THE POLYMERISATION OF ACRYLONITRILE IN AQUEOUS SOLUTION

by

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PREFACE

The work described in this thesis was carried out at the Department of Physical Chemistry in the University of Leeds, where the author was a graduate student from October 1950 to September 1953.

No part of this thesis has been submitted to any other University. Where acknowledgment has not been made in the text, all the work has been carried out by the author. None of this work has been published, but some of it forms a part of other articles (Dainton and James, 1951).

The author wishes to express his sincere thanks to F.S. Dainton, Professor of Physical Chemistry in the University of Leeds, for his direction and encouragement which was forthcoming at all times. Grateful acknowledgment is also made to Dr. D.G.L. James for extensive references to his thesis.

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SUMMARY

The aqueous polymerisation of acrylonitrile, initiated by hydroxyl radicals produced from the photochemical electron transfer $(Fe^{3+}.OH^-) = Fe^{2+} + OH$ at 3130A, has been investigated at 15°C, 25°C, 30°C, 40°C and 50°C.

At 15°C, 25°C and 30°C, assuming a photostationary state in the aqueous phase and in buried centres of the polymer particles, the system was found to obey the rate equation:

$$\frac{-d(m_1)}{dt} = k\, I_o^{0.5} (Fe^{3+}.OH^-)^{0.5} (m_1)^{1.0}$$

At these three temperatures, an attempt was made to evaluate the rate constants and activation energies of propagation and termination by the rotating sector technique. Only lower limiting values were obtained because of the presence of two phases.

Unusually high monomer exponents, found at 40°C and 50°C, are attributed to a changing rate of initiation with monomer concentration.

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BIBLIOGRAPHY

CHAPTER 1. INTRODUCTION.

A. THE NATURE OF THE INVESTIGATION.

This investigation is primarily concerned with elucidation of the reaction of the polymerisation of acrylonitrile in aqueous solution. An attempt has been made, not only to evaluate the rate constants and energetics of the various steps of the reaction, but also to ascertain whether the polymerisation of aqueous acrylonitrile is predominantly a homogeneous or a heterogeneous process. Some attention has also been given to the effect of increased temperature on the polymerisation of acrylonitrile in aqueous solution.

I. Relation to General Chemistry.

As an addition polymerisation provides an excellent example of a kinetic chain reaction, it is important from a physical chemical point of view. With present day advances in the technology of plastics, fibers and rubbers, a more complete understanding of such interesting and useful compounds as acrylonitrile is always welcome.

II. Relation to Photochemistry and Radiation Chemistry.

One of the best tools for detecting the reactive entities created by the radiation of high energy is the polymerisation process. Free radicals, as these reactive entities usually turn out to be, are generally of low concentration and require a sensitive reagent to capture them. Free radical initiated addition polymerisation of vinyl compounds such as acrylonitrile, being long chain in character, provides a very large material amplification of the original step and hence makes them readily detectable by physical chemical means.

III. Relation to the Chemistry of Polymerisation.

Because of the interest in the photochemistry and radiation chemistry of water and its products, research has been directed along the lines of water soluble vinyl compounds. The most useful of these has turned out to be acrylonitrile because of its high solubility and freedom from complicating side reactions and because of the general reproduceability of results obtained when it is used.

Much study has been directed on the actual initiation processes of these aqueous systems. In this work more attention has been paid to the polymerisation process itself, to prove that the method of steady states can be applied to the polymerisation of aqueous acrylonitrile, and to show that the process is a mixture of a homogeneous and a heterogeneous reaction.

B. A BRIEF SURVEY OF POLYMERISATION.

I. Introduction.

In discussing the chemistry of isomers, Berzlius (1833) gave the name "polymer" to those compounds which contained the same atoms in the same proportions but had different molecular weights. High polymer chemistry could be said to have originated with Regnault in 1838 and Goodyear in 1839, but it has only been in this century that a systematic study has been carried out. There are several texts in which the field has been covered in detail. Some of these are: Mark and Tobolsky (1950), Burk and Grummitt (1949), Bawn (1948) and D'Alelio (1952).

Carothers (1940) was the first to distinguish between polycondensations and addition polymerisations. Both Carothers and Chalmers (1934) put polymerisation on firmer theoretical grounds.

Polycondensation or step reaction polymerisation is characterized by the step-wise combination of monomer units with the elimination of some simple molecule, e.g. H_2O, NaCl. Each individual step proceeds at the same specific rate and hence all steps will have the same probability of reaction independent of chain length. Therefore, the degree of polymerisation is chiefly dependent on the duration of the reaction and not on the extent of the reaction. This does not mean, of course, that a step reaction polymerisation always goes to completion and that the degree of polymerisation tends toward infinity.

There is generally a random distribution of molecular weights, influenced, for example, by an excess of reagent, by non-removal of eliminated molecule to prevent back reaction, or by viscosity changes.

Addition or chain reaction polymerisations, because of their complex features, are more interesting and will be considered in greater detail.

II. Addition or Chain Reaction Polymerisation.

Addition polymerisation is the intermolecular combination of unsaturated compounds, usually derivatives of ethylene and butadiene, without the elimination of any simple molecule. Vinyl monomers are most widely investigated, as it is found that even complete substitution at one carbon atom will not hinder polymerisation, but substitution at the second atom will (except in the case of fluorine). However 1,2,substituted ethylenes may take part in copolymerisations.

A monomer reacts to form long chain molecules in which the individual units or segmers are connected by single bonds. Addition polymerisation is a true chain reaction. The initiation step, which is slow, is quite different from the propagation step in contrast to polycondensation. Also in common with other chain reactions, addition polymerisations are very sensitive to the negative or positive catalytic effect of impurities such as oxygen or traces of heavy metals. The molecular weight is also constant and does not show random variations. Hence the degree of polymerisation is not dependent on the duration of the reaction.

Addition polymerisations consist of at least three main steps: initiation, propagation and termination. Other factors will also be considered.

1. Initiation: The opening of the double bond.

There are two types of vinyl polymerisations which depend on the electronic nature of the double bond: radical initiated chain polymerisation, and ion initiated chain polymerisation.

A double bond can be considered in two parts, the first consisting of the σ bonds formed from the maximum overlap of one of the trigonal bonds of the sp_2 hybrid. The other part of the double bond is made up of unhybridized p_z orbitals at right angles to the other three, which overlap to form a π bond having about 70% of the strength in ethylene of the σ bond.

From the molecular orbital treatment of ethylene summarized by Mulliken (1942), it is found that ten of the twelve electrons are localized in pairs in positions between the carbon and hydrogen nuclei and between the carbon nuclei. The remaining two electrons are distributed over the entire molecule.

The opening of the double bond may be visualized by the following processes.

1a. Radical approach:

The odd electron of the free radical attracts the π electron of the double bond which has a spin opposite to that of the free radical and repels the electron with the same spin to the other end of the double bond. The radical then forms an electron pair bond with monomer at one end and effectively transfers its free radical character to the other end.

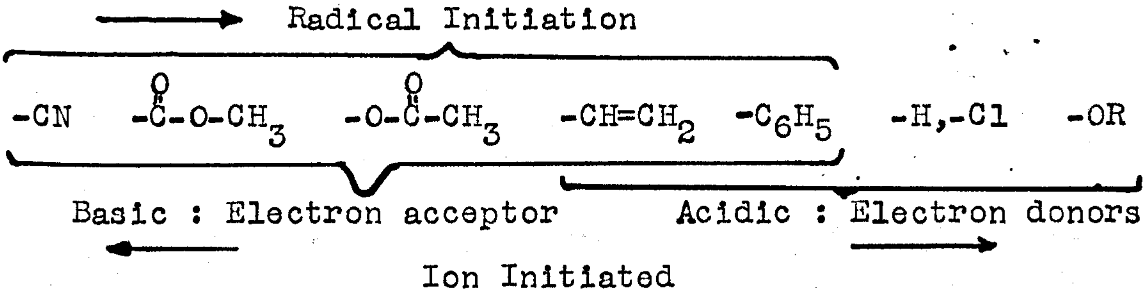
1b. Ionic approach:

(i) A positive ion such as a proton attracts both electrons of the double bond to form a simple covalent bond at one end leaving the far end of the monomer positively charged.

(ii) A negative ion repels both π electrons to the far end of the monomer, thus giving it a negative charge.

Pepper (1952) after Mayo, Lewis and Walling (1948) has summarized the effect of substituent groups on the reactivity of various monomers when subjected to the two types of attack. (Table 101). From the table, it can be seen how the relative electronegativities of the groups

Table 101



$$-CN \quad -\overset{O}{\overset{\|}{C}}-O-CH_3 \quad -O-\overset{O}{\overset{\|}{C}}-CH_3 \quad -CH{=}CH_2 \quad -C_6H_5 \quad -H, -Cl \quad -OR$$

Arrows show direction of increasing reactivity.

affect the overall electronic distribution in a monomer and hence will affect its ability to accept or donate electrons or to undergo radical initiation. Acrylonitrile has been polymerised by a host of free radicals but is not ionically polymerised in aqueous solution where the strongest anion is the hydroxide ion. It is, however, polymerised by a stronger base, the amide ion NH_2^+ (Higginson and Wooding, 1952). The table does not take into account any polarisation that might occur in the presence of highly polar solvents such as water, and so this grouping should not be examined too rigorously.

The energy states of the two labile electrons in ethylene have been considered by Eyring et alia (Hulbert, Harmon, Tobolsky and Eyring, 1943; Eyring and Harmon, 1942).

It is found that two excited states are possible, a triplet internal radical state and an ionic state, with the ionic state above the radical state. A review of experimental data on cis-trans isomerization, olefine dimerization and polymerisation initiation rates by Magee, Shand and Eyring (1941) provides results falling into two classes: *(a)* Those with activation energies of 40 kcals/mole and frequency factors of 10^{11} *i.e.* an ionic transition, and *(b)* Those with activation energies of 20 kcals/mole and frequency factors of 10^{4} *i.e.* a radical transition.

Direct sensitization of monomer is also possible by either photochemical or thermal means and it was this type of process that was considered in early theories. Stuadinger (1932) said that a diradical was formed but this is improbable because of the high activation energy required. A collision mechanism involving two monomer units is more likely. Recent work has proven that chains grow in one direction only in the polymerisation of styrene and methyl methacrylate. (Baysal and Tobolsky 1952, Johnson and Tobolsky 1952).

Since this thesis is primarily concerned with a radical initiated polymerisation, the following sections will be especially concerned with that subject, bearing in mind that analagous steps are postulated for ionic polymerisations.

2. Propagation.

Once a polymerisation has started, propagation follows readily. The propagation step is analagous to the opening of the double bond in the initiation step, the difference occurring in the nature of the radical ion. Since monomers are generally unsymmetrical about the double bond, the question arises as to whether addition to a growing chain is a head to head, or tail to tail mechanism. Evans (1947) has shown theoretically that the activation energy for head to tail addition would be less than for head to head addition and hence would be the most probable mode of reaction. Experimental evidence generally supports head to tail addition. The experiments described by Marvel and Cowan (1939) have shown that head to head addition was favoured in α-haloacrylates. However, Marvel, Weil, Wakefield and Fairbanks (1953) have carried out further investigations and have come to the conclusion that head to tail addition predominates and that their earlier conclusions were unjustified.

Christiansen-Semenov chain theory when applied to polymerisation processes assumes that radicals have a reactivity independent of their chain length and that the lifetime of a growing chain is short compared with the duration of the reaction. Burnett (1950) has shown that experimental evidence supports this view.

3. Termination.

Termination occurs when a growing chain loses its activity without creating another active centre. In radical polymerisations, the most probable terminal reaction is that occurring between two growing polymer radicals, *i.e.* mutual termination. Mutual termination can occur in two ways.

(i) Disproportionation.

$$\sim CH_2CHX\cdot \quad + \quad \sim CH_2CHX\cdot \quad = \quad \sim CH{=}CHX \quad + \quad \sim CH_2CH_2X$$

(ii) Combination.

$$\sim CH_2CHX\cdot \quad + \quad \sim CH_2CHX\cdot \quad = \quad \sim CH_2CHXCHXCH_2\sim$$

Weiss (1947) has shown that radicals of the type found in polymerisations which have appreciable dipole moments are most likely to disproportionate. Melville and Valentine (1950), Bonsall, Valentine and Melville (1953) and Taylor and Bevington quoted in the above, favour disproportionation in styrene and methylmethacrylate especially at high temperatures. Matheson et alia (1951) find that a combination process fits their results best for styrene at 30°C. Arnett (1952) and Arnett and Peterson (1952) postulate termination by combination for methylmethacrylate. Baysal and Tobolsky (1952) assuming 100% initiator efficiency, find that combination occurs in the polymerisation of styrene.

It is becoming increasingly clear that in any particular system, both termination mechanisms can operate at the same time, and it is the temperature at which the reaction is carried out which determines which mechanism predominates, disproportionation being favoured at high temperatures.

Linear termination is also possible in a number of ways: addition of an initiating radical; addition of impurities; or spontaneously. The concept of spontaneous linear termination is important in the polymerisation of acrylonitrile in a non-solvent for the polymer. Here there is a chance of linear termination by the burying of a radical end in a polymer particle.

Termination by ring formation of a long diradical is too improbable to be considered.

4. Other polymerisation steps.

4a. Chain transfer:

A growing polymer chain may transfer its activity to the catalyst, a monomer molecule, a solvent molecule, an impurity, a growing chain other than at the radical end, or a dead polymer chain. One chain is terminated and another one started resulting in a reduction of the average molecular weight.

4b. Chain branching.

When the activity of a growing chain is transferred to another growing chain or a dead polymer chain, branching is said to have occurred.

4c. Cross linking.

The process of mutual combination of two branched chains is called cross linking. If there is no chemical interaction between a polymer and a solvent and they have approximately the same cohesive energy densities, the polymer will be soluble in the solvent. Hence, the large change in cohesive energy densities brought about by branching and crosslinking tend to increase the rigidity and insolubility of a polymer. This accounts for the hardness of dry paint and the elasticity of vulcanized rubber.

Branching and crosslinking are not likely to occur in polymers formed from bifunctional molecules of the vinyl type because the growing chains and dead polymer are generally saturated molecules and present no convenient site for attack. This is, of course, not true for polyfunctional molecules of butadiene type.

5. Degradative chain transfer.

A special type of chain transfer is that known as degradative chain transfer (Bartlett and Altschul, 1945). In this case, the active species formed from the transfer may be stabilized by resonance and therefore become inactive in initiating further polymerisation. Alternatively, two species may be formed, one of which is an inhibitor such as oxygen (Smith 1951). This mechanism may also be advanced to explain the results of Khomikovskii and Medvedev (1948) who found that high persulphate concentrations were necessary to bring about the polymerisation of acrylonitrile.

Degradative chain transfer has also been observed by Bartlett and Nozaki (1946) for allyl acetate and by Hart and Smets (1950) for isoprene acetate. Ihrig and Allyea (1953) have measured the diamagnetic susceptibility of the methylmethacrylate system in the presence of various retarders which serve to promote degradative chain transfer. Radicals were found to be present in concentrations well above that of the chain carriers, thus supporting the above ideas. Air was rigorously removed. Bartlett and Tate (1953), using allyl-1-d_2 acetate showed that a resonance stabilized allyl radical was formed. The rate of reaction was increased twofold in the deuterated form with respect to the undeuterated molecule. If resonance stabilized radical formation did not occur, involving the α-position of the allyl group, the rate would have been unchanged by the presence of D atoms.

6. Depropagation reaction.

Taylor and Tobolsky have pointed out that the principal of microscopic reversibility would lead to the conclusion that not only can an active chain add on a monomer molecule, but under suitable conditions could cast one off as well.

A depropagation step will occur simultaneously with the propagation step. At temperatures at which ΔG has a large negative value, little depropagation will take place. However, at higher temperatures, ΔG will become more positive and the depropagation contribution will increase. When $\Delta G = 0$, the rate of propagation will equal the rate of depropagation and no polymerisation can occur. For addition polymerisations, since both ΔH and ΔS are negative, this leads to a "ceiling" temperature above which polymerisation will not take place (Dainton and Ivin, 1948, 1950). If both ΔH and ΔS are positive, then a "floor" temperature will result (Gee, 1952).

III. The Reaction Mechanism.

Considering only initiation, propagation and mutual termination, the mechanism can be written as follows:

$$X + m_1 = m_1^{*} \qquad (k_i)$$

$$m_1^{*} + m_1 = m_2 \qquad (k_p)$$

$$m_j^* + m_1 = m_{j+1}^* \qquad (k_p)$$

$$m_r^* + m_s^* = P_r + P_s \qquad (k_t)$$

$$\text{or } P_{r+s} \qquad (k_t)$$

If k_p and k_t are independent of chain length and if $C = \sum(m_j^*)$, then:

<u>(a)</u> Using stationary state kinetics, <u>i.e.</u> $\frac{d(c)}{dt} = 0$

Therefore:

$$\frac{-d(m_1)}{dt} = k_p \sqrt{\frac{k_i}{k_t}} \; (m_1)^{1.5} \; (X)^{0.5} \qquad (I)$$

<u>e.g.</u> if $X = S_2O_8^{=}$ (Morgan, 1946)

For thermal initiation [or direct photochemical initiation]

$$X = m_1$$

$$\frac{-d(m_1)}{dt} = k_p \sqrt{\frac{k_i}{k_t}} \; (m_1)^{2.0} \qquad (II)$$

For radical initiation, $\frac{d(OH)}{dt} = 0$

<u>i.e.</u> reduction activation

$$Fe^{2+} + H_2O_2 = (Fe^{3+}.OH) + OH \quad k_1$$

then, $k_1(Fe^{2+})(H_2O_2) = k_1(OH)(m_1) = k_1A^2$

if $(Fe^{2+}) = (H_2O_2) = A$

Therefore, $(X) = (OH) = \frac{k_1A^2}{k_1(m_1)}$

Therefore:

$$\frac{-d(m_1)}{dt} = k_p \sqrt{\frac{k_1 A^2}{k_p}} \, (m)^{1.0} \qquad \text{(III)}$$

(Baxendale, Evans and Kilham, 1946.)

For photosensitized initiation,

$$\frac{d(R)}{dt} = 0 \quad \text{where } R = X.,$$

where $R = OH, Cl, N_3$ (Evans, Santappa and Uri, 1951.)
$= OH, H$ (Dainton and James, 1953.)

and $k_1(OH)(m_1) = n\phi I_a$

where $n\phi$ = number of radicals produced per quantum absorbed if all the radicals formed disappear by initiating chains, and I_a = number of quanta absorbed per cc. per second.

Therefore:

$$\frac{-d(m_1)}{dt} = k_p \sqrt{\frac{n\phi I_a}{k_t}} \, (m_1)^{1.0} \qquad \text{(IV)}$$

Equations (I), (III) and (IV) have been verified by the above mentioned authors; (III) with methyl methacrylate and (I) and (IV) with acrylonitrile.

For a mechanism involving linear termination only with photochemical initiation as in equation (III),

$$\frac{-d(m_1)}{dt} = \frac{n\phi I_a \, k_p}{k_t'(X)} \, (m_1)^{1.0} \qquad X = \text{Radical} \qquad \text{(V)}$$

where $k_t{}'$ = rate constant of linear termination,

and X = concentration of linear termination.

(b) Using non-stationary state kinetics.

Burnett (1950) has summarized the various equations obtained considering the photochemical build up to the steady state in the light period, and the die away from the steady state in the dark period.

Briefly, for a system which follows equation (IV) in the steady state:

For the build up,

$$\frac{d(C)}{dt} = k_1 - k_t(C)^2$$

For the die away,

$$\frac{d(C)}{dt} = -k_t(C)^2$$

On integration, these equations give,

$$\frac{\Delta M}{M} = \frac{k_p}{k_t} \ln(\cosh t/\tau) \qquad \text{(VI)}$$

for the build up,

$$\frac{\Delta M}{M} = \frac{k_p}{k_t} \ln(1+t/\tau) \qquad \text{(VII)}$$

for the die away,

where $\Delta M/M$ = fraction of the monomer consumed,

and = lifetime of the active centres defined by

$$\tau = \frac{(C)\text{steady state}}{k_1}$$

Melville and his group have determined rate constants from the non steady states using very sensitive methods of detection such as change of dielectric constant (Melville and Majury, 1951), or the change of refractive index (Grassie and Melville, 1951). These and similar techniques for measuring lifetime have been summarized by Melville (1952).

The equations which lead to (VI) and (VII) are also used in the development of the rotating sector theory of measuring rate constants to be considered in a later section.

IV. Polymerisation in Aqueous Solution.

1. Introduction.

In the absence of emulsifying agents, acrylonitrile, methyl acrylate, methyl methacrylate, methacrylic acid, styrene, vinylidene chloride, ethylene, 2-nitropropylene and acrylamide have all been polymerised in aqueous media by a variety of free radicals.

The most complete investigations are due to Baxendale, Evans and Park (1946), using methyl acrylate and acrylonitrile initiated by OH radicals from Fenton's Reagent; to Evans, Santappa and Uri (1951) using methacrylic acid, methyl methacrylate and acrylonitrile initiated by OH, Cl and N_3 radicals produced photochemically; and to James (1952) who studied the polymerisation of acrylonitrile initiated by H atoms and OH radicals produced photochemically.

Most interest has been shown, however, in the process of initiation and so, few velocity constants of polymerisation have been determined.

2. Production of initiating free radicals in aqueous solution.

Radicals may be formed in aqueous solution in several different ways. These methods have been detailed in full by James (1952) and will only be summarized here.

2a. Excitation of the monomer.

If light of suitable wavelength is absorbed, or if the reaction is carried out at a high enough temperature, direct production of radicals from a monomer will result.

2b. Homolytic dissociation.

The thermal or photochemical dissociation of peroxide molecules, *e.g.* benzoyl peroxide, hydrogen peroxide (Smith 1951), persulphate ion (Bacon 1946) provides one of the most convenient methods of initiating polymerisation.

2c. Heterogeneous sources.

Parravano has initiated polymerisation by H atoms from the electrodeposition of H_2 on metal surfaces; from metals loaded with hydrogen; from metal hydrides; by the decomposition of hydrazine or palladium and by the decomposition of formic acid on palladium in the presence of oxygen. (1950).

Kolthoff and Ferstandig (1951) activated an otherwise unreactive reduction activation system by electrolytic reduction.

2d. Ionizing radiations.

The polymerisation process has been developed in an attempt to identify the reactive entities produced in the radiation of water. Hydrogen atoms and hydroxyl radicals are the principle species formed in water (Collinson 1952, Collinson and Dainton 1952), but are by no means the only species produced (Betts, Collinson, Ivin and Dainton 1953).

2e. Reduction activation.

This may be a thermal or a photochemical reaction and usually involves the transfer of an electron from a reducing ion to an ion or molecule which possesses no vacant orbital of low energy and dissociates to a radical and an inactive species.

The reducing ion may be cationic or anionic in nature and the reaction may be written generally as follows, using hydrogen peroxide as the electron acceptor.

$$X^{n+} + HOOH = X^{(n+1)+} + OH^- + OH$$

$$X^{n-} + HOOH = X^{(n-1)-} + OH^- + OH$$

Baxendale, Evans and Park (1946), Bacon (1946) and Morgan

(1946), have induced polymerisation by systems operating by one or other of the above mechanisms.

The water molecule may also be reduced to form H atoms,

$$X^{n+} + HOH = X^{(n+1)+} + OH^- + H$$

as described by James (1952), but this is generally a photochemical reaction and will be described in more detail below.

2f. Oxidation of an anion.

The oxidizing agent is generally a cation and electron transfer takes place on dissociation of a cation-anion complex. Unless the cation is a powerful oxidizing agent or the anion a powerful reducing agent, the process is photochemical. By a suitable choice of cation, the electron transfer spectrum of the complex can be brought into a convenient region of the spectra.

C. THE MECHANISM OF PHOTOCHEMICAL ELECTRON TRANSFER.

Since the beginning of the century, ionic reactions involving electron transfer as the primary step, have been recognized as taking part in a great number of chemical reactions. A study of a special type of electron transfer was initiated by the work of Franck and Scheibe (1928), who associated certain absorption bands in the visible and ultraviolet spectra of some aqueous solutions with this step. The concept of electron transfer spectra had arisen in ionic crystals as early as 1896, but it was not extended to the liquid phase until this century.

In order that photochemical electron transfer can take place with considerable probability, the electron donor and acceptor must form a largely electro-valent (ionic or ionic dipole) bond, rather than a covalent (electron pair) bond. For this reason, transfer takes place in gaseous ionic molecules, ionic crystals and simple and complex ions in solution (Rabinowitch, 1942).

When a bond is largely covalent, only electronic excitation results on the absorption of light until shorter wavelengths are reached *i.e.* until sufficient energy is provided to transfer the electron. The complex formed between the vanadous ion and acrylonitrile well illustrates the shift to shorter wavelengths of the actual electron transfer band, while at the same time moving the observed band cut-off towards the visible. In other words, an electronic excitation band of higher extinction is superimposed on, and masks the true electron transfer band.

All complex ions show possible electron transfer bands in the ultraviolet. These are characterized and generally recognized by the large extinction of the order of 10^4, caused by the large "dipole moment of transition"

(Bowen, 1950). This large extinction coefficient is comparable to that of organic dyes and is much greater than that of simple "coloured" inorganic salts. The large increase is usually quite marked so that a wavelength just shorter than the long wavelength cut-off can be associated with the energy necessary for the transfer. It is necessary to use this rather arbitrary procedure because of the difficulty of measuring the wavelength of the peak of the absorption band. As this usually occurs in the vacuum ultraviolet, it is not conveniently located.

Since the energetics of photochemical electron transfer are best approached after consideration of a thermal reaction, this case is presented first. The example cited below is only one of many similar electron transfer reactions, but an understanding of this type leads directly to the photochemical case.

I. Transfer Associated with Bond Breakage.

Bond breakage takes place if the electron is accepted by a molecule and enters an antibonding orbital, or if the molecule donates an electron from a bonding orbital. A good example of this process is the decomposition of hydrogen peroxide in the presence of reduced ions:

$$\mathrm{Fe}^{2+} + \mathrm{HO.OH} = \mathrm{Fe}^{3+} + (\mathrm{HO.OH})^{-} = \mathrm{Fe}^{3+} + \mathrm{OH}^{-} + \mathrm{OH}$$

The mechanism of the reaction is shown in figure 101 as developed by Evans (1950). Curve ABCD is the Morse curve for the dissociation of hydrogen peroxide into two hydroxyl radicals. Curve FCE represents the unstable reaction product $(HO.OH)^-$ which at large values of r dissociates to OH^- and OH. The difference, DE, between the curves is equal to $(E_{OH} + S_{OH^-}) - I_{Fe^{2+}_{aq}}$, where E_{OH} is the electron affinity of the hydroxyl radical, S_{OH} is the solvation energy of the hydroxide ion, and $I_{Fe^{2+}_{aq}}$ is the ionization potential of the reduced state of the aqueous cation when fully hydrated. This is derived from a consideration of the following steps:

$$(1)\quad OH^-_{aq} = OH^-_{g} - S_{OH}$$

$$(2)\quad OH^-_{g} = OH_{g} + e - E_{OH}$$

$$(3)\quad Fe^{3+}_{aq} + e = Fe^{3+}_{aq} - I_{Fe^{2+}_{aq}}$$

Since $(E_{OH} + S_{OH^-}) = 149.7$ kcals/mole (Evans and Uri 1949, Brewer 1950), and $I_{Fe^{2+}_{aq}} = 101.3$ kcals/mole, the distance DE = 48.4 kcals/mole. The height of C above the zero point energy is the activation energy of the forward reaction, the reaction path being BCE.

From the above equation, it can be seen that DE and hence the energy of activation, is governed by the ionization potential of the reduced cation when it is assumed that the presence of the reduced cation does not affect the relative positions of the two curves.

Thus, the rate constants for the decomposition of hydrogen peroxide by Cr^{2+}, ($I_{Cr^{2+}_{aq}}$ = 72 kcal/mole), will be greater than those in the presence of Fe^{2+}, which in turn will be greater than the rate constants for Mn^{2+} ($I_{Mn^{2+}_{aq}}$ = 127 kcals/mole).

The activation energy for the reverse reaction will be low, depending on the height of C above a horizontal line through E. The height of C will depend chiefly on the curvature of the two curves at C.

The overall entropy decrease in the reaction of 1 e.u./mole is due to two factors: a large decrease of 51 e.u./mole because of the increase of effective charge of the system; and a large increase of 50 e.u./mole due to the reduction of the total effective charge on formation of the complex $Fe^{3+}.OH^{-}$. Fortunately, the entropy change in the oxidation of the above ions is approximately the same. Comparison is thus possible because the rate of reaction will be equally influenced by the change of entropy in each case.

The actual values of the thermodynamic functions have been calculated by Evans, Hush and Uri (1952).

II. Transfer to the Water of Hydration.

This mechanism was proposed to explain the results of Weiss (1935), who observed the evolution of hydrogen from an aqueous solution of ferrous sulphate irradiated by ultraviolet light. Franck and Haber (1931) said that an electron would most probably be transferred from a cation (or an anion) to a specific molecule of the hydration sphere. This assumption was embodied in the mechanism of Potterill, Walker and Weiss (1936) to explain Weiss' observation.

$$Fe^{2+}:H_2O \;=\; Fe^{3+} + OH^- + H$$

The combination of the hydrogen atoms accounts for the evolution of gas.

Farkas and Farkas (1938) modified the above reaction to,

$$Fe^{2+}.H_2O \;=\; Fe^{3+}.OH^- + H$$

which is more probable in the light of present day knowledge of the hydrolysis of iron (Olson and Simonson 1949, Rabinowitch and Stockmayer 1942).

There is no direct evidence as to the true nature of the complex, whether it is ionic $Fe^{3+}.OH^-$ or covalent $(FeOH)^{2+}$. For this reason, Bowen (1950) has questioned whether the photochemical process is actually an electron transfer.

Hydrogen evolution is completely suppressed on the addition of a monomer. This can be easily shown even in the presence of air, by the addition of acrylonitrile to an aqueous mixture of zinc in dilute hydrochloric acid.

The potential energy curves are shown in Figure 102. In this case, H_2O replaces H_2O_2 so that the Morse curve ABCD corresponds to the dissociation of water into H atoms and OH radicals. The electron acceptor is now in a solvation sheath about the donor and differs from the previous case in the dissociation energies of the two compounds ($D_{H\ldots OH} \approx 120$ kcal/mole; $D_{HO\ldots OH} = 52$ kcal/mole).

The separation of the curves ABCD and FCE is governed by the same facts as above.

$$(E_{OH} + S_{OH^-} - I_{Fe^{2+}_{aq}})$$

The relative steps shown are for the ferrous ion. However, because of the much greater dissociation energy of water, the activation energy for the reaction represented by the height of C above the zero point energy is much greater than in the hydrogen peroxide case. Hence, electron transfer is immeasureably slow unless brought about by the absorption of light. The magnitude of energy required is shown by the dotted line rising from B to F.

The reactions are also characterized by low quantum yields because of the low energy of activation for the back reaction.

The rates of reaction for the different ions should be in the same order as in the case of hydrogen peroxide since the separation of the two curves is again governed by the ionization potential of the reduced ion. For the transition group the results are summarized in Figure 103. From this figure it is seen that a relationship should exist between the magnitude of the quanta absorbed and the ionization potential. Dainton and James (1951) have shown that a linear relationship does exist when the short wavelength cut-off of the electron transfer spectra is used as a measure of hν and is compared with the redox potential for the ions vanadous, chromous, manganous, ferrous, cobaltous and nickelous. Redox potentials are compared instead of ionization potentials because of lack of knowledge about the latter. Comparison is valid if the entropy changes are approximately equal as in the above group of ions.

Figure 102 illustrates that the ionization potential involved in the separation of the curves needs to be corrected by a term to account for the energy change on the reorientation of the water molecules after light is absorbed. By the Franck-Condon principle, the light absorption is instantaneous and the electron is effectively transferred before reorientation can take place. However, this difference is again approximately the same for each ion of this series and so the error is

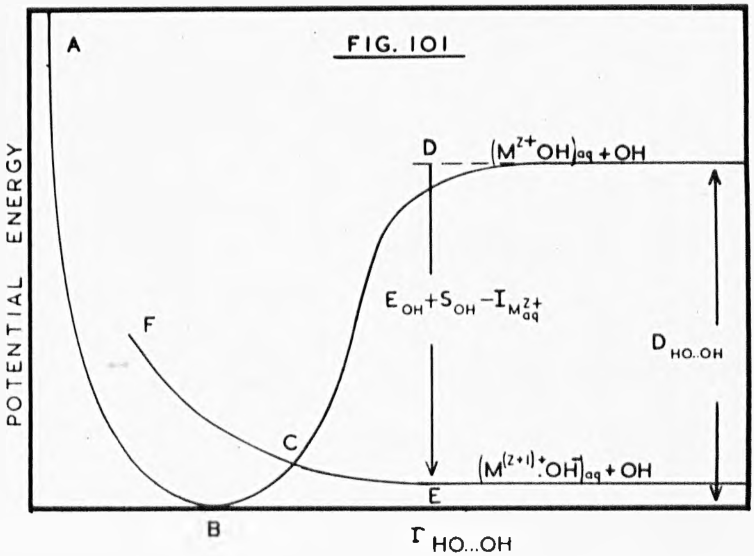


FIG. 101

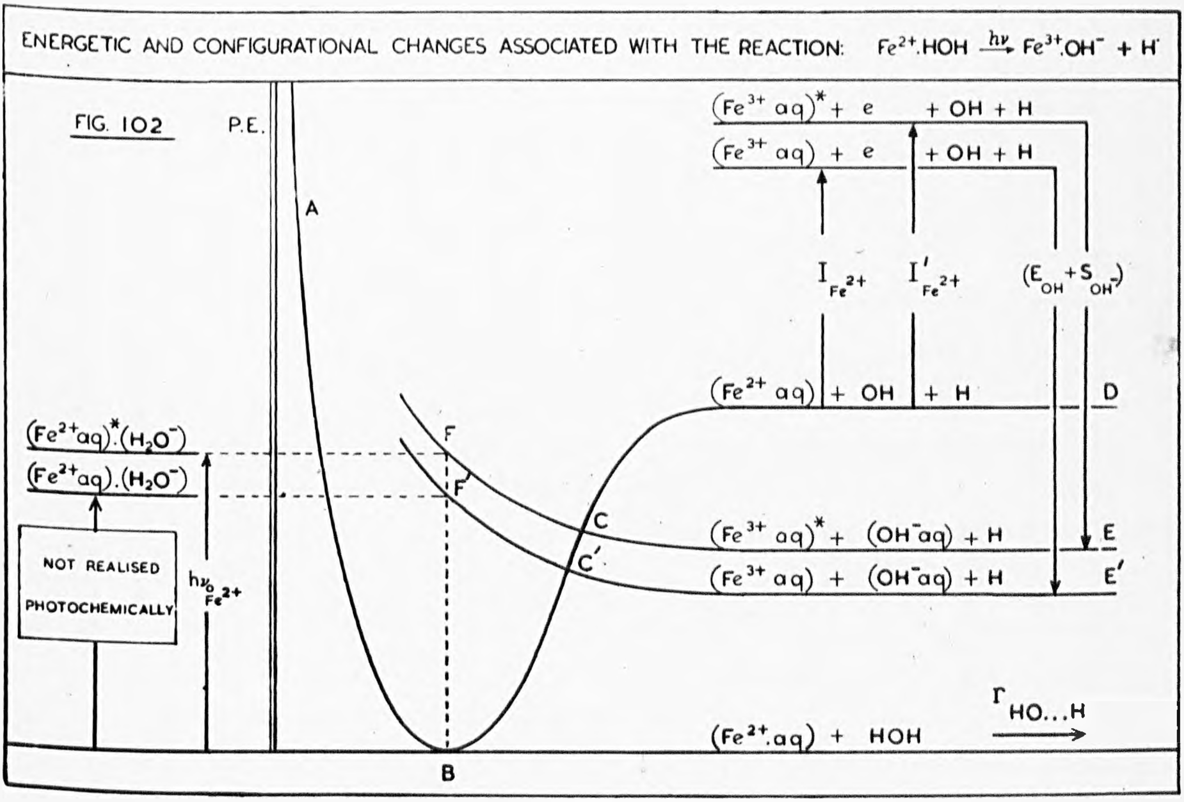
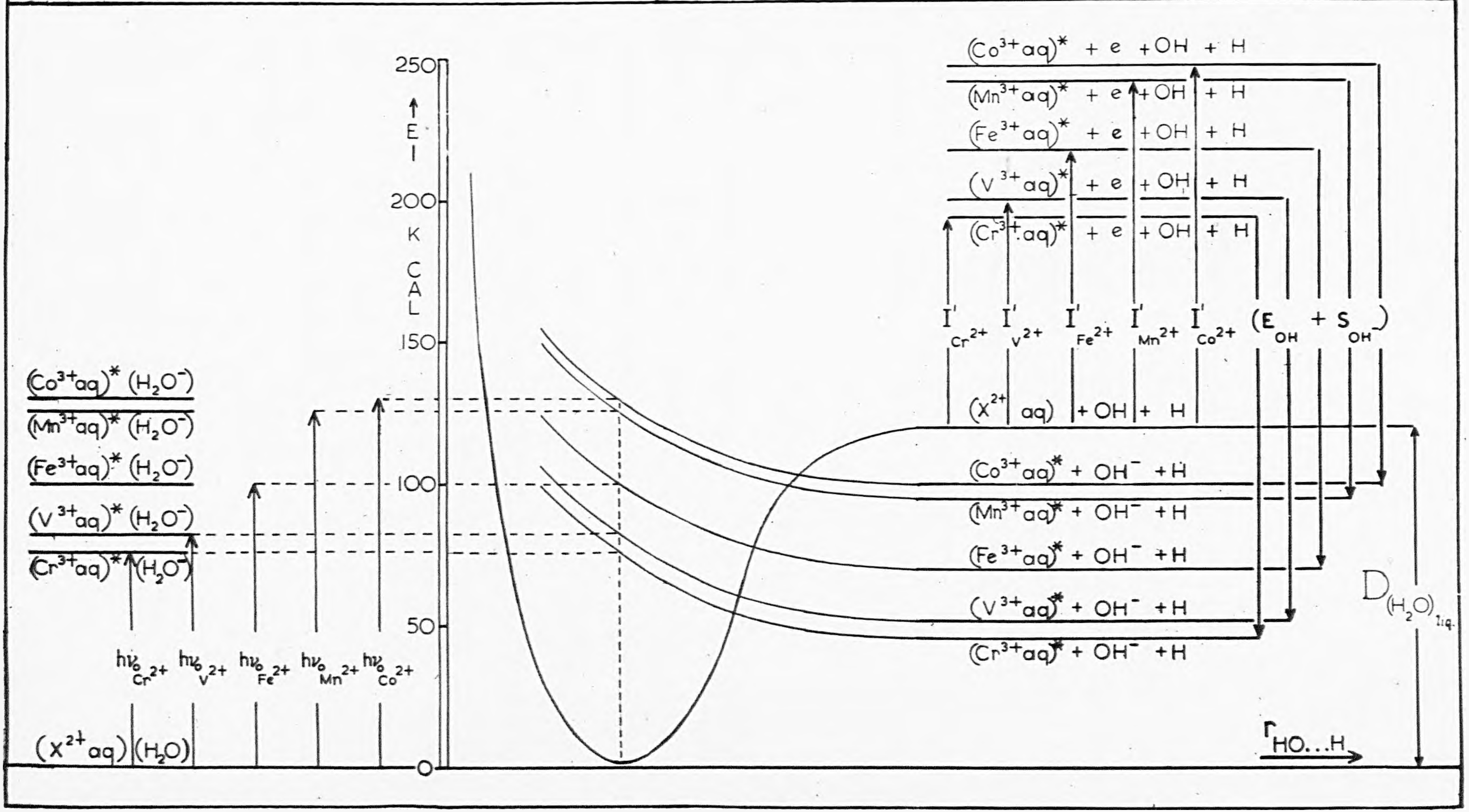

ENERGETIC AND CONFIGURATIONAL CHANGES ASSOCIATED WITH THE REACTION: $Fe^{2+}.HOH \xrightarrow{h\nu} Fe^{3+}.OH^{-} + H^{\cdot}$

FIG. 102

FIG 103 THE ROLE OF THE IONISATION POTENTIAL IN THE REACTION: $M^{Z+}.HOH \xrightarrow{h\nu} M^{(Z+1)+}.OH^- + H^\cdot$



constant and does not affect the validity of the results.

The conclusion to be drawn from this, is that for the same anion, the sum of the solvation and electron affinities remains unchanged, and the separation of the two curves and therefore the energy required to bring about electron transfer is governed only by the ionization potential of the reduced state of the aqueous cation.

III. Transfer from One Ion to Another with an Unlike Charge.

From the point of view of this investigation, this is the most important of electron transfer reactions, as the radicals produced in a transfer of this type were used to initiate the polymerisation of acrylonitrile.

Using ferric iron as an example, the potential energy curves are shown in Figure 104 (Evans and Uri, 1950).

Evans, Santappa and Uri (1951), have shown that a system containing ferric ions at high acid concentrations does not initiate polymerisation. At higher pH's however, the reaction occurs readily and is found to take place through the complex $Fe^{3+}.OH^-$ formed in the following reaction.

$$
\begin{aligned}
Fe^{3+} + H_2O &= Fe^{3+}.OH^- + H^+ \\
Fe^{3+}.OH^- + h\nu &= Fe^{2+} + OH \\
OH + m_1 &= \text{etc.}
\end{aligned}
$$

A similar mechanism is postulated in the presence of hydrochloric acid. Rabinowitch and Stockmayer (1942), have evaluated the thermodynamic functions of this reaction and the equilibrium constant at 25°C is found to be about 5×10^{-3}. The absorption spectra of the $Fe^{3+}.OH^{-}$ was also analysed and found to have a maximum at 3130A corresponding to about 90 kcals/mole.

The complex $Fe^{3+}.OH^{-}$ is weak having a heat of interaction of about 1.5 kcals/mole so that the lower curve shows a shallow minimum only. The separation of the two curves is governed by the same conditions as before but in this case, the curves do not intersect.

The quantum yield of the reaction is low and of the order of 0.05. Back reaction is reduced to a minimum by the presence of monomer which will pick off any radicals that are produced, and by the fact that the products are separated shortly after the light is absorbed and are not in a favourable position for a back reaction. The primary back reaction involving the radical and ion formed from the same ion-pair complex accounts for most of the back reaction. The secondary back reaction occurring from ions after separation will be suppressed by the presence of sufficient monomer.

IV. The Effect of Complexing the Reducing Ion.

Any agent that preferentially complexes with the reducing ion will increase its stability and therefore the magnitude of its ionization potential. This in turn will shift the electron transfer spectrum to shorter wavelengths. Examination of the absorption spectrum may not show this because of the presence of excitation bands of high extinction which will mask the beginning of the electron-transfer band. Polymerisation techniques can be used to locate this band however.

1. Complex between ferrous ion and acrylontrile.

James found that a complex exists between ferrous ion and acrylonitrile which shifted the long wave limit from 2850A to 3000A. Polymerisation was found to take place only when wavelengths of 2900A or shorter were absorbed by the system, thus confirming that this spectral region corresponds to electronic excitation only.

2. The complex between vanadous ion and acrylonitrile.

James found that a much stronger complex existed between the vanadous ion and acrylonitrile; the absorption spectrum is shown in Figure 105. The redox potential of V^{2+}/V^{3+} was also changed by .78 volts in the presence of acrylonitrile.

A mechanism may be postulated which is analagous to the photochemical electron transfer from ferrous ions in water.

If the complex is $(V^{2+}\cdot M_x)$ then the reaction will proceed in the following manner:

$$(V^{2+}\cdot M_x)\cdot HOH + h\nu = (V^{3+}\cdot M_x)(HOH)^- = V^{3+} + xM + OH^- + H$$

The electron is transferred to a water molecule outside the complex and since V^{3+} is not complexed, the products break up as shown. The minimum quantum necessary to produce transfer is greater than that for the uncomplexed ion because of the increased stabilization of the complex. In effect, the electron transfer spectrum may be shifted to shorter wavelengths than that of the uncomplexed ions.

The author of this thesis carried out some experiments to investigate this shift using the technique to be described in the next chapter, and obtained the results shown in Table 102.

The following four systems were considered:

1. 0.001 M V^{2+}, 0.6 M acrylonitrile, 0.5 M $HClO_4$
2. 0.0001 M V^{2+}, 0.6 M acrylonitrile, 0.5 M $HClO_4$
3. 0.001 M V^{2+}, 0.22 M methyl acrylate, 0.5 M $HClO_4$
4. 0.0001 M V^{2+}, 0.22 M methyl acrylate, 0.5 M $HClO_4$

The rates were measured as mm./min. contraction in a 1 mm. capillary.

The large shift in the redox potential indicates that the properties of the vanadous-acrylonitrile system will be essentially that of the complex.

Table 102.

The relative effectiveness of various wavelengths in the initiation of vanadous ion sensitized polymerisation.

	Rate of polymerisation (mm./min.)			
Monomer	0.6 M acrylonitrile		0.22 M methyl acrylate	
(V^{2+})	0.001 M	0.0001 M	0.001 M	0.0001 M
Wavelength, A				
3650	0.000	..	0.000	..
3340	0.000	..	0.001	..
3130 + 3340	..	..	0.003	..
3130	0.001	0.001	..	0.012
3020 + 3130	0.002	..	0.004	..
2537	0.020	..	0.040	..
full light	..	0.030	..	0.5

FIG. 104

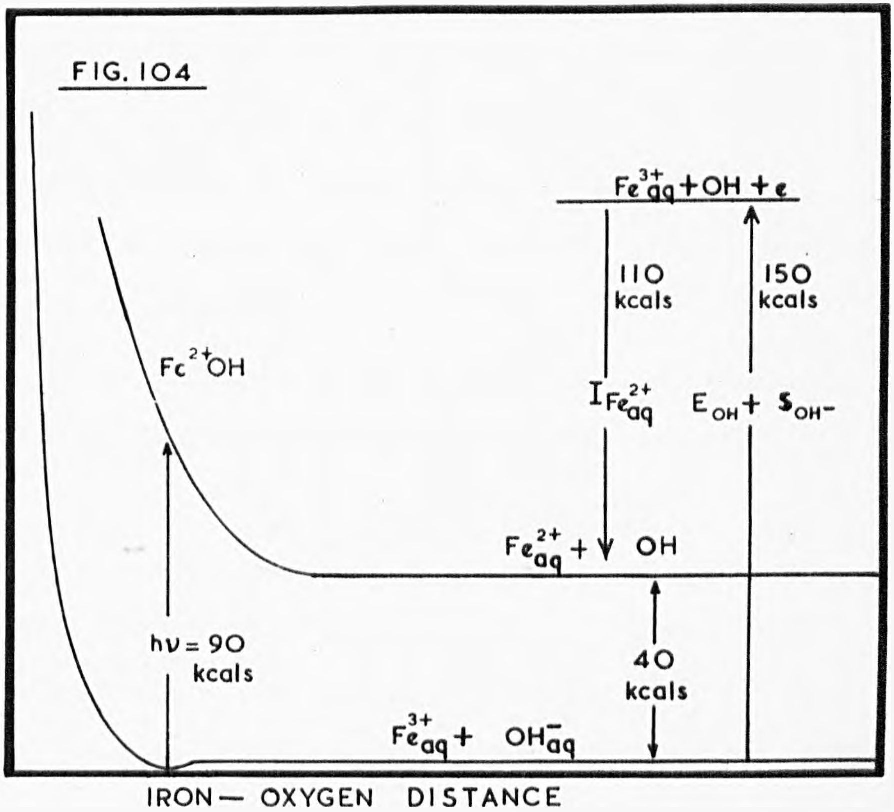
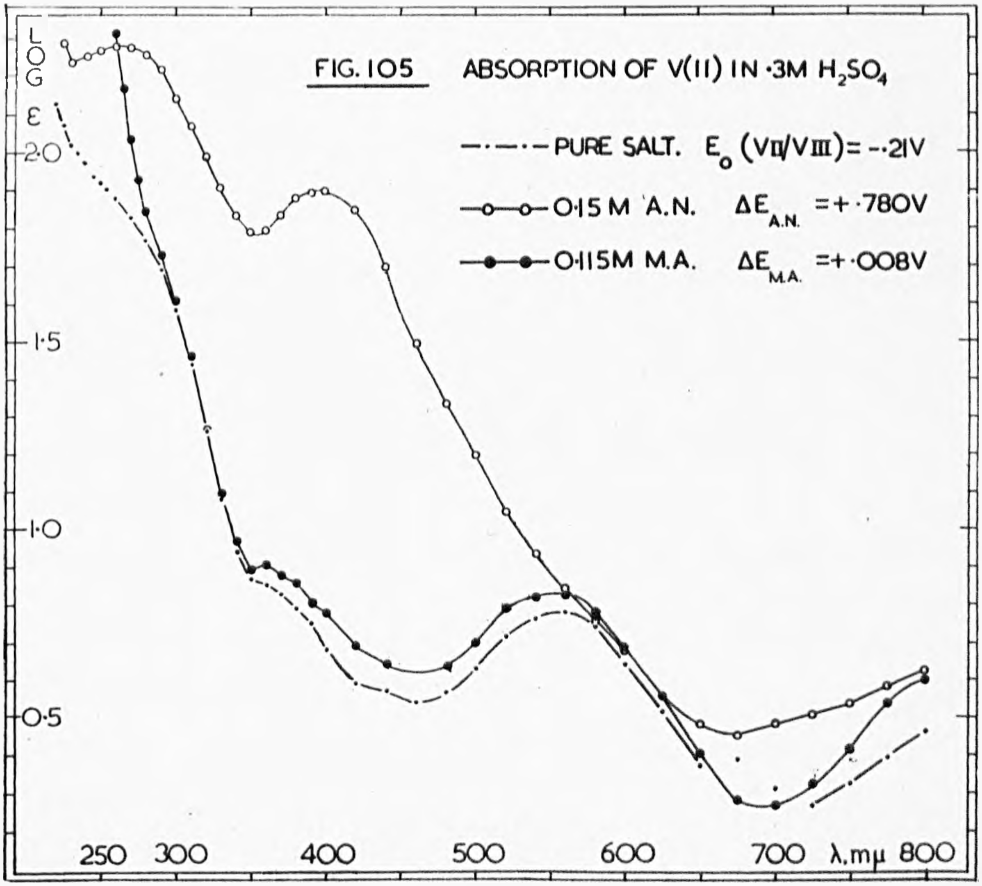


FIG. 105 ABSORPTION OF V(II) IN ·3M H_2SO_4



The experimental results show that the electron transfer spectrum of the uncomplexed vanadous ion lies between 3340A and 3650A, i.e. close to that observed from the absorption spectrum.

Further, the electron transfer spectrum of the complexed vanadous ion is shifted to shorter wavelengths and lies between 3130A and 3340A and so bears out the above theory.

It was also found that the vanadous ion is a more effective sensitizer at lower concentrations and is thus similar to the chromous ion in that respect (James, 1952).

The large shift of the complex spectrum toward longer wavelengths must then be due to electron transfer within the complex, possibly leading to its dissociation. But since no hydrogen atoms are formed, polymerisation can only occur by means of collision or if a dissociated fragment is a radical. Neither is the case in the vanadous-acrylonitrile system.

D. REACTION LOCI IN POLYMERISATION SYSTEMS.

I. Types of System.

Polymerisation systems can be separated into two general classes.

1. Homogeneous systems.

If the polymer is soluble in the monomer or solvent, the system is obviously homogeneous throughout, and the kinetics are relatively simple. All reaction loci are in the liquid phase and for low conversions, steady states are usually obtained. At higher conversions however, the viscosity of the system may increase markedly leading to an "explosive" polymerisation. Examples of this latter phenomena were studied for methyl methacrylate by Trommsdorff (1944) and by Norrish and Smith (1942); and for methyl iso-propenyl ketone by Haward (1948). Matheson et alia (1951b) also noted this effect in methylacrylate.

2. Heterogeneous systems.

Because of the large difference in physical properties between polymer and monomer, most polymers are generally insoluble in their monomers or common solvents. Interesting effects arise if the polymer is swollen by monomer and if the liquid phase is a precipitant or only a poor solvent for a polymer. For a precipitant, there is no significant increase in the viscosity of the system on polymerisation.

Initiation occurs homogeneously in the liquid phase but the loci of propagation and termination depend on individual monomers. Particular examples of each type will be considered.

II. The Polymerisation of Styrene.

1. The emulsion polymerisation of styrene.

An understanding of the part played by soluble, insoluble and swollen polymers can be gained from a consideration of emulsion polymerisation. Harkins (1947), has put forth a detailed description of emulsion polymerisation. Smith and Ewart (1948) have extended this treatment and Smith (1948) has verified the theory for the case of styrene.

The theory is based on systems in which the polymer is swollen by its monomer and the monomer is only slightly soluble in water. Water soluble initiators are used. Styrene in aqueous solution is a good example of this type.

The four phases of an emulsion system are detailed below:

(i) The oil phase, which serves as a reservoir to keep the aqueous phase supplied with monomer and is only a minor locus of propagation.

(ii) The aqueous phase, which contains the dissolved initiator, and only very little monomer (if not appreciably soluble) and is also a minor locus of initiation and propagation.

(iii) The soap micelles, which contain most of the dissolved monomer (depending on the soap concentration). This phase is a major locus of initiation but only a minor locus of propagation. In the presence of soap, the activation energy of initiation for styrene is reduced from 25 kcal/mole in a monomer droplet, to 17 kcal/mole in a micelle. Thus, the micelles compete favourably with the oil phase for the initiator.

Polymer particles are formed in the micelles but after about 10% conversion, they adsorb all the soap and the micelles disappear.

(iv) The polymer particles, which become stabilized against coagulation by soap. These particles, swollen by monomer, become the major locus of propagation. Their number ceases to increase when the micelles disappear from solution. The rate then becomes constant, the particles being supplied with further monomer by diffusion.

Case 2 of Smith and Ewart's theory is the most important. A polymer particle is said to contain either one growing chain or none. If a radical enters a particle already containing a growing chain, termination takes place. The lifetime of a growing chain, and the time interval between the termination of one chain and the initiation of another chain, are thus both equal to the average time interval between successive captures of a free radical. The average number of growing chains per particle is therefore equal to $\frac{1}{2}$, and the rate of reaction is independent of the rate of radical production and dependent on the number of particles.

Smith and Ewart have calculated that the number of particles is proportional to $(R)^{2/5}(S)^{3/5}$ where R = rate of radical production and S = the soap concentration during the micellar stage. This relation was confirmed by Smith.

He also found that the lifetime of a growing chain was 10 - 100 seconds and the degree of polymerisation 10^4 - 10^5. These can be compared with the results of Matheson et alia (1951a) for the bulk polymerisation of styrene (1.3 seconds and 4000 respectively), and it can readily be seen why both the rate and conversion in emulsion are much higher.

Baxendale, Evans and Kilham (1946) suggested that the increased rates were due to a reduced termination constant brought about by the increased viscosity of the system. However, the rate of termination does not enter into the kinetics as long as it remains high (k_t for styrene = 7.2×10^7 (mole/l.)$^{-1}$sec^{-1}; Matheson et alia 1951).

Thus in an emulsion system in which they are swollen by monomer and stabilized against coagulation by a soap layer, the polymer particles are the main locus of propagation and termination and steady states are readily obtained.

2. Aqueous non-emulsion polymerisation of styrene.

Experiments have shown that the non-micellar polymerisation of styrene is essentially the same as in the emulsion case. Polymer particles swollen by monomer remain the major locus of propagation and termination. However, the rate of formation of these particles is very low and the number of particles will be reduced by coagulation so that conditions leading to a steady state are not easily realized (Harkins, 1950).

Bovey and Kolthoff (1950) found the rate proportional to the square of the monomer concentration and the square root of the persulphate initiator concentration, indicating that some measurements are possible.

III. Bulk Polymerisation of Vinyl Chloride.

Bengough and Norrish (1950) have shown that the rate of polymerisation of vinyl chloride initiated by benzoyl peroxide gradually accelerated over the first 40% of the reaction. The increase in rate was attributed to the immobilization of reactive polymer ends on the surface of the polymer, and was roughly proportional to the surface area of the polymer. The polymer may be slightly swollen by the monomer (Arlman and Wagner, 1953). Addition of dead polyvinyl chloride after exposure to air, was found to act as a co-catalyst with benzoyl peroxide. Increased reactivity was not due to the removal of inhibitant. If the remaining monomer was removed from a partially polymerised system and fresh monomer added, the reaction proceeded at the accelerated rate. This catalytic effect disappeared when the reaction took place in the presence of a solvent for the polymer.

Chain transfer from growing chains to the dead polymer was postulated; this lead to an accumulation of immobile centres which were eventually terminated by further transfer to monomer.

Thus the locus of propagation is both in the liquid phase and on the surface of the polymer particle. The part played by the polymer increases with its surface area.

IV. Polymerisation of Vinylidene Chloride.

1. In aqueous solution and emulsion.

Polyvinylidene chloride differs from the above polymers in being crystalline and not swollen by its monomer. Arlman and Wagner (1953) have compared the density of polyvinylidene chloride measured from the volume contraction in a dilatometer with that determined from the X-ray unit cell (Reinhardt, 1943), and found agreement within experimental error.

However, Weiner (1951) in an emulsion polymerisation, found that the solubility of vinylidene chloride could be increased by the addition of dead polymer. The augmented solubility was found to be small and increased much more slowly than the increase in polymer concentration. The increase was also dependent on the soap concentration. This indicates that there may be some absorption, affected by soap, in the polymer lattice.

Steady and higher rates were observed in an emulsion system by Weiner and by Tkachenko and Khomikovskii (1950) after a period of slow reaction. Very slow rates were observed in water alone, but no evidence is available to show if the rate was steady or not (Tkachenko and Khomikovskii, 1950).

Therefore, in spite of the fact that the monomer is only slightly absorbed by polymer, the system is similar to that of styrene. Thus, the main locus of propagation is about the polymer particle.

2. <u>Bulk polymerisation</u>.

Burnett and Melville (1950), investigating the direct photopolymerisation of vinylidene chloride (λ less than 2800A) in bulk and in hexane (a non-solvent for the polymer), found that steady states were attained shortly after illumination was started. The rate was followed dilatometrically over a temperature range of 15°C to 35°C; the limits of temperature control and the volume of the vessels were not recorded. After 40 minutes exposure, the rate began to fall off. Two reasons were advanced to explain this: (a) Formation of polymer particles scatters the incident light and effectively reduces the number of quanta absorbed. (b) The polymer was found to decompose on long irradiation evolving hydrochloric acid.

Using the rotating sector technique, rate constants were evaluated at several temperatures; discussion of this is reserved to a later section.

In contrast to the steady rates observed by Burnett and Melville, Bengough and Norrish (1953) found that the rate steadily accelerated throughout the first 30% polymerisation. The monomer was subjected to repeated distillation and partial polymerisation to remove any impurities that might take part in autocatalysis. The system was initiated by 0.02 - 1.0 M% benzoyl peroxide over a temperature range of 45°C to 75°C. The temperature control was only ±0.1°C, so that there may be a possibility of convection currents in the dilatometer (capacity 0.6 ml.). This would effect the coagulation of the polymer particles and lead to increased occlusion and immobilization of buried centres. There is also a possibility, as pointed out by the authors, of chain transfer to dead polymer resulting in the formation of other immobile centres which could continue growth until terminated by a final chain transfer to monomer, and the initiation of a "free" mobile chain. Conditions leading to a steady state are therefore not easily attained in this system.

Addition of dead polymer, after exposure to air, had no effect. It was thought by Bengough and Norrish that the reactivity was destroyed by air; Bamford and Jenkins (1953) have shown that polyacrylonitrile was deactivated on exposure to oxygen. The inhibiting effect of oxygen on the initiation of polymerisation is well known for styrene (Bovey and Kolthoff, 1947), methyl methacrylate (Burnett and Melville, 1950), vinyl acetate in bulk (Matheson et alia, 1949b) and acrylonitrile in solution (Baxendale, Evans and Park, 1946), when stable peroxides are usually formed. It is probable that similar effects occur with a growing chain.

The only conclusions to be drawn from the negative effect of dead polymer are that it is not swollen by monomer, and chain transfer does not take place.

Thus, it appears that the locus of propagation is both in the aqueous phase and in the polymer particle. Which effect predominates will depend on the number and stability of the particles. If a high degree of coalescence is favoured, steady states may not result because of trapped centres. If coalescence is reduced to a minimum, a steady state in the system of trapped radicals may be possible.

Arlman and Wagner (1953) have added a further step to the formation of a crystalline polymer. They postulate that growing radicals could add to the polymer by the physical process of crystallization rather than by a process of occlusion. This theory should not, however, invalidate any qualitative conclusions reached from a consideration of occluded radicals.

Bamford and Barb (1953) have pointed out that a steady rate does not always mean that steady state conditions exist. In a photopolymerisation of a system involving an insoluble polymer, two opposing effects are possible. The rate may be accelerating as the concentration of the precipitated polymer and trapped centres increases, while at the same time, the number of quanta absorbed is being reduced by the scattering of light. If a balance occurs, a steady rate is possible. In a thermal polymerisation, the second phenomonum does not occur, and continually accelerating rates would be observed. This might account for the contradictory results observed by Bengough and Norrish and by Burnett and Melville.

V. Polymerisation of Methyl Methacrylate.

1. Bulk polymerisation.

As well as those authors mentioned in II.1., the bulk polymerisation of methyl methacrylate has been investigated by Bamford and Dewar (1944) and Matheson et alia (1949a); both groups have determined the rate constants. The most interesting feature has been the increase in rate due to the increased viscosity of the system at high conversions. This was first studied by Schulz and Blaschke (1941, 1942) and subsequently by Norrish and Smith (1942), and Trommsdorff (1944).

The general conclusion is that the termination constant is reduced but that the propagation constant remains unchanged.

2. Aqueous polymerisation.

Because of its relatively high solubility in water (0.15 M = 1.5%) at 25°C, methyl methacrylate is conveniently studied in solution. Baxendale, Evans and Kilham (1946), using Fenton's Reagent as initiator, obtained steady rates after an initial acceleration. The polymer precipitated and rapidly formed a coagulum; polymerisation did not proceed beyond 40%. While the temperature control at 25°C was ±0.02°C, the system was agitated throughout a run, so that coalescence would be favoured. Violent agitation may assist termination and minimize the effect of occluded radicals.

Addition of an emulsifying agent had a profound effect on the reaction. As little as 0.0003% cetyl trimethylammonium bromide doubled the rate and increased the conversion; 1% emulsifier accelerated the rate tenfold and nearly 100% conversion resulted.

This phenomenum, coupled with the fact that the polymer is swollen by its monomer, indicates that the locus of propagation is in the polymer phase. The whole system is similar to the emulsion polymerisation of styrene.

VI. Polymerisation of Acrylonitrile.

1. Bulk polymerisation.

The work of Bamford and Jenkins (1953) has provided the most complete survey of the bulk polymerisation of acrylonitrile. Both thermal and photochemical initiators were used. Most of the experiments were carried out in a temperature range of 25°C to 70°C controlled to ± 0.02°C.

Continuously accelerating rates were observed; the reaction behaved similarly to that of vinyl chloride and vinylidene chloride (Bengough and Norrish, 1950, 1953). Photochemical after effects were detected which were shown to be caused by long living buried centres. Removal of polymer in vacuo did not change the shape of the rate curves and confirmed that the rate increased in the presence of polymer and the initial acceleration was not caused by the slow formation of a monomer-catalyst complex. It was suspected, however, that the polymer retained some of the catalyst which could not be washed free in the filtration. The rate could be reduced to 50% of its value by centrifuging the polymer.

The degree of coalescence was found to play a major part in the occlusion of radicals; the photochemical after effect depends on the extent of reaction. Strong evidence for the occlusion of radicals was obtained when a mixture containing 18% polymer prepared at 25°C was transferred to a thermostat at 60°C. A striking, fast reaction followed which proceeded for at least 8% of the reaction and at forty times the initial rate. By comparison of the monomer concentration before and after the fast reaction, it was proved that a polymerisation had really occurred. Polymerisation could also be initiated in the absence of other catalyst in fresh monomer and in styrene. In the latter case, a block copolymer of styrene-acrylonitrile was obtained in molar proportions of 1:25. The occluded radical effect could be destroyed by exposing the polymer to oxygen for as little as two minutes. Therefore, polyacrylonitrile maintained in vacuo is a catalyst for polymerisation.

The following conclusions may be drawn from this work:

(i) Coalescence and precipitation of polymer play a large part in the termination step, effectively reducing the rate constant of termination.

(ii) Occluded radicals formed by the coiling of the polymer and by coalescence of polymer particles have been shown to exist; their lifetime depends on the degree of coalescence. At 60°C, the increased kinetic motion of these radicals makes them more accessible to propagation and termination.

(iii) The buried radical activity of the polymer particles can be reduced by centrifuging, and completely destroyed by exposure to oxygen.

Consideration of the conclusions noted above readily accounts for the non-steady rates observed.

Ziegler, Dèparade and Kuhlhorn (1950) also observed initial periods of acceleration in the bulk polymerisation of acrylonitrile, as did Chapiro (1950) who initiated polymerisation by γ- or X-rays.

Trommsdorff (1944) observed an "explosive" reaction in the bulk polymerisation of acrylonitrile similar to that of methyl methacrylate.

The reaction was initiated with 0.1% benzoyl peroxide at 60°C, and was so violent that the dilatometer was usually destroyed. In addition, holes and pores developed inside the material which made accurate measurements impossible. These results indicate that termination is diffusion controlled but the weight of evidence is against this.

For the bulk polymerisation of acrylonitrile, therefore, the major locus of propagation is in a coiled polymer particle with the radical ends "in solution" being a minor locus.

2. Aqueous polymerisation.

Whereas emulsifiers and dead polymer accelerate the polymerisation of methyl methacrylate, Khomikovskii and Medvedev (1948) and Khomikovskii (1948) found that these agents had little effect on the polymerisation of aqueous acrylonitrile.

The first two authors found that the rate was lowered by the addition of glass powder or dead polymer.

The latter author investigated the relative effects of potassium palmitate on the polymerisation of methyl methacrylate and acrylonitrile, both catalysed by 0.006 M potassium persulphate. At 40°C, the rate of methyl methacrylate polymerisation was accelerated 40 times by

3% soap, whereas the rate for acrylonitrile at 60°C was reduced 30% with 5% soap. With 8% soap, the rate was reduced to 50% of the full rate and ran parallel with the increase in insolubility of acrylonitrile.

In the absence of emulsifying agents, working at 25°C, James (1952) obtained steady, reproduceable rates for the aqueous polymerisation of acrylonitrile. Monomer concentrations of 0.006 M to 1.2 M were used and chains were initiated by many radicals (chiefly OH and H) produced photochemically from a redox system of the types mentioned in C.II and III. The reaction was followed dilatometrically in quartz cells of capacity 80 ml; the temperature of the bath was controlled to ±0.001°C.

The rate accelerated at first, but after the formation of about 35 mgm. of polymer (one to two hours), the rate became steady and remained so for at least one hour, after which it fell off. No induction periods were observed; polymer could be seen within one minute of commencing illumination and was evenly distributed throughout the cell.

Increasing light absorption was postulated to account for the increasing rates. As the polymer is formed, more light is absorbed because of internal scattering in the cell. If the acrylonitrile concentration is sufficiently reduced (from 0.3 M to 0.006 M) to prevent the formation of large quantities of insoluble polymer while ensuring that all the hydroxyl radicals were captured, James found that the rate of photoreduction of the initiator fell to 71% of its previous value. The scattering power of the polymer is thus equivalent to a 40% increase in the depth of the cell.

If the photopolymerisation was stopped, the after effect allowed to die away and the system reilluminated, the rate of polymerisation was rapidly reproduced only if the polymer had not been precipitated or filtered from the solution. If the polymer was removed by filtration and the clear liquid reilluminated, the original rate curve is reproduced when allowance is made for the consumption of monomer; the rate gradually accelerates to a steady rate and remains so for about one hour.

If the polymer is coagulated and precipitated by disturbing the cell mechanically, a similar result is obtained upon illumination if allowance is made for the fraction of the illuminated volume not occupied by coagulum. Smith (1951) observed the same effects using acrylonitrile in aqueous solution initiated by the photochemical decomposition of hydrogen peroxide.

The after effect which was observed died away to less than 10% of the full rate in one hour.

Rate constants were obtained using the rotating sector technique. The divergence of the intensity exponent from 0.5 to 1.0 has been explained by the introduction of a linear termination step to the kinetics. These aspects of James' work will be considered in more detail in later sections.

From his results and a consideration of other modes of polymerisation similar to those detailed in the above sections, James has come to the conclusion that the major locus of propagation of acrylonitrile in aqueous solution is in the liquid phase (Dainton and James, 1953). This is borne out by the negative effects of added dead polymer, or glass, and of emulsifying agents. Moreover, the rate equation determined experimentally is the same as that for a homogeneous system.

The existence of the photo after effect, the reduction of rate on precipitation of the polymer, and the gradual acceleration to the steady state, show that the polymer particles do play a minor role in the locus of propagation and a major role in the absorption of light.

VII. Conclusions.

A reasonably complete picture of the polymerisation steps is available in the literature already published.

The locus of propagation for a homogeneous system has been shown to be in the liquid phase. When an accelerating rate is observed in such a system, it is due to a reduction in the termination rate because of increased viscosity.

In a heterogeneous system, the locus of propagation is in the polymer particle, if the polymer is swollen by monomer. If the polymer is unswollen by monomer, active centres may become trapped in the lattice and may play more or less important parts, depending on the degree of coalescence and the medium about the particles. In the bulk polymerisation of acrylonitrile, the medium is the monomer itself and hence a large proportion of the reaction can be carried by the particles. In the aqueous phase, the medium is a dilute solution of monomer, and the contribution to the rate from the particles will be correspondingly less. A steady state for the system will be obtained in the aqueous polymerisation, when coalescence is reduced to a minimum. Then steady states can be established in the trapped radicals as well. Uniform production of radicals throughout the system and lack of mechanical disturbance will favour suspension of the polymer particles and establishment of this steady state.

The actual effect of an emulsifying agent in the aqueous acrylonitrile system is not clear. Khomikovskii (1948) has shown that the reduction in rate increases with higher soap concentration. Since the solubility of acrylonitrile increases with higher soap concentrations, it appears that soap immobilizes the monomer and effectively reduces the rate of propagation. Alternately, the polymer particles may be shielded from the monomer by the soap.

Therefore, for the aqueous polymerisation of acrylonitrile photochemically initiated, the major locus of propagation is in the aqueous phase. The polymer particles increase the light absorption and play only a small part in the locus of propagation.

Hence steady states and reproduceable kinetics can be obtained for an acrylonitrile system in water.

The present thesis will proceed from this point and will attempt to evaluate the kinetics of the acrylonitrile reaction at several temperatures as well as to clarify some of the effects noted above.

E. RATE CONSTANTS AND ACTIVATION ENERGIES OF AQUEOUS POLYMERISATIONS.

Dainton, James and Kutschke (1953) have reported the only rate constants for the polymerisation of acrylonitrile. The above authors obtain:

$$k_p = 6.4 \times 10^3 (\text{mole/l.})^{-1}\text{sec}^{-1}$$
$$k_t = 9.2 \times 10^8 (\text{mole/l.})^{-1}\text{sec}^{-1}$$
$$k_t' = 1.1 \times 10^5 (\text{mole/l.})^{-1}\text{sec}^{-1} \quad \text{at } 25^\circ\text{C.}$$

k_t' refers to the rate constant for linear termination. Kutschke's analysis of the sector curve has lead to an evaluation of the proportion of the rate due to trapped radicals. It is found that 25% of the observed rate in continuous illumination is caused by these occluded centres, but no allowance is made for them in the determination of the rate constants.

Evans, Santappa and Uri have determined the value of $k_p/k_t^{\frac{1}{2}}$ for acrylonitrile in aqueous solution initiated by the photoreduction of the $Fe^{3+}.Cl^-$ complex. Their result of 0.156 $(\text{mole/l.})^{-\frac{1}{2}}\text{sec}^{-\frac{1}{2}}$ compares with the value 0.21 $(\text{mole/l.})^{-\frac{1}{2}}\text{sec}^{-\frac{1}{2}}$ for the above work.

Bamford and Jenkins (1953) have evaluated rate constants at 25°C from the photochemical rate and the dark rate after specified periods of illumination. These results are shown in Table 103.

Table 103. Rate Constants for Bulk Acrylonitrile

Time of Irrad'n Minutes	k_p $(\text{mole/l.})^{-1}\text{sec}^{-1}$	k_t $(\text{mole/l.})^{-1}\text{sec}^{-1}$
2	16.9	5.2×10^4
6.7	6.8	0.8×10^4
12	3.6	0.2×10^4

Analagous systems to that of acrylonitrile are difficult to find. Burnett and Melville (1950) found rather startling results for the rate constants and activation energies for the bulk polymerisation of vinylidene chloride, the polymer of which resembles that of acrylonitrile in its crystalline nature. Their results are summarized in Table 104.

Table 104. The Bulk Polymerisation of Vinylidene Chloride

Temp. C°	k_p (mole/l)$^{-1}$sec^{-1}	k_t (mole/l)$^{-1}$sec^{-1}	Eact. prop.	Eact. term	A_p	A_t	Eact. overall
15	2.3	0.23×10^5	25 kcal/mole	40 kcal/mole	10^{16}	10^{30}	5 kcal/mole
25	8.6	1.75×10^5					
35	36.8	18.0×10^5					

The values for the frequency factors are phenomenally high. According to Arlman and Wagner (1953), these results are subject to a systematic error which, however, will not affect the magnitude of the results. Both Burnett and Melville and Matheson et alia (1951b) have summarized the rate constants for many bulk polymerisations.

The rate constants of methyl acrylate (Matheson et alia, 1951b) and butyl acrylate (Melville and Bickel, 1949) in bulk at 30°C, may be compared with those of acrylonitrile. These three monomers are monosubstituted ethylenes and the substituent groups have similar mesomeric and inductive properties (Nozaki, 1947).

The results are summarized in Table 105.

Table 105.

Monomer	k_p (mole/l.)$^{-1}$sec^{-1}	k_t (mole/l.)$^{-1}$sec^{-1}
acrylonitrile	6.4×10^3	9.2×10^8
methyl acrylate	7.2×10^2	4.3×10^6
butyl acrylate	13.8	1.8×10^4

The increase in size of the substituent runs parallel with and may be the principal cause of the decrease in the rate constant.

The reasonable correlation of the results suggests that there is no difference in mechanism in the aqueous polymerisation of acrylonitrile and the homogeneous bulk polymerisation of the acrylates.

CHAPTER 2. EXPERIMENTAL TECHNIQUE.

The experimental procedure may be conveniently divided into four stages:

(1) The preparation and deaeration of a solution.

(2) The transfer of the solution to a quartz dilatometer, and the removal of this dilatometer to a thermostat.

(3) The adjustment of the meniscus to a convenient height.

(4) The illumination and measurement of the rate.

After a preliminary description of the apparatus and chemicals, these steps will be described in greater detail.

I. Purification of Chemicals.

1. Water.

Since certain ions present in trace amounts will exhibit profound effects upon aqueous polymerisation, it is important that the water used in any solution is free from these contaminents. To ensure that all ions, especially iron, are removed, distilled water is allowed to trickle through a column one metre long packed with an acid-base ion-exchange resin, using the procedure recommended by Ackroyd and Kressiman (1950). Bio-Deminrolit was used for most of the work and was discarded after the passage of 200 litres. This was later replaced by

Bio-Deminrolit F which could be regenerated after separation of the acid and base components. Both products were purchased from the Permutit Company of London.

2. Perchloric acid.

Analar perchloric acid was found to contain sufficient trace ions, especially iron, to cause irreproduceable results. Vacuum distillation at 100°C of analar constant boiling perchloric acid was sufficient. The final product, 12 Molar (72%) was stored, in the dark, in a special glass stoppered bottle that had previously been cleaned with a boiling nitric/sulphuric acid solution and steamed out for at least one hour.

3a. Ferric perchlorate.

As this was used in very dilute solution as a photo-catalyst, special care was taken in its preparation. Ferric hydroxide was prepared from analar ferric alum by the method described by Vogel (1951). A double precipitation was carried out redissolving the hydroxide in perchloric acid each time.

For later work, ferric perchlorate, bought from the G. Frederick Smith Chemical Company of Columbus, Ohio, was used without further purification. Both solutions gave identical results.

A stock solution of 2×10^{-2} M in .25 M perchloric acid was prepared and kept in the dark in a specially cleaned volumetric flask. Such a solution was found to be stable for at least two years. More dilute solutions were made from this solution when required, and these were kept under similar conditions. These dilute solutions were stable for at least one month after which time fresh solutions were prepared.

3b. Vanadous perchlorate.

Vanadous perchlorate was prepared by the reduction of analar ammonium vanadate in dilute perchloric acid by zinc amalgam, all in vacuo.. The ammonium vanadate solution was deaerated twice, reduced with zinc amalgam, the zinc amalgam removed, and the deaeration completed. Care was taken not to allow daylight to fall on the mixing vessels after reduction.

4a. Acrylonitrile.

Acrylonitrile, containing stabilizer, was supplied by Lights in two kilogram lots. Water was first removed by cooling the monomer overnight in a stoppered flask at -80°C. Most of the water which is almost insoluble at that temperature crystallizes out (Davis and Wiedemann, 1945). The monomer is then rapidly decanted through a glass wool plug, with minimum contact to air, into a flask which was then connected to the vacuum line. One freezing and decantation, if carefully carried out, was found to be sufficient. The monomer was freed from dissolved air by cooling it again to -80°C. Air in the liquid was then pumped off. The system was isolated and heated to room temperature, then cooled again to -80°C. This cycle was repeated at least three times. Finally, the monomer, at room temperature, was distilled to the pot of the still leaving the last 10% of the crude monomer in the flask. The still was then isolated, the monomer warmed to about 35°C and allowed to reflux. The distillation apparatus consists of a 250 ml. flask, a 10-plate vacuum-jacketed column about one metre long, packed with Fenske helices; a double walled water cooled condenser, and two isolatable receivers.

The distillation was conducted in the absence of air with the source at 35°C - 50°C and the receiver at 0°C. The first and last 25% of the distillate were rejected. The distillate was then exposed to daylight, allowing partial polymerisation to remove any remaining impurities.

4b. Methyl acrylate.

Methyl acrylate was purified by a simple distillation in vacuo. This procedure was found to be adequate for the simple experiments carried out with the vanadous initiation.

II. Apparatus.

1. Vacuum line.

A conventional all glass vacuum line was used for the deaeration of the solutions. A high vacuum was obtained by a one stage mercury diffusion pump backed by an Edwards 150 litre mechanical pump. Pressures were measured on a McLeod gauge which was capable of reading pressures of better than 10^{-4} mm. of mercury.

Tubing of 1 cm. diameter and large bore, good quality taps were used to facilitate the rapid removal of residual air. All the taps and joints on the main line were greased with Apiezon M or N grease.

Liquid air traps on either side of the McLeod gauge and diffusion pump prevented the distillation of mercury into deaeration flasks and the distillation of water and monomer into the pumps.

2. Deaeration assembly.

2a. The deaeration flask.

The deaeration flask, shown in the inset of Figure 201, was a 250 ml. round bottom Pyrex flask, modified so that the neck was constricted and connected to 7 mm. tubing terminating in a B10 joint. About 3/4 of the way up the side of the flask, another B10 joint was fitted so that the two arms were parallel and about 20 cm. long.

The deaeration flask was filled through a small funnel, the stem of which extended well down into the neck of the flask. All glass and quartz vessels were cleaned with a boiling nitric/sulphuric acid solution and were then steamed out for at least one hour. Chromic acid was found to be unsatisfactory for this purpose, as sufficient chromic ions were left on the surfaces to initiate polymerisation.

It was unecessary to reclean the flask after each run; the joints were cleaned of picien and placed on the steamer for at least one hour and then left to dry in the oven.

2b. The adapter.

The adapter was a good quality vacuum tap of large bore, terminated at one end by a B19 cone which plugged into the main vacuum line, and at the other by a B10 socket which was piciened to the side arm of the deaeration flask. This adapter was used to facilitate cleaning which would have been difficult if the tap had been directly connected to the flask.

2c. The quartz cell.

The quartz cell served the dual purpose of reaction cell and dilatometer. It consisted of a short cylinder of 2 cm. internal depth and 7 cm. radius. The faces of the cell were optically flat and well polished. The cell walls were about 3 mm. thick to immunize the effect of variations of atmospheric pressure on the volume of the cell when in vacuo. Out of the side of the cell projected a short B10 socket.

The quartz cell was cleaned in the usual manner about once a month. Polymer tended to precipitate on the face nearest the light, but the effect on the light transmission was negligible. If the accumulation seemed large, the other face of the cell was presented to the light during the next run.

After each run, the cell was washed well with distilled water and steamed for one hour. It was then allowed to drain in an inverted position overnight.

2d. The capillary.

A standard bore Veridia capillary of 1.00 mm. diameter formed the other part of the dilatometer and was connected to the quartz cell with picien. The other end of the capillary was also joined to the central B10 cone of the deaeration vessel with picien.

Thus, when the deaeration assembly was connected to the vacuum line, the flask was upright and the quartz cell inverted and separated from the deaeration flask by the standard capillary.

In this way, a solution could be deaerated, the assembly isolated from the vacuum line by the tap, disconnected, melted, inverted, and the solution allowed to flow into the quartz cell without passing over any greased joints. Picien was found to be completely inert to a solution containing monomer.

3. Optical bench.

A side view of the optical bench is shown in Figure 201.

3a. The mercury lamp.

The mercury lamp, the ultraviolet source of radiation, was provided by the Thermal Syndicate. It was the medium pressure type, capable of operating at 200 V. D.C. The arc is struck by tipping the lamp on its side and allowing liquid mercury to touch the top electrode. The lamp envelope is made of quartz, and passed radiation down to 2000A.

An 11 mm. stop was placed directly in front of the lamp so as to provide as close an approximation to a point source as possible.

The lamp was usually operated at 89 ±2V. D.C. and 2.95 ±.05 amperes; the power was supplied through a current stabilizer.

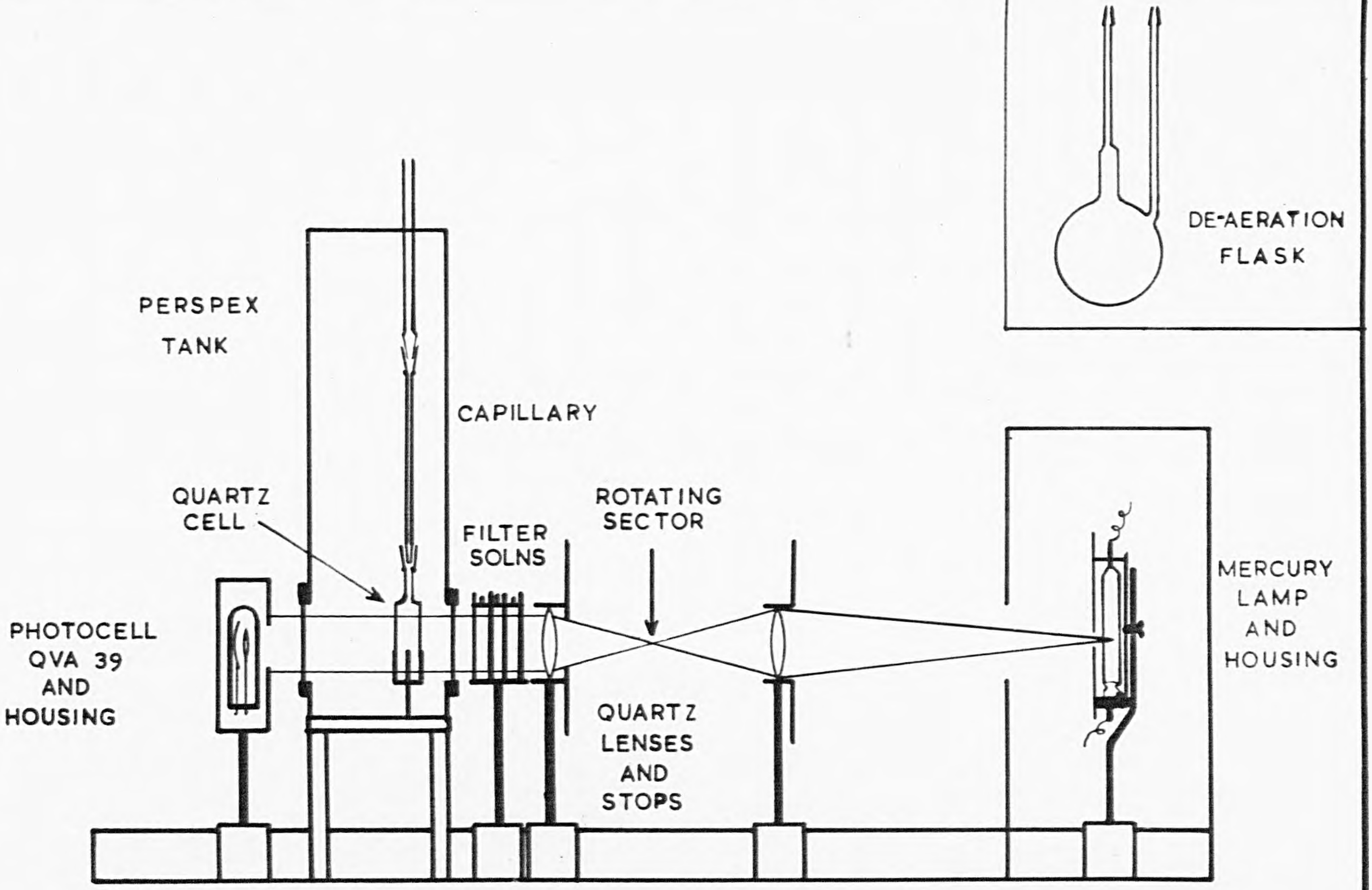


FIG. 201 OPTICAL BENCH SHOWING PATH OF LIGHT BEAM

3b. Mercury lamp current stabilizer.

A diagram of the circuit is shown in Figure 202.

The principle of the stabilizer is as follows:

The voltage from the D.C. mains is passed to the lamp through a parallel resistance. One arm of this is an 18 ohm plus a variable proportion of a 25 ohm fixed resister. The bulk of the current through the other arm is carried by three 12E1 valves; some of the current is also fed to two controlling valves.

If there is a drop in the voltage of the mains, the current through the control circuit also drops. The voltage on the grid of the 6SJ7 becomes more positive and allows more current to flow which in turn raises the potential of the 6F6 grid and finally the grids of the 12E1 valves. Thus more current is allowed to by-pass the fixed resisters and the voltage of the lamp increases to counteract the drop in the mains. For an increase in the mains voltage, the procedure is reversed.

With careful adjustment, the output of the lamp will remain constant for mains fluctuations of ±5 volts. Runs were not carried out in the daytime in winter when the variations were somewhat greater; experiments were then conducted in the evening.

Fluctuations in the intensity of the light at the cell

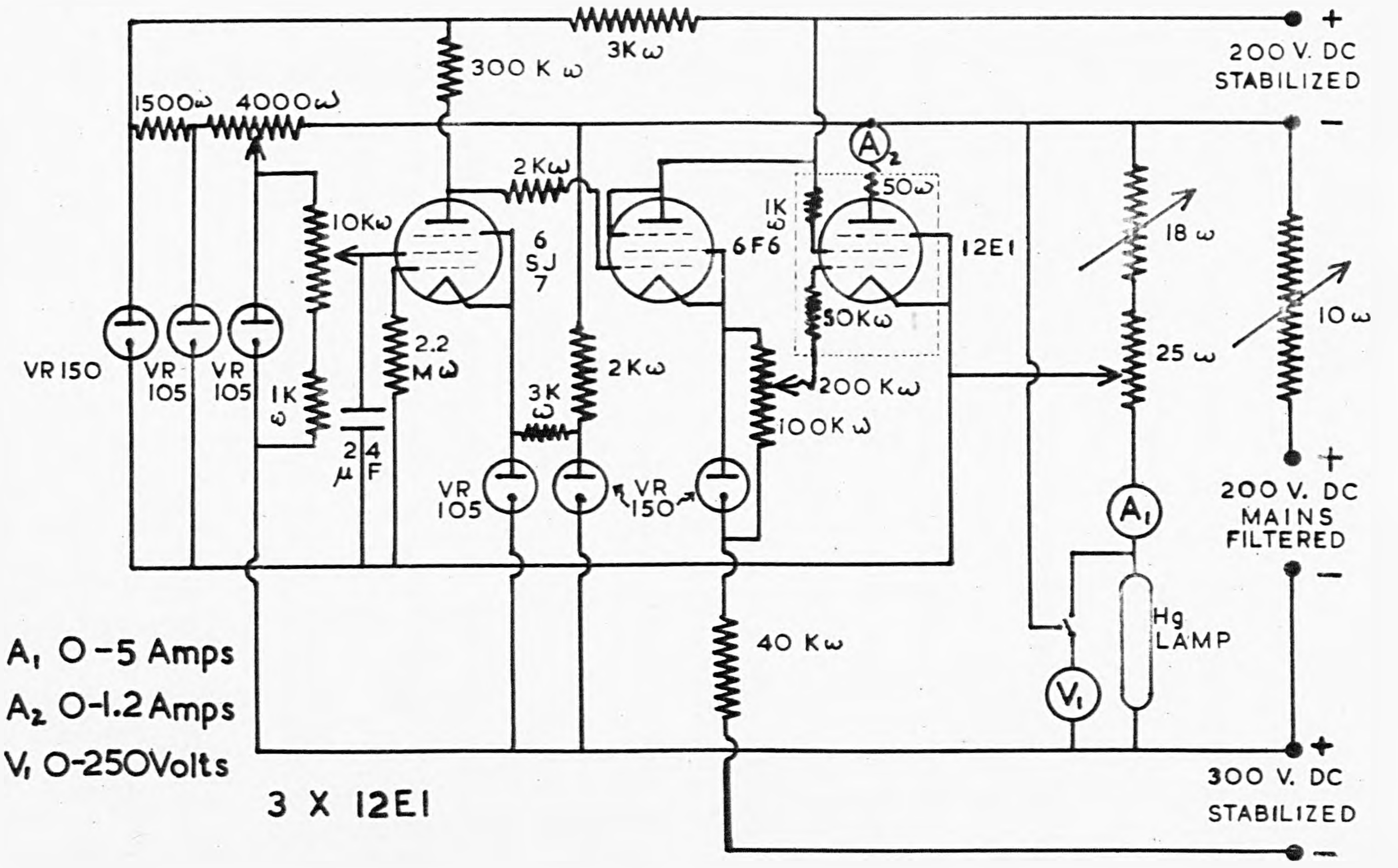


FIG. 202 CURRENT STABILIZING CIRCUIT FOR MERCURY LAMP

were occasionally noted when the fast sector was operated. To remove this beat, the D.C. input was filtered with a large inductance-capacitance circuit, and condensers were placed across the grid of the 6SJ7. No variations could be observed at lower sector speeds.

3c. Lens system.

The first quartz lens (7 cm. focal length) 18 cm. from the lamp stop, brought the light to a focus as shown in the diagram. This light was then gathered through a 3 cm. stop by a second quartz lens (10 cm. focal length), and passed on as a nearly parallel beam to the quartz cell in the thermostat. The transmitted light was measured by a Q.V.A.39 photocell. The two lenses were 19 cm. apart; the second lens was 18 cm. from the centre of the quartz cell.

3d. Filter solutions.

The filter solutions were placed directly behind the second quartz lens. The filter consisted of the following solutions separated by 7 cm. quartz plates.

1.3 cm. 1 M $NiSO_4$, 0.04 M $CuSO_4$ pH about 2.
1.3 cm. 0.008 M K_2CrO_4
1.3 cm. 0.015 M potassium hydrogen phthalate.

It was found that analar grade nickel sulphate contained sufficient iron to be rapidly decomposed at 3130A.

It was removed along with other interfering elements by adding pure hydrogen peroxide to the solution, boiling, cooling slightly, adding dilute sodium hydroxide to give a small permanent precipitate, digesting at the boiling point for ten minutes and filtering. The addition of a small quantity of copper sulphate improved the stability of the solution, only slightly reducing the transmission.

Analar potassium chromate and analar potassium hydrogen phthalate were used without further purification.

The nickel sulphate solution was placed nearest the light source and was found to be stable for several months. The phthalate and chromate solutions were replaced daily.

This assembly was almost monochromatic for 3130A; the transmission was as follows:

A	2970	3020	3130	3340	3650
%T	0	0	38	5.5	0

Since the 3340A line of the mercury lamp has only about one tenth of the intensity of the 3130A line, its contribution was quite negligible.

3f. The thermostat.

The thermostat was made of Perspex, 6 mm. thick. Light was admitted through 10 cm. quartz plates fitted to the tank with rubber gaskets. The internal measurements of the tank were 35 cm. long, 9.5 cm. deep and 53 cm. high, and it was filled with about 20 litres of distilled water.

The quartz cell, placed about 3 cm. from the window nearest the light, was supported in a rubber lined semicircular saddle fixed to the bottom of the tank. With such a deep tank, the dilatometer was completely immersed. Readings were taken on a cathetometer, by observing the meniscus through the tank side.

The temperature was maintained constant to 0.002°C by means of a toluene-mercury regulator, of very large surface to volume ratio. Because of the necessity of good temperature control, a relay circuit of very short time lag was used. A Sunvic relay was found to be unsuitable because of its large time lag. The most satisfactory relay was that employing two thyratrons; 800 ma. could be passed without overloading the circuit. A 250 watt lamp with a series resister was used as the heater. The tank water was stirred by a 24V. D.C. motor attached to the top of the tank.

A National Physics Laboratory standard thermometer was used to calibrate a Beckmann thermometer. By means of a screw on the top of the toluene regulator, the tank could be adjusted to within 0.01°C of any chosen temperature between 15°C and 50°C. It is not advisable to heat Perspex much above 60°C. For the lower temperatures, it was sometimes necessary to cool the water by means of a copper loop at the back of the tank which was fed from a constant head device. About three drops a second were sufficient to keep the tank at 15°C in the winter. In the summer, the lowest temperature attainable was somewhat higher than this, because the temperature of the tap water used in the cooling loop rose to about 17°C.

With the above controls the thyratrons were flickering on and off about every 15 seconds; no variation of temperature could be observed on the Beckmann thermometer.

3g. The photocell.

The photocell was connected to a simple spot galvanometer and deflections of the mirror were recorded from time to time. This photocell was sensitive to the visible radiation passed by the filter solutions, so that readings never dropped exactly to zero.

3h. Rotating sector.

The rotating sector interrupted the light beam at its focus just in front of the second lens. In this way, penumbra errors could be kept to a minimum as the beam was quite narrow at this spot.

Two sectors were used. For determination of the intensity exponent, a high speed sector of 30 cm. diameter from which alternate 90° segments had been cut, was used. The sector rotated at 2000 - 3000 r.p.m., and was mounted on shock absorbers and rubber matting so that the vibrations generated at that high speed were not transmitted to the dilatometer.

For shorter flashing times, a variable speed sector was used. This consisted of a high speed motor geared down with various chains and sprockets. A frame of Meccano supported about 10 axles holding two or three sprockets each. Chains of correct length were fitted and removed from the sprockets. In this way, the rate of rotation of the sector could be altered by tightening the set-screw on a sprocket and fitting its chain. Flashing times of 0.1 seconds to 25 seconds could be obtained with this arrangement. The sector had a diameter of 60 cm. cut in alternate 90° segments so that if the angular velocity was low, the linear velocity of the end of the sector was relatively high. For flashing times of 30 seconds or greater, the sector was hand operated.

The fast sector was timed by a stroboscope. The slow sector was timed with a stop watch or by timing the motor with the stroboscope and from the gear ratios, calculating the rate of rotation of the sector.

31. Wire gauze.

A wire gauze was used to confirm the value of the intensity exponent found using the fast sector. The gauze was placed immediately after the first lens in such a position that the intensity was reduced without focussing the wire mesh on the cell.

The transmission of the gauze was found to be 34.0% for 3130A.

III. Experimental Procedure.

1. Preparation and deaeration of solutions.

One hundred millilitres of solution were prepared for each run. Ten millilitres, i.e. 8.3×10^{-5} M Fe^{3+}, 0.12 M $HClO_4$, of the concentrated stock solution were added to a one hundred millilitre volumetric flask and diluted to volume. The monomer was not added at this stage.

The solution was then transferred to the deaeration flask, the adapter and dilatometer piciened on, and the whole unit connected to the vacuum line.

Vacuum was applied for a second or two in short bursts before freezing, to remove most of the residual air. The solution was then carefully frozen with a dry ice-acetone mixture at -80°C. After freezing the adapter was opened until a vacuum of not less than 10^{-4} mm. of mercury was obtained; a "sticky" vacuum was reached after about fifteen minutes pumping. The tap of the adapter was then closed and the solution warmed to room temperature, then refrozen. This cycle was repeated twice more; a good vacuum was obtained each time. Two runs, mixed in separate flasks, were usually prepared and degassed together.

As the runs were deaerated the day before use, they were stored overnight at -80°C after the third pumping. In the morning, a "sticky" vacuum was again obtained before the addition of monomer.

A known volume of monomer was distilled in from a graduated pipette at 0°C, while the remainder of the line was isolated from the pumps. The graduated pipette was filled by distillation from the partly polymerised monomer in the stock flask. The monomer in the pipette was always water white. From the volume and known density of the monomer, the exact concentration could be calculated.

The deaeration assembly was then disconnected from the vacuum line after closing the adapter tap, and the solution was melted for the last time.

2. Filling the dilatometer.

After melting the solution and giving it a thorough shaking, the whole assembly was carefully tipped over so that the solution in the flask ran into the quartz cell through the capillary. As the solution did not pass over the tap, no grease could enter the system.

The quartz cell filled quickly; occasionally vapour bubbles formed at the cell end of the capillary. These could generally be removed by shaking; in extreme circumstances they could be collapsed by touching the capillary at that spot with cotton wool that had been dipped in the dry ice-acetone mixture.

After all the bubbles had been removed from the quartz cell and capillary, the adapter tap was opened, with the assembly still in a sloping position, allowing the whole system to come to atmospheric pressure. As long as there was plenty of liquid at the top of the capillary, no air reached the main body of the solution.

The dilatometer was then disconnected from the deaeration flask by heating the picien joint, and was then placed in the thermostat. The length of the dilatometer was extended by a B10 joint (as shown in Figure 201) so that the cell could be clamped at the tap and rigidly fixed in position.

A small mercury drop was placed at the top of the capillary before placing the dilatometer in the tank. This drop served two purposes. It prevented any air from passing down the capillary and it dampened any vibrations at the liquid meniscus. Twenty of the 24 - 28 ml. of solution remaining in the deaeration flask were pipetted into a 25 ml. volumetric flask for a blank analysis.

3. The adjustment of the meniscus.

When the dilatometer was placed in the thermostat, it was filled with solution to the bottom of the top joint on the capillary. To get the mercury drop into the capillary and sufficient liquid removed so that a meniscus could be observed, the following procedure was adopted.

A piece of rubber tubing was placed over the end of the tube which was piciened to the top of the capillary, and by means of suction, the dilatometer was contracted sufficiently to push the solution past the drop. On release of the suction, the mercury was pushed down the capillary.

Excess mercury and solution was removed by withdrawing it through a very fine capillary attached by rubber tubing to the water pump. About 2 mm. was the optimum length of the mercury plug. It was best placed so that there was about 1 cm. of liquid above the mercury. A liquid meniscus was found to be much steadier than the meniscus of the drop. If the plug had been any shorter it would have slipped and fallen into the solution; if it was much longer, it tended to stick. The capillary was gently tapped just before a reading to remove any errors of this sort.

Excess liquid above the capillary was removed by a piece of cotton wool on a wire. Draining in the capillary was stopped by touching the meniscus with a fine piece of glass dipped in Teepol. This detergent lowered the surface tension and suppressed any tendency of the meniscus to creep up the side of the capillary.

After about twenty minutes, the level of the meniscus was followed with a cathetometer. Since the solution was generally cooler than the thermostat, cessation of expansion signified thermal equilibrium. Further observations were made to determine if there was any dark rate. With good temperature control, a change of 0.01 mm. could be detected in this manner.

4. The illumination and measurement of the rate.

If no dark rate was observed, the solution was illuminated and timing commenced. The general pattern of the reaction is shown below.

4a. Induction period.

The induction period was always less than one minute with well deaerated solutions. The beginning of the contraction coincided with the first appearance of polymer.

4b. The period of accelerating rate.

A period of accelerating rate followed for all systems.

About 50% of the full rate was reached in twenty-five minutes. For the system 8.3 x 10^{-6} M Fe^{3+}, 0.012 M $HClO_4$, 0.6 M acrylonitrile, at 25°C, the steady rate was reached after about two hours. For systems at 25°C or 30°C, the steady rate was observed after 36 mgm. of polymer had been deposited. The deflection of the photocell was then about 20% of the full deflection. At 15°C, the steady rate was reached after 40 mgm. of polymer had been deposited; the transmission in this case was about 21% of the full transmission. See Figure 203 for a typical rate curve, and Figure 204 for the corresponding transmission of the solution.

Only a few representative points are shown on Figure 203. Readings were taken every minute at the full rates and every two and a half minutes at lower rates. The numbers indicate the rates observed at corresponding points on a graph of much larger scale; the straight line shows the limits of linearity. Deviations which are not so apparent here for the build up and fall off of the rate, are much more obvious on the larger scale.

4c. Steady rate.

A period of steady rate was then observed in the system described above, extending for two hours or until about 100 mgm. of polymer were precipitated.

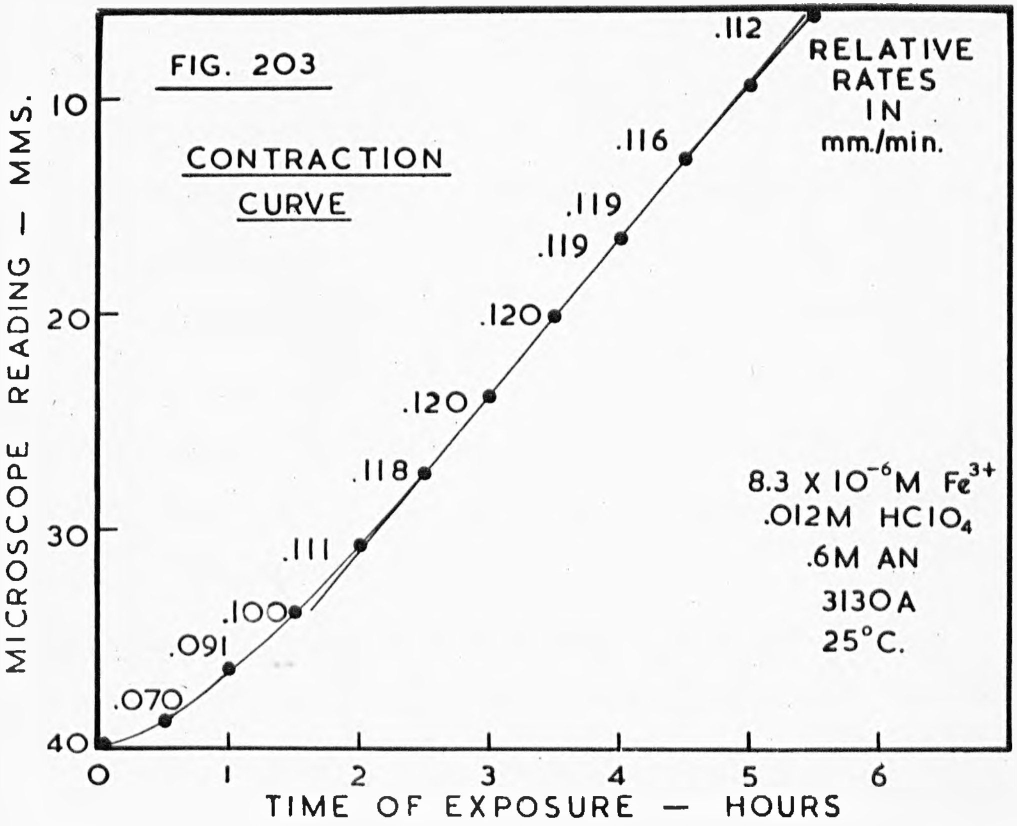


FIG. 203

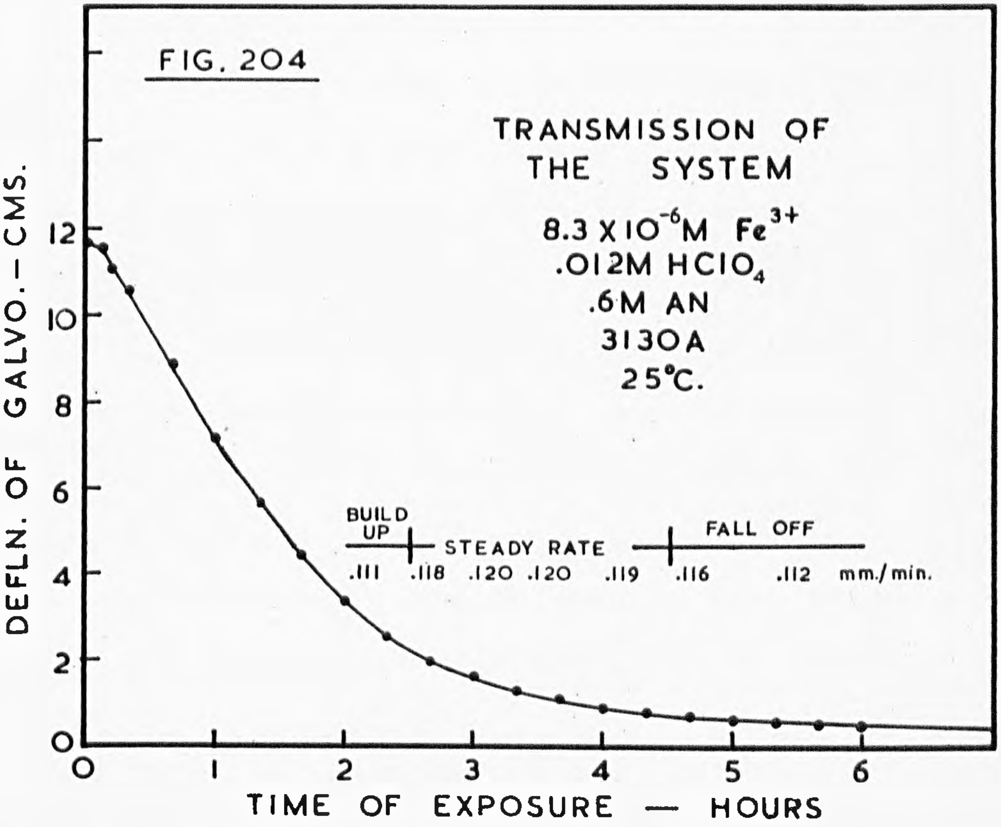


FIG. 204

4d. Period of decreasing rate.

A period of decreasing rate then followed.

4e. Rotating sector.

The rotating sector was introduced during the steady rate period. The full light rate was measured before and after the interrupted rate. Five minutes after the introduction of the sector, the rate became steady at the lower value.

IV. The Physical Appearance of the Polymer in Suspension.

Within two or three minutes of the beginning of an irradiation, a thin, homogeneous cloud of polymer could be seen in the light beam. As the reaction proceeded more polymer was formed and the cloud became more dense, as indicated in Figure 204. However, after about four hours of illumination in such a system as shown in the above figure, the polymer could be seen to sag, taking up a parabolic shape when viewed from the side. It did not precipitate equally throughout the cell; it stuck to the parts of both faces which were directly exposed to the light beam, and settled in the middle. In the space above the sagging polymer, which was still exposed to the light beam, fresh polymer could be seen forming. No definite coagulation of the polymer could be seen at the bottom of the cell, but it was noticeably denser here than at the top.

The onset of the decreasing rate was not marked by any visible change in the appearance of the polymer.

For a cell and stem volume of 80 ml. (2 cm. deep by 7 cm. in diameter), the total illuminated volume was 62.5 ml. (2 cm. deep by 6.4 cm. in diameter).

V. Determination of the Rate of Initiation.

The rate of initiation of ferric sensitized polymerisation was measured from the rate of formation of the ferrous ion.

At the end of an irradiation, the polymer was filtered off and 20 ml. of the filtrate were transferred to a 25 ml. volumetric flask. The blank solution obtained as described in Section II.2, was also analysed to give the zero time ferrous concentration.

The following analar reagents were added to the two solutions in strict order: 1 ml. 0.2 M ammonium fluoride; sufficient 5 M ammonium acetate to give a pH of about 4; 1 ml. of 0.2% o-phenanthroline.

The solutions were then diluted to volume and the optical density was measured, in 4 cm. cells at 5100A, within fifteen minutes.

The results for each temperature will be given in the next chapter.

VI. The Determination of the Intensity of Illumination.

Uranyl oxalate was prepared from analar uranyl nitrate and oxalic acid, and was recrystallized from water. A solution of 0.005 M $UO_2C_2O_4$ and 0.025 M $H_2C_2O_4$ was used; 75 ml. were placed in a 2 cm. deep standard quartz reaction cell and exposed with constant stirring to radiation of 3130A for periods of approximately 24 hours. All the light was absorbed at these concentrations. About 10% decomposition occurred in this time; the oxalic acid concentration was determined before and after exposure by direct titration with 0.00985 M $KMnO_4$ (Farkas and Melville, 1939).

The amount of light of 3130A incident on the cell was found to be 1.40×10^{15} quanta/second, or 2.32×10^{-9} $Nh\nu$/second; these results have an error of ±2% from three determinations. The radiation had 12% of the intensity used by Evans, Santappa and Uri (1951), or slightly less than that used by James.

VII. Standardization of the Capillary.

In order to determine the absolute rates of reaction, it was necessary to know the relative contraction in the capillary corresponding to the formation of a certain weight of polymer.

The standardization was carried out by weighing the insoluble polymer after a month's drying in a vacuum dessication over anhydrous magnesium perchlorate.

At least three determinations were made at each temperature, except at 40°C. The overall error in each case was about ±2%. For a capillary of 1.00 mm. diameter, the results are shown in Table 201; the value for 40°C is interpolated.

Table 201. Standardization of the capillary.

Temperature degrees C.	Wt. of polymer for 10.0 mm. contraction	Density of Monomer g/ml.
15.0	34.1 mgm.	0.811
25.0	30.4 "	0.800
30.0	29.9 "	0.795
40.0	27.8 "	0.784
50.0	26.1 "	0.773

James obtained an average value of 30.5 mgm. for 10.0 mm. contraction at 25.0°C.

From this contraction factor, the density of the polymer can be obtained. A density of 1.01 g/ml. (error of 1%) was obtained from all five temperatures, indicating that the variation in the factor depends only on the difference of the density of water at that temperature. The density of water is found to vary linearly with the above calculations. The density of these dilute solutions is assumed to be the same as that of water.

Bamford and Jenkins (1953) obtained values of 1.04 gm./ml. from measurements of polymer density "by standard methods."

VIII. Standardization of Dilute Ferric Perchlorate Solutions.

The dilute ferric solution was standardized colorimetrically as described in Vogel (1951) page 647. Results were reproduceable within 1% after a period of six months. The ferrous ion content of the solution was observed periodically at the same time as measurements were made for the rate of initiation and was never greater than 4% of the total iron concentration, i.e. for 8.3×10^{-6} M Fe^{3+}, the ferrous ion concentration was not greater than 3×10^{-7} M.

CHAPTER 3. THE EXISTENCE OF A PHOTOSTATIONARY STATE.

A. VERIFICATION OF THE RATE EQUATION FOR 15°C, 25°C AND 30°C.

From the arguments and data presented in Chapter 1, it is seen that the polymerisation of acrylonitrile in aqueous solution should be a homogeneous photochemical reaction capable of reaching a steady state. The rate of reaction should therefore be describable by Equation IV assuming mutual termination to be occurring exclusively.

i.e. $$-\frac{d(m_1)}{dt} = k_p \sqrt{\frac{n\phi I_a}{k_t}} \, (m_1)^{1.0} \qquad \text{(IV)}$$

Non-steady states may arise from several causes: (i) the variation of the rate constants with the degree of reaction; (ii) a non-steady state in isolated loci; (iii) the formation of catalysts or inhibitors during the reaction. These effects show themselves in continuously accelerating and irreproduceable rates; induction periods and long after effects; and variable and unusual values for the monomer and intensity exponents.

None of these effects were observed at 15°C, 25°C and 30°C.

I. Reproduceability of Observed Rates of Reaction.

As noted in Chapter 2, Section III.4, the reaction accelerated for a relatively long time but a steady rate was finally reached. The results were reproduceable; at 15°C, for a total of 26 runs at the same concentrations, the average deviation was 5%; at 25°C, for 14 runs, the average deviation was 4%; at 30°C, for 13 runs, the average deviation was 6%. No induction periods were observed in well deaerated solutions.

The exact rates will be given in the next chapter.

II. The Monomer Exponent.

For the Fe^{3+} system at 3130A and the temperatures 15°C, 25°C and 30°C, the monomer exponent was found to be 1.0. See Figure 301.

Deviations from an exponent of 1.0 are observed at monomer concentrations of less than 0.6 M. At low concentrations, i.e. 0.3 M, it was observed that polymer was forming so slowly that it precipitated to the bottom of the cell. After three hours, the transmission of the system had only dropped to about 60% and remained constant, instead of the 20% observed at the steady rates for higher concentrations. Hence sufficient polymer was not formed to increase the light absorption to a degree found at higher concentrations. With less light being absorbed, lower rates were observed than would be predicted from an exponent of 1.0.

Polymer settled very slowly at higher concentrations also, but it was being formed at a sufficient rate to maintain constant light absorption. See Chapter 4.

James found a monomer exponent of 1.0 for acrylonitrile at 25°C initiated by Fe^{2+} (2537A and full light); Fe^{3+} (2537A); and I^- (2400A). The lowest concentration used in these experiments was 4.5 M; no deviations from linearity were observed.

III. The Intensity Exponent.

A value of 0.5 was found for aqueous acrylonitrile at all three temperatures. The intensity was varied by means of the fast sector and the wire gauze. The fast sector reduced the intensity 50%, the gauze 66%. The results are shown in Figure 302.

IV. The Initiator Exponent.

The rate of initiation was varied by changing the pH of the solutions. Evans, Santappa and Uri (1951) have shown that in a Fe^{3+} system, the photoactive species is the complex $Fe^{3+}.OH^-$. Using the thermodynamic functions evaluated by Rabinowitch and Stockmayer (1942), the exact concentration of this complex was calculated at various acid strengths at the three temperatures. An exponent of 0.5 was obtained in all cases; see Figure 303.

FIG. 301

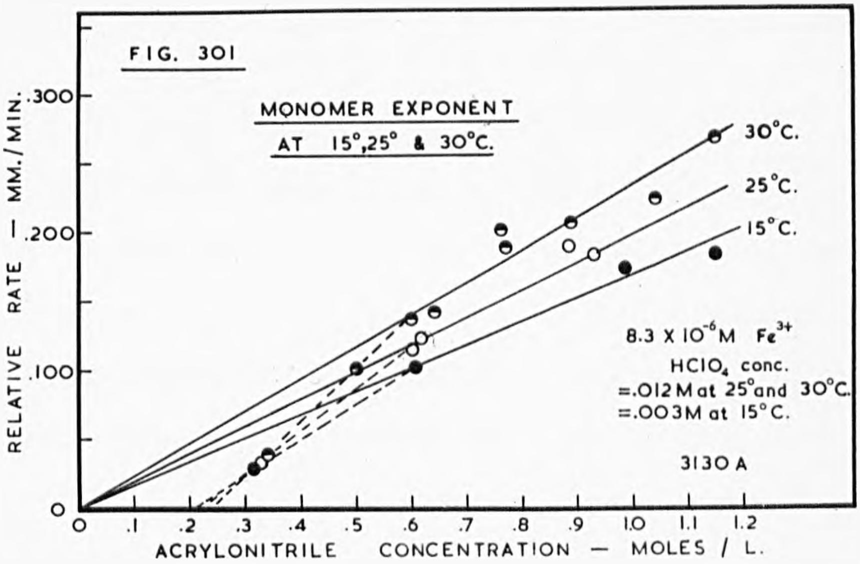


FIG. 302

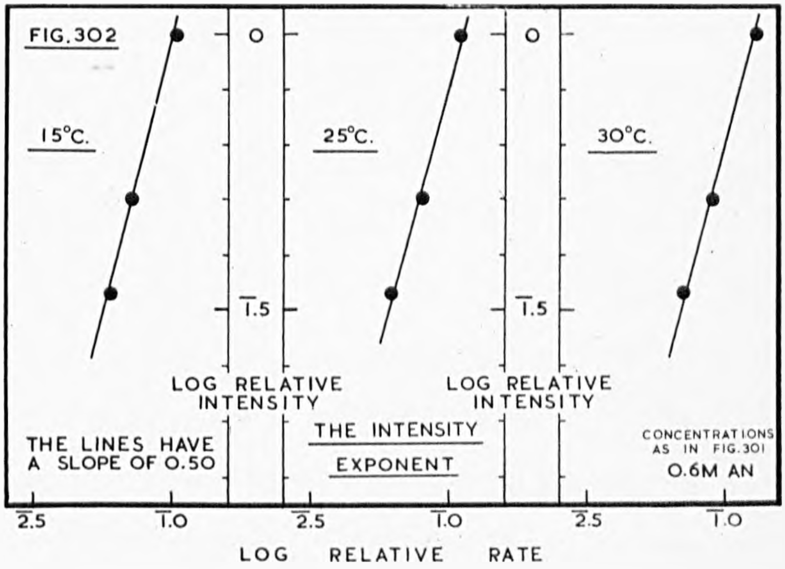
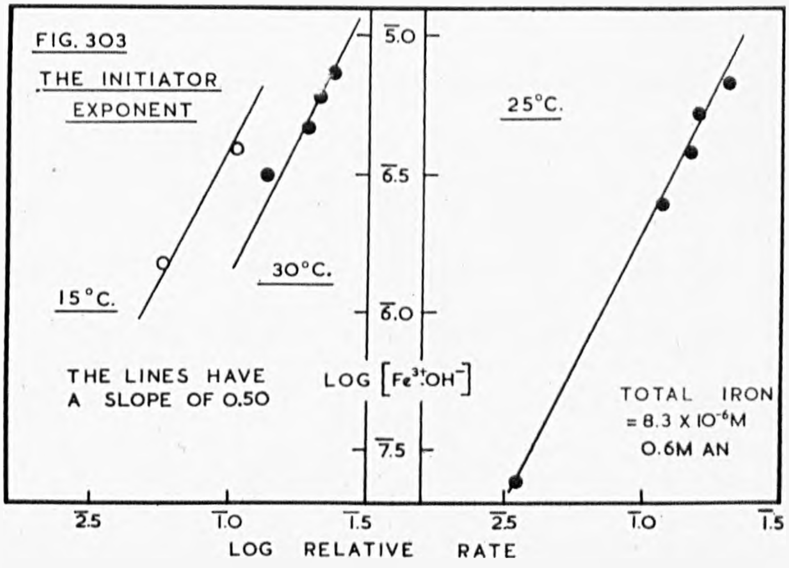


FIG. 303



B. EVIDENCE FOR THE SIMULTANEOUS OCCURRENCE OF HOMOGENEOUS AND HETEROGENEOUS REACTIONS IN THE SYSTEM.

The above results supply partial verification of the homogeneous rate equation. Attempts at further proof have led to a reinterpretation of the mechanism and to a reinterpretation of the effect played by the polymer particles.

I. The Rate of Initiation.

The rate of initiation was determined as described in Chapter 2, Section V. The results are shown for the three temperatures in Figures 304, 305 and 306. The graphs obtained at 15°C and 25°C do not pass through the origin as the actual measured optical densities are plotted, the value at zero time being due to the initial ferrous concentration and reagent blank. Hence the zero time reading is effectively the origin. The calculation of the rates of initiation will be given in Chapter 4.

It is to be noted from Figs. 304, 305 and 306, that the rate of initiation is constant from zero time.

II. Buried Centres of Polymerisation.

Bamford and Jenkins (1953) have shown that polyacrylonitrile particles contain propagating centres. Observations on the aqueous system show that buried centres are also present.

1. Photochemical after effect.

It will be shown in Chapter 4, that the lifetime of a growing chain is of the order of one second in the homogeneous phase. Thus, within a minute after irradiation has ceased, most of these chains will have disappeared. However, a gradual die away of rate is observed, falling off to about 10% of the full rate in one hour. Dainton, James and Kutschke (1953) also observed this. Assuming only mutual termination, they were able to fit a theoretical curve to the experimental points and evaluated the lifetime of these buried centres in the dark.

The equation is of the form:

$$-\Delta h = A \log (1 + Bt)$$

where $B = \frac{1}{\theta}$, and where θ = the lifetime of the buried centres. See Equation VII of Chapter 1.

This equation was fitted to 15 die away curves measured at 15°C, 25°C and 30°C at various durations of exposure. The results are shown in Table 301 for the system 8.3×10^{-6} M Fe^{3+}; 0.6 M acrylonitrile; 0.003 M $HClO_4$ at 15°C and 0.012 M $HClO_4$ at 25°C and 30°C; 3130A. Figure 307 shows a typical die away and its calculated curve.

From the table it can be seen that the lifetime of the centres increases with the duration of exposure until

Table 301. Lifetimes of Buried Centres.

Temperature °C		Duration of Exposure to Light - hrs.	Lifetime e, seconds
15°C		1.0	100
		2.0	200
		2.2	300
	steady rate reached	3.0	300
		3.4	300
		3.6	300
25°C		1.0	60
		2.0	100
	steady rate reached	2.8	160
		3.2	210
		3.3	170
		3.5	170
30°C	steady rate reached	2.3	160
		3.4	100 ??
		3.6	170

the steady rate is reached. Then the lifetime is effectively independent of the exposure time.

It is also to be noted that the average lifetime after the steady rate is reached is greater at 15°C than at 25°C and 30°C. This is likely a temperature effect, but the lower acid concentration necessary to increase the rate of initiation at this temperature may also affect it indirectly.

James considered at one time, that this die away was a cooling effect; the heat released on polymerisation would maintain the cell at a temperature slightly above that of the bath. On terminating illumination, the cell slowly cooled, resulting in a contraction.

However, James and Dainton (1953) show that the amount of heat released is negligible. The heat of polymerisation is 17.3 kcal/mole (Tong and Kenyon, 1947); the rate of reaction is about 2 x 10^{-6} mole/l. sec^{-1} and the volume of the cell is 80 ml. The total decrease in volume to be expected would not exceed a few thousandths of a millimetre when the light is turned off. This is quite within the experimental error of the microscope readings.

2. Resurgence of Reactivity.

A similar experiment to that of Bamford and Jenkins (1953) was undertaken. The system 8.3 x 10^{-6} M Fe^{3+},

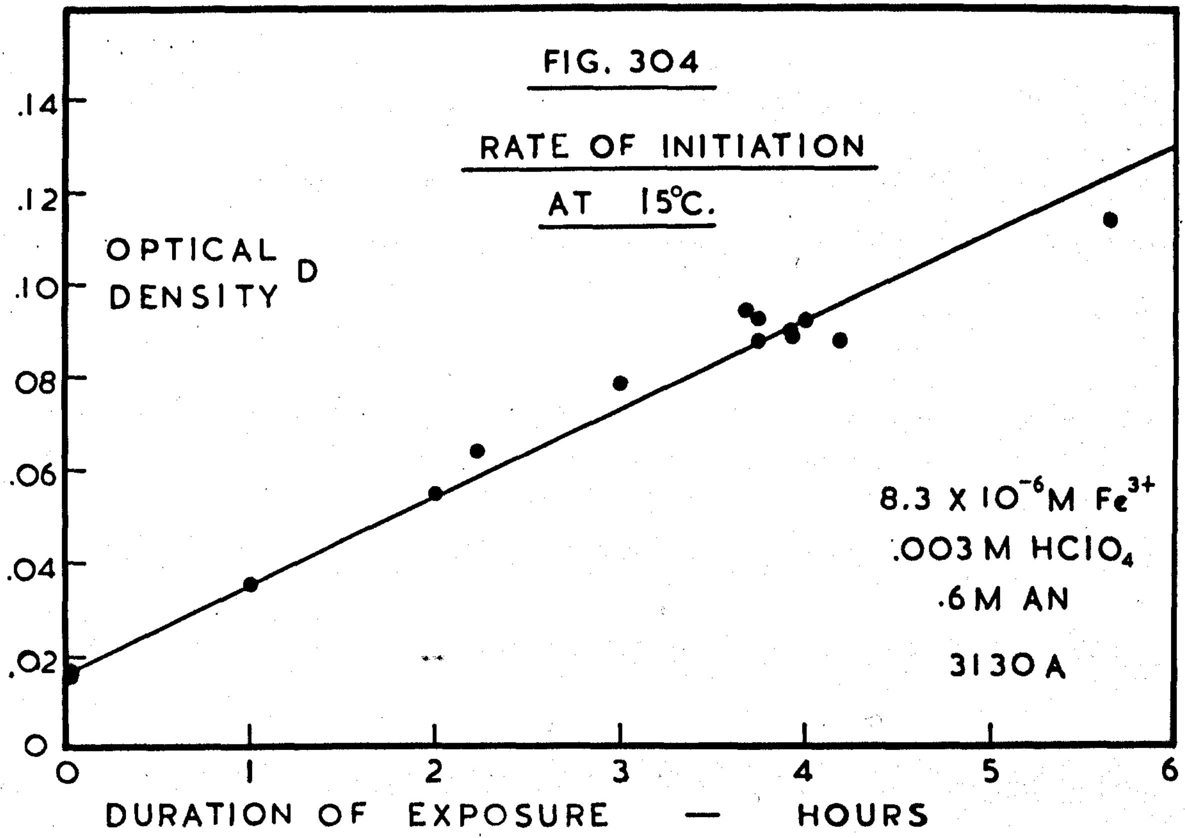


FIG. 304

RATE OF INITIATION AT 15°C.

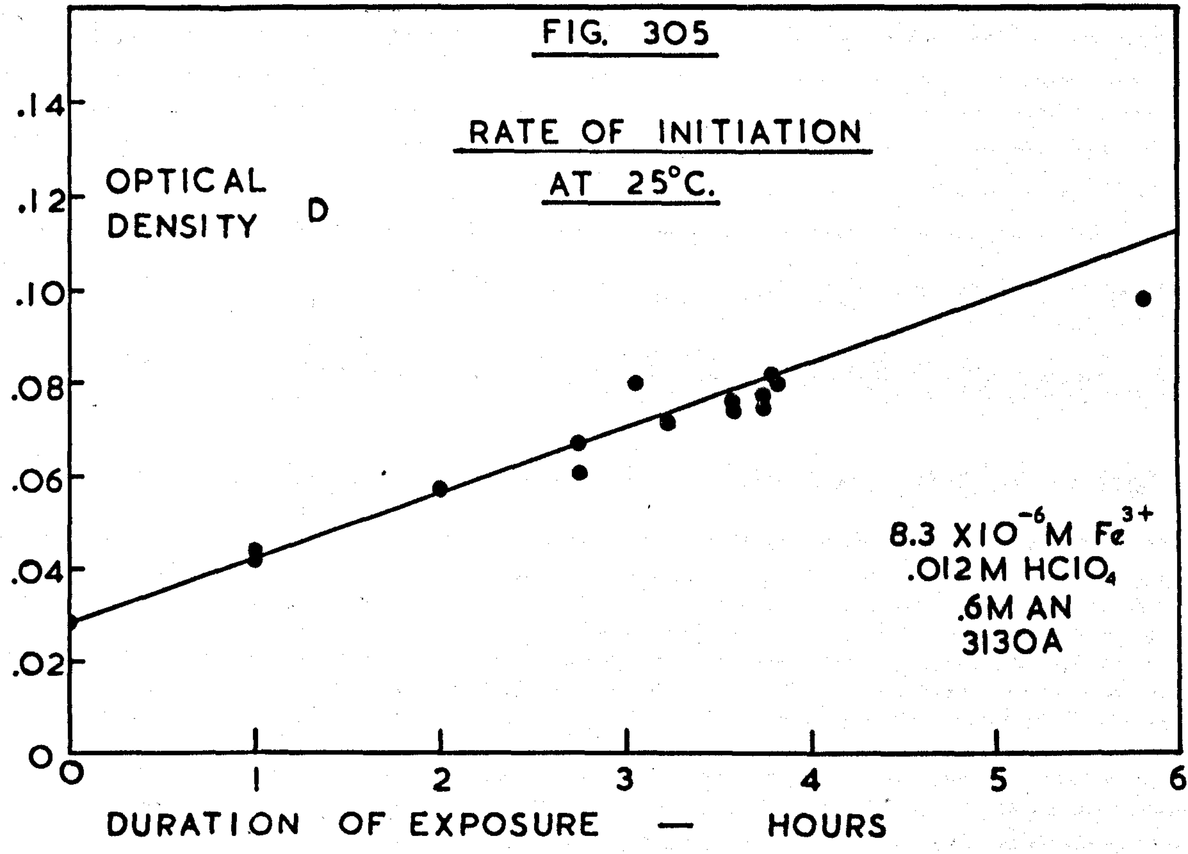


FIG. 305

RATE OF INITIATION AT 25°C.

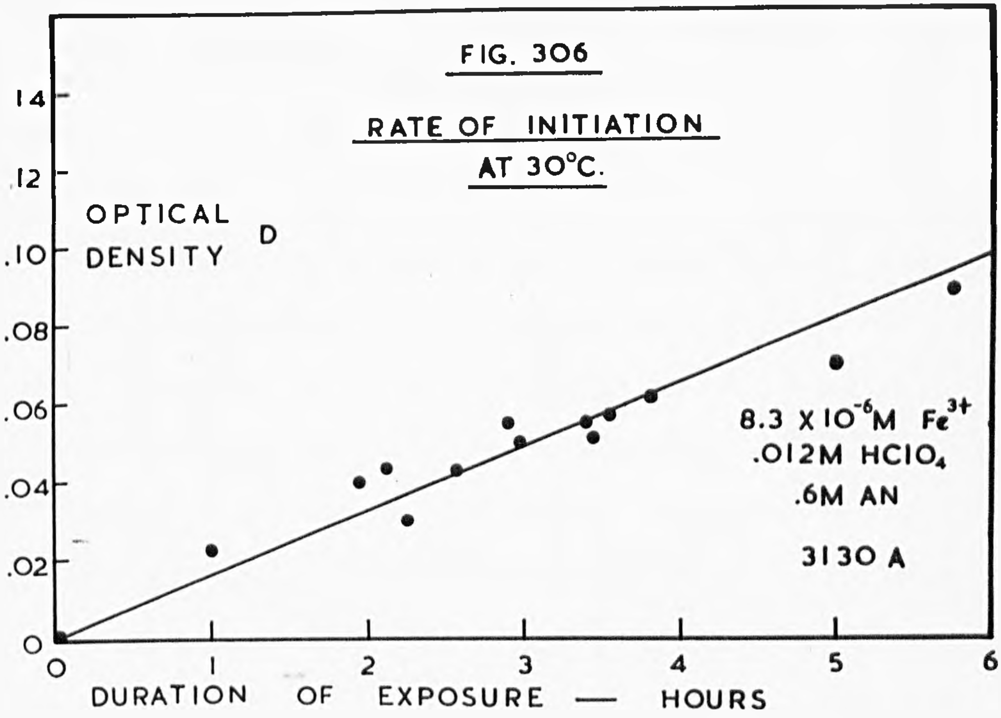


FIG. 306

RATE OF INITIATION AT 30°C.

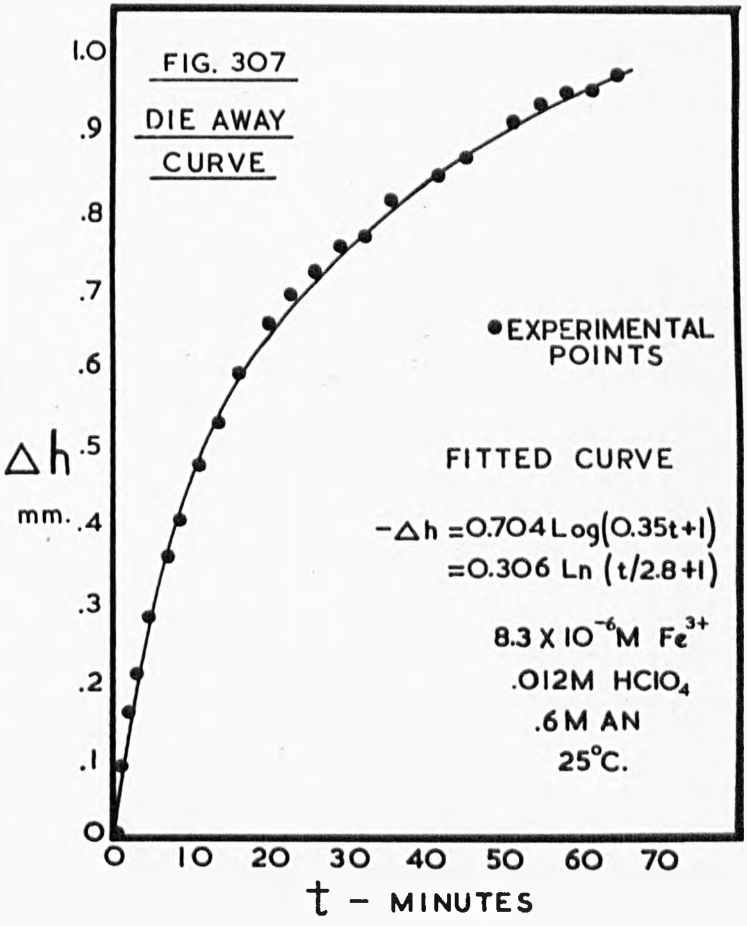


FIG. 307

DIE AWAY CURVE

0.012 M $HClO_4$ and 1.0 M acrylonitrile was illuminated, at 25°C, in a quartz cell in vacuo for three hours. It was estimated that 82 mgm. of polymer would form in that time.

The mixture was transferred, still in vacuo, to a spiral, pyrex dilatometer of large surface area (volume 60 ml.). This was then placed in a thermostat, in the dark, at 50°C. From observations of the cessation of expansion, thermal equilibrium was found to be established in about five minutes. A rapid rate was observed; the results are summarized in Table 302. Zero time refers to the start of the readings.

Table 302. Rates observed in a system at 50°C from polymer prepared at 25°C.

Time minutes	Relative Rate mm./min.
10	.171
20	.245
30	.117
50	.087
90	.072
120	.064

Estimated photo rate
at 25°C = 2.59 mole/l. sec^{-1}
= 0.17 mm./min.

Photo rate that would be observed in the same system at 50°C
= 0.43 mm./min.

About 1% polymerisation occurred in the two hours of observation.

The rates are seen to reach a peak and then slowly to decay.

3. Addition of polymer to a fresh run.

The system 8.3×10^{-6} Fe^{3+}, 0.006 M $HClO_4$, and 0.6 M acrylonitrile was irradiated, at 25°C in vacuo, in a quartz cell for two and a half hours. It was estimated that 52 mgm. of polymer would form in that time.

The polymer was then separated from the liquid phase by filtration under vacuum. This polymer, without exposure to air, was then added to a fresh solution of composition 8.3×10^{-6} M Fe^{3+}, 0.012 M $HClO_4$ and 0.6 M acrylonitrile. The whole mixture was placed in a standard dilatometer and a run carried out as if the polymer were not present.

Most of the pre-prepared polymer settled to the bottom of the cell to a depth of about one centimetre and a half. The remainder of the solution was slightly clouded from a fine suspension of polymer. Thus the cell contained a mixture of coagulated and suspended polymer. A slight dark rate of $.14 \times 10^{-6}$ mole/l. sec^{-1} was observed before irradiation. This may be due to two causes:
(i) an after effect as described in Chapter 3, Section II.1 or (ii) initiation of polymerisation caused by impurities picked up from the large vacuum assembly necessary for the

separation of polymer. It is suspected, in this case, that the dark rate was caused by impurities. The effect on the light rate will be negligible if one estimates the error from the square root of the difference of the squares of the rate. For a 10% dark rate, the error is only 1%.

On turning the light on, the transmission of the system was found to be only about 50% of that of a clear solution. The transmission rapidly dropped and a steady rate was observed within one and a half hours, instead of the usual two and a half hours required for a system of this type. The steady rate observed was 1.89×10^{-6} mole/l. $\sec^{-1}$; the rate of a system without initially added polymer at the same monomer concentration is 1.8×10^{-6} mole/l. $\sec^{-1}$, so the two rates are the same within experimental error. The slight increase in rate is not considered to be significant.

III. Emulsifying Agents.

1. Acrylonitrile.

An attempt was made to repeat the experiments of Khomikovskii (1948). One per cent sodium stearate, purified by filtration, was added to a system 8.3×10^{-6} M Fe^{3+}, 0.012 M $HClO_4$, and 0.6 M acrylonitrile. Very low rates were observed; see Table 303.

The mixture was quite fluid and very silky in

Table 303. The polymerisation of acrylonitrile in the presence and absence of soap at 25°C and 3130A.

% Soap	Absolute Rate mole/l. $sec^{-1} \times 10^{+6}$	% Transmission of system
1%	.37 at first, .14 after 2 hours	½%
1%	.30 at first, .15 after 2 hours	½%
0	1.73 steady rate after 2½ hours	As in Fig. 204

appearance; the transmission of the cell was very low throughout the observations.

2. Methyl methacrylate.

It has been shown that emulsifying agents have a profound effect on the polymerisation of methyl methacrylate. A similar system to that mentioned above was exposed to 3130A, using methyl methacrylate in place of acrylonitrile. Pure methyl methacrylate was obtained from Dr. K.J. Ivin of this laboratory. The results are summarized in Table 304.

The rate of polymerisation of methyl methacrylate is apparently unchanged by the presence of soap, while the rate of polymerisation of acrylonitrile is reduced to about one fifth.

The results for methyl methacrylate are contrary to

Table 304. The polymerisation of methyl methacrylate in the presence and absence of soap at 25°C and 3130A.

MMA conc. moles/l.	Fe^{3+} conc. moles/l.	HClO$_4$ conc. moles/l.	Soap conc. %	Relative max. rate mm./min.	Trans. of cell %
.14	8.3×10^{-6}	.0012	1%	0.95	½
.28	8.3×10^{-6}	.012	1%	0.99	½
.14	8.3×10^{-6}	.0012	-	0.91	similar to AN runs
.14	4.2×10^{-6}	.012	-	0.44	

what has been found previously for systems not photo-initiated. Because of the low transmission of the mixture, it is felt that the light absorption is reduced considerably below that of a simple acrylonitrile system in which there is no soap. The equivalence of the rates for methyl methacrylate in the presence and absence of soap is fortuitous.

Khomikovskii (1948), studying the aqueous persulphate catalyzed polymerisation of acrylonitrile, has shown that it took a 5% soap solution to reduce the rate 30%, and an 8% soap solution to reduce the rate 50% at 60°C. From this it is seen that a 1% soap solution would have little effect on the rate at 60°C; and it might be inferred that the same conclusion would hold at 25°C.

In effect, the light absorption is reduced by about twenty-five fold (assuming homogeneous kinetics) and lowers the observed acrylonitrile rate by one fifth. Therefore the true emulsion rate of polymerisation of methyl methacrylate for an intensity comparable to that observed in the absence of soap, should be about five times that actually measured; this is more in line with other experimental results.

The rates for the aqueous non-emulsion polymerisation of methyl methacrylate were very high, and not steady. This system is more complex than that of acrylonitrile and would require more study, when photoinitiated, both in the aqueous phase and in emulsion in order to obtain more reliable results.

IV. Discussion.

From Figures 304, 305 and 306, the rate of initiation of the aqueous acrylonitrile system is seen to be constant from zero time. This can only mean that the light absorption must be effectively constant from a time shortly after the illumination is started and that it remains so throughout the period of accelerating rate and the period of constant rate.

James, who also found a linear rate of initiation from zero time, postulates that the acceleration of rate to the steady period is caused by increasing light absorption from increasing polymer formation. If this were the case, the rate of initiation should also show an increase. When the steady rate is reached, the rate of initiation should then become linear. Extrapolation of this linear rate would not go through the origin.

If the light absorption is constant, then what is causing the accelerating rate? The accelerating rate must be due to the slow establishment of a steady state in the buried centres of the polymer particles. A steady state in the homogeneous phase is established shortly after the start of the illumination. A steady rate occurs when both systems reach a steady state.

Light absorption is constant at a higher level than would be obtained in a clear solution. This high level of absorption is reached shortly after the first polymer is formed.

With increasing polymer formation and coalescence, light, instead of passing through the cell, is scattered in all directions. The increase in absorption due to scattering is, however, offset by the inability of the light to penetrate very far into the cell before being scattered. As more and more polymer is formed, more light is scattered but less can penetrate to any depth, resulting in constant absorption throughout the reaction.

The rate falls off at the end of the steady period, not because of reactant consumption, but because the balance between scattering and absorption is disturbed. Insufficient light enters the cell to maintain the absorption at the high level created by scattering. The results show, as illustrated in Figures 203 and 204, that the rate falls off much more rapidly than can be accounted for by consumption of reactants. At the end of the steady period, 4½ hours after the start, less than 3% of the monomer has been consumed. In the next hour, the rate drops 8%. In the same period, the initiator concentration will have changed much less than that of the monomer concentration.

Further evidence to support the work of Bamford and Jenkins was presented in Section B.II.1,2 and 3.

The photochemical after effect was shown to be due to the propagation and mutual termination of long lived buried radicals. The lifetime of these buried centres is found to be independent of the duration of exposure after the steady rate is reached, inferring that the concentration of these radicals has become constant in the period of the steady rate. For exposures of shorter duration, in which less polymer is formed, the buried centres must be more accessible to termination, even though they are in lower concentration. Hence, it appears that the degree of coalescence has some bearing on the lifetime of the buried radicals. Those buried centres formed in the steady rate period, being in the presence of more coalesced polymer, have a longer lifetime.

The burst of activity from polymer prepared at 25°C and then observed at 50°C, must be due to the greater accessibility of these buried centres at higher temperatures. The results observed were not so striking as those of Bamford and Jenkins because of the difference of environment in the two cases, and the slightly lower temperature of the aqueous system.

The addition of polymer to a fresh run illustrates that the rate is not increased by the presence of polymer as in the case of systems in which polymer is swollen by monomer. This confirms that the locus of propagation for "free radicals" is in the aqueous phase.

The effect of emulsifying agents on the aqueous polymerisation is not conclusive, but appears to support these conclusions.

Also, the presence of polymer particles accelerates the attainment of a steady state of buried centres by favouring coalescence. The overall result is that a steady rate is reached in a shorter time than without initial polymer. In other respects, the two systems are the same.

V. Conclusions.

From the experiments described above, it has been proven that buried centres of considerable lifetime do exist. The only reasonable interpretation correlating a linear rate of initiation with a gradually accelerating rate of reaction is that light absorption is constant from zero time, and the increasing rate is due to the slow attainment of a steady state in these buried centres. The lifetime of these buried centres is dependent on the degree of coalescence but independent of the duration of exposure after a steady rate is reached.

The effect of adding polymer to a run is not to increase the light absorption, but to assist in coalescence and to accelerate the attainment of a steady state in the buried centres.

Therefore, a true steady state does occur in the aqueous polymerisation of acrylonitrile. However, the steady state is not simple, but consists of two systems, one predominantly homogeneous and the other predominantly heterogeneous, both of which contribute to the observed rate. The homogeneous reaction may be described as that in which the growing chains are effectively free and "in solution"; the heterogeneous reaction that in which the growing chains are buried in polymer particles and are immobilized.

The mechanism of the $Fe^{3+}.OH^-$ photoinitiated polymerisation of acrylonitrile should include steps for this heterogeneous propagation and termination. A linear mechanism as postulated by James is also included.

$$Fe^{3+}.OH^- + h\nu = OH + Fe^{2+} \qquad \phi Ia$$

$$OH + m_1 = m_j$$

$$m_j + m_1 = m_{j+1} \qquad k_p$$

$$m_r + m_s = P_{r+s} \text{ or } P_r + P_s \qquad k_t$$

$$m_p + Fe^{2+}.H_2O = m_pH + Fe^{3+}.OH^- \qquad k_t'$$

$$M_j + M_1 = M_{j+1} \qquad K_p$$

$$M_r + M_s = P_{r+s} \text{ or } P_r + P_s \qquad K_t$$

M_j = trapped centre

M_1 = concentration of the monomer available to trapped radicals.

This mechanism will be described by an equation similar to that assuming homogeneous kinetics, provided that the Fe^{2+} ion concentration is low i.e. that there is little linear termination. Catalyst and intensity variations will still give an exponent of 0.5, as both phases are initiated in the same manner. Since the monomer exponent is 1.0, then the monomer concentration about the particles must be the same as that in the homogeneous phase <u>i.e.</u> $M_1 = m_1$

Thus it can be said that Equation IV is verified, in the form,

$$\frac{-d(m_1)}{dt} = k\, I_o^{0.5} (Fe^{3+}.OH^-)^{0.5} (m_1)^{1.0} \qquad \text{(IVa)}$$

but it is seen that the rate constants incorporated in k, are made up contributions from both the homogeneous and heterogeneous reactions.

Whether the two systems can be separated and whether their relative rate constants can be evaluated are the subjects of the next chapter.

CHAPTER 4.

THE EVALUATION OF THE RATE CONSTANTS AND ACTIVATION ENERGIES OF THE POLYMERISATION OF ACRYLONITRILE IN AQUEOUS SOLUTION AT 15°C, 25°C AND 30°C.

I. Introduction.

It has been shown in Chapter 3, that the aqueous polymerisation of acrylonitrile can be described by the equation,

$$\frac{-d(m_1)}{dt} = k\, I_o^{0.5}(Fe^{3+}.OH^-)^{0.5}(m_1)^{1.0} \qquad (IVa)$$

which is a form of Equation IV.

It now remains to attempt an evaluation of the separate rate constants. The most convenient method has been to use a rotating sector to measure the lifetimes of the growing chains.

II. Refinements in the Theory of the Rotating Sector.

1. Homogeneous systems.

Kutschke (Dainton, James and Kutschke, 1953), working in this laboratory, has developed a general solution of the rotating sector theory.

A simple theory involving mutual termination only, has been presented by Dickinson (1941). Special cases have been considered by Rice (1942), Bateman and Gee (1948), Matheson et alia (1949a) and Burns and Dainton (1950).

Case I of Kutschke's treatment involves thermal as well as photochemical initiation, and is not applicable to this system.

Case II, which treats a mechanism involving both linear and mutual termination in the absence of any thermal reaction, can be applied to the aqueous acrylonitrile system.

Let the subscript c refer to continuous illumination and a bar refer to intermittent illumination. Then the steady rate

$$R_c = \frac{-d(m_1)}{dt} = k_p(m_1)C_c$$

and the intermittent rate

$$\overline{R} = k_p(m_1)\overline{C}$$

where $C = \sum m_j^*$.

Therefore, $\dfrac{\overline{R}}{R_c} = \dfrac{C_c}{C} = \dfrac{\text{steady rate}}{\text{intermittent rate}}$

is the experimentally measured ratio.

The variation of $\overline{R}/R_c$ with respect to the ratio flashing time to the lifetime of the chains b, is described by the function $\rho(o,\delta)$ shown in detail in Table 401 (Equations VIII and IX).

The dimensionless quantity δ may be related to functions of more physical significance. In continuous illumination, the rate ~~of linear~~ radical disappearance

Table 401. The Function: The variation of the ratio of the interrupted rate to the full rate, with respect to the logarithm of the ratio of the flashing time to the lifetime of the chain.

$$\rho(0,\delta) = \frac{1}{p+1}\left(1 + \frac{1}{b}\ln\left[1 + \frac{1-\delta}{2\delta}\left(1 - \exp(-2\delta p b')\right)\frac{z(0,\delta)-\delta}{1+z(0,\delta)}\right]\right) \qquad \text{(VIII)}$$

$$z(0,\delta) = \frac{\frac{1}{2}(1-\delta^2)}{\coth b' + \delta\coth\delta p b'}\left\{1 + \left[1 + \frac{4\delta}{(1-\delta^2)^2}(\coth\delta p b')(\coth b')\left[1+\delta^2+\delta\left((\coth b')(\tanh\delta p b') + (\coth\delta p b')(\tanh b')\right)\right]\right]^{\frac{1}{2}}\right\} \qquad \text{(IX)}$$

$$\rho(0,\delta)_{b\to\infty} = \frac{1}{p+1} \qquad \text{(XI)}$$

$$\rho(0,\delta)_{b\to 0} = \frac{1}{p+1}\left(1 + p\,\frac{-\delta(p+1)^{\frac{1}{2}} + (p\delta^2+1)^{\frac{1}{2}}}{(p+1)^{\frac{1}{2}} + (p\delta^2+1)^{\frac{1}{2}}}\right) \qquad \text{(XII)}$$

$$\rho(0,0) = \frac{1}{p+1}\left(1 + \frac{1}{b}\ln\left[1 + \frac{pb}{1 + \frac{2(pb\coth b + 1)}{pb + [p^2b^2 + 4pb\coth b + 4]^{\frac{1}{2}}}}\right]\right) \qquad \text{(X)}$$

$$p = \frac{\text{duration of the dark period}}{\text{duration of the light period}} \qquad b = \frac{\text{flashing time}}{\text{lifetime of chain}} \qquad b' = \frac{b}{1-\delta}$$

= 1 for the sectors used here.

is $V_1 = k_t'(B)C_c$, where (B) = the concentration of the linear terminating species. The rate of quadratic radical disappearance is $V_2 = k_t(C_c)^2$. The total rate of disappearance of centres is $V = V_1 + V_2$ from which it can be shown that,

$$\frac{V_1}{V} = \frac{2\delta}{1+\delta} \quad \text{and} \quad \frac{V_2}{V} = \frac{1-\delta}{1+\delta} \qquad \text{(XIII)}$$

2. A combination of a homogeneous and a heterogeneous system.

The long photo after effect and other phenomena have shown that buried centres are also chain carriers.

If two photochemical initiated chain carriers are independently propagated and terminated within the same system, the sector curve will exhibit a plateau for values of the flashing time which lie between the different lifetimes of the two chain carriers. Therefore, from the complete mechanism given in the conclusions of Chapter 3, the steady total rate in continuous illumination,

$$R_c = k_p(m_1)C_c + k_p(M_1)D_c$$

$$\text{where } D = \sum M_j^* \text{ and } C = \sum m_j^*.$$

For intermittent illumination,

$$\overline{R} = k_p(m_1)\overline{C} + k_p(M_1)\overline{D}$$

where the bar and the subscript c have the same meaning as before.

Therefore the ratio of the intermittent rate to the continuous rate is now given by,

$$\frac{\bar{R}}{R_c} = \frac{\frac{\bar{C}}{C_c} + g\frac{\bar{D}}{D_c}}{1+g} = \frac{\rho(o,\delta) + g\rho(o,o)}{1+g} \qquad \text{(XV)}$$

where $g = \dfrac{K_p(M_1)D_c}{k_p(m_1)C_c}$, which is independent of the flashing (XVI) time, but dependent on the physical condition of the polymer present.

3. Evaluation of the theoretical sector curve.

In Equation XIV, $\rho(o,o)$ is the function describing the lifetime curve of the buried centres assuming mutual termination only; $\rho(o,\delta)$ is the function describing the lifetime curve of the chain centres in the homogeneous phase assuming both linear and mutual termination.

The symbol g may be evaluated from the value $\bar{R}/R_c$ at the plateau, using Equation XV, and assuming $\rho(o,\delta) = \rho(o,\delta)_\infty = 0.50$ (Equation XI), and $\rho(o,o) = 0.707$ at this point.

From the value of g so obtained, $\rho(o,\delta)_o$ can be determined from the intercept of the sector curve at very short flashing times, i.e. when $b \rightarrow 0$, by a second application of Equation XV.

It can be shown from Equation XII, that,

$$\delta = \frac{(1 - (p + 1)\rho^2(o,\delta)_o)}{p - (p + 1)(1 - \rho(o,\delta)_o)^2} \qquad \text{(XVII)}$$

Using the above value of $\rho(o,\delta)_o$, δ can be determined.

From this value of δ, $\rho(o,\delta)$ can be obtained; $\rho(o,o)$ may be similarly calculated (Equation X). By combining these in Equation XV, the theoretical sector curve can be constructed, fitted to the experimental points and the lifetimes, corresponding to mutual termination, of both the homogeneous and heterogeneous chains determined.

III. The Results.

1. The concentrations used were as follows:

At 15°C, 8.30×10^{-6}M Fe^{3+}, 0.003M $HClO_4$, 0.60M acrylonitrile.
At 25°C, 8.30×10^{-6}M Fe^{3+}, 0.012M $HClO_4$, 0.60M acrylonitrile.
At 30°C, 8.30×10^{-6}M Fe^{3+}, 0.012M $HClO_4$, 0.60M acrylonitrile.

Fe^{2+} not greater than 3×10^{-7} M in all cases.

2. The Illuminated volume.

The illuminated volume of the system was 63 ml; the total volume of the cell and stem was 80 ml.

3. The rate of polymerisation.

The values of the relative rates at each temperature are shown in Table 402..

From these, the average rate and average deviation can be calculated. This is then converted to absolute units.

The absolute rates are calculated from the

Table 402. The rate of polymerisation.

Temperature	Relative Rate mm./min.		
15°C	.115	.106	Average rate
	.104	.105	= 0.105 mm./min.
	.106	.104	
	.104	.105	Average deviation
	.106	.0924	= .005
	.105	.121	
	.105	.107	Absolute rate
	.101	.108	= 1.80×10^{-6} (moles/l) sec^{-1}
	.106	.107	
	.101	.110	
	.101	.110	
	.0998	.102	
	.111	.103	
25°C	.108	.111	Average rate
	.110	.121	= 0.114 mm./min.
	.108	.112	Average deviation
	.112	.115	= .005
	.117	.112	
	.126	.120	Absolute rate
	.114	.116	= 1.73×10^{-6} (moles/l) sec^{-1}
30°C	.147	.128	Average rate
	.137	.132	= 0.135 mm./min.
	.146	.132	Average deviation
	.144	.123	= .006
	.139	.137	
	.134	.131	Absolute rate
	.129		= 2.01×10^{-6} (moles/l) sec^{-1}

shrinkage factors given in Table 201 of Chapter 2, and the known illuminated volume.

4. The rate of initiation.

If D is the increase in the measured optical density of the colorimetric solutions corresponding to a time t in minutes, then ,

$$\frac{d(Fe^{2+})}{dt} = \frac{25}{20}.\frac{0.25}{11100}.\frac{80}{63}.\frac{1}{60}.\frac{D}{t} = 5.96 \times 10^{-7} \frac{D}{t}$$

The results are summarized in Table 403.

Table 403. The rate of initiation.

Temp. °C	D/t min^{-1}	Absolute rate (mole/l)sec^{-1}	$\frac{1+\delta}{1-\delta}$	$\frac{dOH}{dt}$ = Q,(mole/l) sec^{-1}
15	3.16×10^{-4}	1.88×10^{-10}	1.41	2.65×10^{-10}
25	2.20×10^{-4}	1.31×10^{-10}	1.05	1.38×10^{-10}
30	2.68×10^{-4}	1.59×10^{-10}	1.57	2.50×10^{-10}

The values in column 2 are obtained from Figures 304, 305, and 306.

The Equation,

$$\frac{d(OH)}{dt} = Q = \frac{1+\delta}{1-\delta}.\frac{dFe^{2+}}{dt}$$

also follows from Kutschke's treatment. This is to allow for the consumption of Fe^{2+} in a linear termination step. The constant δ is derived from the intercept as described in Section II.3. The evaluation is given in the next section.

5. The sector curves.

The experimental ratios and the calculated sector curves are shown in Figures 401, 402 and 403, for the systems described above.

The plotted ratios are obtained by interrupting the light during the steady rate period and then measuring the reduced rate. If there was a variation in the steady rate in that time, the average steady rate was used in the ratio. The points given at $\log t_f = \bar{3}.0$ are those obtained from the wire gauze. The ratio that would be obtained using the fast sector, to give the same value of the intensity exponent, is plotted. The points at $\log t_f = \bar{3}.7$ are from the fast sector running at 3000 r.p.m.

At least five minutes were required for the rate to fall to the lower value.

From the experimental ratios, it is seen that the intensity exponent, evaluated from very short flashing times, is slightly greater than 0.5. This effect is not marked at 25°C, but is prominent at 15°C and 30°C. For $\bar{R}/R_c = 0.707$, the intensity exponent is 0.50; for

$\overline{R}/R_c = 0.68$, $n = 0.55$. This variation is within the experimental error of the calculation of the intensity exponent as in Figure 302, but it does play an important part in the derivation of the sector curve.

James (1952) has shown that at high concentrations, ferrous ion acts as a linear terminator in a manner illustrated in the mechanism presented in Chapter 3, page 318. A linear terminating step leads to an intensity exponent at some intermediate value between 0.50 and 1.0, depending on the ferrous concentration. For ferrous ion concentrations of not greater than 5×10^{-7} M, James found an intensity exponent of 0.51 at 25°C. Figure 402 shows that this is also true in this work at 25°C, where the ferrous concentration is not greater than 3×10^{-7} M.

No explanation can be offered for the deviations at 15°C or 30°C, other than to say that, for the lower acid concentration and temperature in the first case, and for the higher temperature in the second case, the above limits on the ferrous concentration may not hold.

The experimental intercepts and plateaux, and the constants calculated from them by Equations XIV and XVI are shown in Table 404.

Table 405 gives the theoretical values of $\overline{R}/R_c$ calculated from these constants.

Table 404. Derivation of the sector curve constants.

Temp. °C	Intercept	Plateau	$\rho(o,\delta)_o$	g	δ	% linear termination
15	0.687	0.630	0.661	1.30	.169	29
25	0.704	0.618	0.700	1.32	.0244	5
30	0.678	0.625	0.646	1.16	.221	36

Table 405. Theoretical sector curves.

Log b.	$\bar{R}/R_c$ calculated		
	15°C	25°C	30°C
$\bar{2}.000$	0.687	0.704	0.678
$\bar{1}.000$	0.687	0.704	0.678
$\bar{1}.477$	0.686	0.703	0.677
0.000	0.679	0.698	0.669
0.301	0.666	0.688	0.655
0.602	0.650	0.674	0.638
1.000	0.633	0.652	0.623
1.778	0.620	0.627	0.606
2.000	0.611	0.618	0.594
2.301	0.598	0.612	0.574
2.602	0.578	0.600	0.548
3.000	0.550	0.579	0.517

The theoretical curves and experimental points were fitted together and the points at which $\log b = 0$ were compared with the actual flashing times. While the results at long flashing times are not very reliable, some estimate can be made of the lifetimes of the buried chains.

6. The lifetime of the growing chains.

If subscripts 1 and 2 refer to cases of linear and mutual termination respectively, the related lifetimes are connected by the expressions:

$$\tau_1 = \frac{1-\delta}{2\delta}\cdot\tau_2; \quad \frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}; \quad \tau = \frac{1-\delta}{1+\delta}\cdot\tau_2$$

where τ is the overall lifetime of the growing chain.

The lifetime of the buried centres, e, can be determined approximately, from the lower half of the sector curve. The results are tabulated in Table 406.

Table 406. Lifetimes of the growing chains.

Temp. °C	Log τ_2	τ_2 secs.	τ_1 secs.	τ secs.	e sector curve seconds	e from die aways seconds
15	0.40	2.51	6.17	1.78	100	300
25	0.04	1.10	22.0	1.05	100	170
30	0.28	1.19	3.37	1.22	60	170

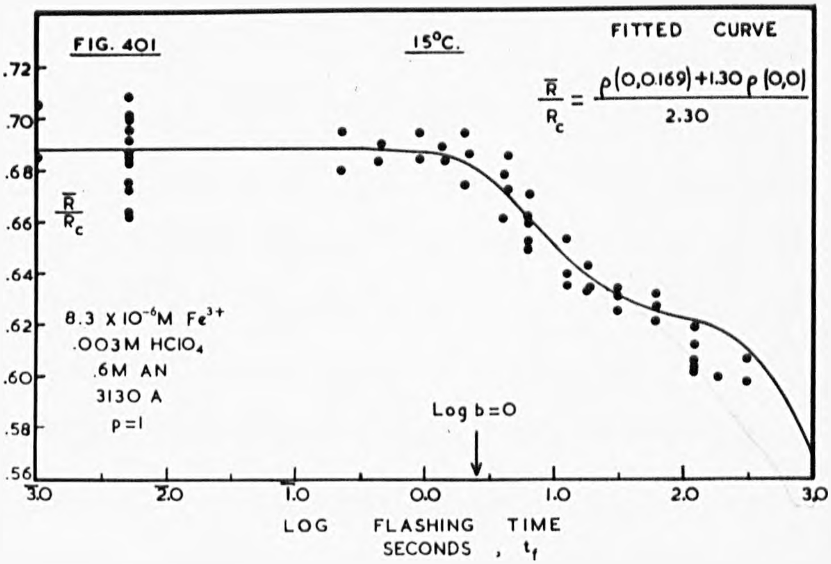


FIG. 401

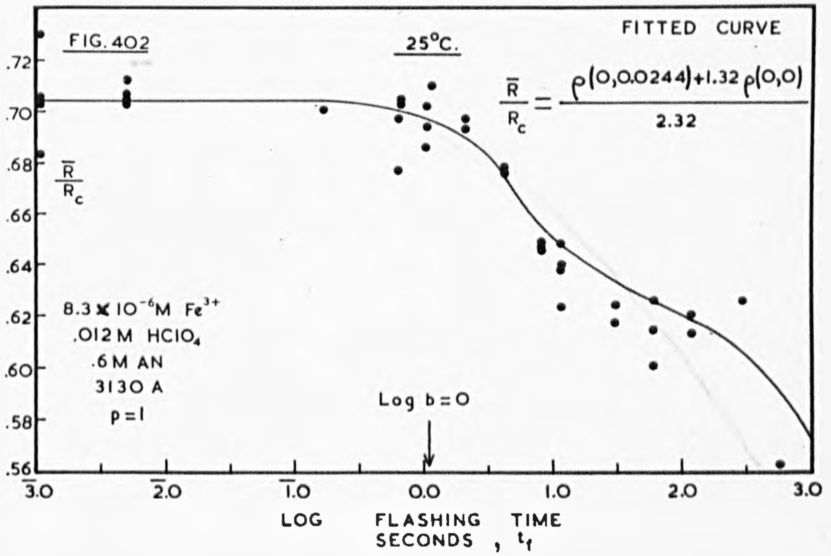


FIG. 402

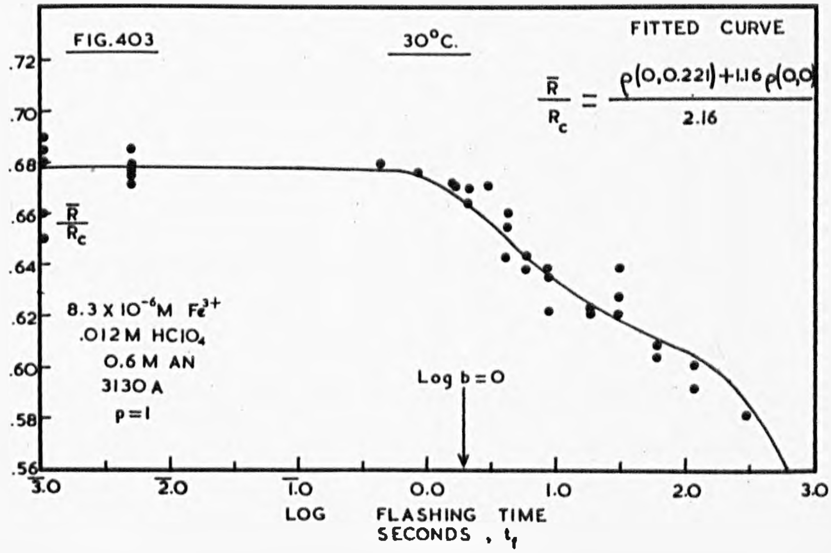


FIG. 403

IV. Evaluation of the Rate Constants and Activation Energies.

1. The activation energy of polymerisation, $E_p - \frac{1}{2}E_t$.

Since the concentration of the initiating complex varies with the temperature, two arbitrary concentrations, near those actaully used, were chosen. At these concentrations, the absolute rate at each temperature could be calculated. The logarithms of the absolute rate against the reciprocal of the absolute temperature are plotted in Figure 404. Both give a reasonable, straight line. The activation energy, $E = E_p - \frac{1}{2}E_t$, has a value of 4.8±0.2 kcal/mole for both concentrations.

2. Rate constants of propagation and termination at 15°C, 25°C and 30°C.

Assuming the existence of a photostationary state, the rate constants may be evaluated from the following equations:

$$C_s = \tau Q; \qquad \frac{-d(m_1)}{dt} = k_p(m_1)C_s; \quad \tau_2 = \frac{1}{k_t.C_s}; \quad \tau_1 = \frac{1}{k_t'.(B)}$$

$$k_p = \frac{-d(m_1)/dt}{\tau.Q.(m_1)}; \quad k_t = \frac{1}{Q.\tau.\tau_2}; \quad k_t' = \frac{1}{(B).\tau_1}$$

where C_s = the concentration of the growing chains under steady illumination.

Q = rate of formation of unit chains per unit volume.

(B) = the concentration of the linearly terminating species.

Substituting the values given in Tables 402, 403 and 406, and since $(m_1) = 0.60$ M, and letting $(E) = 3 \times 10^{-7}$ M, the following rate constants are obtained. The total rate is used for $-d(m_1)/dt$. James' values at 25°C are also quoted.

Table 407. The rate constants from the total rate.

Temp. °C	k_p (l/mole) sec^{-1}	k_t (l/mole) sec^{-1}	k_t' (l/mole) sec^{-1}	$k_p/k_t^{\frac{1}{2}}$
15	6.6×10^3	8.5×10^8	5×10^5	0.23
25	2.0×10^4	6.3×10^9	2×10^5	0.25
James' values	6.4×10^3	9.3×10^8	1.1×10^5	0.21
30	1.1×10^4	1.7×10^9	10×10^5	0.26

The logarithms of these values are plotted against the reciprocal of the absolute temperature in Figure 405 (k_p overall) and Figure 406.

The points do not fall on a straight line. Only by incorporating James' results can an approximation be obtained. This gives a value to the activation energy of propagation of 6±2 kcal/mole and a frequency factor of about 10^8. The plot for the rate constant of mutual termination is no better. The values in this case are 7±2 kcal/mole for the energy of activation and a frequency factor of about 10^{14}. The limits of accuracy of the activation energies are only estimated; the actual errors are probably much greater.

Since there is little linear termination in this system, the values of k_t' will also have a large error. For this reason, they are not plotted.

An attempt could be made to evaluate the rate constants of the buried centres from their lifetimes, assuming that the monomer concentration was the same about the buried radical as in solution. However, it is felt that there are too many errors to give results of any value.

V. Discussion.

It can be calculated, from Equations XIV and XVI, that over 50% of the rate is carried by the buried centres (Table 408). If this is the case, then only the rate associated with the homogeneous polymerisation can be used for calculating the homogeneous rate constants.

A correction should also be made to Q, the rate of formation of unit chains per unit volume, but it is not known what proportion of the light goes to initiate chains that will effectively remain "in solution". This rate cannot be divided with the data available here. Also, it is naive to assume that the homogeneous system is distinct from the heterogeneous system. A chain may start growing "in solution", and at some point in its growth become occluded, thus becoming a heterogeneous centre.

If k_p is recalculated using only the homogeneous rate of polymerisation, other factors remaining unchanged, lower limiting values can be obtained. See Table 408.

For the same reason, the values of k_t are only limiting values. However, k_t', although inaccurate, will be real. Since an equation assuming mutual termination exclusively, gives a good fit for the die away of buried centres, it can be inferred that there is little linear termination in the buried radicals. Hence, the values used to calculate k_t' refer to the homogeneous phase only.

The same corrections are applied to James' results.

Table 408. The lower limit of the values of the propagation rate constant.

Temp °C	Total rate (moles/l) sec^{-1}	Fraction of rate in homo. phase	Homo. rate (moles/l) sec^{-1}	k_p (l/mole) sec^{-1}
15	1.80×10^{-6}	0.43	7.8×10^{-7}	2.9×10^{3}
25	1.73×10^{-6}	0.43	7.5×10^{-7}	8.6×10^{3}
James' values	2.18×10^{-6}	0.76	1.7×10^{-7}	4.9×10^{3}
30	2.01×10^{-6}	0.46	9.3×10^{-7}	5.1×10^{3}

These values are plotted as k_p homogeneous, in Figure 405. They give an activation energy of 7±2 kcal/mole, and a frequency factor of about 10^9 which is within the experimental error of the first determination. Again the errors are estimated and are probably larger than quoted.

If we assume that the proportion of the reaction carried by the buried centres is the same at the three temperatures, then while the rate constants are only limiting values, the activation energies may still be roughly correct. The experimental results seem to bear this out (Table 408, column 3, and the homogeneous plot of Figure 405).

As has been shown in Chapter 1 Section E, few rate constants or activation energies have been evaluated for systems similar to acrylonitrile. The ratio $k_p/k_t^{\frac{1}{2}}$ agrees well with the work of James and Evans, Santappa and Uri (1951). Except for the results of Burnett and Melville (1950) on vinylidene chloride, the activation energy of propagation in radical polymerisation systems is generally between 2 and 7 kcal/mole; and the activation energies of mutual termination are between 0 and 5 kcal/mole. The former agrees with E_p calculated from this work, but the termination activation energies are generally smaller than calculated here. However, the value of

7 kcal/mole for E_t probably includes a contribution from the buried centres.

The frequency factors of propagation are of the same order as those in other polymerisations, but the frequency factor of termination is perhaps high, in common with, but not as high as, the values of Burnett and Melville (1950). The cause of the high result is likely the same in both cases.

The value $E_p - \frac{1}{2}E_t = 4.8$ kcal/mole is comparable to those reported in the literature and may be a real value, as pointed out above.

Table 406 compares the lifetimes of the buried centres, measured from the sector curve, with those from the die away equation. It is to be noted that the lifetimes measured in the illuminated system are shorter than those in the dark. This is probably due to termination between chains "in solution" with buried centres in the polymer particles. The lifetime again appears to decrease with increasing temperature.

Further evidence for the steady state in the polymer particle is provided by observation of the time required for the rate for total illumination to fall to the rate for interrupted illumination. If the chains were completely homogeneous with a lifetime of one second, the rate would fall to the lower rate almost instantaneously. Observations show, however, that at least five minutes are required before the reduced rate becomes steady.

VI. Conclusions.

From the evaluation of the constants of the theoretical sector curve it can be seen that more than half of the rate is carried by the buried centres. Hence, in order to evaluate rate constants, the rate must be partitioned between the homogeneous and heterogeneous systems. However it is not possible to do this with the rate of initiation (the rate of formation of chains per unit volume) as it is not known how many chains remain "in solution" throughout, nor when a homogeneous chain becomes a heterogeneous chain. Therefore, the evaluation of the rate constants, using the homogeneous portion of the rate, but the overall rate of initiation, will only lead to the lower limit of these values. The results are summarized in Table 409.

The activation energies may have real values, however, if the proportion of the homogeneous rate is the same at the three temperatures considered. The frequency factors are less reliable.

Table 409. Limiting values of the rate constants.

Temp. °C	k_p (l/mole)sec^{-1}	k_t (l/mole)sec^{-1}	k_t' (l/mole)sec^{-1}
15	2.9×10^3	8.5×10^8	5×10^5
25	8.6×10^3	6.3×10^9	2×10^5
30	5.1×10^3	1.7×10^9	10×10^5

The results may be summarized as follows:

$$E_p = 7 \pm 2 \text{ kcal/mole} \qquad A_p = 10^9$$

$$E_t = 7 \pm 2 \text{ kcal/mole} \qquad A_t = 10^{14}$$

$$E_p - \tfrac{1}{2}E_t = 4.8 \pm 0.2 \text{ kcal/mole}$$

It is seen that a mathematical analysis of the sector curve does predict that a large proportion of the rate is carried by the buried centres in the coalesced polymer particles. Since steady rates are observed, this confirms that a steady state is established in the buried radicals and confirms, in general, the conclusions of Chapter 3.

Therefore the polymerisation of acrylonitrile in aqueous solution is capable of reaching a steady state. This steady state is not simple as it is composed of a homogeneous and a heterogeneous contribution.

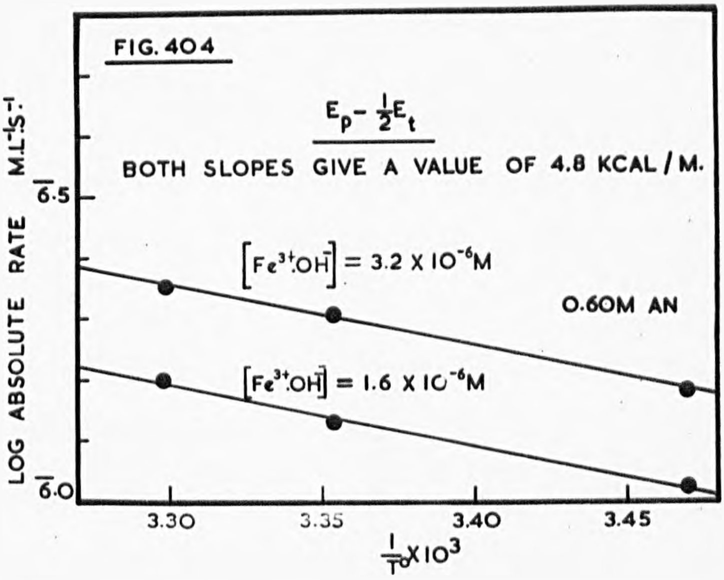


FIG. 404

$E_p - \frac{1}{2}E_t$

BOTH SLOPES GIVE A VALUE OF 4.8 KCAL / M.

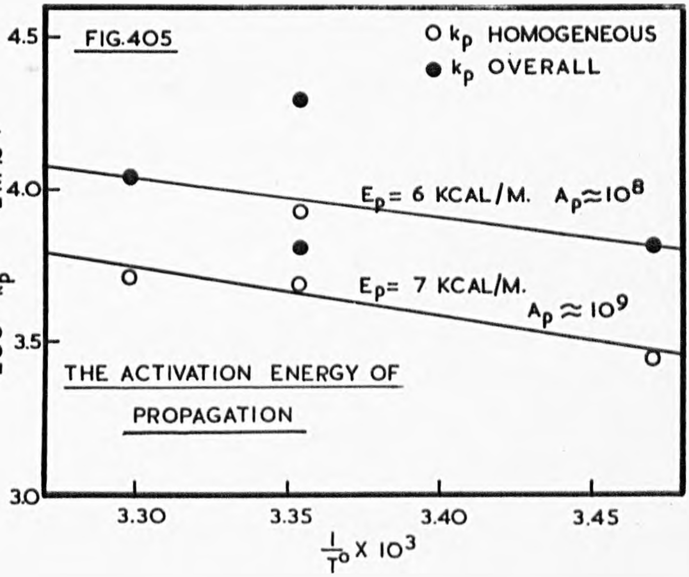


FIG. 405

THE ACTIVATION ENERGY OF PROPAGATION

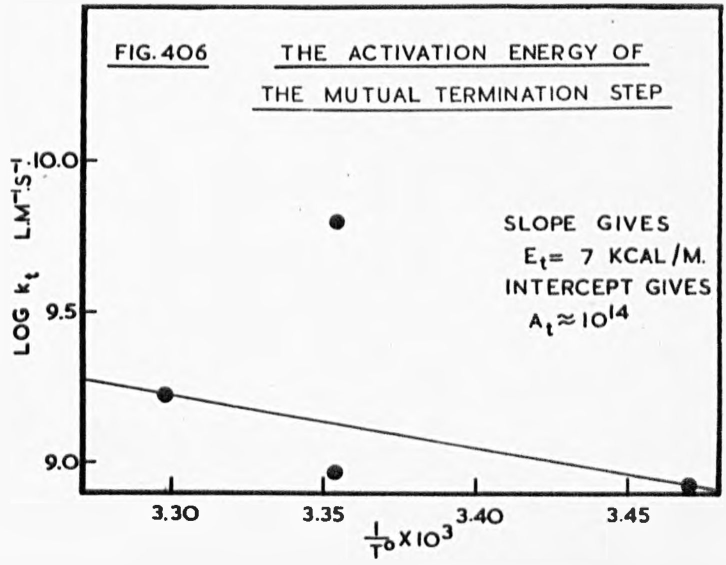


FIG. 406

THE ACTIVATION ENERGY OF THE MUTUAL TERMINATION STEP

Calculations of the experimental results obtained in such a system, lead to the lower limits of the values of the rate constants of propagation and mutual termination in the homogeneous phase.

Calculations on the heterogeneous system involve too many untried assumptions to be of value.

The activation energies obtained from these constants may be real. The frequency factors are also lower limiting values. The results for E_p and A_p are in general agreement with those in the literature; those for E_t and A_t are somewhat higher than those reported.

CHAPTER 5. SOME RESULTS AT 40°C AND 50°C.

I. Introduction.

In order to get as accurate values of the activation energy as possible, it is necessary to do measurements at widely separated temperatures. With this end in view, an aqueous acrylonitrile system was exposed to irradiation at 40°C. However, strange results were observed. The system would not polymerise at low monomer concentrations, but polymerised exceedingly quickly at high monomer concentrations. The intensity and initiator exponents remained the same.

II. The Intensity Exponent.

A value of 0.5 was found at both 40°C and 50°C for the system 8.3 x 10^{-6} M Fe^{3+}, 0.012 M $HClO_4$ and a constant monomer concentration. Both the fast sector and a wire gauze were used as in Chapter 3, Section A.III.

III. The Initiator Exponent.

The rate of initiation was again changed by varying the pH of the solution. The monomer concentration was kept constant at each temperature. The few results that were obtained show that an exponent of 0.5 is probably correct. See Figure 502.

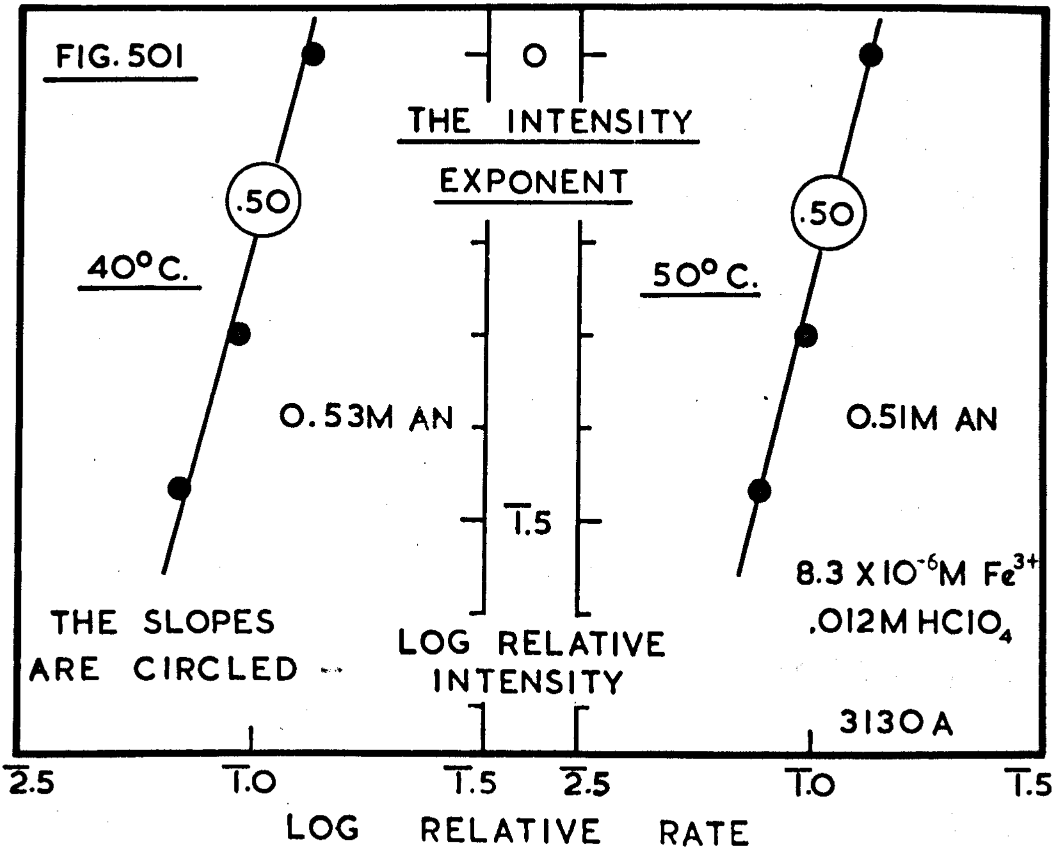


FIG. 501

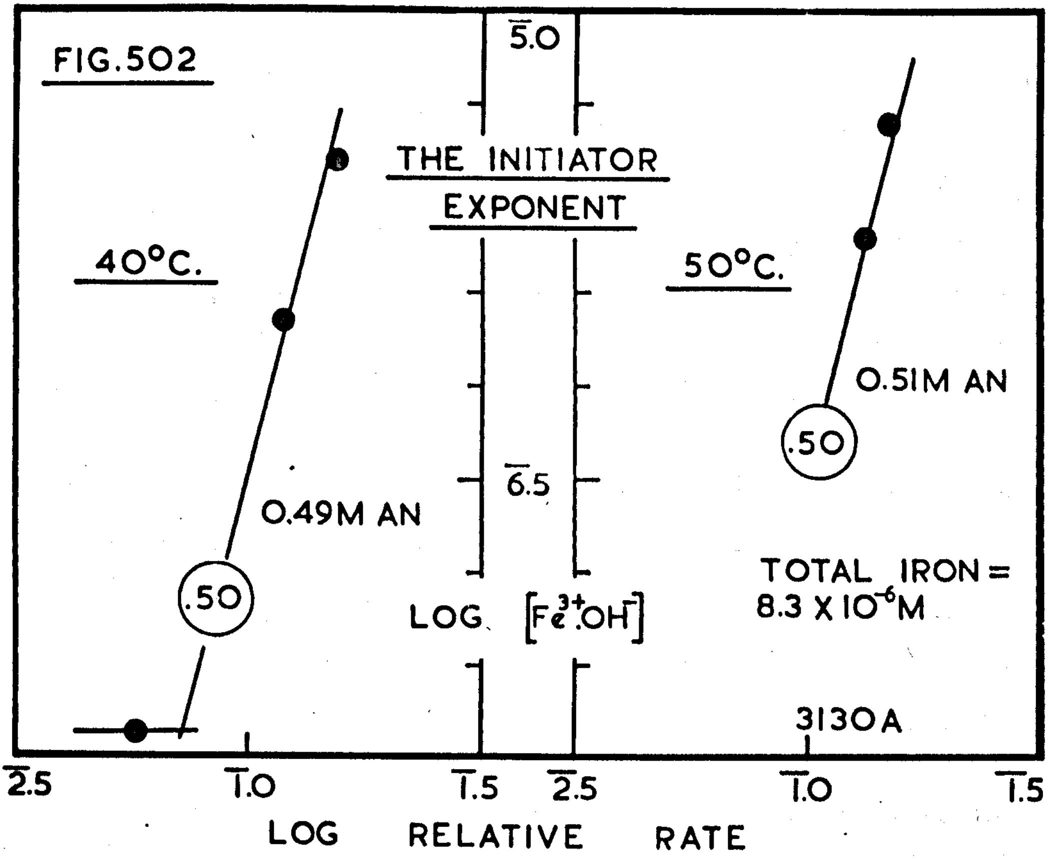


FIG. 502

IV. The Monomer Exponent.

The rate of polymerisation at 40°C was investigated over the complete range of monomer concentrations available in aqueous solution. The initiator concentration was kept constant. The results are shown in Figure 503. The points seem to fall on a straight line which does not pass through the origin. It is to be noted that there is no discontinuity in the results as was the case at the lower temperatures (Figure 301).

The intercept on the monomer axis is similar to that observed by Dainton and Ivin (1950), which lead to an explanation in terms of the ceiling temperature of the reaction. See Chapter 1, Section B.II.6. The ceiling temperature is

$$T_c = \frac{\Delta H}{\Delta S} = \frac{\Delta H}{\Delta S^o + R\ln(m_1)} \quad \text{when } \Delta G = 0.$$

The standard state refers to unit concentration; the monomer is assumed to behave ideally. ΔH and ΔS refer to the prevailing monomer concentration.

Hence the ceiling temperature depends on the monomer concentration and is lower at low monomer concentrations.

It was thought at one time, that the results, shown in Figure 503, were due to a ceiling temperature effect, but the following calculations show that this is not likely true.

From the table of entropies given in Dainton and Ivin (1950), it can be seen that the entropy of polymerisation of vinyl monomers in solution is about -28 cal/degree.mole. The heat of polymerisation of acrylonitrile has been measured by Tong and Kenyon (1947) as -17.3 kcal/mole. The heat of solution of acrylonitrile in water can be estimated from the solubility data of Davis and Wiedemann (1945) as about 3.5 kcal/mole. At 40°C, the intercept is at a monomer concentration of 0.3 M.

With this data, an estimate of the ceiling temperature can be made.

$$T_c = \frac{-17{,}300 + 3{,}500}{-2.8 + 2.30\log(0.3)} = \frac{-14{,}000}{-30} = 470^{\circ}\text{Absolute}$$
$$= 200^{\circ}\text{C}.$$

Therefore, it appears that the observed phenomenum is not due to a ceiling temperature effect.

Similar experiments were carried out at 50°C. A straight line with a steeper slope, but the same intercept, was obtained (Figure 504). If there was a true ceiling temperature effect, the intercept would have been shifted to a higher monomer concentration.

The logarithm of the rate was plotted against the logarithm of the monomer concentration to see if there was any change in the monomer exponent (Figure 505).

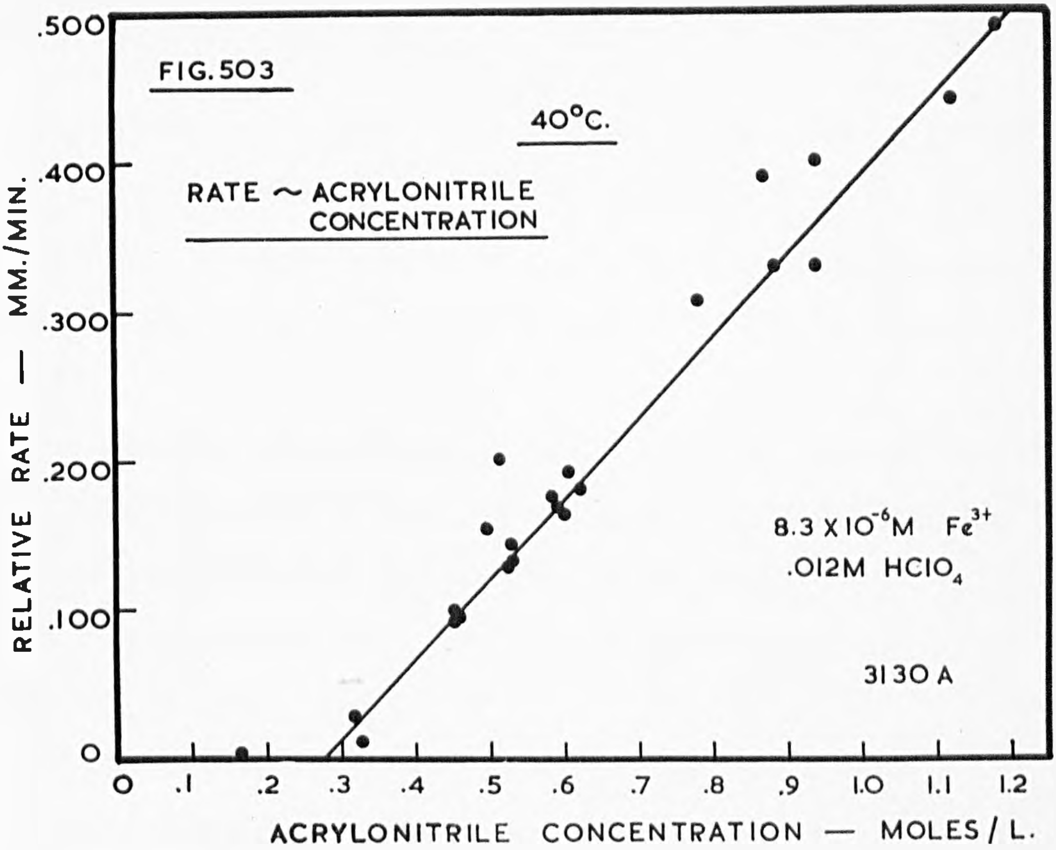


FIG. 503

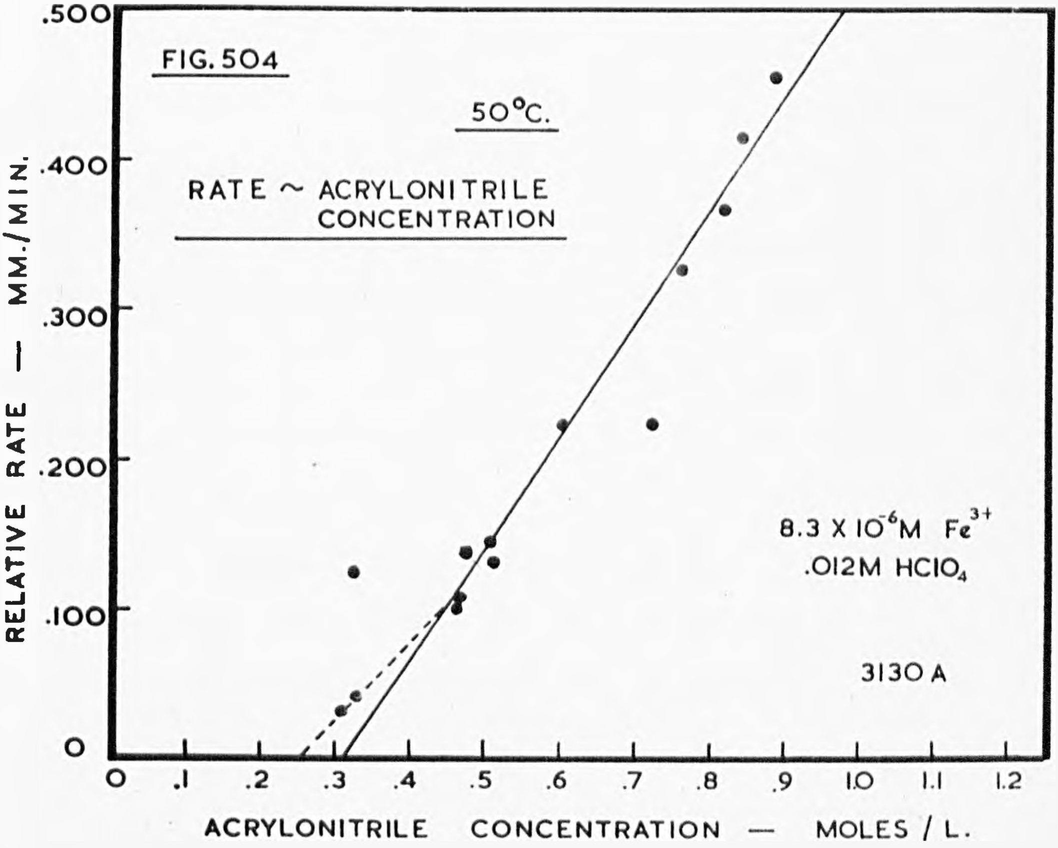


FIG. 504

The monomer exponent could then be calculated from the slope. The value at 40°C is 1.6; at 50°C it is 2.2. The results at low monomer concentrations do not fall on the straight line, but they are subject to the largest error.

Khomikovskii and Medvedev (1948) found a monomer exponent of 2.44 at 60°C for a persulphate initiated system. Cooper (1953) found a monomer exponent of 2.0 at 25°C for acrylonitrile initiated in aqueous solution by diazonium salts.

Matheson (1945) has shown that monomer exponents of up to 1.5 are possible without postulating a monomer-initiator complex. Monomer-monomer interaction will predict an exponent of 2.0. However, no probable mechanism has been devised as yet for an exponent greater than 2.0. It is even more difficult to correlate a change of monomer exponent from 1.0 to greater than 2.0 without any change in the initiator or intensity exponent.

These unusual results must be due to some heterogeneous effect.

V. The Physical Appearance of the Polymer.

At monomer concentrations of less than 0.4 M polymer was formed so slowly that it precipitated to the bottom of the cell, as was the case for low monomer concentrations at 15°C, 25°C and 30°C. (See Chapter 3, Section A.III). Precipitation of polymer was more marked for higher concentrations at 40°C and 50°C than at the lower temperatures. The polymer became thread-like in appearance; vertical filaments seemed to form in the cell. The transmission through the cell was measured as before. It was found to be high at low monomer concentrations, but appeared to be normal above 0.4 M acrylonitrile.

VI. The Rate of Initiation.

The rate of initiation was determined as at the other temperatures; the solutions were analysed colorimetrically for the rate of increase of ferrous concentration. The increase in optical density at various monomer concentrations is shown in Figures 506 and 507. The results plotted at short exposure times were those of the monomer concentration of 0.9 M or greater, i.e. those runs that reached a steady state quickly. In general, the duration of exposure increases with decreasing monomer concentration.

The rate of initiation at 15°C, 25°C and 30°C was determined at a constant monomer concentration of 0.6 M.

Most of the results seem to fall on a straight line not through the origin. A few results at short exposure

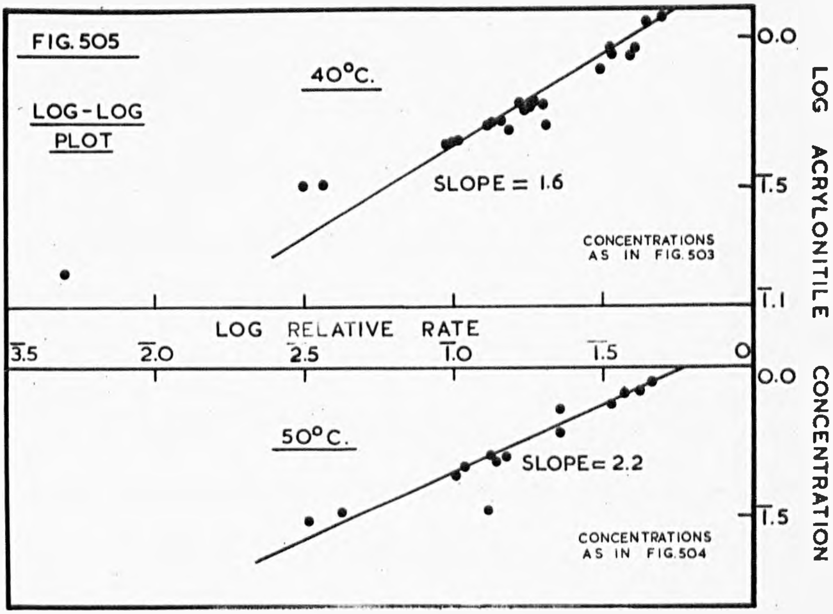


FIG. 505

LOG-LOG PLOT

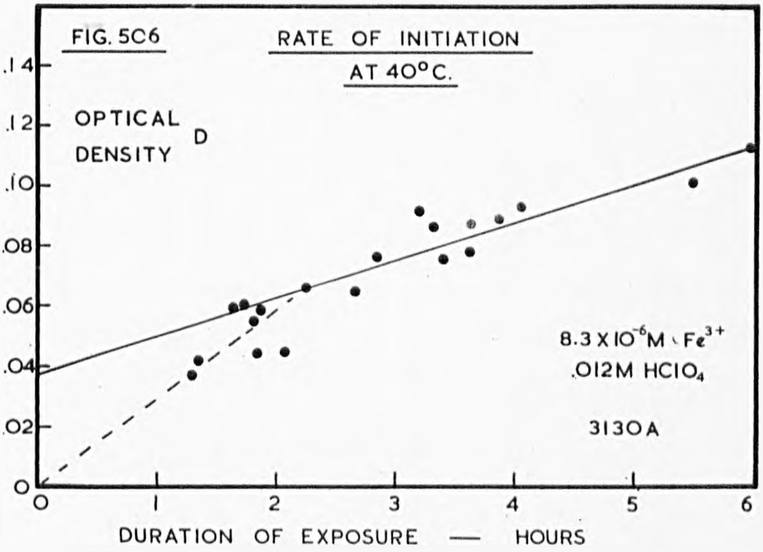


FIG. 5C6

RATE OF INITIATION AT 40°C.

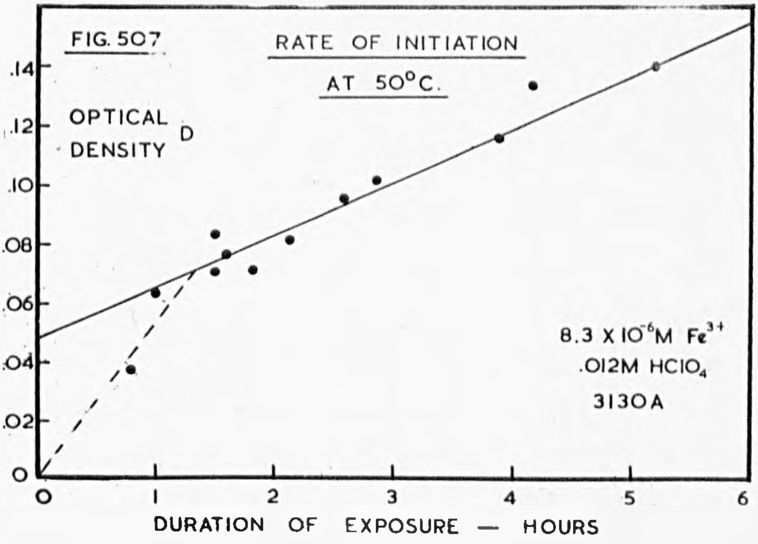


FIG. 507

RATE OF INITIATION AT 50°C.

times fall below this line and can be extrapolated to the origin which must be a point on these graphs.

VII. The Effect of Soap on Acrylonitrile at 40°C.

One per cent sodium stearate was added to the system 8.3×10^{-6} M Fe^{3+}, 0.012 M $HClO_4$ at monomer concentrations of about 0.8 M. The results are shown in Table 501. Low rates, as compared to systems in the absence of soap, were observed. The rates were not reproduceable, and were very sensitive to impurities.

Table 501. The effect of soap on acrylonitrile at 40°C.

Rate (mole/l)sec^{-1}	Acrylonitrile concentration	Rate in the absence of soap (mole/l)sec^{-1}
4.0×10^{-7}	0.79 mole/l.	38×10^{-7}
3.5×10^{-7}	0.81 mole/l.	40×10^{-7}
7.3×10^{-7}	0.84 mole/l.	42×10^{-7}
12.0×10^{-7}	0.79 mole/l.	38×10^{-7}

The rate determining factor was not thought to be a chemical effect of the soap on the propagation step, but rather a physical effect of the soap on the absorbed light intensity. The transmission of the system containing soap was of the order of ½%, which is the same as a similar system at 25°C.

No experiments were carried out using methyl methacrylate at this temperature.

VIII. Lifetime of Buried Centres at 40°C and 50°C.

Equations, assuming mutual termination only, were fitted to seven die away curves at these two temperatures for the system 8.3×10^{-6} M Fe^{3+}, 0.012 M $HClO_4$. The results are summarized in Table 502. A steady rate had been reached in each case.

Table 502. Lifetimes of the buried centres.

Temp. °C	Monomer conc. mole/l.	θ from the die away - seconds
40	.33	150
	.49	300
	.58	240
	.59	150
	.78	240
50	.46	860 ??
	.51	750 ??

These lifetimes are, in general, longer than those observed at the lower temperatures, even though it was shown that at 30°C the buried centres had a shorter lifetime than those at 15°C.

IX. Discussion.

It is almost impossible to derive a reaction mechanism of polymerisation in which the initiator and intensity exponents are 0.5 while the monomer exponent is variable and is greater than 1.0. However, if one considers the reaction from a physical point of view, a plausible explanation is possible.

It was observed at 25°C in Figure 301, that the monomer exponent was 1.0. This exponent depended on an extrapolation of results at monomer concentrations greater than 0.5 M. At lower monomer concentrations, the rate was lower than expected, due to precipitation of the polymer and the reduction in the intensity of the light absorbed.

At monomer concentrations greater than 0.6 M, the level of the absorbed light intensity is increased and kept constant by the presence of large quantities of polymer. At low concentrations, the polymer forms too slowly to build up and maintain a sufficient bulk to keep the light of absorption at this high level.

At 40°C and 50°C, this may be the case over the whole range of monomer concentrations available in aqueous solutions. In other words, the rate of light absorption and hence the rate of initiation, is dependent on the monomer concentration over the whole range, rather than only up to 0.6 M as at the lower temperatures. The graphs shown in Figures 503 and 504 correspond, therefore, to the dotted lines of Figure 301. This explanation will account for an increasing monomer exponent with increasing temperature. At higher temperatures, the monomer will precipitate more rapidly; the rate of precipitation will depend on the difference in density between the monomer and the polymer. It was shown in Chapter 1, that the polymer density was constant up to 50°C. The density of the solution decreases with increasing temperatures.

The results of Khomikovskii and Medvedev, while not affected by changing light intensity, may be explained by the high rate of precipitation at 60°C.

Further evidence in favour of this heterogeneous effect is found in Figures 506 and 507. Points corresponding to a high monomer concentration *i.e.* those of short duration of exposure, fall on a line through the origin, while those of lower monomer concentration fall below this line. The overall effect is a discontinuity. The results would best be described by a curve starting at the origin. The rate of initiation would be a line from the origin to the points corresponding to the various monomer concentrations.

At a constant monomer concentration, the points would fall on a straight line through the origin for various durations of exposure, but the slope of this line would increase with increasing monomer concentration. For systems at 15°C, 25°C and 30°C, the rate of initiation is constant and a normal monomer exponent of 1.0 is found at all concentrations above 0.5 M acrylonitrile.

The longer lifetimes observed in the buried polymer particles may be due to increased coagulation brought about by the less stable polymer particles. Even though the polymer molecules may have more kinetic energy at these temperatures, they may be occluded to a higher degree than at 30°C.

X. Conclusions.

If the above postulates are correct, a monomer exponent of 1.0 would be obtained at 40°C and 50°C if the polymer suspension was stable. The high and variable monomer exponents measured in this system are, therefore, only apparent values because of the changing rate of initiation with monomer concentration; and the changing rate of precipitation of polymer with temperature.

Since an intensity exponent and an initiation exponent of 0.5 are found, the reaction is probably describable by Equation IVa, but the system is again complex.

BIBLIOGRAPHY

Akeroyd and Kressiman (1950), Chem. and Ind., 69, 189.

Arlman and Wagner (1953), Trans. Far. Soc., 49, 822.

Arnett (1952), J. Amer. Chem. Soc., 74, 2027.

Arnett and Peterson (1952), J. Amer. Chem. Soc., 74, 2031.

Bacon (1946), Trans. Far. Soc., 42, 140.

Bamford and Barb (1953), Disc. Far. Soc., 14, 245.

Bamford, Barb and Jenkins (1952), Nature, 169, 1044.

Bamford and Dewar (1946), Nature, 158, 380.

Bamford and Jenkins (1953), Proc. Roy. Soc., A216, 515.

Barb (1952), Disc. Far. Soc., 12, 273.

Bartlett and Altschul (1945), J. Amer. Chem. Soc., 67, 812, 816.

Bartlett and Nozaki (1946), J. Amer. Chem. Soc., 68, 1495, 1686.

Bartlett and Tate (1953), J. Amer. Chem. Soc., 75, 91.

Bateman and Gee (1948), Proc. Roy. Soc., A195, 391.

Bawn (1948), The Chemistry of High Polymers, Butterworths.

Baxendale, Evans and Park (1946), Trans. Far. Soc., 42, 668.

(1946), J. Polymer Sci., 1, 466.

Baysal and Tobolsky (1952), J. Polymer Sci., 8, 529.

Bengough and Norrish (1949), Nature, 163, 325.

(1950), Proc. Roy. Soc., A200, 301.

(1953), Proc. Roy. Soc., A218, 149.

Berzlius (1833), Jahresber., 12, 63-64.

Betts, Collinson, Ivin and Dainton (1952), Annual Reports, 49, 34.

Bonsall, Valentine and Melville (1953), Trans. Far. Soc., 49, 686.

Bovey and Kolthoff (1950), J. Polymer Sci., 5, 487.

Bowen (1950), Quart. Revs., IV, 236.

Brewer (1950), National Nuclear Energy Series, IV-19B, 76.

Burk and Grummitt (1949), High Molecular Weight Inorganic Compounds, Interscience.

Burnett (1950), Quart. Revs., IV, 292.

(1950), Trans. Far. Soc., 46, 772.

Burnett and Melville (1950), Trans. Far. Soc., 46, 976.

Burns and Dainton (1950), Trans. Far. Soc., 46, 411.

Carothers (1940), The Collected Papers of W.H. Carothers on High Polymeric Substances, Interscience.

Chalmers (1934), J. Amer. Chem. Soc., 56, 912 and earlier papers.

Chapiro (1950), J. Chim. Phys., 47, 747, 764.

Collinson (1952), Dissertation, Cambridge.

Collinson and Dainton (1952), Disc. Far. Soc., 12, 212.

Cooper (1953), Chemistry and Industry, 17, 407.

Dainton and Ivin (1948), Nature, 162, 705.

(1950), Trans. Far. Soc., 46, 331.

Dainton and James (1951), J. Chim. Phys., 48, 1.

(1953), Disc. Far. Soc., 14, 244. 12, 277.

(1953), Unpublished results.

Dainton, James and Kutschke (1953), Unpublished results.

D'Alelio (1952), Fundamental Principles of Polymerisation, Wiley.

Davis and Wiedemann (1945), Ind. Eng. Chem., 37, 482.

Dickenson (1941) in Noyes and Leighton, The Photochemistry of Gases, Reinhold, p. 206.

Evans (1947), J. Chem. Soc., 263.

(1950), Tilden Lecture, J. Chem. Soc.

(1951), Disc. Far. Soc., 10, 1.

Evans, Hush and Uri (1952), Quart. Revs. VI, 186.

Evans, Santappa and Uri (1951), J. Polymer Sci., 7, 243.

Evans and Uri (1949), Trans. Far. Soc., 45, 224.

(1950), J. Soc. Dyers Colourists, 709.

Farkas and Melville (1939), Experimental Methods in Gas Reactions, MacMillan, p. 254.

Farkas and Farkas (1938), Trans. Far. Soc., 34, 1113, 1120.

Franck and Haber (1931), Sitz. Preuss. Akad. Wiss, 250.

Franck and Schiebe (1928), Z.f. physik. Chem., A139, 22.

Gee (1952), Trans. Far. Soc., 48, 515.

Goodyear (1838), see Mark and Tobolsky, 2nd edition, p. 444.

Grassie and Melville (1951), Proc. Roy. Soc., A207, 285.

Harkins (1947), J. Amer. Chem. Soc., 69, 1428.

(1950), J. Polymer Sci., 5, 217.

Harmon and Eyring (1942), J. Chem. Phys., 10, 557.

Hart and Smets (1950), J. Polymer Sci., 5, 55.

Haward (1948), J. Polymer Sci., 3, 10.

Higginson and Wooding (1952), J. Chem. Soc., 760, 774.

Hulbert, Harmon, Tobolsky and Eyring (1943), Ann. N.Y. Acad. Sci., 44, 371.

Ihrig and Allyea (1953), J. Amer. Chem. Soc., 75, 2917.

James (1952), Dissertation, Cambridge.

James and Dainton (1953), Unpublished results.

Johnson and Tobolsky (1952), J. Amer. Chem. Soc., 74, 938.

Khomikovskii (1948), Doklady Akad. Nauk. U.S.S.R. 60, 615.

Khomikovskii and Medvedev (1948), J. Chem. Phys. U.S.S.R. 22, 1027.

Kolthoff and Ferstandig (1951), J. Polymer Sci., 6, 563.
Magee, Shand and Eyring (1941), J. Amer. Chem. Soc., 63, 677.
Mark and Tobolsky (1950), Physical Chemistry of High Polymeric Systems, 2nd edition, Interscience.

Marvel and Cowan (1939), J. Amer. Chem. Soc., 61, 3156.

Marvel, Weil, Wakefield and Fairbanks (1953), J. Amer. Chem. Soc., 75, 2326.
Matheson (1945), J. Chem. Phys., 13, 584.

Matheson, Auer, Bevilacqua and Hart (1949a), J. Amer. Chem. Soc., 71, 497.

(1949b), J. Amer. Chem. Soc., 71, 2610.

(1951a), J. Amer. Chem. Soc., 73, 1700.

(1951b), J. Amer. Chem. Soc., 73, 5395.

Mayo, Lewis and Walling (1948), J. Amer. Chem. Soc., 70, 1529.

Melville (1952), Liversidge Lecture, J. Chem. Soc., 1547.

Melville and Bickel (1949), Trans. Far. Soc., 45, 1049.

Melville and Majury (1951), Proc. Roy. Soc., A205, 309.

Melville and Valentine (1950), Trans. Far. Soc., 46, 210.

Morgan (1946), Trans. Far. Soc., 42, 169.

Mulliken (1942), Rev. Mod. Phys., 14, 265.

Norrish and Smith R.R. (1942), Nature, 150, 336.

Nozaki (1947), Disc. Far. Soc., 2, 337.

Olson and Simonson (1949), J. Chem. Phys., 17, 1322.

Parravano (1950), J. Amer. Chem. Soc., 70, 185, 628, 3856, 5546.

Pepper (1952), Seminar, Leeds, Unpublished.

Potterill, Walker and Weiss (1936), Proc. Roy. Soc., A156, 561.

Rabinowitch (1942), Rev. Mod. Phys., 14, 112.

Rabinowitch and Stockmayer (1942), J. Amer. Chem. Soc., 64, 335.

Regnault (1838), Ann. Chim. (2), 69, 157.

Reinhardt (1943), Ind. Eng. Chem., 35, 422.

Rice (1942), J. Chem. Phys. 10, 440.

Schulz and Blaschke (1941), Z. physik. Chem., B50, 305.

(1941), Z. electrochem. angew. physik. Chem., 47, 749.

(1942), Z. physik. Chem., B51, 75.

Smith P. (1951), Dissertation, Cambridge.

Smith W.V. (1948), J. Amer. Chem. Soc., 70, 3695.

Smith W.V. and Ewart (1948), J. Chem. Phys. 16, 592.

Staudinger (1932), Der hochmolekularen org. Verbindungen.

Taylor and Tobolsky (1945), J. Amer. Chem. Soc., 67, 2063.

Tkachenko and Khomikovskii (1950), Doklady Akad. Nauk. U.S.S.R. 72, 543.

Tong and Kenyon (1947), J. Amer. Chem. Soc., 69, 2245.

Trommsdorff (1944), B.I.O.S. Report 363, Item 22.

Vogel (1951), Quantitative Inorganic Analysis, 2nd edition, Longmans.

Weiner (1951), J. Polymer Sci., 7, 1.

Weiss (1935), Nature, 136, 794.

(1947), Disc. Far. Soc., 2, 104.

Ziegler, Deparade and Kuhlhorn (1950), Liebig's Ann., 567, 151.