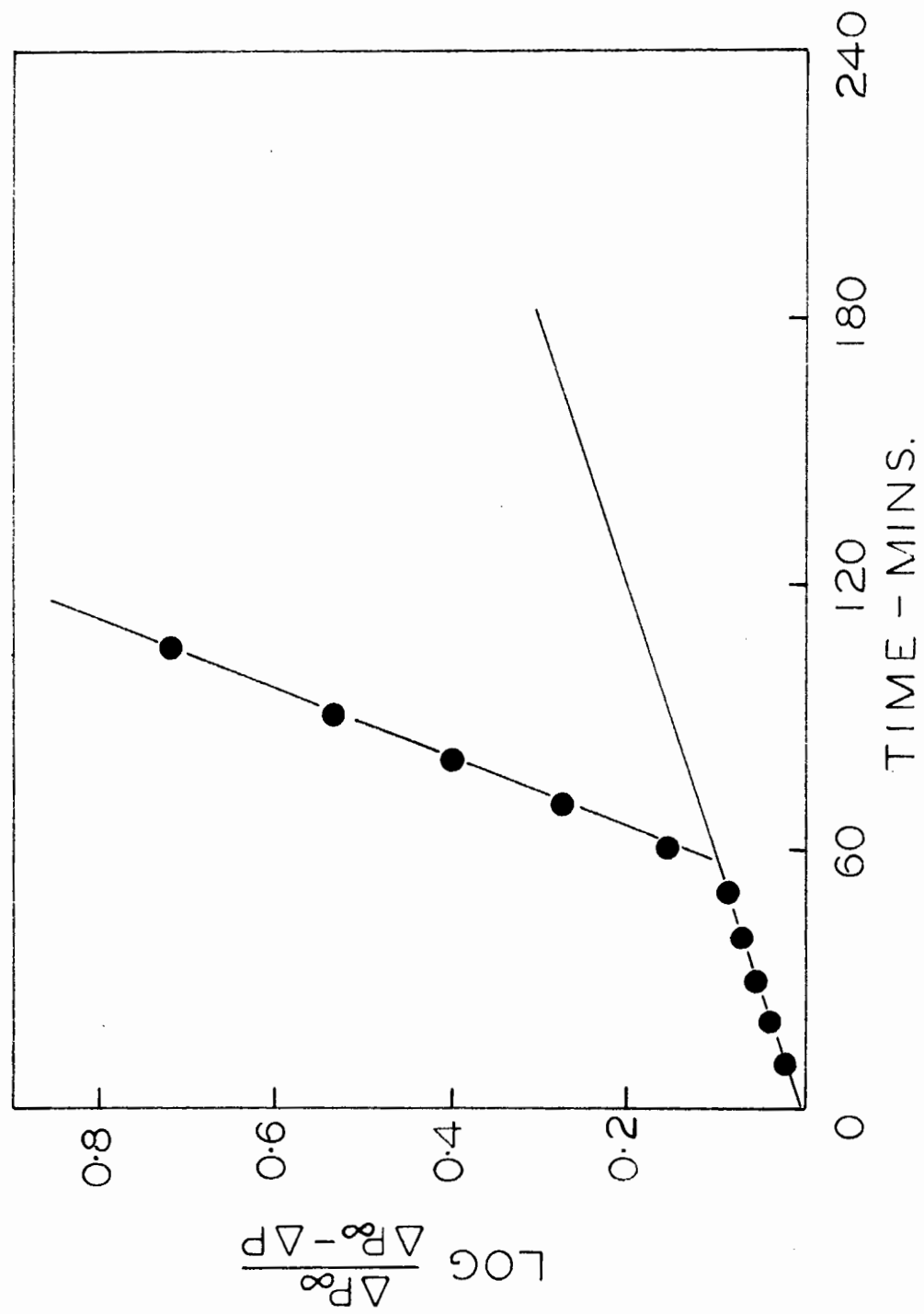
TABLE V

**A COMPARISON OF THE RATE CONSTANTS k' FOR THE SYSTEM
NITROGEN-METHYL BENZOATE AT $30^{\circ}C$. WITH AND WITHOUT
AN ELECTRIC FIELD (2000 VOLTS) FOR DIFFERENT
METHODS OF FILLING THE CELL ($30^{\circ}C$.)**

Experiment Number	$\triangle P_{\infty}$ mm. Hg.	k_o' sec.$^{-1}$	k_f' sec.$^{-1}$	Ratio k_f'/k_c'	Remarks
1	157.8	0.00170	0.0127	7.46)	Cell filled in
2	164.6	0.00240	0.0158	6.59)	usual way
3	90.5	0.00142	0.00433	3.05)	Cell filled
4	81.8	0.00147	0.00366	2.49)	under vacuum
5	165.8	0.00170	0.00348	2.04)	Liquid saturated
6	168.2	0.00136	0.00324	2.38)	in cell

two cell apparatus for this system, the rate constants themselves
were markedly different.

To determine what effect the condition of the cell walls
had on the out-gassing reaction, three different methods were
examined for introducing the gas-liquid solution into the cell.
The first method was the one already in use and described in
detail previously. In the second method, a dropping funnel was
fitted with a 10/30 glass joint and placed in the filling outlet
of the cell. The stop-cock was closed and the cell evacuated for
about 24 hours. The saturated solution was then transferred to
the dropping funnel and introduced into the evacuated cell by
opening the stop-cock. The funnel was removed and the glass joint
cleaned with a swab as usual. The third method was simply to
resaturate the liquid in the cell after leaving it under reduced
pressure for about 24 hours following an experiment. To permit a
ready comparison of results, the nitrogen-methyl benzoate system
was used in all of the following out-gassing experiments.

The results of two experiments using each method are
listed in table V. The first method (experiments 1 and 2) resulted
in somewhat higher than average control rates, and much higher field
rates. The second method (experiments 3 and 4) gave slightly lower
control rates and much lower field rates. The final pressure increases
obtained under these conditions were much lower, which was undoubtedly
due to the release of dissolved gas into the vacuum during the filling

process; quite violent bubbling and some foaming were noticed. The rates obtained in experiments 5 and 6, using the third method of filling, were about the same as those obtained using the second method; the final pressure increases, however, were normal.

In all of these experiments an unexpected sudden increase in pressure occurred during the period in which the bath temperature was lowered. It was especially noticeable in experiments 1 and 2, where the greatest field effect was obtained (c.f. fig. 18). This increase in rate during cooling suggested that convection was a major factor to be considered, and several experiments were made to determine the importance of temperature gradients.

For the first of these, the regular method of saturating the solvent externally to the system was used. The out-gassing was allowed to proceed at $30^{\circ}C$ for 50 mins. At this time the bath temperature was lowered quite rapidly to $25^{\circ}C$, held constant for 80 mins., and then raised again to $30^{\circ}C$. for the remainder of the experiment. Neglecting the difference in ΔP_{∞} for the two temperatures, log. $\Delta P_{\infty} / (\Delta P_{\infty} - \Delta P)$ was calculated (using ΔP_{∞} for $30^{\circ}C$.) and is plotted against time in fig. 20. The rate constants, determined as the slopes of the three-straight lines shown, were found to be

k_1' $(30^{\circ}C.)$ mm.$^{-1}$	k_2' $(25^{\circ}C.)$ mm.$^{-1}$	k_3' $(30^{\circ}C.)$ mm.$^{-1}$
0.00188	0.00137	0.00178

Figure 20.

Variation of Log. $\Delta P_\infty / (\Delta P_\infty - \Delta P)$ with Time for the System Nitrogen-Methyl Benzoate at 30°C. and at 25°C., and Under Conditions of Cooling and Heating

0	- 50 mins.	steady at 30°C.
70	- 150 mins.	steady at 25°C.
170	- 240 mins.	steady at 30°C.
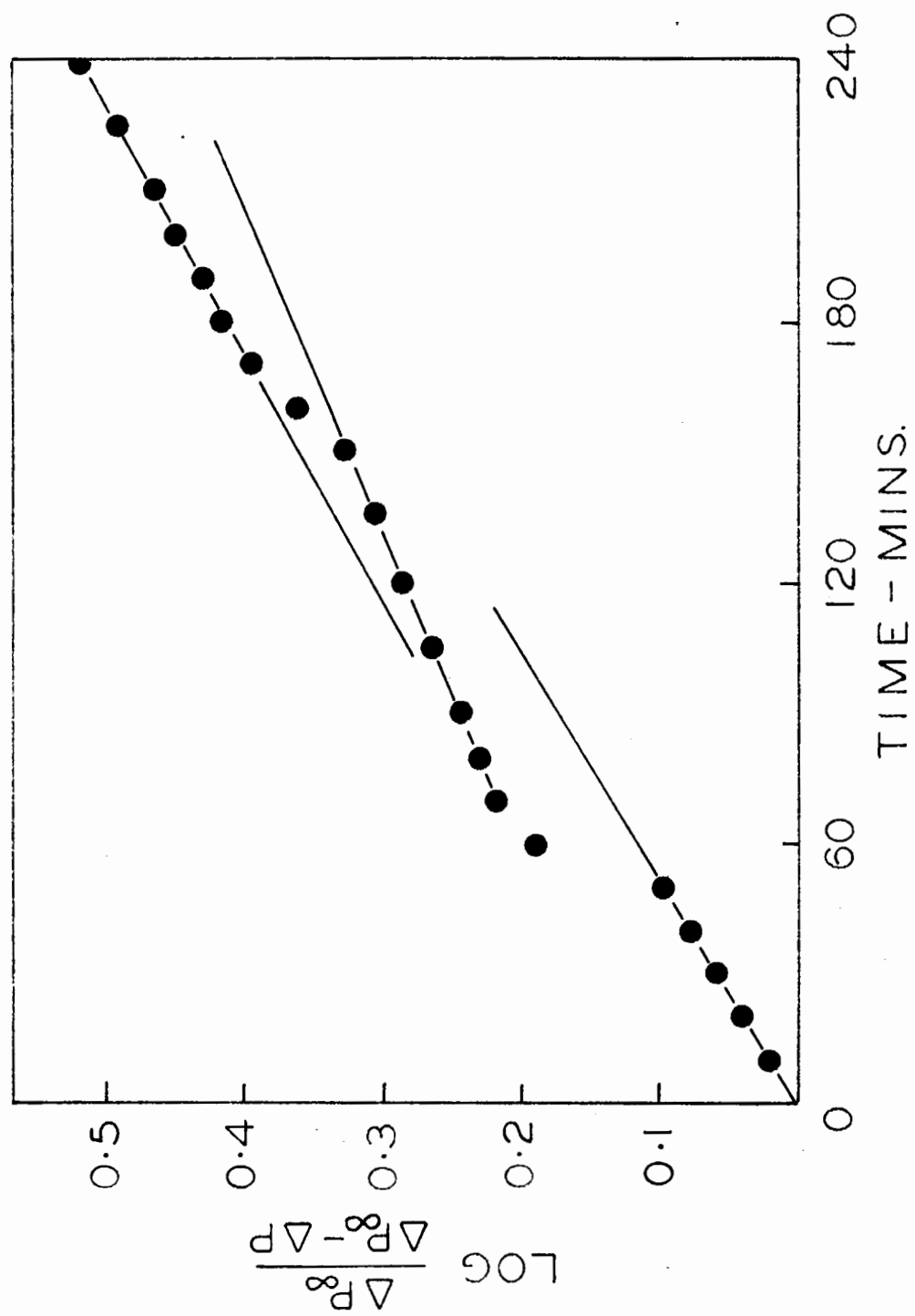
Very abrupt changes in rate between the straight portions of the graph in fig. 20, and the lower rate obtained at 25°C. again indicated a convection effect, for which even stronger evidence was obtained in the following experiments.

The "core" of the cell was closed at the top and bottom using rubber stoppers sealed around the edges with DeKhotinsky cement. Two holes in the upper stopper were fitted with glass tubing for the circulation of a coolant. The inlet tube extended almost to the bottom stopper, and the outlet tube was flush with the inner face of the top stopper. The inlet tube was supplied with tap water at a constant pressure by connecting it in parallel with an overflow tube dipped into a mercury column. The outlet tube was connected to the drain. With the water supply cut off completely, the cell with stagnant water in the "core" was allowed to come to temperature equilibrium with the bath. The nitregen-methyl benzoate solution was prepared in the usual way and trans-ferred to the cell. The out-gassing was allowed to proceed under thermal equilibrium conditions at 30°C. for 50 mins. Tap water, at a temperature of 8°C. was then turned on and left running until the out-gassing was completed. The outlet water temperature was 14°C. giving an average temperature of 11°C. on the inside cell wall, and a difference of 19°C. between the two walls. When the pressure reached a steady value, the tap water was turned off and the pressure was determined again after thermal equilibrium had been established.

Log $\Delta P_\infty / (\Delta P_\infty - \Delta P)$ was calculated for each part of this experiment using the appropriate value of ΔP_∞, and the rate constants were determined in the usual way to be

$$k' \text{ (thermal equilibrium)} = 0.00184 \text{ min.}^{-1}$$

$$k' \text{ (temp. gradient } 19^\circ C.) = 0.0139 \text{ min.}^{-1}$$

The ratio of these rates is 7.55 and would be somewhat larger if a correction were made for the lower average temperature of the solution during the second part of the experiment.

The question then arose "Was the field effect due entirely to disturbance in the thermal conditions of the system, or was the field acting in some way to aid in the formation of nuclei, or the release of gas at the nuclei?" It was reasoned that if the temperature gradient caused by the field were responsible for the entire effect, the field should have little or no effect on a system already subject to a strong temperature gradient. On the other hand, if the field were acting to aid the formation of nuclei, or the release of gas at the nuclei, the pre-existence of a strong temperature gradient should not entirely eliminate the field effect. An answer to this question was obtained in the following experiments.

The rubber stoppers used previously to close the "core" of the annular cell were replaced by polystyrene plates, and oil from a second constant temperature bath was introduced by gravity feed to

obtain the desired temperatures on the inner wall of the cell. The temperature gradient was produced by lowering the cell bath temperature and raising the temperature of the oil flowing through the "core" in such a way that a temperature of 30.0°C was recorded by the thermocouple. The liquid was saturated with gas in the cell as described previously (method 3) to obtain the slower rates found under these conditions; this allowed three rates to be determined in one experiment.

In the first experiment of this type, the out-gassing was allowed to proceed under thermal equilibrium at 30.0°C. for 60 mins. At this point the cell bath temperature was decreased to 26.0°C., and oil from the other bath (at 42.0°C.) was allowed to flow through the "core". The outlet temperature of this oil was 40.0°C., giving an average inner wall temperature of 41.0°C., and a temperature difference of 15.0°C. across the cell. The thermocouple temperature remained at 30°C. After 150 mins. both bath temperatures were reduced by 2.0°C., and after 160 mins. the field was turned on and adjusted to 2000 volts. After 165 mins., the solution temperature, measured by the thermocouple method, was 31.5°C. To save time, since the reaction was proceeding at quite a sufficient rate, the solution temperature was returned to 30.0°C. by lowering the voltage to 1500 volts. After 260 mins. the field was turned off and the system was returned to thermal equilibrium at 30.0°C. The results of this experiment (fig. 21), and those of a similar experiment using a 25.0°C temperature difference between the cell walls, and an electric field of

Figure 21.

Variation of Log. $\Delta P_{\infty}/(\Delta P_{\infty} - \Delta P)$ with Time for the
System Nitrogen-Methyl Benzoate with a Temperature
Gradient (15°C.) and in a Field of 1500 Volts (30°C. Av.).

    0 - 60 mins.   normal conditions

   70 - 260 mins.   15°C. wall temp. difference

160 - 260 mins.   1500 volts
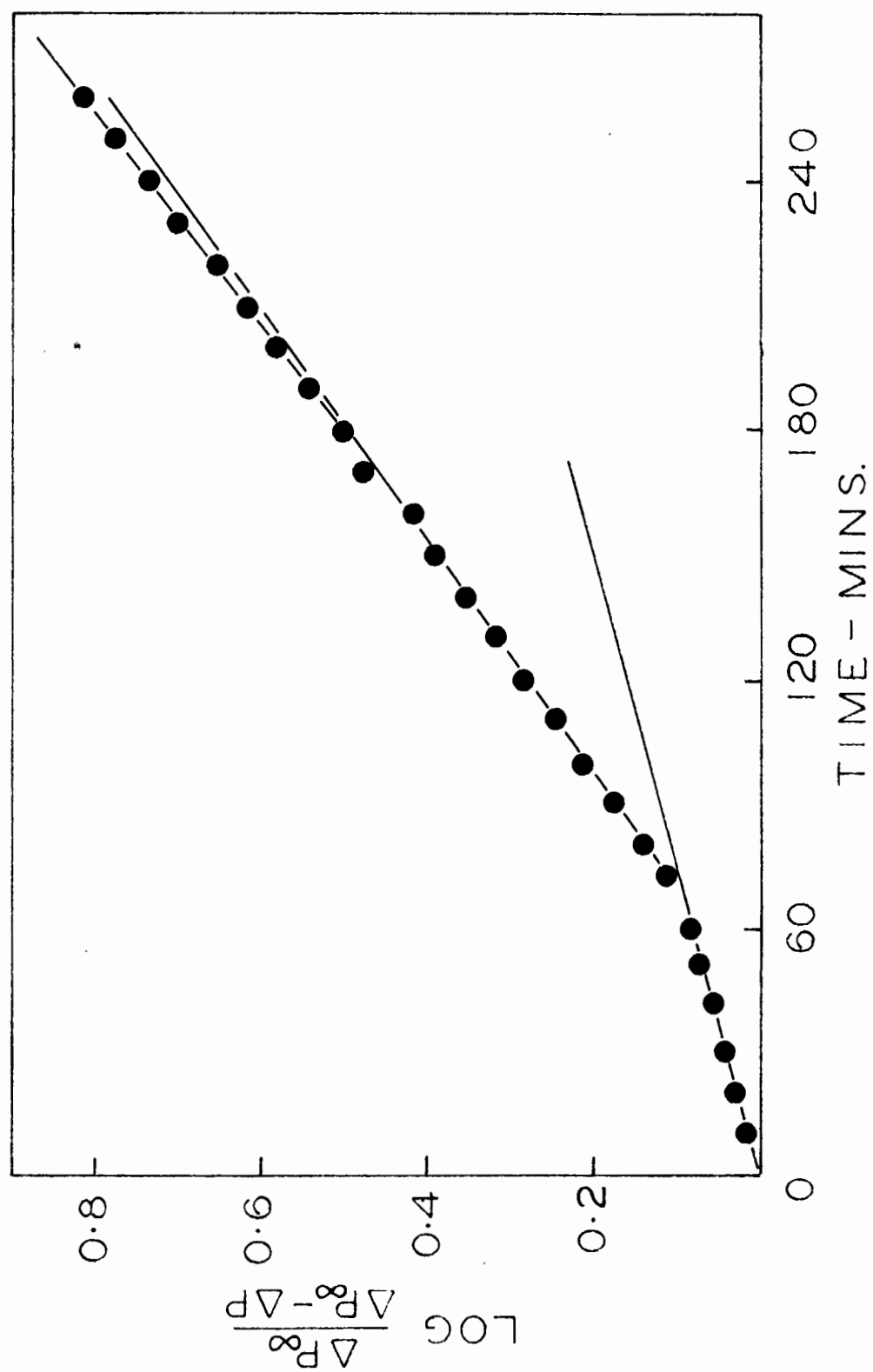
1700 volts, (fig. 22) did indeed show that as the temperature gradient was increased, the field effect was decreased and disappeared altogether with a temperature difference of 25°C. between the cell walls.

Final evidence that mixing was the basic cause of acceleration, whether it was caused by the field, by a temperature gradient, or mechanically, was obtained in two experiments in which mechanical stirring was substituted for the temperature gradient.

The cell was opened at the bottom and a ring type stirrer (3 mm. pyrex rod) was placed in the cell with its shaft extending out the 10/30 pyrex joint. A short piece of soft iron rod was attached with scotch tape to the end of the stirrer shaft, and the glass stopper for the 10/30 joint was replaced by a long piece of tubing sealed at the top. The stirrer was moved up and down by a small electromagnet surrounding the sealed tube and actuated by a string connected through a system of pulleys to a motor driven eccentric.

The cell was placed in the bath and filled to the top of the electrodes with methyl benzoate (about 85 ml.). To duplicate the previous two experiments, the pressure was reduced and left for 24 hours. The ball and socket joint was then disconnected and the liquid was saturated with nitrogen. The joint was cleaned and connected to the pressure measuring system, and the experiment was started in the usual way. After 40 mins. the stirrer was turned on with a period of about 13 secs. The out-gassing proceeded very

Figure 22

Variation of Log.$\Delta P_{\infty}/(\Delta P_{\infty} - \Delta P)$ with Time for the
System Nitrogen-Methyl Benzoate with a Temperature
Gradient (25°C.) and in a Field of 1700 Volts (30°C. Av.).

    0 - 60 mins.   normal conditions

   70 - 220 mins.   25°C. wall temp. difference

150 - 220 mins.   1700 volts
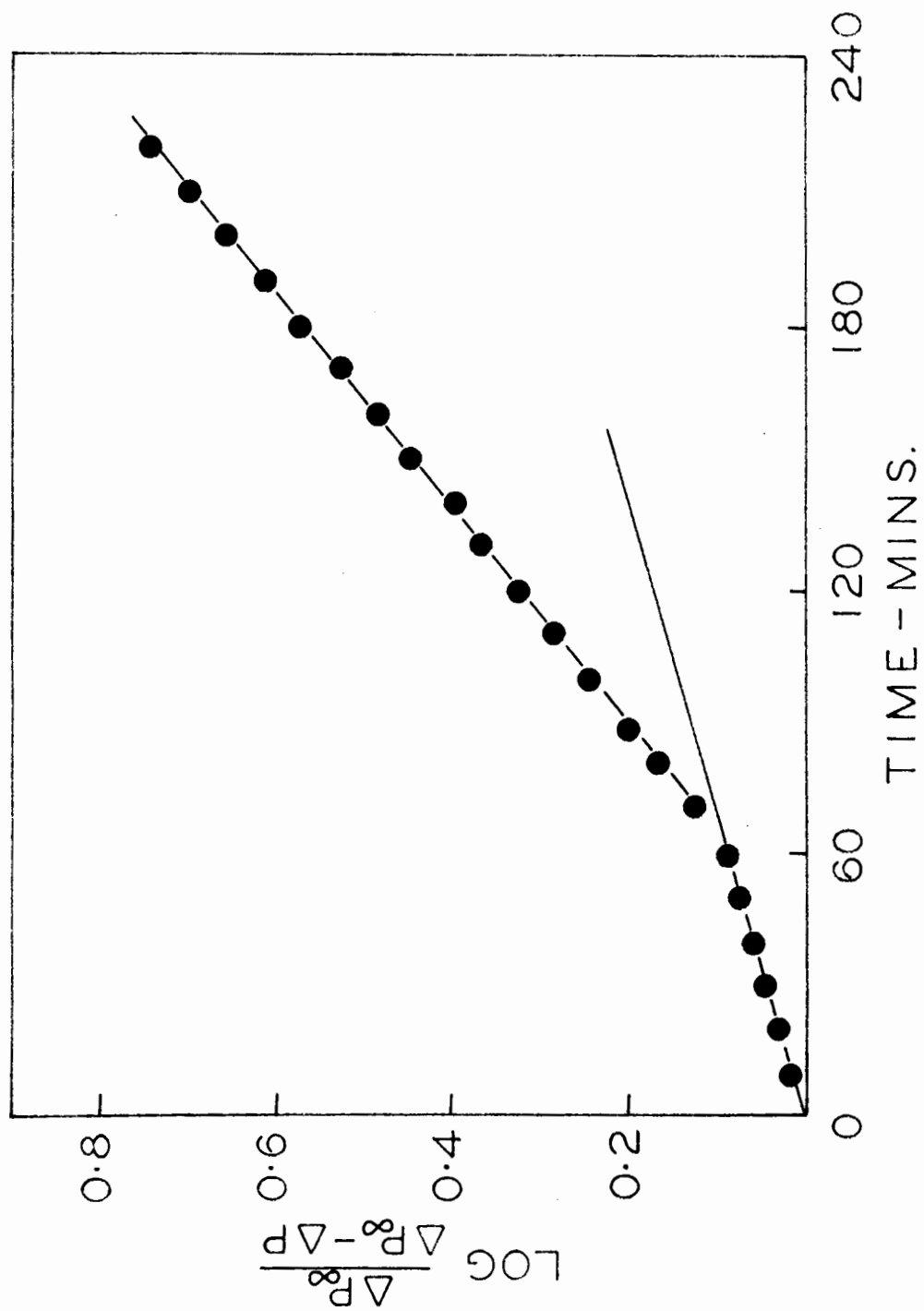
rapidly, and after 55 mins. the bath temperature was lowered to 27.5°C. The field was turned on at 60 mins. and adjusted to 2000 volts. After 120 mins. the field was turned off, and when the pressure reached a steady value the stirrer was turned off. The first order plot for this experiment (fig. 23) shows no field effect in the presence of stirring.

The various rate constants and the final pressure increases obtained in this and the two preceding experiments are listed in table VI. Values are also shown for an experiment in which the stirring period was reduced to 1 sec. The short duration of this experiment did not permit use of the field; the results are shown only as an indication of the effectiveness of stirring in this type of process. The small values of ΔP_{∞} for the last two experiments were caused by the increase in the volume introduced by the stirring mechanism.

The results obtained thus far made several points clear.

1. The field caused a very marked acceleration of the rate of out-gassing of an otherwise stagnant solution.

2. The field had no effect on the out-gassing of a solution agitated, either by a sufficiently large temperature gradient or by mechanical stirring.

3. Strong evidence was found for the existence of temperature gradients of considerable magnitude within the solutions in the electric field. These temperature gradients would in turn give rise to convection currents.

Figure 23.

Variation of $\text{Log.}\,\Delta P_\infty / (\Delta P_\infty - \Delta P)$ with Time for the
System Nitrogen-Methyl Benzoate with Stirring and
in a Field of 2000 Volts (30° C. Av.).

0 - 40 mins.	normal conditions
40 - 120 mins.	stirred (period 13 secs.)
60 - 120 mins.	2000 volts.
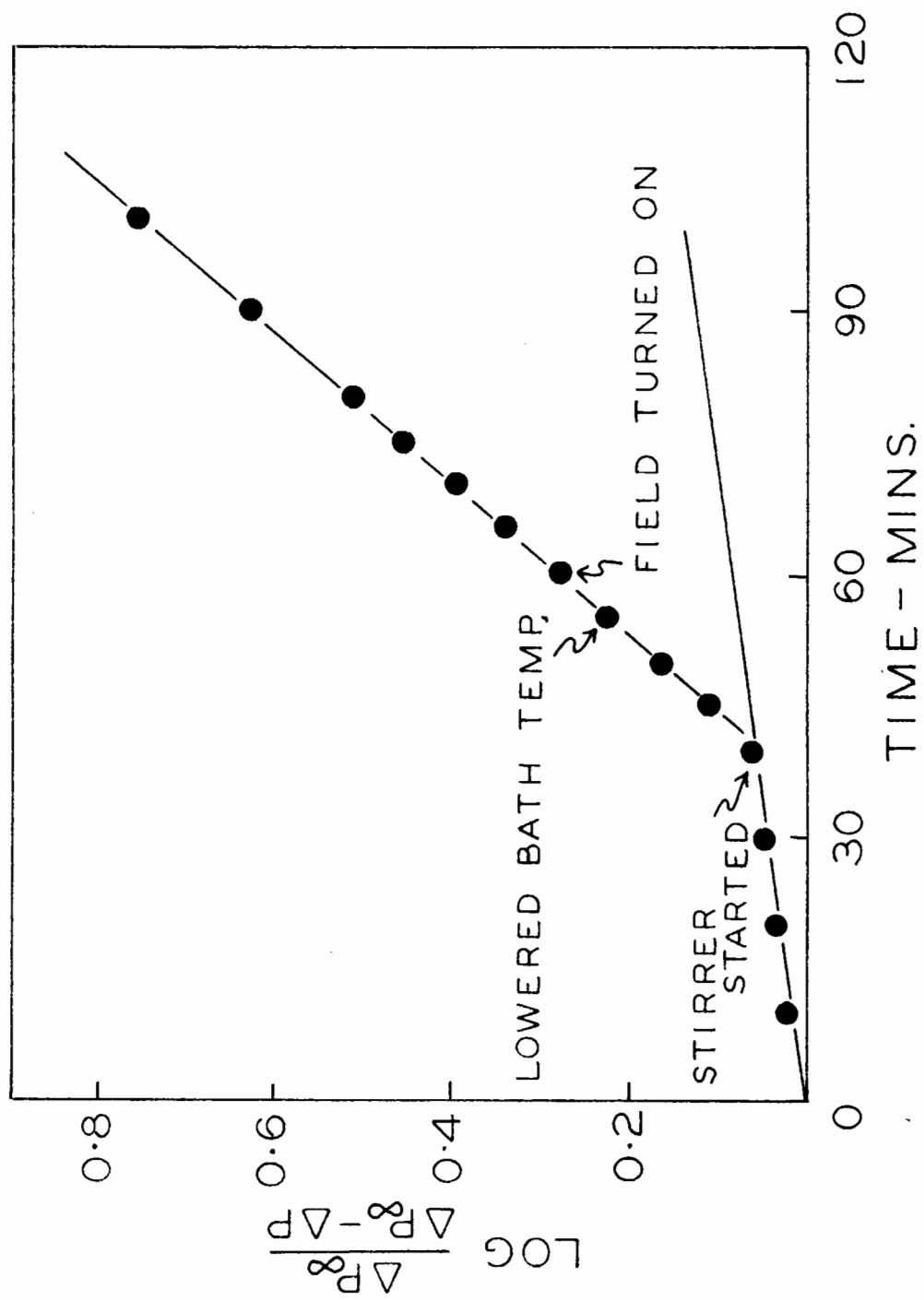
TABLE VI

THE FINAL PRESSURE INCREASES AND RATE CONSTANTS
FOR THE SYSTEM NITROGEN-METHYL BENZOATE
UNDER VARIOUS CONDITIONS (30°C. Av.)

Experiment No.	$\triangle P_\infty$ mm. Hg.	k_x' min.$^{-1}$	x	Ratio k_x'/k_1'	Condition
1	165.3	0.00133	1	1.00	Thermal Equilibrium
		0.00358	2	2.69	Temp. Gradient -15°C.
		0.00392	3	2.95	Temp. Gradient -15°C.
					+ Electric Field 1500 V.
2	165.0	0.00144	1	1.00	Thermal Equilibrium
		0.00416	2	2.89	Temp. Gradient -25°C.
		0.00416	3	2.89	Temp. Gradient -25°C.
					+ Electric Field 1700 V.
3	76.0	0.00130	1	1.00	Thermal Equilibrium
		0.0118	2	9.08	Stirred - Period 13 sec.
		0.0118	3	9.08	Stirred - Period 13 sec.
					+ Electric Field 2000 V.
4	78.2	0.00130	1	1.00	Thermal Equilibrium
		0.0762	2	58.5	Stirred - Period 1 sec.

Further experimental evidence for the existence of
temperature gradients in the solutions in the presence of the
field was obtained using the thermocouple as a probe. Temperatures
were measured in the manner described previously, except that the
thermocouple was held directly in the liquid by a second operator
instead of being placed in the well. A temperature difference in
the order of 1 to 2°C. was found between the walls and the center
of the liquid. This difference was believed to be quite signifi-
cant considering the crudeness of the method; the thermocouple
occupied about one fifth of the cell width, and also, its insertion
into the liquid undoubtedly caused appreciable mixing. Both of
these factors would tend to reduce the measured difference in
temperature relative to the actual difference.

Considering the importance of temperature to chemical
reaction kinetics, the existence of this relatively large tempera-
ture gradient was a matter of utmost concern in the present investi-
gation. As discussed in the next section, control and field reactions
would be thermally equivalent only under certain specified conditions,
one of which requires that the reaction be zero order. A second
condition involves the relation between the uniform temperature
in the control cell and the temperature distribution in the field
cell; a satisfactory approximation for the type of field used in
this work is obtained when the control temperature is equal to the
volume average temperature in the field.

The polymerization of styrene is zero order, and was reported

by Bryce et al (30) to be inhibited in the type of fields employed
in this study. Their investigation included the first serious
attempt to measure and control reaction temperature in an electric
field, but the thermometer method used by them was inadequate as
indicated earlier. Acceleration of this reaction had also been
reported, and it seemed desirable to study it further, with determina-
tion of the field reaction temperature by the thermocouple method
which was believed to approximate quite closely the volume average
value.

The polymerization of styrene

The polymerization of styrene was studied in the same
apparatus used for the out-gassing experiments, with the pressure
measuring system disconnected. The bath temperatures were raised
to 80°C. - the control bath was maintained for the purpose of
comparing temperatures.

The styrene was distilled from the inhibitor (tertiary
butyl catechol) at a temperature of 25°C. and a pressure of 10 mm. Hg.,
and stored in a flask at 0°C. for 1 day prior to use. Thiophene free
benzene and analytical reagent grade benzoyl peroxide were used;
other reagents were of C.P. grade.

A catalyst concentration of 1 g. per 1. was used because

a large field effect was obtained by Bryce et. al. (30) at this
level. The styrene was polymerized in bulk by dissolving the
desired amount of catalyst in 100 ml. of styrene, and trans-
ferring 85 ml. to the cell in the constant temperature bath.
Following a 60 min. induction period without stirring, samples
(1.5 - 2 g.) were withdrawn every 20 mins. for 3 hours. Each
sample was weighed and dissolved in 10 ml. of benzene containing
a trace of hydroquinone (short-stop). The polymer was precipitated
by adding 50 ml. of methanol, and the solvents and unpolymerized
styrene were distilled off under vacuum at $65 - 70^\circ$ C. The dried
polymer was weighed and the percent conversion was calculated.
Time was measured from the end of the induction period.

The effect of the field and the effect of stirring on
the polymerization were determined by 4 experiments using the fol-
lowing procedures.

In the first experiment, the polymerization was continued
without stirring or application of the field for 80 mins., at which
time the bath temperature was lowered to 77.8° C. and the field was
turned on and adjusted to the maximum strength (3600 volts). In the
second, the field was turned on and adjusted to 3600 volts immediately
following the induction period. After 80 mins. the field was turned
off, and the bath temperature was reset at 80° C. For the third
experiment, the polymerization was allowed to proceed without
stirring or application of the field for 80 mins., at which time

the stirrer was started with a period of 1 sec. In the last experiment the field was turned on at 3600 volts immediately following the induction period, and left on for the remainder of the experiment. After 85 mins. the stirrer was started with a period of 1 sec.

The percent conversion was plotted against time for each experiment, and in every case the rate of polymerization appeared to decrease during the second part of the experiment. A careful examination of the plots indicated that in each case a straight line could easily be drawn through all the points except the first two which were always low, as illustrated in Fig. 24. The rates of polymerization (% conversion per hour), determined from the slopes of these straight lines, are listed in table VII. The average rate of the stirred reactions, with and without the field, was about 5.9 as compared with about 5.2 for the unstirred reactions. The stirred reaction was unaffected by the field; whereas the unstirred reaction was faster when the field was applied during the first stage than it was when the field was applied later.

Also shown in table VII are the results of experiment No. 5 in which the induction period was extended to 2 hours to avoid the initial low points. The field was turned on for 80 mins. immediately following the induction period; and turned

Figure 24.

Variation of % Conversion with Time for the Bulk
Polymerization of Styrene at 80°C. with a Catalyst
Concentration of 1.101 g. per 1. (1 hr. induction period).

    0 - 80 mins.   no field

80 - 170 mins.   3600 volts
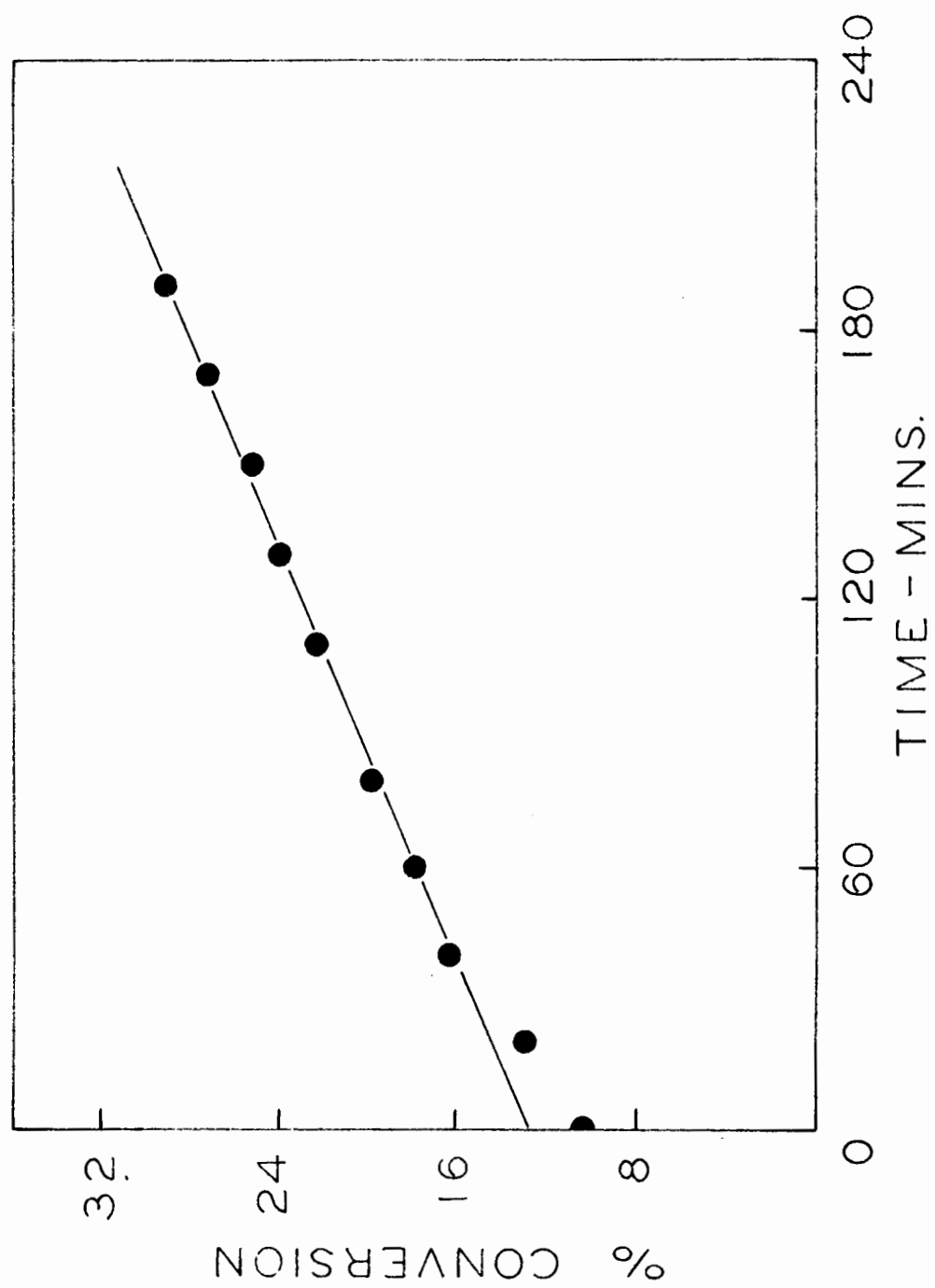
TABLE VII

THE RATE OF POLYMERIZATION OF STYRENE IN ENVIRONMENTS AS SHOWN

Experiment No.	Initial Condition	Final Condition	Rate % Con./Hr.	Induction Period
1	No field No stirring	3600 Volts No stirring	5.05	1 hour
2	3600 Volts No stirring	No field No stirring	5.40	"
3	No field No stirring	No field Stirred	5.87	"
4	3600 Volts No stirring	3600 Volts Stirred	5.85	"
5	3600 Volts No stirring		5.58	2 hours
		No field No stirring	5.06	

Best combined rate 5.30

off for the remainder of the experiment. Temperatures were adjusted as usual, and no mechanical stirring was used. The % conversion - time plot for this experiment is shown in fig. 25. The two straight line segments are much more definitely defined than in the first four experiments, and the individual rates are listed in the table along with the rate obtained from the best single line.

The results of all the styrene experiments indicated that the polymerization was accelerated by stirring, whether by mechanical means or otherwise. The faster rate obtained in experiment No. 2 as compared with No. 1 may be explained as follows. The amount of stirring caused by the field depends upon the temperature gradient and the viscosity. The dielectric nature of the system is not greatly altered during the polymerization process, so that the temperature gradient remains roughly constant. The viscosity of the styrene, however, increases very considerably during polymerization, and a reduction of stirring results. This will be further discussed in the next section.

Figure 25.

Variation of % Conversion with Time for the Bulk
Polymerization of Styrene at 80°C. with a Catalyst
Concentration of 1.098 g. per l. (2 hr. induction period).

0 - 80 mins.   3600 volts

80 - 180 mins.   no field
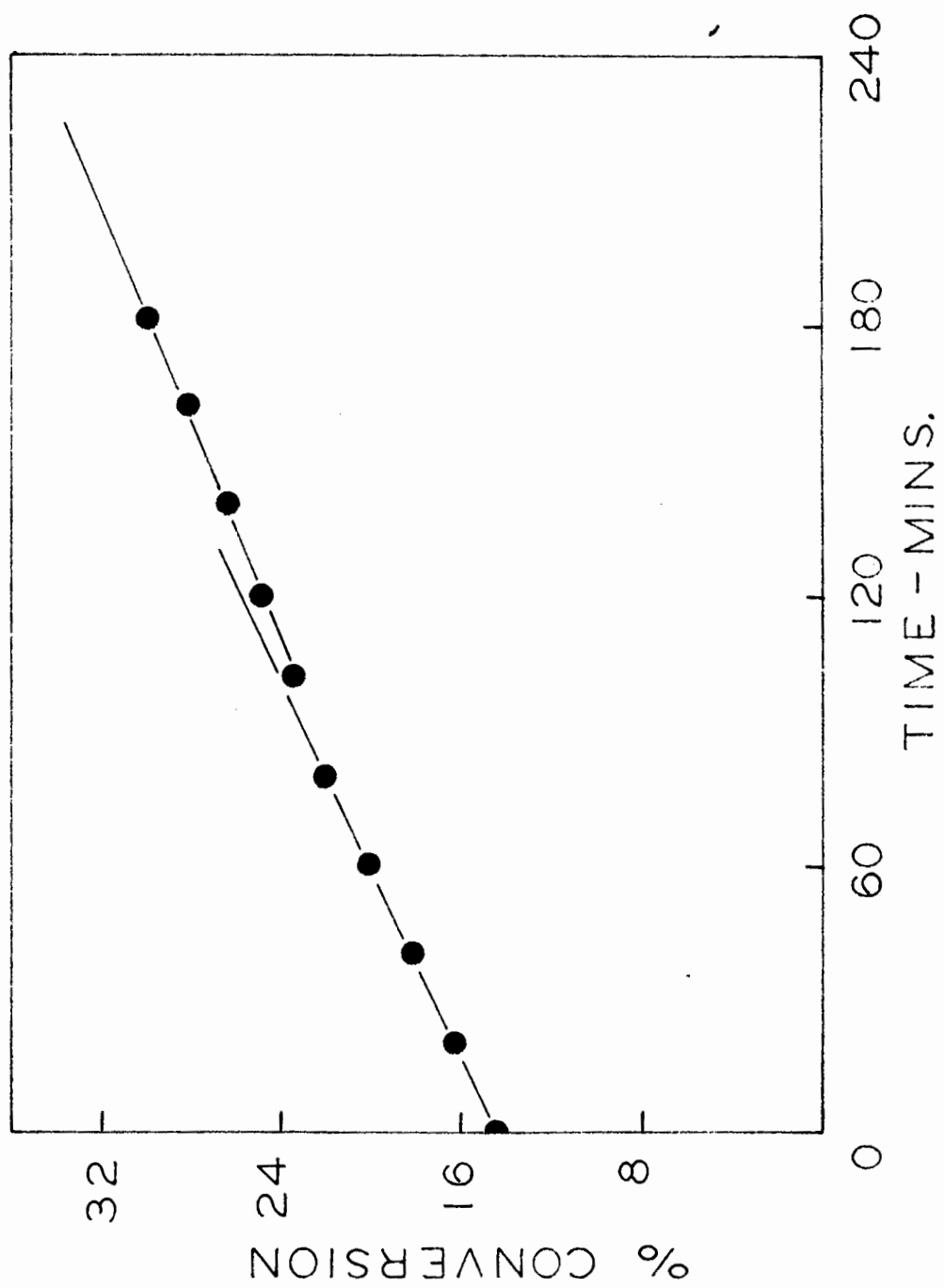
DISCUSSION

The out-gassing process

The conclusions based on the out-gassing experiments are
directly relevant to a discussion of the results obtained in the
experiments on chemical reactions and it will contribute to clarity
if the out-gassing experiments are discussed first. As mentioned
in the introduction, earlier workers have demonstrated the depen-
dence of gas evolution from liquids on the presence of certain types
of nuclei, such as foreign particles, microbubbles, and even
certain conditions existing at the container walls. The critical
nature of the cell wall is demonstrated by the results listed in
table V. When the cell was exposed to the laboratory atmosphere
prior to being filled, the normal thermal out-gassing proceeded at
a slightly faster rate than it did when no exposure occurred. The
effect of the field on the out-gassing under the two different
conditions was even more striking. Exposure of the cell to the
laboratory atmosphere resulted in a large field effect $(k_f'/k_c' \doteq 7)$
compared with the value obtained when no exposure occurred $(k_f'/k_c' \doteq 2)$.
These results support the conclusions of Harvey et. al. (43) con-
cerning the condition of the cell walls, but visible bubbles were
not formed at the walls under the conditions of the present investi-
gation, and their role in the out-gassing process remains obscure.

The much greater field effect in the exposed cell suggests that some factor other than condition of the cell wall is even more effective in controlling the out-gassing rate. For the normal thermal process the rate is largely controlled by this other factor, and a change in the condition of the cell wall has a relatively small effect. In the presence of the field, however, the effectiveness of the second factor is reduced, and a change in the condition of the cell wall has a large effect on the rate.

If the general view is accepted that gas can escape from solution only at certain active centers (nuclei), the following possible stages must be considered:

1. The formation and destruction of nuclei

2. The release of dissolved gas at a nucleus

3. The diffusion of dissolved gas to the nuclei

Micro-bubbles, and possibly certain other micro-nuclei which are dispersed throughout the body of the liquid, will be destroyed in the first phase of the out-gassing, by being carried to the surface with the first macro-bubbles formed on them. This leaves only heavy foreign particles and the cell walls as sources of nuclei for the major part of the process, or in a clean system, only the cell walls. The formation of nuclei is a little more difficult to picture, but Harvey et. al. (43) succeeded in demonstrating that cracks formed in the walls during out-gassing acted

as nuclei, whereas cracks made previously did not.

The mechanism by which gas is released at a nucleus is somewhat vague. It has been suggested that the nucleus is merely a pre-existing gas-filled space into which dissolved gas can evaporate. Certainly this would appear to be true where micro-bubbles are the nuclei, and the practise of using inverted capillary tubes to prevent bumping in boiling liquids lends support to the idea.

If gas is released only at certain active centers, the dissolved gas around such centers will be depleted very quickly, and subsequent diffusion of more dissolved gas to the centers will be necessary to maintain the process. Mixing would then be expected and is found to accelerate the out-gassing process. The rate of out-gassing is increased by a factor of 9 for relatively slow mechanical mixing and by a factor of 60 for faster mixing (experiments 3 and 4, table VI).

Neglecting the initial out-gassing centered on micro-bubbles located in the body of the liquid, the rate of out-gassing appears to depend jointly on the condition of the cell walls and on the migration of dissolved gas to the walls. The effect of the field on the out-gassing process may then be ascribed simply to absorption of energy from the field, with the production of temperature gradients, hence convection currents that carry dissolved gas to effective wall nuclei. Consideration must now be given, therefore, to the thermal effects of alternating fields.

The temperature of a dielectric in an alternating electric field

The electrical energy stored in an ideal dielectric in an electrostatic field is given by

$$u \; = \; \frac{k \; E^2}{8}$$

where u = energy per unit volume

    k = specific inductive capacity of the dielectric

    E = field intensity

It is a potential energy resulting from an instantaneous displacement current within the dielectric, and is completely recoverable on removal of the field. When an alternating field is applied to such a dielectric the current leads the applied emf. by a 90° phase angle, and no power is absorbed. For actual dielectrics this is no longer true; there are, in addition to the displacement currents, conduction currents and absorption currents. Conduction results from the presence of a small number of charged particles (ions, electrons, etc.) in the dielectric, and is relatively constant over a short period of time. As in any conductor, electrical energy is converted into heat. The nature of absorption currents is not completely understood, but they are known to involve molecular orientations and deformations, and the conversion of electrical energy into heat. When an alternating electric field is applied to a real dielectric, the current leads the voltage by a phase angle somewhat less than 90°,

and power is absorbed by the dielectric in proportion to the cosine of the phase angle, which is also called the power factor.

The absorption of power from an alternating electric field by a dielectric material is given by (50)

$$W = 1.4 \ f \ E^2 \ e''$$
$$= 1.4 \ f \ E^2 \ e' \cos \phi \tag{1}$$

where   W   is the power absorbed in watts per inch^3

f   is the frequency in Mc. per sec.

E   is the voltage gradient in Kv (rms) per inch

e'' is the loss factor

e' is the dielectric constant

$\cos \phi$ is the power factor

This power is absorbed by the material as heat which must be subsequently removed from the system to avoid a continuously rising temperature. If the dielectric surface is maintained at a constant temperature, a temperature gradient will be established such that energy is conducted from the material at the same rate that it is absorbed. Neglecting, for the moment, the convection currents which undoubtedly occur in a liquid under these conditions, the temperature T for this steady state condition satisfies the differential equation

$$\nabla^2 T = - \frac{W}{K} \tag{2}$$

where   W   is the rate of power absorption (as heat)

K   is the thermal conductivity

Written in terms of cylindrical polar coordinates, r, Θ, and z this becomes

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} = -\frac{W}{K}$$

Neglecting end effects, symmetry considerations require that T should not change with z or Θ, so that the equation becomes

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} = -\frac{W}{K} \tag{3}$$

which may be rewritten

$$\frac{d}{dr}\left(r\frac{dT}{dr}\right) = -\frac{Wr}{K}$$

The solution of this equation with the boundary condition

$$T = To \text{ for } r = R_1 \text{ (inner wall)}$$
$$r = R_2 \text{ (outer wall)}$$

gives the temperature as

$$T = To + \frac{W}{4K}\left[R_1^2 - r^2 + \frac{R_2^2 - R_1^2}{\ln \frac{R_2}{R_1}}\ln \frac{r}{R_1}\right] \tag{4}$$

The maximum temperature occurs at

$$r_m^2 = \frac{R_2^2 - R_1^2}{2\ln \frac{R_2}{R_1}} \tag{5}$$

In the type of cell used in this investigation, the maximum temperature exists very close to the center of the cell, and is given by

$$T_m = To + \frac{c}{K} \cdot f\ E^2\ e'\ \cos \phi \qquad (6)$$

where c is a constant incorporating the bracketed radius function in equation 4, and a conversion factor for the units of W. The actual temperature gradient $\frac{dT}{dr}$ is a function of r, but for the purposes of this investigation the maximum temperature difference

$$T_m - To = \frac{c}{K} \cdot f\ E^2\ e'\ \cos \phi \qquad (7)$$

is equally important, and it will be used throughout.

The assumptions necessary for the derivation of equation 4 are too extensive to permit an accurate calculation of the temperature at various points within the liquid, but the qualitative relation between $(T_m - To)$ and other factors such as E, e', etc. may be obtained from equation 7. However, although thermal conductivity and dielectric constant are listed for a number of liquids, power factors have been reported for a very limited number of substances, primarily those used as dielectrics in the manufacture of condensers. Also, convection currents caused by the temperature gradient would act to decrease the final steady-state value of $(T_m - To)$ through the mass motion of hot liquid away

from the center of the cell. A second result of this convection would be the introduction of vertical temperature gradients.

The existence of a horizontal temperature gradient is confirmed by the results of the experiment in which the thermo-couple was used as a probe placed directly in different parts of the cell. The temperature difference measured in this way is quite small (about $1 - 2^{\circ}$C.), but it is pointed out that the large relative width of the probe, and the mixing caused by its intro-duction into the liquid both act to lower the measured difference in temperature. The main point of interest here is the actual demonstration of a horizontal temperature gradient.

The magnitude of $(T_m - To)$ is better estimated from the results of the out-gassing experiments, and this may now be done as an explanation of the effect of the field on the out-gassing process

An explanation of the field effect

The field effect (k_f'/k_c') depends upon the dielectric constant of the liquid as shown in fig. 17. The temperature gradient changes with this property in the same general way, as indicated in equation 7 developed above. The out-gassing depends upon the migra-tion of dissolved gas to the walls, which normally occurs by a

process of diffusion. It seems fairly obvious that at least a part of the field effect is due to convection currents initiated by the temperature gradient established by the field. The nature of the temperature gradient is such that convection will carry liquid up the center of the cell and down the walls making the slower process of diffusion unnecessary.

This mechanism will explain the results in table V for the different methods of filling the cell. For the normal thermal out-gassing, diffusion of the gas to the walls is the main rate controlling step, and differences in wall activity cause only small differences in the rate of the process. In the field, however, diffusion is replaced by convection, and the activity of the walls becomes rate controlling. Under these conditions differences in the activity of the walls cause much larger differences in the rate of out-gassing. Hence the relatively small change in k_c' produced by different methods of filling the cell, and the relatively large change in k_f'.

There is also the possibility that the field affects the wall activity as a rate controlling factor; either by increasing the activity of nuclei already present, or by creating additional nuclei. If this were the case, some field effect should remain even in the presence of stirring other than convection. On the other hand, if the field acts only through the convection currents set up, its effect would be negligible in the presence of sufficient

agitation. The results in table VI show that the convection caused by a temperature difference of 25°C. between the cell walls completely nullifies the field effect, as does also sufficient mechanical stirring. A temperature difference of 15°C. between the cell walls is not quite sufficient to nullify the effect of the field.

Since, as above, the field affects the rate of out-gassing only through the convection currents set up by the temperature gradient which is established, the magnitude of the temperature gradient can be estimated by comparing the accelera-tion caused by the field with the acceleration due to a thermally produced temperature gradient. The results in table VI indicate that a field of 2000 volts is roughly equivalent to a temperature difference of 10 - 15°C. across the cell, or 5 - 7°C. from the center of the cell to the walls.

A temperature difference of this magnitude is extremely important in investigations of a kinetic nature, and this aspect of the problem must now be considered.

Kinetic studies in alternating electric fields

The kinetics of chemical reactions are normally studied under conditions of a constant, uniform temperature throughout the

reacting medium. Under these conditions the rate of a reaction of the simple type

$$n\ B\ \longrightarrow\ Products$$

is given by the equation

$$-\frac{d\ c}{d\ t}\ =\ k\ c^n \qquad\qquad (8)$$

where c is the concentration of B at time t, and n and k are called the order and rate constant respectively, for the reaction. Integration gives c as a function of t,

$$c\ =\ Co\ e^{-kt} \qquad\qquad n = 1$$
$$c\ =\ \left[\frac{Co^{n-1}}{1 + (n-1)\ Co^{n-1}\ kt}\right]^{\frac{1}{n-1}} \qquad n \neq 1 \qquad \Bigg\} \ (9)$$

Where the reaction is taking place in a constant volume V (essentially valid for a liquid system), the total amount of material present at time t is given by

$$q\ =\int_{V}\ C\ d\ V\ =\ C.V \qquad\qquad (10)$$

In this case the reaction can also be described by

$$-\frac{d\ q}{d\ t}\ =\ -\ V\ \frac{dc}{dt}\ =\ Vkc^n\ =\ k'q^n \qquad\qquad (11)$$

in which $V^{n-1} k' = k$. Integrated expressions equivalent to
equations 9 give q as a function of t.

The rate constant varies with temperature T roughly
according to the Lewis (or Arrhenius) equation

$$k = A e^{-E/RT} \qquad (12)$$

in which A is a constant known as the frequency factor, E is the
activation energy and R is the gas constant. More accurate
expressions have been developed, but this one will serve for the
present purpose.

The temperature of a dielectric in an alternating electric
field is a function of position, as indicated in equation 4 previously.
Under these conditions k, and hence also C which is a function of k
(equation 9), both vary with position. Equations 8 and 9, there-
fore, describe the reaction only at any given point in the system,
and the overall reaction in the cell must be described by the fol-
lowing expression, in which * indicates a quantity which varies with
position.

$$- \frac{dq}{dt} = - \frac{d}{dt} \int_V C^* \, dV = - \int_V \frac{dc^*}{dt} \, dV = \int_V k^* c^{*n} \, dV \qquad (13)$$

This expression will be equivalent to equation 11 for the reaction
at uniform temperature only if

$$V \ K \ C^n \quad = \quad \int_V k^* \ C^{*n} \ d \ V \qquad (14)$$

i.e. only if the uniform temperature T is chosen so that $k \ C^n$ is equal to $\frac{1}{V} \int_V k^* \ C^{*n} \ d \ V$, the volume average of this expression for the non-uniform temperature.

For a zero order reaction, $n = o$ and the required condition is

$$k \ = \ \frac{1}{V} \int_V k^* \ d \ V \qquad (15)$$

Substitution of the expression for k (equation 12) yields

$$e^{-E/RT} \quad = \quad \frac{1}{V} \int_V e^{-E/RT^*} \ d \ V$$

To ensure that a zero order control reaction is thermally equivalent to the field reaction, the control temperature must satisfy

$$T \ = \ \frac{-E}{R \ \ln \ \frac{1}{V} \int_V e^{-E/RT^*} \ d \ V} \qquad (16)$$

Similar reasoning shows that for a first order reaction, the uniform temperature must be chosen to satisfy the condition

$$e^{-(E/RT \ + \ A \ t \ e^{-E/RT})} \ = \ \frac{1}{V} \int_V e^{-(E/RT^* \ + \ A \ t \ e^{-E/RT^*})} \ d \ V$$

The occurrence of t in this expression suggests that the rates
of the over-all reaction under the two different conditions can
be made equivalent only at a given instant of time. This means,
in fact, that for a first order reaction, it is impossible to
choose a temperature to ensure thermal equivalence of the control
and field reactions. This is also true of higher order reactions.

Even for zero order reactions, T^* must be determined
as a function of V for substitution into equation 16, and the
resulting integral determined. Considering the complicated
expression for T in equation 4, this would appear to be a most
difficult task.

However, for a small temperature range the rate
constant may be approximately expressed by

$$k = k_1 + a (T - T_1)^m$$

where k_1 and T_1 are corresponding values of the rate constant and
temperature at some point within the existing range. Even with
$m = 1$ the average error in k over the temperature range may be
made quite small by the proper choice of a and T_1, and substitution
of the linear function

$$k = k_1 + a (T - T_1) \tag{17}$$

into equation 5 gives

$$k_1 \;+\; a\,T \;-\; a\,T_1 \;=\; \frac{1}{V} \int_V (k_1 + aT^* - aT_1)\; d\,V$$

whence

$$T \;=\; \frac{1}{V} \int_V T^*\, d\,V \tag{18}$$

This means that control and field reactions will approximate to thermal equivalence if

    1 - the control temperature is adjusted to be the volume average of the field temperature

    2 - the field is not sufficiently strong to cause very large temperature differences in the system

    3 - a zero order reaction is chosen

      The effects of stirring and of oxygen on the reaction should also be considered if a true field effect is to be isolated. Reactions affected by mixing must be stirred mechanically at a sufficient rate to ensure that the effect of convection caused by the field will be negligible. Schlapfer et. al. (51) have found that even in a practically stagnant column of water, the absorption of oxygen depends upon convection, except for a thin layer near the surface. In a system capable of reacting with oxygen, the oxygen concentration will depend upon the rate at which it is used up, and the rate at which it is absorbed. Such a system will be very

sensitive to mixing, whether of mechanical origin, or as a result
of convection currents established by an electric field.

It is interesting to recall here the color effect
reported by Russel and Winkler (36). Although some inhibition of
the decomposition of benzoyl peroxide in toluene solution appeared
to be caused by an alternating electric field, the appearance of
an orange color occurred much earlier in the "inhibited" system.
The color did not arise when nitrogen was bubbled through the
system, and it seems probable that the phenomenon was caused by
a more rapid absorption of oxygen in the presence of the field.

The polymerization of styrene in an alternating electric field

The foregoing discussion demonstrates that the poly-
merization of styrene should be suitable for study in electric
fields. When benzoyl peroxide is used as the catalyst at a con-
centration of about 1 g. per l., the reaction is zero order, with
an activation energy of about 15,000 cal. per mole. The error
introduced by using equation 17 for k is not excessive for this
value of E and the low dielectric constant of styrene (about 2.5)
ensures that the temperature gradient in a given field strength
will be less than that obtained with many liquids. The major
problem is to determine the volume average temperature in the field.

The existence of convection currents makes calculation of the average temperature based on equation 4 quite inaccurate. If the field bath temperature is used, the control reaction temperature will be lower than the volume average temperature in the field, and an apparent acceleration will result. This may explain the increases in rate found in a number of investigations (26 - 28), but the pre-activation found by Liechti (27) remains inexplicable. On the other hand, the method used by Bryce et. al. (30), in which a thermometer is placed in the center of the liquid with only the bulb immersed, does not seem adequate. Russel and Winkler (36) succeeded in showing that a thermometer (alcohol or mercury) placed in an alternating electric field registers too high. Further, as indicated by the out-gassing experiments, the top central portion of the liquid is considerably hotter than the average, due to field heating and convection. In this case, the control reaction takes place at a temperature slightly higher than the volume average temperature in the field, and an apparent inhibition is obtained.

The thermocouple-potentiometer method devised by Russel and Winkler, and used in this investigation appears to be the most satisfactory one for determining the temperature. Interaction of the field and the thermocouple is prevented by momentarily turning off the field. The temperature gradient is temporarily eliminated through stirring set up by introduction of the thermocouple, which is immersed to the mid-point of the liquid. Under these conditions,

a reasonably accurate determination of the volume average tempera-
ture of the liquid in the field is obtained.

The results given in table VII indicate that the effect
of a field of 3600 volts per cm. and 1.5 megacycles on the polymeri-
zation of styrene, if it exists at all, is not great enough to be
noticeable in the presence of concurrent mixing.

Other physico-chemical determinations

The arguments presented above concerning the temperature
of dielectric materials subjected to alternating electric fields
have significance not only for chemical kinetics, but for any
physico-chemical determination that depends on temperature. Viscosity,
surface tension, vapor pressure, solubility, and equilibrium all
vary with temperature, and the investigation of any one of these
properties in an electric field would require also a determination
of the volume average temperature, or possibly some function of
temperature.

The only property which has been widely studied under
the action of various types of fields is viscosity. Increases and
decreases in viscosity in both electric and magnetic fields are
reported, as well as the absence of any effect (52 - 60). Various
materials were used, including a number of organic liquids and

solutions, but the most widely studied were substances exhibiting
the liquid crystal state (para azoxy anisole etc.). Different
effects were obtained depending on the orientation of the field
(E or H) relative to the velocity gradient in the liquid.

Again, no mention is made of the determination of
temperature in the field. However, viscosity changes in the
order of 275 percent are reported, and while some part of this
is undoubtedly due to temperature in some cases, a 100 percent
increase produced by a d.c. field of 10,000 volts per cm. can
not be entirely attributed to incorrect temperature determination.
It is also noted that where bath temperature is adopted as the
field temperature, an apparent decrease in viscosity should be
obtained. It appears likely that fields (electric or magnetic)
do affect viscosity, possibly to a considerable extent. However,
in the absence of definite information concerning temperature
determinations, quantitative results are open to criticism.

Suggestions for further work

A more complete evaluation of the temperature gradient
and convection currents existing in liquids subjected to electric
fields would be made possible by

> 1) out-gassing experiments using a less critical
> cell material (polystyrene, lucite, etc.) and

subsequent determination of the dielectric

constant and loss factor of the liquids

used.

2) experiments using a rectangular cell and

a dilute suspension of fine particles of

almost the same density as the liquid to

permit visual evaluation of convection

currents.

The results of this investigation concerning the effect

of the field on the polymerization of styrene should be extended to

at least a few other zero order reactions, including some in the

gas phase; dielectric heating in gases is much smaller than in

liquids.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. An apparatus was built to follow the decomposition of
benzene-diazo-acetate in solution by measuring the pressure
of the nitrogen evolved in a constant volume system -
the evolution of air from solution occurred simultaneously
due to an initial decrease in pressure to protect the
system. One of two otherwise similar cells was fitted with
electrodes for application of an electric field.

2. The rate of pressure increase for a concentration of 0.4 g.
per l. was greatly accelerated by an electric field of 3000
volts per cm. and 1.5 megacycles. The effect of the field
decreased rapidly as the concentration was increased, and at
1.6 g. per l. the acceleration was barely discernible. The
greatest effect was obtained for the gas evolution alone.

3. The evolution of gas from supersaturated gas-liquid solutions
was studied in the same apparatus, and also in a modified
apparatus comprised of only one cell. The effect of the
electric field on this process was studied first by comparing
the results in two cells, one of which had the field applied,
and later by applying the field to the process after the
control rate had been established.

4. The rate of out-gassing was found to be slower for more
   viscous liquids, but the relation was not well defined. It
   was dependent to some extent on the condition of the cell
   walls, being slightly faster when the cell was exposed to
   the laboratory atmosphere prior to filling. Stirring
   caused a marked increase in the rate of the process,
   especially in the exposed cell. Convection currents intro-
   duced thermally by temperature differences of 15 and 25° C.
   across the cell were quite effective, but fast mechanical
   stirring increased the rate by a factor of 58.

5. An electric field of 3000 volts per cm. increased the rate
   of evolution of nitrogen from toluene by a factor of about
   5, and had roughly the same effect for oxygen and hydrogen.

6. An electric field of 2000 volts per cm. increased the rate
   of nitrogen evolution from a number of organic liquids by
   factors ranging from about 2 for liquids like toluene and
   xylene (dielectric constant about 2.3) to about 6 for
   liquids like o-dichlorobenzene and methyl benzoate
   (dielectric constant about 7). The effect of the field was
   greater when the cell walls were exposed to laboratory
   atmosphere prior to filling. The field had no effect on the
   process when mechanical stirring was used, nor in the
   presence of a temperature difference of 25° C. between the
   cell walls; a slight effect remained with a temperature
   difference of 15° C.

7. Evidence was obtained to support the view that a significant temperature gradient was maintained by the field, and that the acceleration of the rate of out-gassing was essentially due to the resulting convection currents.

8. The bulk polymerization of styrene catalyzed by benzoyl peroxide was reinvestigated in the presence of an electric field of 3600 volts per cm. and 1.5 megacycles. The conditions showing maximum effect in the investigation by Bryce et. al. (30) were duplicated, and the method devised by Russel for determining the average temperature in the field was used. No measureable effect was found.

9. The significance of the temperature gradient to reaction kinetics was discussed in detail, and it was shown that only for zero order reactions is it possible to have thermally equivalent conditions in the presence and absence of an electric field.

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