The photolysis of acetone

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THE PHOTOLYSIS OF ACETONE

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ABSTRACT.

The literature dealing with the primary processes in the photolysis of acetone with ultra-violet light has been reviewed and the important areas where reliable data exists have been identified. Gaps in the knowledge necessary for a complete description of the process have also been noted and measurements have been made which made possible a much fuller description of the primary process. An apparatus has been constructed which measures the light emission from the excited states formed by electronically excited acetone and the effect of temperature, acetone pressure, oxygen, iodine and Xenon on the excited states has been measured. Quantum yields of methyl iodide from the photolysis of acetone at 3130Å have been measured by a technique devised specially for this work and by combining these results with the light emission work an over-all mechanism has been produced which embraces both sets of data. The role of the triplet excited state has been shown to be more important than was postulated before this work commenced and the results obtained indicate that the mechanism of the primary process must be more complex than previous workers had supposed.

INTRODUCTION.

Many reports on the u.v. photolysis of acetone have appeared in the literature. The work was originally given special attention because the photolysis of acetone provides a convenient source of methyl radicals. Later investigation showed that when pure acetone vapour above 100°C is photolysed at 3130Å, the quantum yield of acetone decomposition, Φ_d is close to unity and the overall reaction gives two methyl radicals and a molecule of carbon monoxide. The measurement of the amount of carbon monoxide formed found application as a convenient actinometric standard.

The study of u.v. absorption and light emission (phosphorescence and fluorescence) has provided useful information concerning the excited states produced before decomposition.

The importance of elucidating the mechanism of energy distribution in the acetone molecule before the primary split into an acetyl and a methyl radical was demonstrated by Martin and Sutton (4). They showed that when acetone vapour above 100°C is photolysed at 3130Å in the presence of iodine, the primary quantum yield for decomposition, Φ_d is reduced to a value well below unity.

Most workers have studied either the light emission or the photochemical yields of products under various conditions and have produced mechanisms which were aimed primarily at explaining the results in the particular field investigated. The present work is directed towards extending the measurement of both the light emission and the de-exciting effect of iodine in an attempt to elucidate a mechanism which will account quantitatively and simultaneously for the light emission and photochemical yield date.

CHAPTER I.

THE PHOTOLYSIS OF ACETONE - A REVIEW.

The published work in this field is so voluminous that the whole of it cannot be reviewed here (for reviews see 1,2,3). Only those sections which are basic to the whole subject or of direct application to the work contained in this thesis will be discussed.

The Primary Process in Acetone Photolysis.

The primary process will be taken to comprise the events between the absorption of a photon and the disappearance of the molecule or its return to its original state.

The energy absorbed will be re-distributed in one of the following ways;

a. Chemical reaction or decomposition,
b. Light emission (fluorescence or phosphorescence),
c. Conversion to thermal energy either by collision or internal conversion.

Useful information on the primary process will be given by the following types of data.

(1) The absorption spectrum will indicate the energy absorbed and taken with the bond strengths in acetone may exclude certain modes of dissociation. A truly continuous absorption spectrum indicates that all the excited molecules dissociate within a vibration period. Discrete absorption implies that light emission from the de-activation of the excited state is possible.

(2) Fluorescence and phosphorescence. Light emission will give information about the excited states formed. The emission spectra will be useful in the same way as in (1). The effect of pressure, temperature, wavelength and added gases on the

excited states may be studied by means of the light emission,

(3) The nature of the reaction products.

The number of possible mechanisms can be limited to those which can give the observed reaction products. The products formed when foreign molecules (e.g. scavengers such as iodine, oxygen or nitric oxide) are present, are also useful in this respect. When scavengers are added their possible effect in changing the primary process must be considered.

(1) Spectroscopic Information.

The Absorption Spectrum.

Acetone shows a broad region of absorption associated with the carbonyl group between about 3500Å and 2300Å and another starting at and continuing below 2000Å. Very little photochemical work has been done at wavelengths below 2000Å: the wavelengths most investigated have been 3130Å and 2537Å which fall in the first of these absorption regions. These absorption regions are now recognised (50) as being associated respectively with a $\pi^* \leftarrow n$ and a $\pi^* \leftarrow \pi$ or $\sigma^* \leftarrow n$ transition in the carbonyl group of the molecule.

Some structure has been reported (24, 20, 25) at about 3130Å but at the resolutions used it is uncertain whether there exists solely a discrete spectrum or whether there is an underlying continuous absorption. There is a suggestion of the fuzziness in bands which is typical of predissociation of the upper state. The excited state(s) produced by absorption at 3130Å is capable of light emission (see next section) and this virtually requires structure in the absorption at these wavelengths. As the wavelength is decreased to below 3130Å the absorption spectrum becomes more and more diffuse until, by 2537Å the absorption is probably truly continuous and this is consistent with the observation that at that shorter wavelength no light emission occurs and the primary quantum yield for decomposition $\Phi_d=1$ (26, 27) Measurements of the absorption coefficient in the region below 3000Å shows a gradual increase to a maximum at about 2750Å (25) followed by a decrease until absorption caeses at about 2300Å. This behaviour is characteristic of absorption to a continuum but it is visually apparent that this overall trend is modified in that the are subsiduary maxima. It is worth noting that, because of the many low vibrational frequencies in the acetone ground state the natural Maxwell-Boltzman distribution will populate appreciably several vibrational levels in the absorbing molecules and lead to complications in the absorption spectrum.

The difficulties in the interpretation of absorption spectra of polyatomic molecules are very great. Some success has been achieved with highly symmetrical molecules such as pyridine (13, 14) and benzene (15, 16, 17), and with the relatively simple molecule of formaldehyde (18, 19). Acetone is not highly symmetrical and no detailed interpretation in terms of the primary process has yet been achieved.

The Emission Spectrum.

When excited by light of 3130Å acetone emits light in the region of 3800Å to 4700Å with a maximum intensity at about 4550Å (34, 35, 36, 37, 28, 39). The wavelength of the maximum intensity is sensitive to changes in temperature and the presence of certain gases (see later). An emission, often described as "the green phosphorescence", has been shown to originate in biacetyl which is a major photolysis product at temperatures below about 70°C.

In the earlier work biacetyl was sometimes present as impurity in the acetone. At 50°C the ratio of the total true emission from acetone ("the blue emission") to the absorbed intensity has been shown (39) to be about 2 x 10^{-3}.

There is a gap of 300Å between the long-wavelength limit of absorption (at about 3500Å) and the short-wavelength limit of emission (about 3800Å) showing that energy is lost in the excited state between the formation of the state by absorption and its subsequent emission: the 0,0 transition can be tentatively placed at 3600 ± 200Å. This behaviour is of course usual. As the excited states are usually more loosely bound than ground states, the Frank-Condon principle ensures that absorption occurs to a highly vibrationally excited state of the upper electronic state and this vibrational excitation is degraded (by collision or internally) before emission.

Flash excitation followed by a subsequent study of the decay of emission has shown (35) that, at 25°C, the emission is of at least two kinds: a long-lived component, the phosphorescence, with a half life of about 2 x 10^{-4} seconds, and a short-lived component, the **fluorescence**, with a half-life of about 8 x 10^{-6} seconds. This last figure agrees very well with the mean lifetime of about 3 x 10^{-6} seconds of the excited state estimated (38) from the integrated absorption coefficient. This also suggests that the fluorescence originates from the same state as that produced by absorption.

At 25°C the phosphorescence:- (35)

(a) contributes about 90% of the emission intensity.

(b) has some demonstrable structure.

(c) is not quenched by hydrogen or nitrogen.

(d) is strongly quenched by oxygen, nitric oxide and biacetyl.

(e) is quenched by rise in temperature, being virtually eliminated by 150°C.

Since the phosphorescence can be quenched by reagents such as oxygen and nitric oxide which do not effect the fluorescence, the fluorescence can be studied in isolation by quenching the phosphorescence. Phosphorescence, however, can only be studied by a difference technique i.e. by measuring the difference between the quenched and unquenched systems.

The intensity of the fluorescence:-

(a) is unquenched by oxygen or nitric oxide.

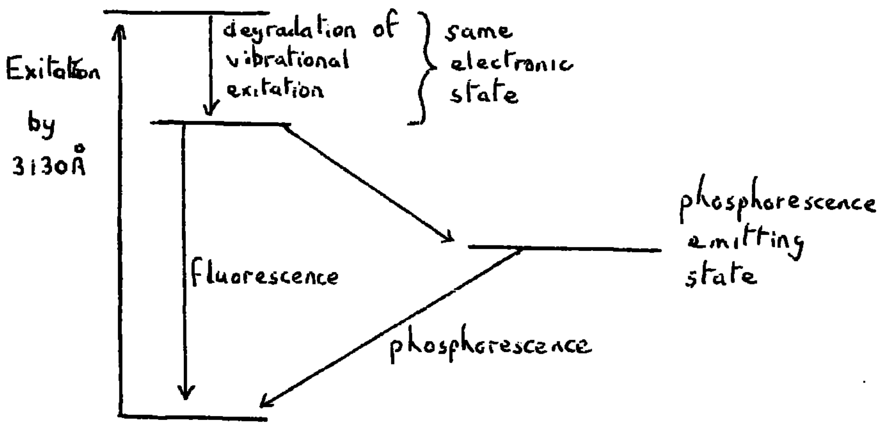
(b) is almost independent of temperature over the range 25°C — 150°C.

(c) may or may not be quenched by acetone - the reports are conflicting.

(i) Groh, Lackey and Noyes (35) report that the fluorescence is quenched, the results supporting the Stern-Volmer mechanism (i.e. the inverse of the fluorescence efficiency is proportioned to the acetone pressure).

(ii) Heiklen's data (43), published at about the time work for this thesis was commenced, suggested that the fluorescence efficiency is independent of the acetone pressure. It should be noted that the mechanism proposed by Heiklen includes a step which would require the fluorescence to be quenched by acetone (his equation 5A)

From the results summarised in the above sections on light emission the following schematic relations of the absorbing and emitting states seems beyond question.



On the evidence of their life-times the fluorescence emitting state has been postulated to be a singlet and the phosphorescence emitting state to be a triplet.

Because the fluorescence intensity is unaffected by whether the phosphorescence is quenched or unquenched it may be deduced that

a) The fluorescence is emitted from an excited state which preceeds the phosphorescing state

b) The arrow showing the transition from the singlet to the triplet is, in practice, irreversible.

The spectroscopy of related compounds.

A study by ~~Heiklen (43)~~ Ausloos and Murad (44) of the light emission from trifluoracetone, after u.v. absorption, has shown that for this molecule (which resembles acetone closely in its photochemistry) the fluorescence efficiency is independent of acetone pressure, temperature or incident wavelength. The absence of effect of acetone concentration and temperature on the fluorescence efficiency are stated to be comparable to his results (mainly unpublished) obtained for acetone. This data indicates, contrary to Groh, Luckey and Noyes (35), that the fluorescence is not quenched by acetone. At 3130Å and 30°C the phosphorescence was found by ~~Heiklen~~ Ausloos to be quenched by both acetone and trifluoracetone but the Stern-Volmer relationship (see previous section) was not followed in either case. A decrease in phosphorescence yield was found to occur with decrease in the incident wavelength in the region from 3130Å to 2652Å. No light emission occurs at 2537Å. The major difference found by ~~Heiklen~~ Ausloos between the emission from acetone and trifluoracetone was the existence of a resonance fluorescence in the case of trifluoracetone.

The mechanism proposed for acetone photolysis by ~~Heiklen~~ Ausloos from the results for both acetone and trifluoracetone is similar to that proposed by Groh, Luckey and Noyes for acetone (35). It shows an important difference, however, in that the steps responsible for the removal of the singlet state are not dependent on acetone pressure.

Weir (45) has studied the light emission from diethyl ketone - biacetyl mixtures. Light emission from pure diethyl ketone is in part due to emission from the biproprionyl formed in photolysis (analogous to biacetyl in acetone photolysis). Weir showed that there exists also a "blue" emission due solely to diethyl ketone but found it too weak to study quantitatively. The qualitative effect of reduction in the blue intensity with addition of oxygen suggested that there was a triplet contribution to the light emission as is found in the acetone case. At 2537Å no light emission was observed

Thus such results as could be obtained with pure diethyl ketone showed that the photolysis resembles acetone photolysis.

The effect of adding biacetyl to the diethyl ketone photolysis was to decrease Φd and increase the emission from excited biacetyl. Energy transfer is proposed from an excited triplet in the ketone to the biacetyl. The formation of a proprionyl radical from the singlet state is postulated and it is shown that it has enough energy to decompose into $C_2H_5^{\cdot}$ and $CO^{\cdot}$. The facts reported are analogous to those which have been reported for acetone and a mechanism was proposed similar to that proposed by Noyes et al. for acetone.

(2) The Photochemistry of pure acetone.

(a) The Energetics

Absorption of 3130Å by acetone provides about 91 Kcals per mole. The energy required to break the C-C bond in acetone has been put at between 68 and 80 Kcals per mole. Thus sufficient energy is supplied to cause decomposition but it is unlikely that any of the products will be produced in a highly excited state. This is especially true if they are produced from a second electronic state (e.g. a triplet) which is energetically closer to the ground state than the first (the singlet).

(b) Products and Mechanism

The principle products of the photolysis of pure acetone with light of 3130Å are as follows:

At room temperature: Major products C_2H_6, biacetyl
Minor products CO, CH_4, and others

At 100°C : Major products CO, CH_4
Minor products C_2H_6 and others

There is common agreement that the above products are to be accounted for by the following mechanistic steps:

$CH_3\ CO\ CH_3 \xrightarrow{h\nu} CH_3^{\cdot} + CH_3\ CO^{\cdot}$ 1

$2CH_3^{\cdot} \longrightarrow C_2\ H_6$ 2

$2CH_3\ CO^{\cdot} \longrightarrow$ biacetyl 3

$CH_3\ CO^{\cdot} \longrightarrow CH_3^{\cdot} + CO$ 4

$CH_3^{\cdot} + Ac \longrightarrow CH_4 + CH_3\ CO\ CH_2^{\cdot}$ 5

At room temperature reactions 2 and 3 (which being free radical - free radical reactions will have zero activation energy) dominate the others and account for the high ethane and biacetyl yields. The low CO and CH_4 yields at room temperature are due to the fact that few methyl radicals or CH_3 CO radicals survive to undergo reactions 4 and 5. At temperatures above 120°C reaction 5 (which has an appreciable activation energy) competes effectively with reaction 2 and this accounts for the high methane yield and the depression of the ethane yield at these temperatures. The higher temperature also increase the rate of reaction 4 so that a high yield of CO results and the biacetyl yield becomes vanishingly small. Indeed at temperatures $>$100°C it is common to combine 4 and 1 and write $CH_3\ CO\ CH_3 \longrightarrow 2\ CH_3^{\cdot} + CO$.

Other secondary reactions are necessary to explain the formation of the minor product (e.g. acetaldehyde, Me Et CO and at 250°C ketene and C_2H_4 (11)) and to account for the fate of radicals such as $CH_3\ CO\ CH_2^{\cdot}$ (3)

$CH_3^{\cdot} + CH_3\ CO\ CH_3 \longrightarrow CH_4 + {}^{\cdot}CH_2\ CO\ CH_3$

${}^{\cdot}CH_2\ CO\ CH_3 \longrightarrow {}^{\cdot}CH_2\ CO + CH_3^{\cdot}$

$2\ CH_3\ CO^{\cdot} \longrightarrow CH_2\ CO^{\cdot} + CH_3\ CHO$

$CH_3^{\cdot} + CH_3\ CO^{\cdot} \longrightarrow CH_4 + {}^{\cdot}CH_2\ CO$

$CH_3^{\cdot} + {}^{\cdot}CH_2\ CO\ CH_3 \longrightarrow C_2\ H_5\ CO\ CH_3$

$2\ {}^{\cdot}CH_2\ CO\ CH_3 \longrightarrow (CH_2\ CO\ CH_3)_2$

But in all these secondary reactions there is never any suggestion other than that $CH_3^{\cdot}$ and $CH_3\ CO^{\cdot}$ are the first radical species to appear in the system after the photo-absorption process. The possibility that

$$CH_3\ CO\ CH_3 \xrightarrow{h\nu} C_2\ H_6 + CO \qquad (X)$$

may occur by a molecular process can be discounted since small amounts of iodine (an efficient radical trap - see later) can suppress the $C_2\ H_6$ and CO yields and this would not be possible if $C_2\ H_6$ and CO were being formed without a radical intermediary as in (X) (At wavelengths below about 2000Å, hydrogen begins to appear as a product, but the absorbed quantum at these wavelengths is sufficiently energetic to break the C - H band and alternative photo-absorption steps become possible).

The quantum yield of decomposition, Φ_d, has been measured with 3130Å incident radiation.

$$\Phi_d = \frac{\text{No. of molecules of acetone decomposed}}{\text{No. of quanta absorbed}}$$

and varies from 0.3 at room temperature to 1.0 at 120°C (1) (the latter value being maintained up to 300°C (9, 10)). This effect was explained originally by suggesting the additional back reaction

$$CH_3^{\cdot} + CH_3\ CO^{\cdot} \longrightarrow CH_3\ CO\ CH_3 \qquad (Y)$$

which is, of course, not amenable to detection since the product is already present in large excess, but the work of Herr and Noyes (12) shows that this alone may be too simple an explanation. They measured Φ_d at various acetone pressures and found that:

(a) the value of $\Phi_d = 0.3$ at 25°C, for acetone pressures over 100 mm, rose and tended towards unity as the acetone pressure was decreased.

(b) a similar effect was observed at 75°C, although the low value of Φ_d was maintained to lower acetone pressures.

(c) at 100°C (when $\Phi_d \doteqdot 1.0$) acetone pressure had no effect on Φ_d.

(d) at very low acetone pressures (below 10 mm) wall effects begin to complicate the picture.

A naive explanation might be that acetone is necessary as a third body for the radical recombination step (Y) above but it is then difficult to see why,

(e) acetone should assist reaction (Y) - reducing the apparent decomposition - and not assist (2) and (3) above (which are also radical recombinations) hence enhancing decomposition. It begins to appear that the acetone may be capable of modifying the yield of reaction (1) itself. When it is realised that absorption of 3130Å light produces an electronic transition essentially located in the CO group, yet all the evidence is that the primary step of chemical significance is the rupture of a C-C bond, it is clear that equation (1) must be much more complicated than the simple representation above (as is in fact known from the spectroscopic data dealt with previously which shows that at least two electronically excited states need to be taken into account) and some interference by acetone in the processes which occur before the rupture of the C-C bond becomes a distinct possibility.

3. The photolysis of acetone iodine mixtures.

Iodine is known to be an efficient radical trap. It would therefore be expected to trap the primary products found and if the low values of Φ_d observed at lower temperatures (e.g. 0.3 at 25°C) were arising because

$$CH_3\,CO\,CH_3 \xrightarrow{h\nu} CH_3^{\cdot} + CH_3\,CO^{\cdot} \qquad (1)$$

was proceeding with $\Phi_d = 1$ but an apparent Φ_d of 0.3 being measured because of the interference by the back reaction

$$CH_3^{\cdot} + CH_3\,CO^{\cdot} \longrightarrow CH_3\,CO\,CH_3 \qquad (Y)$$

then Φ_{MeI} values of about unity would be expected (or even higher if $CH_3 \cdot CO.I$ leads to $CH_3.I$ in the analysis).

In early work done by Gorin (6, 7) on the system at high temperatures the value for Φ_{MeI} was measured as unity. Workers since that time have been unable to reproduce his analytical results (5) and and the value of the Φ_{MeI} is almost certainly too high due to errors in analysis.

Benson and Forbes (5) established the absence of biacetyl and ethane in the photolysis of acetone-iodine mixtures at 60°-140°C but the yields of CO which they found are higher than is now accepted to be the correct result in view of later work (4, 8).

The papers by Pitts and Blacet (8) and Martin and Sutton (4) are ~~and~~ the most important papers in the field of acetone - iodine photolysis and, taken together, their results have enabled important deductions to be made on the primary process in acetone photolysis.

Methyl iodide was the main product isolated. Acetyl iodide was probably formed with nearly the same yield but neither sets of workers could produce quantitative data on its yield since $C\overset{H}{\cancel{O}}_3$ COI is so labile as to defy analysis. No ethane was detected and only small amounts of CO (of the order $\Phi_{CO} = 0.01$). Methyl iodide yields increased with increase in temperature and decreased with increase in acetone or iodine pressure.

The work of Pitts and Blacet was done at iodine pressures which were always in excess of 2 mm. By measuring $\Phi\ CH_3I$ at $80^{\circ}C$ and $177^{\circ}C$ they showed that the effect of temperature increase is to increase $\Phi\ CH_3I$ and they also showed that $\Phi\ CH_3I$ increases as the wavelength of the incident light is decreased. This latter observation is interesting in that the phosphorescence (see previously) shows the opposite trend and these two observations taken together suggest the possibility that both de-activation by iodine at 3130Å and the phosphorescence originate from the same electronic state (the triplet) which becomes less important as the incident wavelength decreases in favour of an electronic state which decomposes directly (the singlet).

The papers by Martin and Sutton (4), as well as containing the important results for ΦCH_3I and ΦCO mentioned above, also reported the results of using light of longer wavelength mixed with the 3130Å which was usually employed. The function of the longer wavelength light was to provide a high concentration of $I^{\bullet}$ in the system. It was found that only a slight increase in $\Phi\ CH_3I$ occurred and the result was used (see later) to estimate the life-time of the long-lived excited state proposed in their mechanism. Martin and Sutton analysed their results by assuming that the methyl radicals (which gave rise to the methyl iodide found in their analysis), were formed only by one of the steps.

$$CH_3\,CO\,CH_3 \longrightarrow CH_3^{\cdot} + {}^{\cdot}CO\,CH_3$$

or

$$CH_3\,CO^{\cdot} \longrightarrow {}^{\cdot}CH_3 + CO.$$

If this is the case then $\Phi_d = \Phi_{CH_3I} - \Phi_{CO}$ and as Φ_{CO} was always found to be small compared to $\Phi\,CH_3I$ then it is possible to write, less exactly

$$\Phi_d = \Phi_{CH_3I}$$

The most significant facts established by the above work are that Φ MeI is much less than unity at higher iodine pressures and only begins to rise as the pressure of I_2 is decreased to very low values. The observation that reducing the amount of the radical trap should increase the primary quantum yield is startling, paradoxical and clear evidence that step (1) above is being interfered with before the primary bond rupture.

The following mechanism was proposed by Martin and Sutton. It shows an interesting resemblance to the mechanism produced for light emission data (see earlier) in that two electronically excited states are postulated.

The absorption by acetone (A) of a quantum of radiation forms an electronically excited state (A') which, in pure acetone, decomposes almost completely above 100°C giving Φ d =1.

$$A + h\nu \longrightarrow A' \qquad (1a)$$

$$A' \longrightarrow \text{Products} \qquad (2a)$$

A' is postulated to be susceptible to partial deactivation by iodine (1b), in competition with (2a)

$$A' + I_2 \longrightarrow A'' + I_2 \text{ (or 2I)} \qquad (1b)$$

A'' is a second electronically excited state which retains enough energy to decompose.

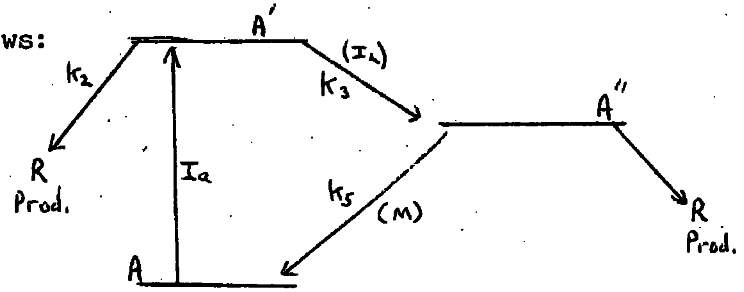
$$A'' \longrightarrow \text{Products} \qquad (2b)$$

A'' is postulated to be susceptible to deactivation by collision with acetone or iodine in competition with (2b).

$$A'' + M \longrightarrow A + M$$

Where $M = (A) + (I_2)$

The mechanism may be summarised diagramatically as follows:



A = acetone molecule in its ground state.

A' and A'' electronically excited states.

R = radicals.

No vibrational levels are shown.

Except for the small amount of CO mentioned previously, the radicals react with I_2 or $I^{\cdot}$ to give methyl iodide and acetyl iodide. The absence of ethane in the products proves that the direct split into ethane and CO does not occur.

By the usual steady state treatment the equation:

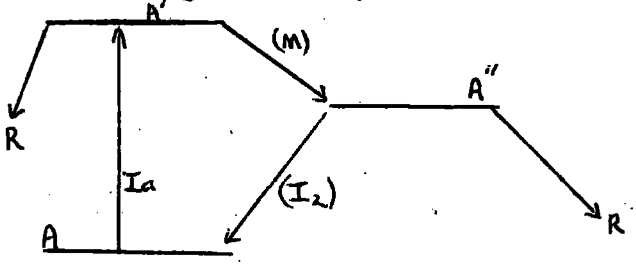
$$\Phi_{CH_3I} - \Phi_{CO} = 1 - \left\{1 + \frac{K_2}{K_3\,(I_2)}\right\}^{-1} \left\{1 + \frac{K_4}{K_5\,(M)}\right\}^{-1}$$

is obtained where $M = (I_2) + (A)$

assuming equal efficiencies of I_2 and A for de-activating A''.

This equation gives good agreement with the experimental results which were obtained.

Brown (29) proposed a different mechanism which can be represented diagramatically thus



i.e. the role of iodine and M in the Martin and Sutton mechanism are interchanged in the de-activation step from A' to A''. This gives a similar mathematical treatment to Martin and Sutton's mechanism but makes the important change that A'' is still produced even in the absence of iodine. This is important in any attempt to correlate this work with the light emission results (see later). In the absence of iodine, de-activation of A' or A'' by collision could account for the behaviour of Φ d at low temperatures, the split of A' or A'' into radicals competing much more favourably above 100°C.

The Martin and Sutton paper provided interesting information on the extent of the reaction $CH_3\,CO\,CH_3 \longrightarrow C_2H_6 + CO$. It had been suggested that a fraction of the acetyl radicals were formed with sufficient energy to decompose via $CH_3\,CO \longrightarrow CH_3^{\cdot} + CO$, before reacting in any other way. Assuming that the radicals arising from A' are equivalent to those formed in the photolysis of pure acetone, they set up an upper limit of 1% to the fraction of acetyl radicals which decompose via $CH_3\,CO \longrightarrow CH_3^{\cdot} + CO^{\cdot}$. This was done by extrapolating the ratio $\Phi\,CO / \Phi\,(CH_3)_1$ to infinite acetone pressure. $\Phi\,(CH_3)_1$, (the quantum yield of CH_3I originating in A'), is given by

$$\Phi (CH_3)_1 = \frac{1}{\left\{ 1 + \frac{K_3}{K_2} (I_2) \right\}}$$

The results from the use of light of 3130Å mixed with longer wavelengths were used to estimate the lifetime of A''. The slight increase in $\Phi CH_3 I$ which was found was attributed to the reaction of iodine atoms with A'' and a lifetime of at least 10^{-5} seconds was postulated for A''.

Making a reasonable estimation of the collision diameter for the action between A' and iodine and assuming each collision is effective an estimate of 4×10^{-7} seconds was made for the half-life of A'. The half-life so calculated prompted the identification of A' with the first excited state in the light emission mechanism of Groh, Luckey and Noyes.(35)

A'' could not be identified with the second excited state in the light emission mechanism for obvious reasons. It was suggested that A'' might be a complex aggregate of acetone and iodine.

The revised mechanism of Brown (29) suggests that A'' is an electronically excited state of acetone and possibly the triplet postulated in light emission experiments. Brown suggested that the study of the effect of iodine on the acetone phosphorescence would help to choose between his mechanism and that of Martin and Sutton.

4. The Photolysis of Acetone - Biacetyl mixtures.

Okabe (33) has shown that biacetyl effects both the light emission and the photochemistry of acetone.

Heicklen and Noyes (42, 43) have investigated the photolysis of acetone below 70°C using low conversions in an attempt to prevent the results from being complicated by the in-situ production of biacetyl. They have also used the same technique to study light emission and quantum yields of acetone - biacetyl mixtures at low temperatures. Their more important results may be summarised as follows:

(1) Biacetyl removed that part of the emission from acetone which is removed by oxygen i.e. the phosphorescence.

(2) The fluorescence yield changed little with acetone pressure and relatively little with incident wavelength in the range 2800Å - 3130Å.

(3) The phosphorescence diminished with decrease in wavelength in the same range.

(4) Using incident light of wavelength 3130Å the phosphorescence decreased with increase in acetone pressure. At the other wavelengths used the phosphorescence increased as the acetone pressure was increased.

(5) Φ_d was calculated from analysis of the amounts of carbon monoxide, biacetyl and ethane present. Φ_d was found to be decreased by the presence of quite small pressures (0.08 mm) of biacetyl. At higher biacetyl pressures a saturation effect was found and Φ_d became constant as the biacetyl pressure was further increased.

(6) With photolysis of pure acetone to low conversions (less than 0.3%) Φ_d increased with temperature. The carbon monoxide yield also increased with temperature but changed little with acetone pressure. Light intensity had little effect on the yields.

(7) The addition of biacetyl lowered the ratio C_2H_6/CO.

The results were interpreted in terms of an energy transfer between the excited triplet formed in acetone photolysis and the biacetyl molecule: the acetone phosphorescence and photo-decomposition is thus diminished by removal by reaction of the triplet with biacetyl before decomposition or light emission can occur.

Heiklen (42) postulated that the reduction of the ratio C_2H_6/CO by addition of biacetyl could be due to the fact that dissociation from the acetone singlet state when the triplet is fully quenched is mainly by the step

$$CH_3\ CO\ CH_3^{*} \longrightarrow 2\ CH_3 + CO$$

whereas in the absence of biacetyl the triplet provides methyl radicals by way of

$$CH_3\ CO\ CH_3^{**} \longrightarrow CH_3 + CH_3\ CO$$

It is interesting to note that at 40°C the addition of sufficient biacetyl reduced Φ_d to about one third of its value in the absence of biacetyl. As the effect of the biacetyl is almost certainly to de-activate the triplet in acetone (as Heiklen postulates) then Heiklen's results suggest that the rôle of the triplet is vastly more important than had been postulated by previous workers. The importance of the triplet state formed at 3130Å will be further discussed in the light of results to be reported later in this thesis on the emission from acetone - iodine mixtures and the quantum yield of methyl iodide in acetone - iodine mixtures.

The Photolysis of Acetone - Oxygen Mixtures.

Only those papers dealing directly with the effect of oxygen on the primary process in the photolysis of acetone will be dealt with in this review. The literature dealing with the products formed by reaction of oxygen with the products of the photolysis is voluminous and sometimes contradictory. With oxygen present, oxidations (possibly involving chain mechanisms) begin to make their appearance and quantum yields more than unity for products become commonplace.

The effect of oxygen on the emission of light from acetone has been dealt with in a previous section. That evidence established beyond reasonable doubt that oxygen removes the emission from the triplet. The mechanism for the quenching of triplet emission can be postulated as being either de-activation of the triplet state by oxygen or reaction of the oxygen with the triplet state to form products. The analysis of the products formed in the photolysis of acetone - oxygen mixtures can provide data which is useful in deciding the role of oxygen in the primary process. However the interpretation of the data is made difficult by the complexity of the product formed.

Marcotte and Noyes (30, 31) have analysed the products formed in the photolysis of acetone - oxygen mixtures above 100°C. They found that as the oxygen pressure was reduced to 0.04 m m, Φ CO approached a maximum value of about 3. At higher oxygen pressures, up to 0.3 m m, the sum of Φ CO and Φ CO_2 remained constant at about 3. They also found that at temperatures where Φ_d is close to one for pure acetone (above 100°C) then the addition of oxygen had little effect on the light emission.

Marcotte and Noyes propose that their results are consistent with Φ_d taking a value of unity in the presence of oxygen above 100°C. The value of Φ CO = 3 at the lowest oxygen pressures is explained by postulating that one molecule of CO is formed from dissociation of the acetyl radical and one from each of the methyl radicals produced. At higher oxygen pressures CO_2 which is found is proposed as being formed solely from the CO. Thus the previous value of Φ CO = 3 is replaced by Φ CO + Φ CO_2 = 3 and this is taken as evidence that oxygen reacts with the products of decomposition of the acetone molecule and Φ d = 1.

The apparent lack of effect of oxygen on the light emission at temperatures above 100°C was used as evidence that oxygen has no effect on the decomposition of the excited acetone molecules - if oxygen were effective in de-exciting the state(s) responsible for decomposition it should also reduce the light emission from those states. This argument is only valid, however, if the state which is responsible for light emission is the same as that which decomposes or is de-excited by oxygen. If the light emission were from a state (the singlet) which is formed before the state (the triplet) which reacts with the oxygen (by decomposition or de-excitation), then the presence or absence of oxygen could not be expected to modify the light emission. The suggestion by Marcotte and Noyes that above 100°C the rate of decomposition of acetone in photolysis at 3130Å is so high that de-activation by oxygen must be small in comparison is still open to question. If the postulate that Φd =1 above 100°C for acetone - oxygen mixtures is true then the role of the oxygen in the mechanism must be very different to that of iodine in the acetone- iodine system (see previously).

Brown (29) has produced results which could be significant in indicating the primary action of oxygen in the photolysis of acetone - oxygen mixtures. He photolysed mixtures of acetone, oxygen and iodine and measured the yield of products formed. Using the assumption that methyl radicals formed in the primary process react either with iodine or oxygen to form methyl iodide or formaldehyde, Brown calculated the quantum yield for decomposition of acetone from the expression

$$\Phi_d = \Phi_{CH_2O} + \Phi_{CH_3I} \qquad (19)$$

He observed that as the iodine pressure was reduced at constant oxygen pressure the yields of oxygen containing products rose and also that, as expected, Φ_d increased. The increase of Φ_d, however, was actually greater in the presence of oxygen than in the case of iodine alone. Brown interpreted these results as indicating that oxygen was competing with iodine for the second excited state in acetone (the triplet) but that its function was one leading to dissociation rather than de-activation. These deductions are only sound if the above equation (19) on which they are based, is valid.

Mitchell (32) has also investigated the effect of adding iodine to the photolysis of acetone - oxygen mixtures. He found that iodine caused a reduction of not more than a factor of 10 in his measured values for Φ_{CO} and Φ_{CO_2} but Φ_{CH_2O} is reduced by a factor of 300. He also found that Φ_{CH_3I} increased with increase in oxygen concentration at constant iodine concentration.

The relatively large effect of iodine on Φ_{CH_2O} compared to its effect on Φ_{CO} and Φ_{CO_2} indicated that formaldehyde might not be a direct product of the action of oxygen with methyl radicals but that it is produced from a secondary radical - perhaps acetonyl. This throws considerable doubt on the equation (19) on which Brown's results are based.

Mitchell's observation of the increase of $\Phi\,CH_3\,I$ as oxygen concentration is increased at constant iodine concentration can be explained most simply in terms of the primary process as being due to an oxygen dependent decomposition step competing with de-activation by iodine. However the increase in $\Phi\,CH_3\,I$ could also arise from the reaction of oxygen with the acetyl iodide.

Thus a general review of the photolysis of the oxygen - acetone system reveals little firm data on which to base a mechanism for the role of oxygen in the primary processes. Whether the oxygen reacts with the acetone triplet to form products or by de-excitation of the triplet, or both, remains an open question. The reaction products in the system are so complex that a solution by means of photochemical yield determinations appears to be a difficult task.

Summary.

Established data on the primary process in the u.v. photolysis of acetone can be listed as follows:

(a) The excited state formed by absorbing a quantum of energy loses some of that energy before emitting light.

(b) At least two electronically excited states are found with lifetimes of about 10^{-4} secs (the triplet) and $10^{-\overset{6}{8}}$ (the singlet).

(c) The short-lived state is not appreciably affected by temperature, oxygen, nitric oxide or biacetyl.

(d) The long-lived state is quenched by acetone, oxygen, nitric oxide and biacetyl or heating above 100°C.

(e) The primary split is into a CH_3 and a $CH_3\,CO$ radical. Above 100°C the $CH_3\,CO$ radical is unstable with respect to decomposition into CH_3 and CO.

(f) The quantum yield of CO is close to one above 100°C.

(g) Iodine de-excites at least one of the excited states thereby reducing decomposition.

The most important points which are either in dispute or which need further clarification may be listed.

(1) The spectroscopic data, although of prime importance in the progress which has been made in establishing the mechanism, is too complex to provide on its own further insight into the mechanism unless more refined measurements can be made.

(2) The relative importance of the two excited states is not known.

(3) The effect of acetone on the singlet state requires further investigation in view of the conflicting data in the literature on whether or not the singlet is quenched by acetone.

(4) The mechanism of the inter-action of iodine with the excited state(s) is not known.

(5) More quantatitive data is required on the quenching of the long-lived emission by acetone and other gases, especially at high temperatures.

(6) The determination of chemical yields in the acetone - oxygen system has not established the role of oxygen in the primary process.

(7) While many mechanisms have been proposed to explain small sections of the data available, a satisfactory mechanism embracing both light emission and quantum yield data has not yet emerged.

AIMS OF THE PRESENT INVESTIGATION.

Although several papers on the light emission from acetone existed at the beginning of this investigation, much important information was lacking. In particular, the quenching of the phosphorescence by temperature and addition of gases such as oxygen and nitric oxide has not been fully investigated and light emission at elevated temperatures had not been studied in any detail. The main reason for this was probably that the emission from acetone is so weak that previous investigators were unable to take quantitative measurements when part of the intensity was quenched. No doubt the same explanation can be put forward to explain the confusion in the literature concerning the effect of acetone on the fluorescence efficiency. The papers by Groh, Luckey and Noyes, contain conflicting results to those reported by Heiklen.

It appeared that an investigation of the effect of iodine on the light emission might enable the mechanism proposed by Brown for the acetone - iodine system to be confirmed.

The original aim was to construct an apparatus capable of investigating quantitatively the light emission of acetone vapour, either pure or in the presence of oxygen or iodine. It was also intended to investigate light emission at and above 100°C where most of the chemical yields have been determined; the intention being to attempt to find a mechanism to fit quantitatively both the light emission and quantum yield results.

The final part of the work involved the development of a new technique for determining ΦCH_3I in the acetone iodine system at 3130Å over a range of iodine pressure greater than has previously been reported. From the values of ΦCH_3I obtained it was intended to demonstrate that the ratios of constants derived in the light emission results give theoretically calculated values of ΦCH_3I which agree with those found experimentally.

Throughout the investigations reported in this thesis the line of investigation followed was that which seemed most likely to produce information useful in elucidating the primary process involved in the photolysis of acetone at 3130Å. With this in mind the investigation of light emission was discontinued at a stage where the emission of acetone at 3130Å had been fairly fully investigated, so that ΦCH_3I could be studied. The goal at which the work was aimed was the collection of results which would allow a mechanism to be developed which would account both quantitatively and simultaneously for the light emission and the photochemical yield data.

CHAPTER II.

EXPERIMENTAL TECHNIQUE.

A. Materials Used.

Acetone.

Trotman-Dickinson and Steacie have observed that in the direct photolysis, analar grade acetone gives results consistent with those from "purified" analar acetone. A fresh unopened bottle of analar grade acetone was procured at the outset and was stored in a cool dark place. The acetone was dried over magnesium sulphate and distilled into the storage bulb. The acetone was tested for the presence of unsaturated compounds by reaction with dilute potassium permanganate solution at room temperature. It gave no reaction. It was also tested for biacetyl by the addition of hydroxylamine which would form dimethyl glyoxime with any biacetyl present. The formation of dimethyl glyoxime was tested for by the formation of the coloured nickel complex. This test is sensitive to about one part in ten thousand for biacetyl. No biacetyl was detected.

Before use the acetone was outgassed by prolonged pumping at - 78°C. The storage bulb was blackened to prevent any formation of biacetyl by sunlight.

Oxygen.

The oxygen used was taken directly from a cylinder from B.O.C. It did not contain impurities which absorb or emit light of the wave-lengths used in these investigations.

Iodine.

Analar grade iodine was used without further purification except to outgas it thoroughly to guarantee that it was free from oxygen trapped in the crystals. This was done by ~~altneratively~~ alternately subliming the iodine in its reservoir then freezing it down and pumping to a high vacuum. This manoeuvre was repeated 30 times.

Xenon.

Spectroscopically pure xenon was used directly from a B.O.C. phial.

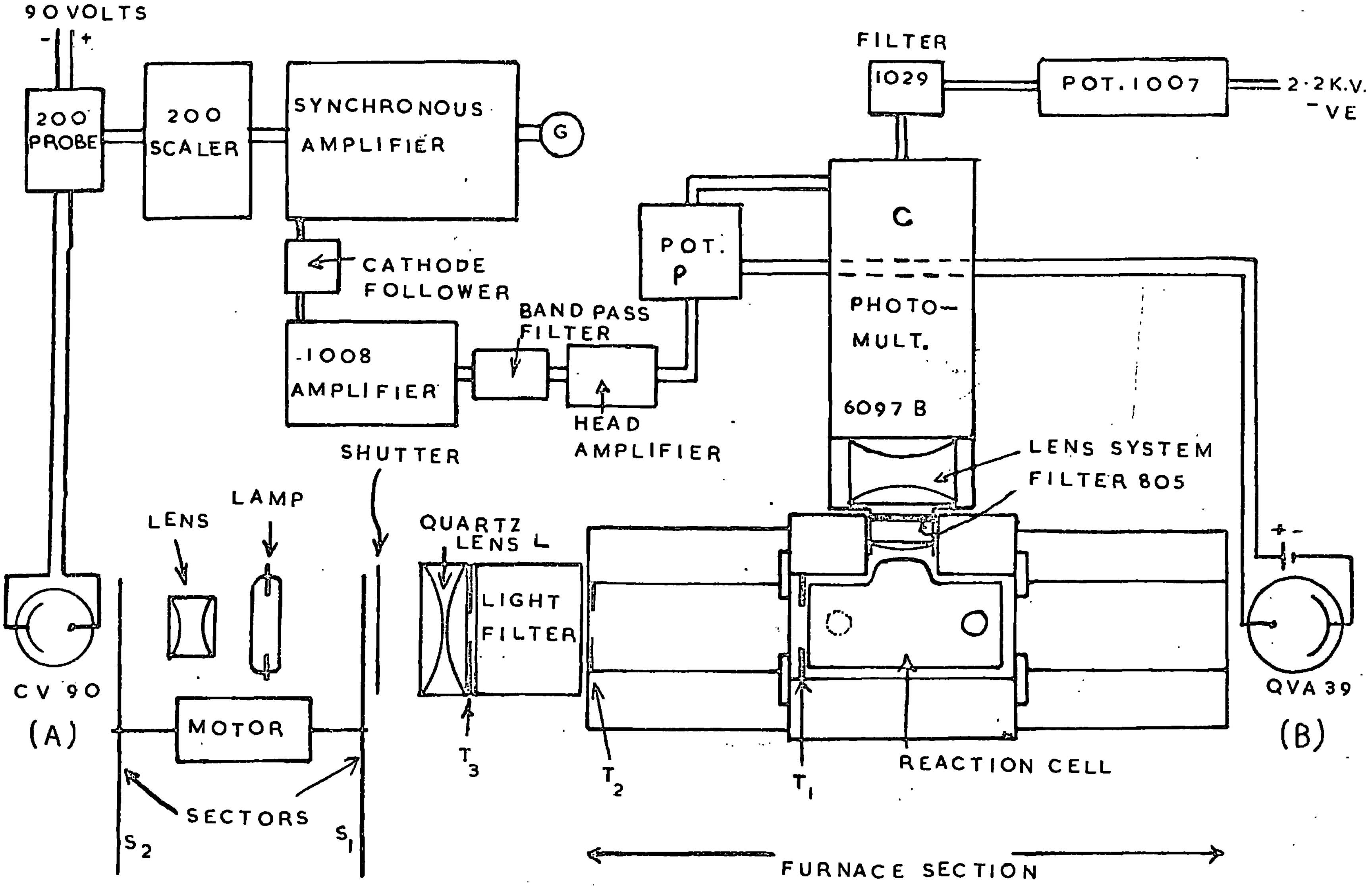


Fig. 1 Light emission apparatus

Fig. 1 Light emission apparatus

B. Apparatus and Experimental Method for Light Emission Measurements.

The apparatus is shown schematically in fig. (1). The details are as follows:

The u.v. source was a Phillips mercury vapour lamp, rated at 100w A.C., but for reasons which will be explained later, it was necessary to run this from a D.C. supply. The lamp was powered from the 120 D.C. mains available in the laboratory, the supply being further smoothed by the circuit of fig. 2A (to reduce the 100 c.p.s ripple remaining from rectification of 50 c.p.s mains). The inductance used (about 10 Henries) was the primary of a transformer and the resistance was set so that the lamp dissipated about 30w when warmed to the operating temperature.

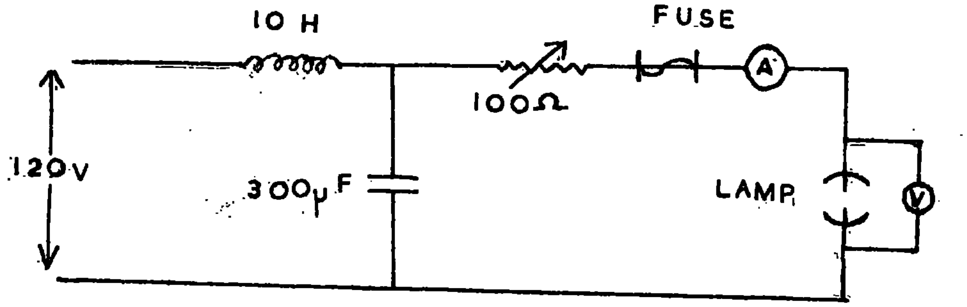
The light passing through the cell fig. (1) was collimated by the quartz lens system L, (focal length 5") and the stops T_1, T_2 and T_3 so that a parallel beam of diameter 0.5 cm passed through the centre of the cell. The stops prevented quite a large fraction of the light from entering the cell but this was found to be necessary if the amount of light scattered into the photomultiplier was to be kept to a reasonably low level.

Light of wave-lengths near 3130A was obtained by the use of the following filter system:

(1) A disc shaped quartz cell 1 cm. between the plane polished faces which contained a solution of potassium chromate (0.2gms/litre) to which 0.2 gms/litre of sodium hydroxide had been added to prevent dichromate formation.

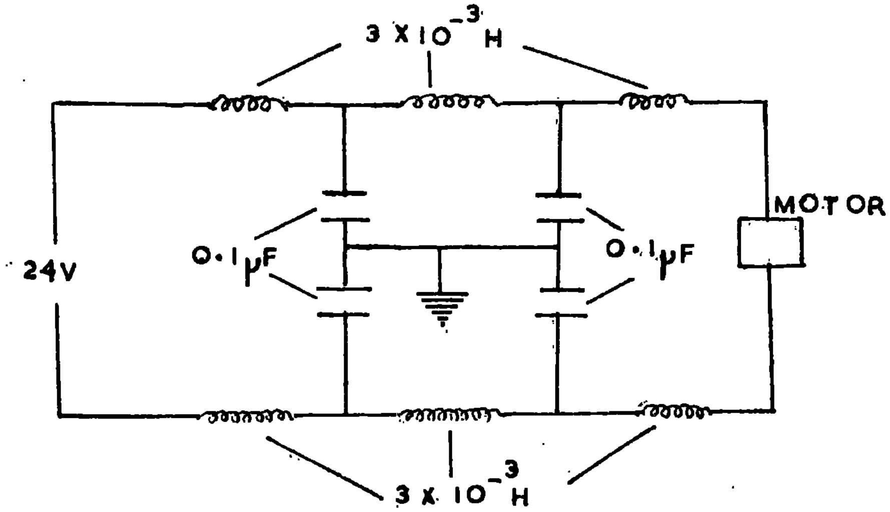
(2) Two layers of Chance OX7 glass filter each layer being 2mm. thick. One of the Chance filters was incorporated as one face of the chromate cell.

FIG. 2A



10 H
FUSE
A
100Ω
120V
300μF
LAMP
V

FIG. 2B



3 X 10^{-3} H
MOTOR
0·1μF
24V
0·1μF
3 X 10^{-3} H

(3) A disc shaped quartz cell 1 cm between the plane polished faces which contained nickel sulphate of strength 50gms/litre.

The transmission spectrum of the filter system was measured in a Unicam (SP500) spectrophotometer and is shown in fig. (3). The filter system was effective in eliminating all lines except those close to 3130Å in the emission spectrum for a mercury lamp run at medium pressure (i.e. at or just less than one atmosphere). It will be noted that a great deal of intensity has been forfeited in order to gain purity of the light used. This was considered worthwhile as it seemed from previous work (43) that the mechanism of the photolysis may depend critically on wave-length.

The sectors S_1 and S_2 were driven at about 5000 r.p.m. by an electric motor run from a 24 volt DC supply. This supply was smoothed, using the circuit shown in fig. (2B) to reduce electrical interference in the amplifier. The sector S_1 cutting the irradiating beam had three 60° segments cut out symmetrically, whilst sector S_2 had just twice as many 30° segments removed. The reason for this is to be found in the electronic set-up used and will be explained later. The whole motor and lamp section of the apparatus was enclosed in a removable aluminium box with suitable openings for the emergent u.v. beam. The purpose of the box was to screen the laboratory generally from the u.v. light and also as a safety measure in case of an accident with the rapidly moving sector plates.

The furnace consisted of a solid aluminium block which was halved and drilled to contain the cell and its connecting tubes. At each end of the furnace a heavy copper tube was fixed coaxially with the light beam. When the whole assembly was heavily lagged the

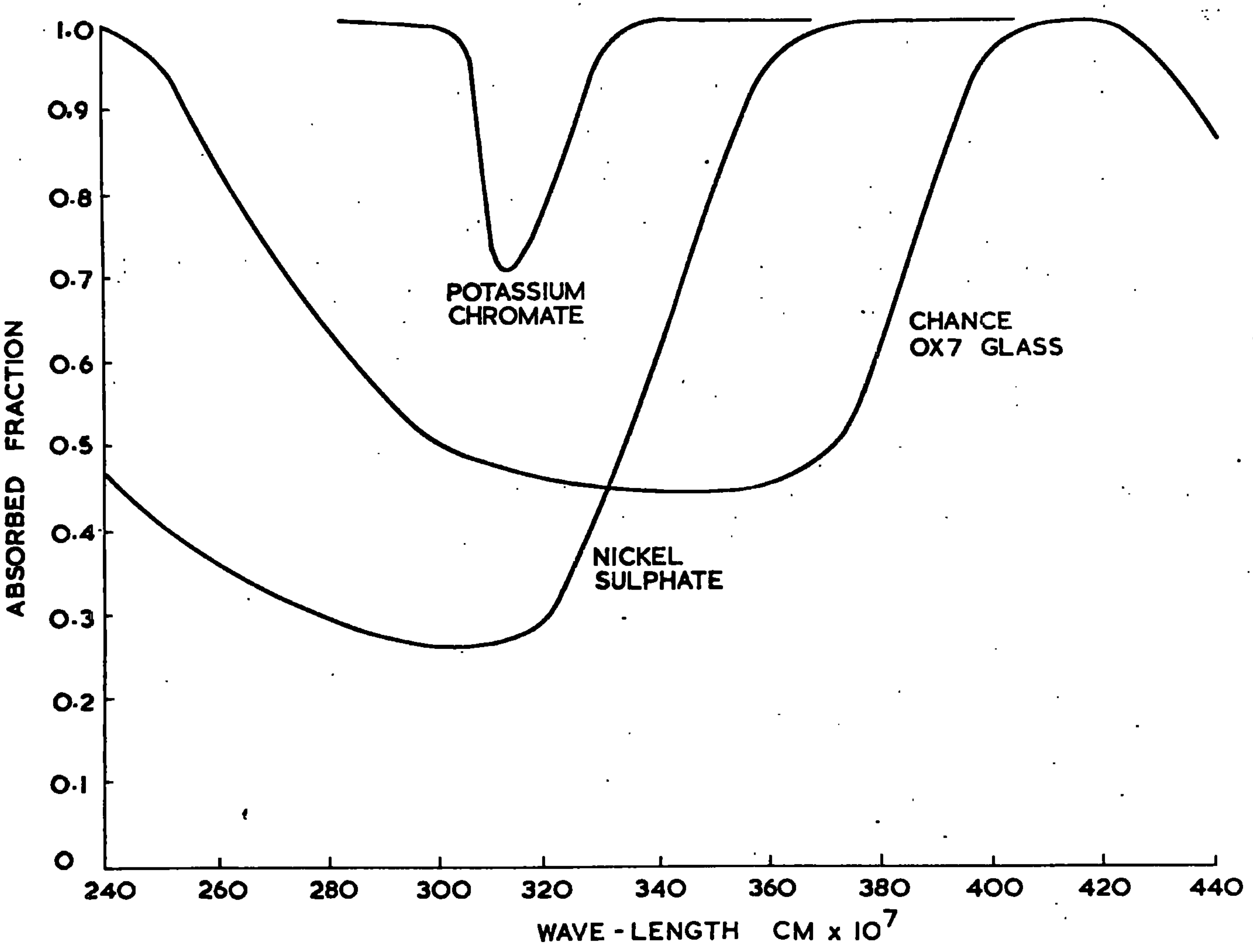


Fig. 3 Filter transmission

copper tubes served to prevent any sharp temperature gradient at the edge of the aluminium block. The internal surfaces of all the furnace section were painted black with "A dag" colloidal graphite to prevent any stray external light from being reflected into the photomultiplier. The aluminium block portion of the furnace was heated by two 150W Edwards pump heaters connected in series. The power supplied was 110V AC from a mains transformer and the temperature controlled manually to about ± 2°C over the range ambient to 150°C by a variable 175 ohms resistance in series.

Photocells.

Cell (A) fig.(1) which produced a trigger signal for the scaler (see later for explanation) was a caesium-cathode Mullard CV 90 photocell. The required 90V for the cell was supplied from a dry battery.

The chopped beam focussed by the lens system between the sector blades fell onto A giving an output signal through the probe unit to the A.E.R.E. type 200 scaler.

Cell (B) was used to measure the intensity of the u.v. beam after passing through the cell. It was a Cintel QVA 39 photocell contained in a quartz envelope. A potential of 20 volts was provided by a small battery which was contained in a metal box to screen it from AC pick-up. Cell (B) was also contained in a steel box containing a window through which the cell could "see" along the axis of the quartz cell.

The photomultiplier (C) was an E.M.I. type 6097B contained in a metal box which acted both as an electrical shield and light excluder. Electrical leads to (C) passed through Plessey plugs on the metal box. Light emitted from within the reaction cell passed through the lens onto the photomultiplier cathode. The Ilford 805 filter between the lens and the photomultiplier stopped all u.v. below 3800A and transmitted more than 80% of the light above 4000A.

The E.H.T. supply to the photomultiplier was supplied from an A.E.R.E. type 1007 power pack and potentiometer which gave any voltage up to 2KV to a tolerance of 1%. A filter was incorporated between the photomultiplier and the potentiometer to eliminate a.c. voltages. The filter was an E.H.T. 1029 type modified for use with standing current by replacing the 10 megohm resistances by 0.5 megohm resistances. The circuit including the photomultiplier is shown schematically in fig.(1).

Light Emission Measurements.

The low fluorescence/phosphorescence efficiency makes this quantity a difficult one to measure with accuracy and this is especially true at temperatures above about 50°C where the phosphorescence is substantially quenched. Previous work has all been subject to considerable limitations in the range of experimental conditions over which reliable data could be collected because of the limitations imposed by these problems. The difficulties are twofold.

(1) Because of the low fluorescence/phosphorescence efficiency considerably more effective gain must be built into the emission detection system compared to that for the detection of the exciting light and there are problems in ensuring that this gain is constant or that variations are properly allowed for.

(2) With the exciting intensities practicable, the fluorescence/phosphorescence emission is so small that the signal to noise ratio

in the emission detection system is inevitably poor.

The detection system used in this work attempts to overcome these difficulties to a greater extent than has been previously achieved in the following ways:

(1) The currents from the photomultiplier and the photocell B are compared before any amplification (apart from that inherant in the photomultiplier) on the potentiometer P, details of which are given later. Briefly the potentiometer is so arranged that when its output is nulled the potentiometer reads directly the ratio

$$\frac{\text{Photomultiplier current}}{\text{Photocell B current}}$$

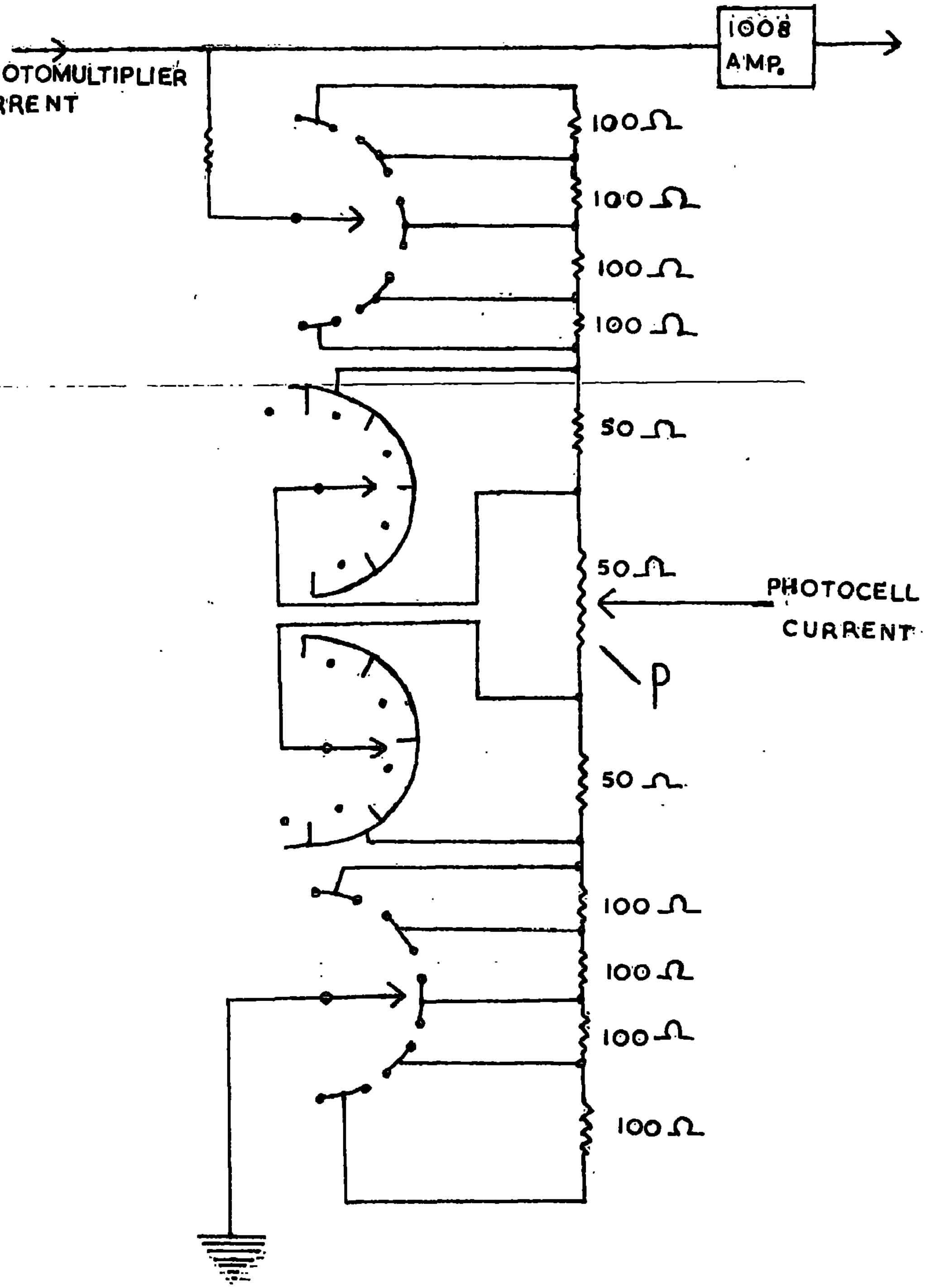
and this reading is equivalent to the light emission efficiency.

By comparing the currents directly in this way fluctuations in light output of the lamp are discounted.

(2) The amplifier system is used only as a null-detection device: this discounts any minor changes in gain since such changes only affect the sensitivity with which the null point can be detected.

(3) Included in the amplifier system is an extremely narrow bandwidth amplifier which is synchronously locked to the chopping frequency of the light beam. (This is the reason for the use of the sectors S_1 and S_2 and the use of intermittent rather than continuous illumination). The function of this unit is to provide gain only at the frequency of the chopped beam and a very narrow band of frequency on either side of this. Noise, which covers the whole spectrum of frequencies, is therefore in general not amplified by this unit. Since the amplifier is locked to the frequency of the signal of interest,

b)



a) SCHEMATICALLY

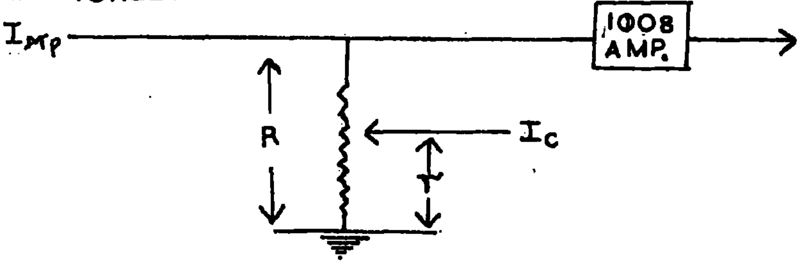


Fig. 4 Potentiometer

the effect of this unit is to give a great improvement in the signal to noise ratio.

The Potentiometer P.

The arrangement of the potentiometer is shown schematically in fig. 4a.

The photomultiplier current, i_p, flows through the whole resistance of the potentiometer, R, and the photocell current, i_c, flows <u>in the opposite</u> sense through part of this resistance, r. When the potentiometer output is nulled (i.e. at ground potential) then clearly:

$$i_p . R = i_c . r$$

and when this null point has been obtained, the ratio of the two currents can be read from the potentiometer since:

$$\frac{r}{R} = \frac{i_c}{i_p}$$

To achieve accuracy in reading the potentiometer it is constructed as shown in fig. 4b. Coarse adjustment of r is by the 10 - position ganged switch S, and fine adjustment by the precision linear potentiometer P.

The Amplifier System.

The output of the potentiometer was fed to an A.E.R.E. type 1008 Head amplifier and from this via a band-pass filter to the main 1008 amplifier. The band-pass was tuned to approximately the frequency of the light seen by photocell B and the photomultiplier (precise tuning was pointless since the speed of the sector motor was not accurately controlled). The function of the filter is to eliminate noise at frequencies different from the signal frequency and also, much more importantly, to remove harmonics of the signal frequency before the synchronous amplifier where such harmonics would cause malfunction. The output of the main 1008 amplifier feeds the synchronous amplifier whose output was displayed on a centre-zero spot galvonometer. Synchronization of the amplifier is ensured by the signal from the photo cell A which is applied to an A.E.R.E. type 200 scaler. The large amplitude antiphase square waves from the anodes of the first binary stage are used as the tuning switch signals for the synchronous amplifier. The synchronous amplifier is described in more detail in Appendix I.

Oxygen-Acetone Measurements.

It is an often reported fact (42, 33) that, in the photolysis of pure acetone below 80°C, biacetyl is produced. Biacetyl is excited to a strongly emitting triplet state by 3130Å so that the trace amounts formed could interfere seriously with measurements of light emission from acetone. Because of this it was intended to use a flow system at temperatures below 100°C. However, it was found that the light emission was independent of flow rate and, even with no flow through the cell, no build-up of light emission could be detected in 30 minutes irradiation. This rather surprising result can probably be explained by the facts; (1) the light intensity was very small; (2) the volume of the irradiated portion of acetone along the axis of the cell was very small compared to the total volume of acetone enclosed in the reaction cell part of the apparatus. The fact that a static system could be used made the reading of pressures much more accurate and convenient than would have been the case in the flow system. It was never found necessary to pass u.v. through the cell for more than one

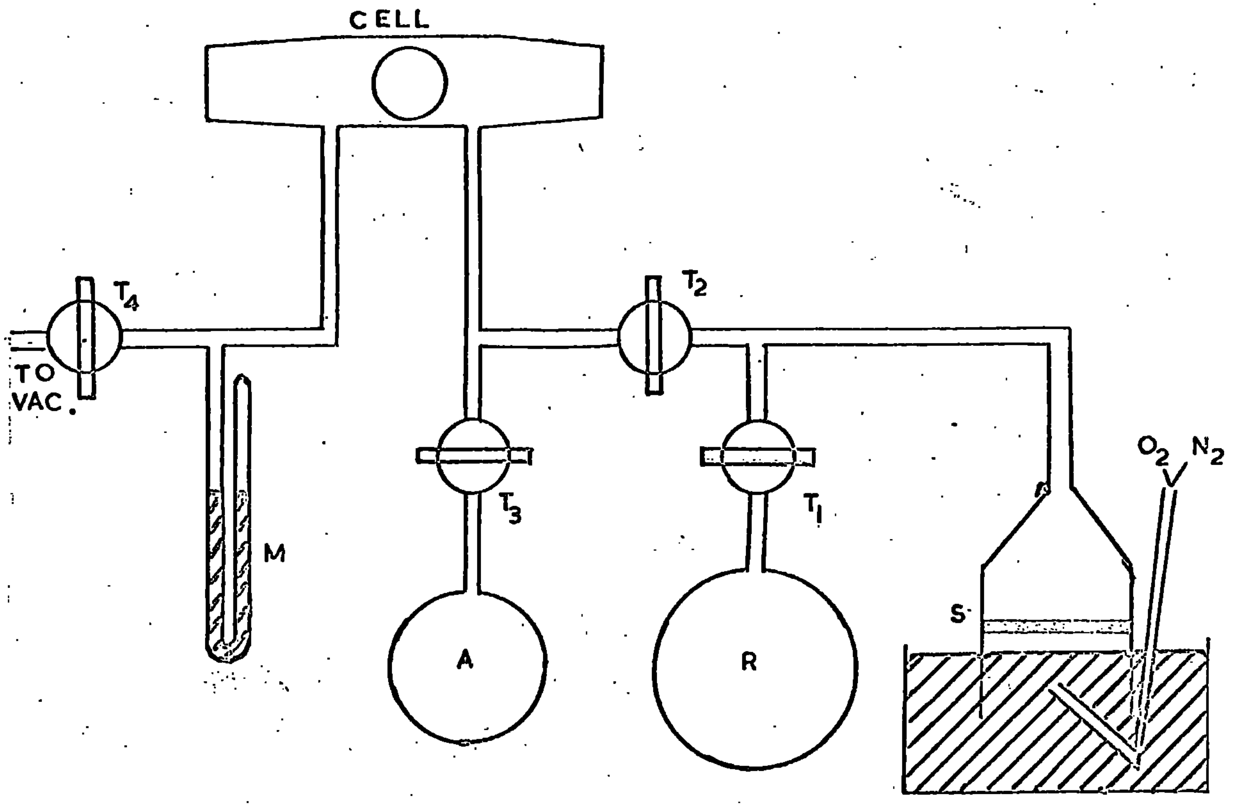


Fig. 5 Cell filling apparatus

minute to take a reading and, as an added precaution, a new batch of acetone was used for each reading.

The apparatus used for filling the cell with acetone or acetone/oxygen mixtures is shown in fig. (5).

The cell was constructed from pure silica by Thermal Syndicate Limited. It was 6 cms long, slightly barrel-shaped of diameter 2 cms. Each end was plane polished and a plane polished window 2 cms in diameter in the centre of the T shaped cell enabled the light emitted perpendicular to the incident beam to enter the photomultiplier. The silica cell was joined to the rest of the apparatus by graded silica-pyrex seals. The side tubes on the cell were heat insulated over a distance of 2" where they emerged from the heat insulation enclosing the aluminium block in which they rested. Colloidal graphite was painted over the connecting tubes between T_2, T_3, T_4 and the cell to prevent stray light from entering the photomultiplier along the tubes. The surface of the cell except for the windows was also covered with colloidal graphite.

The electrical heating of the aluminium block which enclosed the cell was controlled manually to about $\pm 2^{\circ}C$. The temperature of the cell was measured by a N.P.C. calibrated thermometer seated in a recess in the block close to the cell. A lens was used to assist in reading the scale behind the manometer M. The purified acetone was stored in the bulb A.

It has previously been reported (30) that nitrogen has no effect on the emission or absorption of light in acetone photolysis. This was confirmed in preliminary experiments with the apparatus then the oxygen which was used in the acetone-oxygen runs was diluted with nitrogen so that small oxygen pressures could be measured more accurately on the manometer M.

Oxygen and nitrogen were introduced into the evacuated apparatus by means of the sinter S dipping into the mercury trough. With T_4 and T_3 closed and T_1 and T_2 open, the pressure of oxygen and nitrogen introduced was adjusted until a ratio of one part of oxygen to nine parts of nitrogen was obtained in a total pressure of 25 cms Hg. After mixing overnight T_1 was closed and the cell part of the apparatus was evacuated. R was a 2 litre flask.

Mixing in the reaction cell was allowed to occur naturally when oxygen and acetone were used. The side tubes between the cell and the taps T_2, T_3 and T_4 were kept as short as possible to minimise the time required for mixing. In the low acetone pressure runs only a minute or two was needed for mixing (as indicated by the measured light emission efficiency) to be complete. Up to twenty minutes was allowed for the highest acetone pressures.

Experimental Proceedure.

The technique for a typical measurement using a mixture of acetone and oxygen was as follows:

The electronics side of the apparatus was switched on and allowed to "warm up" for at least half an hour. This included the lamp which needed to be primed by bringing the discharge from a leak testing coil close to the quartz envelope before it would strike. The discharge was kept a few centimet~~ers~~res away from the envelope to avoid puncturing it. As soon as the lamp was lit the sector motor was started since the sector blades had a cooling effect on the lamp and the lamp must, of course, be brought to a stable operating condition with the cooling operating in the same way throughout the experiment.

With the input to the synchronous amplifier removed from the 1008 output and grounded, VR_3 (see fig. I, in Appendix I.) was adjusted to balance the synchronous amplifier itself. Restoring the connection to the 1008 output, and with the shutter of fig. (1) in place to exclude light from photocell B and the photomultiplier, the signal due to the photomultiplier dark current was balanced out using the potentiometer. With the cell evacuated the shutter was now removed. A small reading on the galvanometer was usually noted due to light scattered from within the cell and the oven and this too was balanced out using the potentiometer. The potentiometer reading necessary to balance out both the photomultiplier dark current and the effect on light scatter must be subtracted from all subsequent emission readings: it was much less than 1% of the acetone emission signal at room temperature but at higher temperatures the correction, of course, became more important.

When acetone alone was used it was introduced into the cell by allowing it to escape past T_3 with T_2 and T_4 closed until the requisite pressure, as measured by M was obtained. The acetone was left for a few minutes to attain the temperature of the cell, then the shutter was raised and a reading was taken. The shutter was then lowered and the acetone discarded by opening T_4.

To introduce a known mixture of oxygen and acetone to the evacuated cell, the oxygen, which was always at a much lower pressure in the cell than acetone, was introduced first by means of T_2.

For the low pressures of the synthetic oxygen mixture which were needed it was found easier to keep a fairly low pressure between T_2 T_1 and S., so that a relatively low pressure difference existed across T_2 which could be used to make small increases in the manometer reading until the requisite pressure was obtained. T_1 was used to top up the pressure in the volume T_1 T_2 S when it became depleted. The acetone was introduced after the oxygen by opening T_3 carefully and letting acetone excape past it into the cell until the required total pressure was obtained.

It had been thought that this procedure might lead to the contamination of the acetone reservoir with oxygen vapour. However, usage proved that this did not occur and the initial method of introducing the acetone first and freezing it down in a cold finger before introducing the oxygen was discontinued. Mixing was found to be quicker when the acetone was not frozen down and dispensing with the cold finger reduced the volume in which the gases had to mix.

For a series of fully quenched readings, volume T_1 T_2 S was filled with pure oxygen which was used instead of the synthetic mixture in R. This served both to conserve the mixture in R and to reduce mixing times. The exact oxygen pressure was not critical for fully quenched readings.

The effect of change of incident intensity on the results obtained could be studied by both altering the power dissipation of the lamp and by interposing various gauges of wire gauze in the incident light beam. The maximum effect of these measures was to reduce the incident intensity by a factor of two.

Xenon - Acetone Measurements.

The effect of xenon on the light emission of acetone was studied using apparatus identical with that used for the oxygen acetone measurements except that R in fig. (5) was replaced by the xenon phial. The phial was mounted behind two taps to ensure against leakage into the xenon when the apparatus contained an atmosphere of air (as it did for instance when T_2 was re-greased). The volume between T_2 T_1 and S was evacuated and used to introduce xenon into the cell in exactly the same way as in the oxygen case. No difficulty was encountered in measuring the xenon pressures used as pressures of several cms of Hg. were used in each case. Temperatures in the range 20° to 150°C were studied.

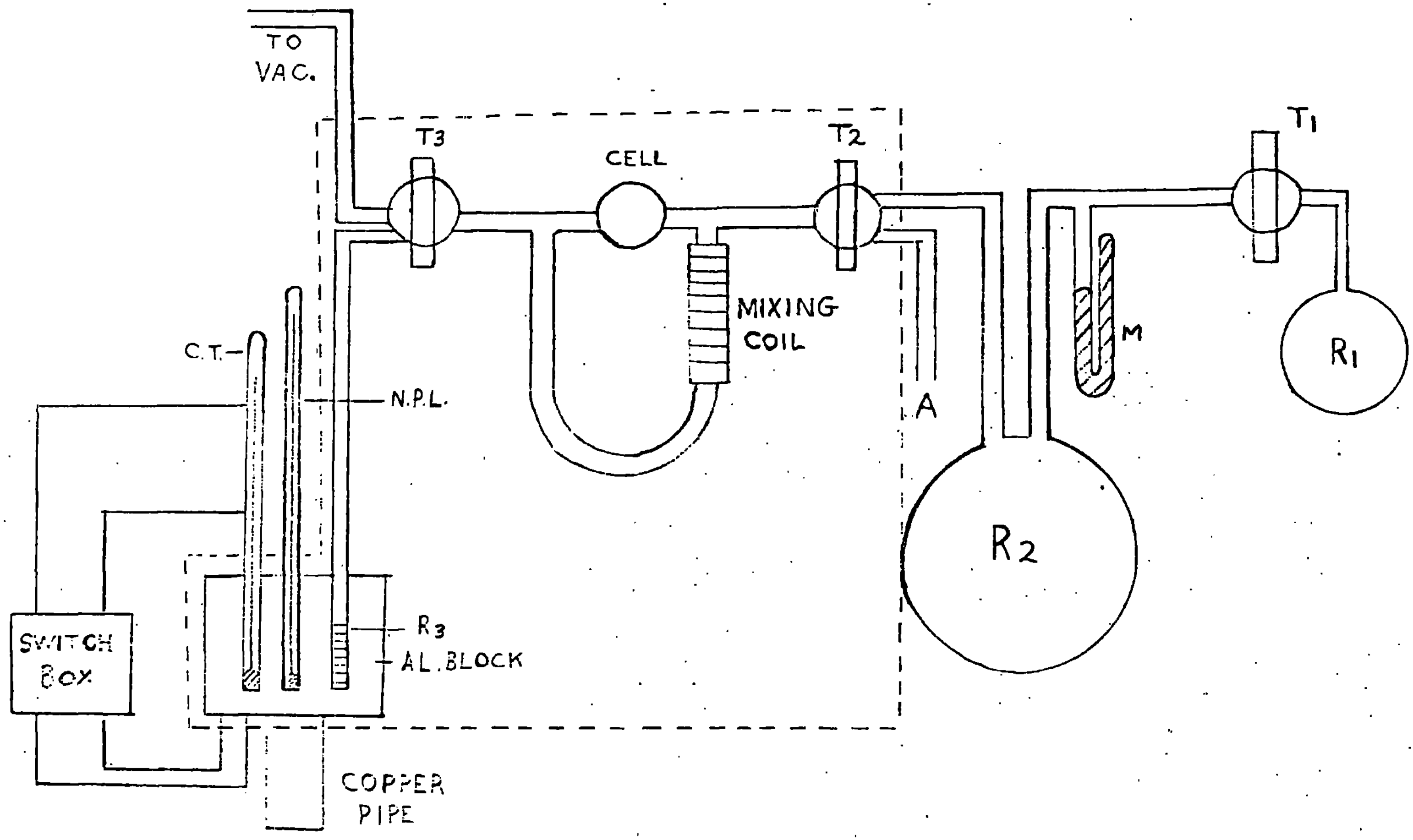


Fig. 6 Acetone-iodine cell filling apparatus

Acetone - Iodine System.

The reactivity of iodine, notably towards hydrocarbon grease and mercury, makes its use in a vacuum system especially difficult. A solution to this problem used previously in this laboratory, was to construct a tapless portion of the apparatus which could be detatched from the main apparatus before the iodine was released by means of a break-seal. This technique, although sound, is rather time consuming in that each reading requires a considerable amount of glass blowing and the prior preparation of a carefully measured amount of iodine.

The effect of iodine on silicone grease was investigated and the rate of attack was found to be slow at room temperature - several days elapsed before any sign of reaction was observed. Above 100°C attack was quicker but in all cases it appeared that the iodine dissolved in the silicone grease without causing breakdown in the grease. In view of these results it was decided to introduce the iodine into the cell by means of a pyrex tap using silicone grease as the lubricant.

The apparatus for filling the cell as modified for the acetone/iodine measurements, is shown in fig.(6) and fig.(7). R_1 is the acetone reservoir, R_2 is a 5 litre flask.

To reduce the actual mixing time which had been encountered in the oxygen/acetone system, a convection mixing heater was fixed to the cell portion of the apparatus. This is shown in fig.(7). One limb of the convection mixer was heated to 120°C by a supplementary heating coil. The cell was heated by the oven described previously

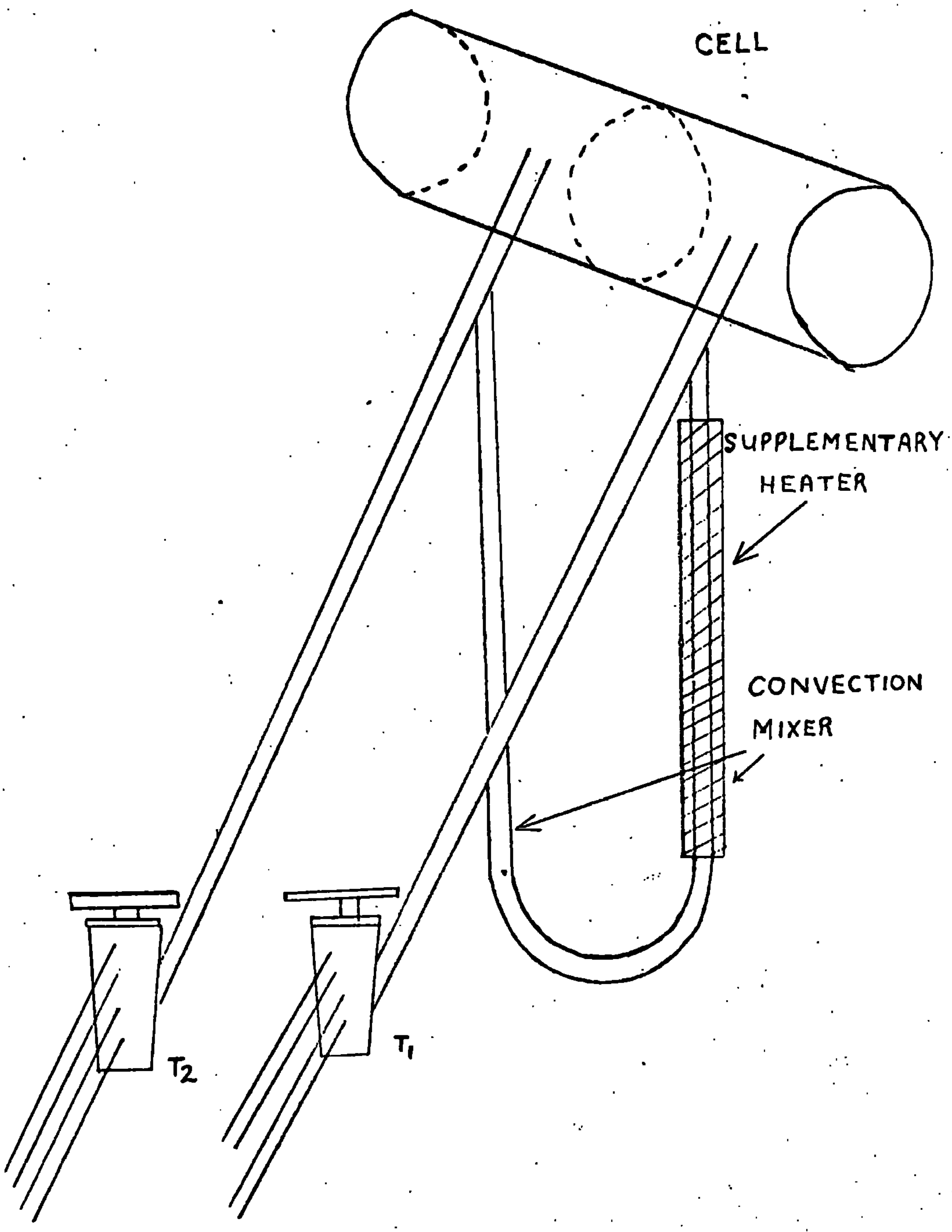


Fig. 7 Convection mixer

in the acetone/oxygen section and all the connecting tubes and the taps T_2 and T_3 enclosed in the dotted line in fig.(6) were heated by electrothermal tapes wrapped round them. Glass tape was used as extra insulation and all the tubes were wrapped with aluminium foil and copper wire to ensure that no cold spots were left.

The iodine reservoir was contained in a large cylindrical aluminium block 15 cms in diameter. The tube containing the iodine sat in a hole bored 7 cms into the block. Two similar holes contained an N.P.L. calibrated thermometer and a contact thermometer. The contact thermometer controlled the current through an Edwards mercury pump heating strip wrapped round the side of the aluminium cylinder. The 250 volt output from the contact thermometer control was taken to a transformer and the 80 volts output from the transformer was used for the heater. A 61 ohms rheostat connected in series with the 350 ohms of the heater could be adjusted so that, with the top and sides of the block heavily lagged, the periods when the heating current was "on" and "off" were approximately equal.

A copper pipe 6" long and $1\frac{1}{2}$" in diameter was screwed into the bottom of the block. This pipe could either be heated with a small gas flame or cooled in a cooling bath to effect large changes in the temperature of the reservoir fairly rapidly. Pulped asbestos fibre was used to insulate the top of the aluminium block. When wet this material could be built up round the heating tape on the tube from the iodine reservoir to provide good insulation at the point where the heating tape stopped.

The contact thermometer kept the temperature of the aluminium block constant to within 0.1°C at temperatures above room temperature. The contact thermometer could not be used for temperatures below room temperature but with a little practice it was found to be possible to keep the temperature constant to ± 0.1°C by judicious use of the cooling mixture applied periodically to the copper tube.

The holes containing the two thermometers and the iodine reservoir were situated close to the centre of the block within 3 cms of each other. Each hole was a close fit for the glass tube sitting in it so that the thermal contact was good.

Acetone was introduced into the cell at the desired pressure by first filling the volume T_1, R_2, T_2 to the correct pressure as measured by M. The volume T_1, R_2, T_2 is so large compared to the volume of the cell that the acetone could then be introduced into the cell by momentarily opening T_2 (with T_3 and T_1 closed) without appreciable change in pressure.

The pressure of iodine in the cell was controlled by carefully adjusting the temperature of the reservoir containing the iodine which was always maintained as the coldest part of the system. A graph relating vapour pressure of iodine to temperature was constructed using the formula (46).

$$\log P = 20.75878 - (2986.21241)\,T^{-1} - 40.847264 \times 10^{-3}T + 42.66239 \times 10^{-6}T \quad \text{where } T = \text{degrees absolute.}$$

From the graph constructed the pressure of iodine in the cell could be quickly calculated at any given temperature. A variation of 0.2°C in temperature gave an error of less than 1% in iodine pressure. The temperature was kept constant to ± 0.1°C. The taps were maintained at about 60°C which ensured that they were at all times warmer than the iodine reservoir and the rate of iodine attack on the tap grease was quite low.

A test was made to measure the time required for iodine vapour to reach its equilibrium pressure under conditions of temperature and volume similar to those to be used in the actual experiments. An approximate replica of the quartz cell and its side arms was constructed in pyrex with a tube leading to an iodine reservoir as in the finished apparatus. This pyrex cell was placed in a Unicam spectrophotometer and the time required for iodine vapour to fill the evacuated cell portion after the tap to the reservoir was opened was noted. It was found that equilibrium was reached in less than 15 seconds with the reservoir dipping into a beaker of water at room temperature. Thus the two minutes which was subsequently used on the actual apparatus for equilibrium to be reached was known to be sufficient.

In a typical experiment using an iodine/acetone mixture the iodine was introduced first, through the two-way tap T_3. With T_3 closed the two-way tap T_2 was opened momentarily to fill the cell with acetone at a pressure indicated by M. Two minutes were allowed for mixing of the components then the shutter was raised and a reading was taken. At the pressures used mixing always occurred in less than two minutes. Attempts to estimate the mixing time on the apparatus failed because it was less than the response time of the galv~~o~~anometer.

After prolonged usage the silicone grease on the tap T_3 developed a light brown colour apparently due either to reaction with iodine or by iodine dissolving in the silicone. It was essential to check that the interaction of the iodine and the silicone grease did not produce a volatile species which would quench the fluorescence/

phosphorescence emission. This was done by checking at regular intervals throughout the whole course of the acetone/iodine experiments that the light emission from pure acetone in the cell was the same as that measured at the start of the experiments i.e. before iodine was introduced. The usual procedure after having made a measurement using an acetone/iodine mixture was to evacuate the cell through T_3 to cold traps. The emission of a known pressure of pure acetone was then measured as a check that all the iodine had been removed before another acetone/iodine mixture was made up and measured.

In the course of modifying the apparatus for use with iodine the photomultiplier was enclosed in a light-tight metal box so as to reduce the correction necessary due to dark current from the photomultiplier. When measurements were subsequently taken at the higher temperatures the air inside the box became hot and caused a rise in the background reading on the photomultiplier as it became warm. To eliminate this effect extra water cooling coils were fitted to the photomultiplier.

At the beginning of the iodine series of runs the cell was dismantled from the apparatus, cleaned and replaced. The subsequent re-alignment increased the sensitivity of the measurements by increasing the amount of emitted light reaching the photomultiplier cathode from the cell.

C. Methyl Iodide Quantum Yields.

Introduction.

In order to clarify and describe more fully the primary steps in the photolysis of acetone it is necessary to use and explain the quantum yields of the species produced as well as account for the mechanism of light emission. A complete understanding of the mechanism would allow the scheme to be produced which accounts similtaneously for both light emission and quantum yield results. At the end of the series of measurements of light emission results it was decided to confirm and extend the work which had been done on the formation of methyl iodide in acetone/iodine photolysis as this data seemed most likely to be of use in devising, in conjunction with the light emission results, a comprehensive account of the important steps in the photolysis of acetone.

In order to measure the quantum yield of methyl iodide (Φ_{CH_3I}) it is necessary to measure the ratio of the number of moles of methyl iodide formed to the number of quanta absorbed. The number of quanta absorbed in the photolysis of pure acetone above 100°C can be measured by measuring the yield of CO. However in the case of the photolysis of iodine/acetone mixtures the iodine has been shown (4) to interfere radically with the production of CO and so it is not possible to use CO production as an actinometric standard. It is necessary to determine the number of quanta absorbed in the photolysis of iodine/acetone mixtures by performing a separate experiment under the same conditions to measure the production of CO from pure acetone.

It was decided to measure the amount of methyl iodide formed by a radiochemical technique using I_2^{131} in the photolysis and measuring the amount of methyl iodide produced by counting the radioactive methyl iodide formed and comparing it with an I_2^{131} standard. In order to apply this analytical approach it was necessary to prepare I_2^{131} and to establish, in preliminary experiments, a technique for the separation of methyl iodide from all other photolysis products which contain I^{131}.

The preparation of I_2^{131}

I^{131} was available as a solution of NaI^{131} in thiosulphate. It was necessary to convert the active iodide into elemental iodine and introduce a known amount of elemental iodine, labelled with I_2^{131} into the photolysis cell. It was decided to use the technique which has been used previously (39, 32) of preparing active palladous iodide which can be decomposed by heat to give elemental iodine.

$$I^- \xrightarrow{\mathrm{Pd}\overset{\mathrm{Cl_2}}{\cancel{\mathrm{SO_4}}}} \mathrm{Pd}\,I_2 \longrightarrow \mathrm{Pd} + I_2$$

This technique has the advantage that the elemental iodine is labelled with I^{131} and at the same time a known mass of elemental iodine is introduced into the photolysis cell.

Active palladous iodide was prepared by precipitation from a 1% solution of palladous chloride (Johnson, Mathey and Co. Ltd.) in 1% aqueous hydrochloric acid. Active potassium iodide, prepared by the addition of a calculated amount of potassium iodide carrier solution to carrier free I^{131} (Radiochemical Centre, Amersham), was added as a 1% solution and the resulting precipitate was allowed to stand overnight before centrifuging. (Slightly less than the calculated equivalent of potassium iodide was added so that no iodide was left in solution) Iodine ions left in solution would represent both a waste of active iodine and a potential health hazard. After several washings with $\frac{N}{1000}$ hydrochloric acid, the precipitate was dried in an oven at 100°C and stored in a closed vessel in an enclosure built from lead bricks. 10 mg of palladous iodide was calculated to give a pressure of approximately 1 mm of iodine in the reaction vessel at 100°C. The required amount was weighed out in the thimble A fig.(8) which was then glass-blown into position. With U immersed in liquid air the apparatus was pumped to a high ~~volume~~ vacuum. The constrictions C_1 C_2 were degassed by heating with the hand torch then C_1 was sealed off. B was then immersed in liquid air and the palladous iodide was decomposed by heating A. C_2 was then sealed and the phial drawn off. The sinter S (No.1) ensured that flakes of palladium were not carried through to B with the iodine.

Preliminary Experiments.

Preliminary experiments were performed to establish a technique to separate methyl iodide from the other iodine containing products in the iodine-acetone system. From previously reported work on this system (4, 5, 6, 7, 8) it seemed likely that the products are methyl iodide and acetyl iodide. Acetyl iodide is unstable (several attempts to determine it have reported non-reproducible results) but it does not break down to give methyl radicals (4). Thus it seemed probable that after photolysis the iodine would be present as either molecular iodine, methyl iodide, acetyl iodide or hydrogen iodide. Of these only methyl iodide would not be expected to be strongly absorbed by alumina.

Apparatus used.

(1) **Chromatography** apparatus. The construction of the chromatography apparatus, which used argon as the carrier gas and a

radioactive detector head will be described in Appendix 2. In this application it was used simply as a qualitative analytical tool.

(2) The irradiation apparatus. In the preliminary experiments the irradiation cell was a cylindrical quartz flask with a B19 socket neck. A pyrex stopcock with a B19 cone on each end served both as a stopper for the flask and as a connecting device for attaching the flask to a gas handling system.

(3) Radioactivity counter. The counter used in the preliminary experiments was exactly the same as for the main measurements and will be described later.

<u>Experiments.</u>

In the preliminary experiments mixtures of acetone (about 200 cms pressure) and iodine (about 1 mm pressure) were exposed to the u.v. lamp for periods of up to one hour at 100°C. For those irradiations the dichromat~~ic~~e filter was omitted to increase the intensity of the incident light. After irradiation the flask was transferred to a vacuum line and the contents were frozen down into a thimble of 5 m m. bore glass tube. The glass tube was cut and a rubber bung was inserted. The contents of the thimble were warmed by the heat of the hand and as soon as they were liquid a sample was injected onto the column of the vapour phase chromatography apparatus. Using an 8 ft colmn of 30-60 mesh firebrick (diameter 1 cm) loaded with 40% by weight of tricresyl phosphate, the column was run at 90°C with a flow rate of 40 cc of argon per minute. The sample from the irradiation gave three peaks.

Synthetic mixtures of acetone and methyl iodide were passed through the column under the same experimental conditions as outlined above and from a comparison of retention time two of the three peaks found in the analysis of the products of the acetone/iodine mixture were identified as acetone and methyl iodide. The other peak [illegible], which occurred immediately after the air peak was ascribed to hydrogen iodide. No trace of iodine was found - it having either been absorbed strongly by the stationary phase or it reacted with the firebrick.

The irradiation was repeated and the products were passed through a 20 cm long alumina column, 5 cm bore, before being put on the chromatography column. No peak ascribed to hydrogen iodide was found in this case, the only two peaks formed being those corresponding to acetone and methyl iodide.

To establish that alumina is efficient in absorbing iodine a mixture of acetone vapour and iodine containing I^{131} was passed through the alumina column. All the activity was retained in the column.

To establish that acetyl iodide does not pass through an alumina column an aliquot of the photolysed mixture was taken from the solution which was counted after passing through the alumina. The sample taken was passed through the chromatography column, collected in a cold trap and re-counted. No loss of activity was found. This experiment eliminated the possibility that acetyl iodide could be passed by the alumina column but retained by the chromatography column.

The degree to which methyl iodide is retained by alumina was studied in preliminary experiments by photolysing a mixture of active iodine and acetone. The products were passed through the

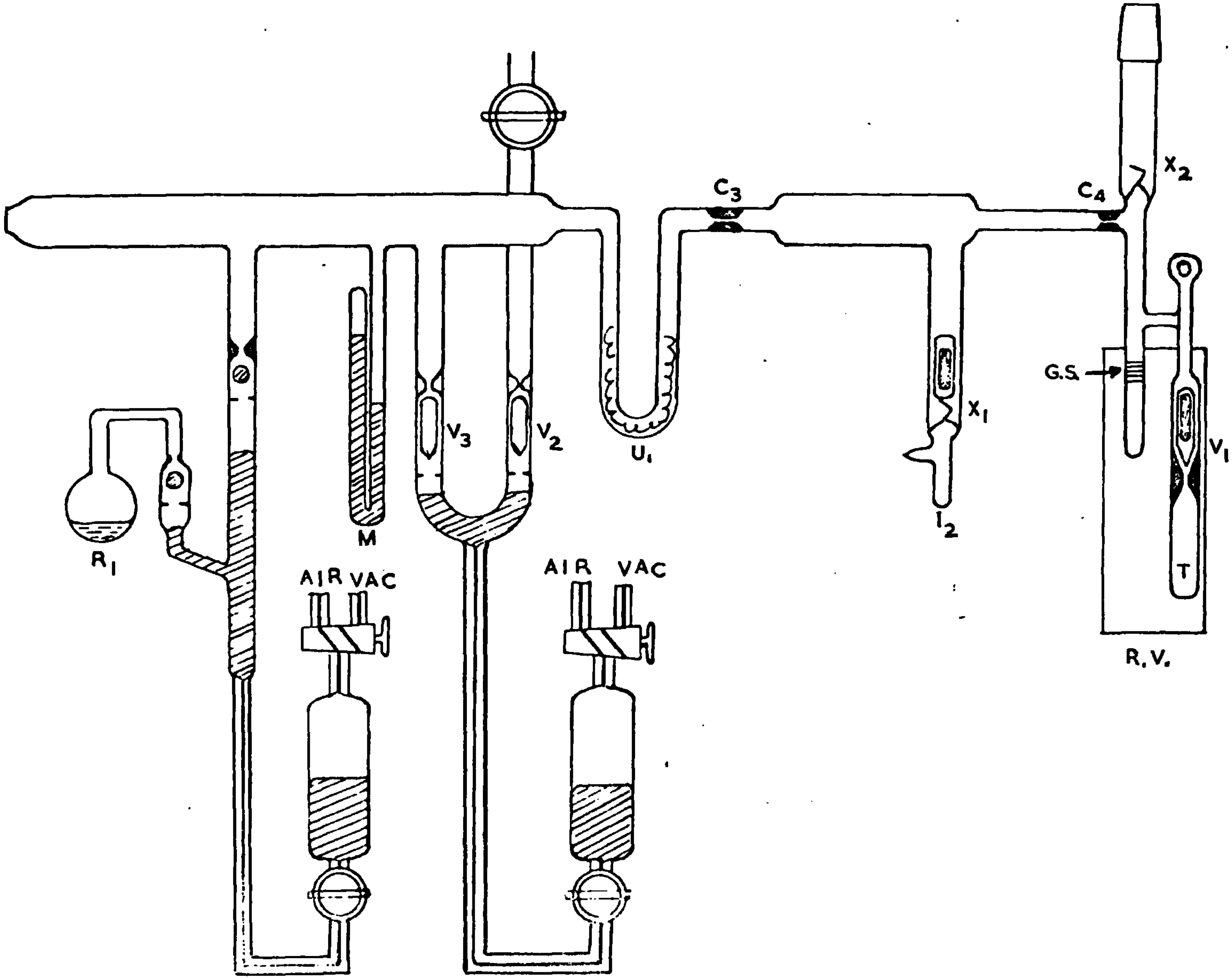


Fig. 9 Cell filling apparatus

alumina column and then counted in the scintillation counter (see later for counting technique). The products were then passed several times through the column and counted after each operation in a similar container. The count remained constant throughout, demonstrating that methyl iodide is not retained by alumina.

Attempts to remove activity from the column by prolonged evacuation and passing air through it failed; thus it was established that of the reaction products containing iodine in the photolysis of acetone/iodine mixtures, methyl iodide is the only iodine containing molecule not retained by an alumina column.

Experimental Procedure in Preparing a Sample for Irradiation.

The procedure for preparation of a known mixture of acetone and iodine will be described; the procedure when iodine was omitted is then obvious.

The reaction vessel R.V. fig.(9) was carefully cleaned by filling it with a chromic - sulphuric acid mixture before each irradiation. The cleaning mixture was removed completely by about fifteen successive washings with about 400ccs of distilled water, particular attention being paid to the side arm section. Rapid removal of washing water from the cell was achieved with the aid of a water pump.

The apparatus to the right of U_1 fig.(9) was then assembled. The active iodine was prepared as previously described. The cell was evacuated, special attention being paid to removing all residual water, and the cut-off V_2 V_3 raised to isolate the cell from the main vacuum line. Acetone was then introduced into the cell from R_1 until the required pressure was registered by M. C_3 was constructed especially so that one touch of the flame from the hand torch was sufficient to enable it to be sealed and drawn off. The volume between C_3 and C_4 was kept constant in each run and the amount of acetone finally contained in the cell could be calculated from a knowledge of this volume. Any error in the estimation of this volume (about 35ccs) was small compared to the volume of the reaction cell (664ml). With C_3 drawn off the acetone was condensed in the side arm T and the valve V_1 was closed by removing the magnet which held it open.

The break-seal X was opened by dropping on it a plunger constructed from soft iron encased in pyrex. The iodine liberated was condensed on the lower end of the vessel which was cooled in liquid air. C_4 was then drawn off.

The iodine was vapourised first by running warm water over the main body of the cell. When all the iodine was vapourised the acetone was allowed to warm up and the vapour pushed past V_1 to mix with the iodine vapour. In this way the possibility of reaction between liquid acetone and iodine was eliminated.

The vessel was cleaned externally with a dilute soap solution, special attention being given to the removal of grease from the end windows. It was then dried, polished and transferred to the irradiation oven.

Irradiation.

The optical bench and furnace used were exactly the same as used by Brown and modified by Mitchell (29, 32) and will not be described here.

The lamp-filter combination employed in the light emission experiments was again used. The light from the lamp passed through a 200cc spherical quartz flask filled with distilled water. The position of this flask was adjusted until a nearly parallel beam was obtained through the cell. The shutter was placed between the flasks and the filter system. The filter system was thermally insulated by being separated from the quartz window of the oven by an air gap of 2 cm. The reaction vessel lay horizontally in the oven on the two glass covered metal bars and was effectively filled by the u.v. beam. The cell consisted of a cylinder 24 cms long and 6 cms external diameter with plain polished ends. The side arm was connected to it by a quartz-pyrex seal.

Previous workers having reported slight variation in intensity of the lamp output, ~~so~~ it was decided to construct a constant current supply. The basic circuit for this was taken from that given by Elliot and Radley (47). A slight modification was introduced to prevent damage to the relay contacts by the high current when the arc was struck. This consisted of an extra resistance in the lamp circuit which was shorted out by another relay when the lamp began to warm up. This device gave a reproducible constant current of 0.6 amps.

The transmitted beam was measured by a selenium barrier-layer photocell (Evans Electro Selenium Ltd.) placed one centimeter from the rear face of the furnace. This photocell has been shown (29) to give an output current which is directly proportional to the indicent light energy when the resistance in the circuit is less than 200 ohms. It was connected directly across a Unipivot microammeter (basic movement 111ohms). The photocell was mounted on a chair and could be placed about one centimeter from the furnace window in an accurately reproducible position.

Irradiation Procedure.

The filter solutions were inspected before each run. The potassium chromate and the nickel sulphate solutions never showed signs of deterioration but the chromate was replaced for each irradiation because the transmitted spectrum is particularly dependent on the strength and purity of this component.

The lamp was switched on at least half an hour before irradiation in order to warm up.

The chromate filter cell and the photocell both tended to warm up slightly if left in position close to the furnace at 100°C. This caused a drop in intensity of light passed by the chromate of about 2% after three hours and a drop in the efficiency of the photocell of the same order in the same time. To eliminate this effect the chromate cell and the photocell were not placed in position close to the furnace until just before an irradiation was commenced. In the longest irradiations (30 minutes) no appreciable fall in intensity was noted. Light, other than the u.v. transmitted through the cell, was prevented from reaching the photocell by means of an opaque cloth which enclosed the whole of the photocell end of the apparatus.

When the reaction cell was transferred to the oven at 100°C, the temperature, as recorded by a thermometer inserted into the oven, returned to 100°C in about 15 minutes. A further 30 minutes was allowed before an irradiation was commenced to ensure that the cell and the whole of its contents had attained that temperature. The temperature of the oven was constant to within 1°C.

At the end of an irradiation the lamp was switched off and the reaction cell transferred to the analytical apparatus.

Analysis.

Carbon Monoxide Analysis from Pure Acetone Irradiations.

The photolysis of pure acetone at 120°C can be used as an actinometric standard. Analysis of the amount of carbon monoxide produced enables the number of quanta absorbed to be calculated since one molecule of carbon monoxide is produced for each quantum absorbed. The amount of carbon monoxide produced was measured by measuring the volume of non-condensable gases then oxidising the CO to CO_2. The CO_2 was condensed by a cold trap and the volume of the remaining gases was measured so that the amount of carbon monoxide could be calculated by difference. Iodine pentoxide was used for the oxidation of the carbon monoxide. At a temperature of 140°C the reaction

$$I_2O_5 + 5\,CO = I_2 + 5\,CO_2$$

proceeds rapidly. Neither methane nor ethane is attacked at this temperature.

Materials used.

The iodine pentoxide was "analar" grade which was dried by heating at 200°C for two days before use. When first used it gave off a gas which was condensable. This gas was probably water vapour. After pumping for one day at 145°C the gas ceased to be given off and a good vacuum could be maintained.

Apparatus.

The apparatus used is shown in fig.(10). The U tube U_2 was packed with granules of iodine pentoxide. Each end of the U tube was packed with silver gauze to remove liberated iodine. The temperature of U_2 was maintained at 145°C ± 1°C by means of electrothermal tape controlled by a Sunvic Energy Regulator (type TYB). The length of the tube G (fig.10 inset) was marked at three distances approximately 3 cms, 6 cms and 9 cms from V_1. Before the apparatus was constructed the volume between each of the marks and V_1 (with the ball seated) was measured by weighing with mercury in the usual way.

Procedure.

Preliminary experiments with samples of pure carbon monoxide and methane introduced via T_3 established that at 145°C a sample of about 10 micromoles of carbon monoxide was completely oxidised in 90 minutes by the circulation technique to be described later. Approximately the same amount of methane was unaffected after 150 minutes using the same technique. In the actual measurements of the amount of carbon monoxide produced in the photolysis of pure acetone, T_4, T_3 and T_2 (fig.10) were closed and the cell was joined to the vacuum line by means of a B14 joint at J. T_2 was then opened and the apparatus pumped down to a high vacuum. Liquid air traps were then placed round D and B and the seal X_2 (fig.9) was broken. For the higher pressures of acetone the bottom of the cell was cooled in liquid air to reduce the vapour pressure in the cell before X_2 was broken. As the cell warmed up the acetone transferred to D and B (fig.10) slowly, thus ensuring that no acetone escaped past these traps.

Non-condensable gases were transferred to the section to the left of T_3 by means of the Toepler pump. A seal was made at V_1 by means of a ball bearing held down to a ground seal by 10-15 cms. head of mercury. A similar seal at V_2 but with a head of only 1 or 2 cms. of mercury acted as a non-return valve. The seals were seated with the help of a magnet. About 30 strokes were usually needed to transfer the non-condensable gases into the section between V_1 and V_2.

The amount of gas in G was determined by measuring the pressure of a known volume. By using the calibrated volumes selectively a large pressure difference (i.e. several centimeters) could be obtained for measurement with a cathetometer. The correction for surface tension made by measuring the heights of the menisci and using the formula in the I.C.T. was usually found to be negligible because the meniscus heights were of nearly the same size and the pressure difference was always in the region of a few centimeters.

The gas was then circulated slowly through the iodine pentoxide, carbon dioxide being condensed out by immersing U_1 in liquid air. Using V_1 as a non-return valve the gas was circulated for two hours.

After complete oxidation of the CO the non-condensable fraction was collected in G and its pressure measured again. The amount of carbon monoxide originally present was found by subraction. This method gave more consistent (and smaller) results than the direct measurement of the CO_2 formed. The discrepancy between the two readings can probably be attributed to water vapour coming off the iodine pentoxide or condensable material from the tap grease.

Methyl Iodide.

No B14 joint was attached to the cell for acetone/iodine runs. A soft iron plunger enclosed in glass was placed in X_2 (see fig.9) and the cell was glass-blown onto the analysis line at Y. (fig.10). The counting tube (to be described later) was attached at J by a B14 joint and, with T_3 shut T_2 T_5 and T_4 were opened and the apparatus evacuated.

Liquid air traps were placed round D and B then the plunger was raised with a magnet and dropped to open X_2. The contents of the cell passed into U_3 which was a U tube 20 cms. in length containing aluminium oxide. Products not stopped by the alumina were either condensed in D and B (methyl iodide and acetone) or pumped away (a little CO perhaps).

The drawn out limb at Z was broken when the cell was highly evacuated and the cell allowed to fill with air before it was sealed again. The cell was again evacuated through the alumina column. This last operation ensured that no methyl iodide was left on the column but all was transferred to D or B.

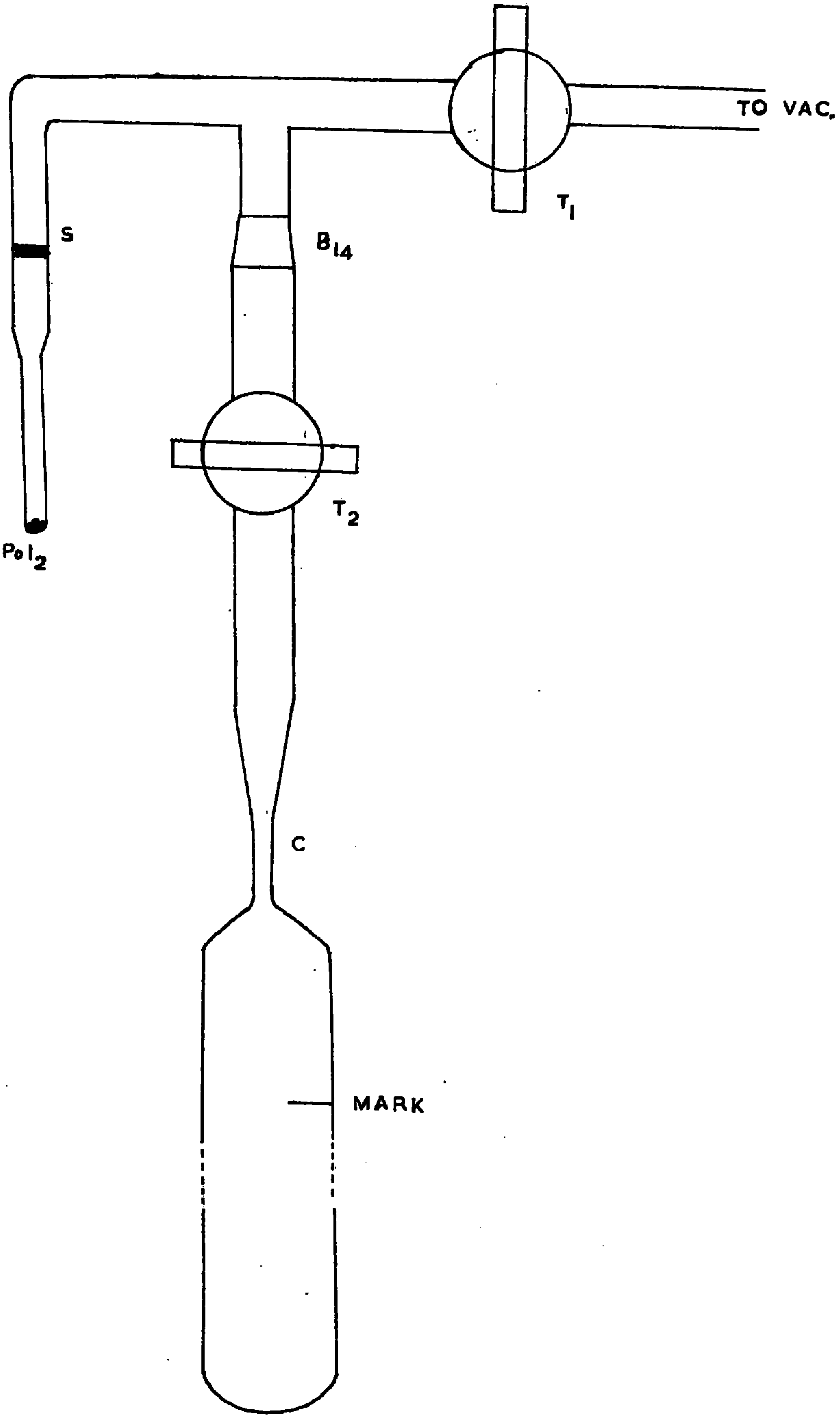
To transfer the contents of D and B to the counting tube (C.T), T_4 was closed and, when a high vacuum was obtained, T_2 was closed. (fig.10). The liquid air was removed from D and B and a liquid air trap placed round C.T. When the contents of D and B had distilled into C.T. the tap T_5 was closed and the counting tube removed from the apparatus at J. Acetone was poured into the open limb of the counting tube and T_5 opened so that it filled the tube to a fixed mark. The tube was then warmed to room temperature and shaken vigorously to mix the contents before they were counted.

Counting Technique.

The counting tubes, (fig.10) were constructed from a thin walled pyrex test tube of diameter 15 mm. They fitted snugly into a sodium iodide well-crystal scintillation counter through a hole of 15 mm clearance in the roof of the lead castle.

Highly stabilised H.T. was applied to the photomultiplier from 1007 type potentiometer. The output from the photomultiplier was

Fig. 11 Preparation of I^{131} standard



amplified by a head amplifier and a linear pulse amplifier. Before recording on the scaler the pulses passed through a pulse analyser, (type N101), the window of which was centred on the 0.33 Mev I^{131} photopeak.

The counting apparatus was used purely to make comparative measurements (see below) and the active solutions to be compared were always counted close enough together in time so that decay of the I^{131} ($t_{\frac{1}{2}}$ = 8 days) was negligible.

Preparation of a Standard I^{131} solution. (fig.11).

The palladous iodide used to prepare the standard was the same source as that prepared and used for the iodine used in the acetone/iodine photolysis. The preparation of a standard of known iodine content and of the same specific activity as the iodine used in the photolysis experiments, enables the amount of methyl iodide collected in the analysis to be determined by simple comparative measurements. The amount of active palladous iodide needed to give a solution of approximately the same activity as expected for the methyl iodide solution was calculated from Sutton's results. Twenty five times this amount was weighed in a tube on a semimicro balance and fixed below sinter S (No.1), by glass blowing. With U immersed in liquid air T_1 and T_2 were opened and the apparatus evacuated to a high vacuum. $T_{\cancel{2}1}$ was closed and with the counting tube C.T. immersed in liquid air the palladous iodide was heated with the hand torch. The iodine was condensed rapidly in C.T. there being little time for it to react or dissolve in the silicone grease on the taps.

When all the palladous iodide was decomposed $T_{\cancel{1}2}$ was closed and the counting tube removed from the apparatus at the joint B14. The iodine was transferred into a 250cc graduated flask by repeated washings (about 15) with 10cc portions of acetone. The solution in the flask was then made up to the mark and shaken well. Acetone from the graduated flask was poured into the open limb of C.T. and T_{12} was opened carefully until the level in the counting tube reached the 10cc level mark placed on C.T. The fixed mark on all the counting tubes i.e. the standard and those which contained methyl iodide, was at exactly the same level.

The standard I^{131} solution was to be kept for a period of weeks (until all the palladous iodide source was used in photolysis experiments or the activity became too low to count) so the construction C was sealed off to eliminate any possibility of slow reaction between the iodine solution and silicone grease. The standard solution thus contained a known amount of iodine in the same volume of solution with the same geometry as the active methyl iodide solutions. The amount of iodine in the methyl iodide solutions could then be easily determined by comparative counting of the two solutions.

Health Aspects.

Health hazards in these experiments can be ascribed to

(1) the possible harmful effects of u.v. on the eyes

(2) the radio-active hazard of using I^{131}.

All experiments were conducted in the open laboratory (as opposed to a room which could be evacuated during an irradiation) so it was necessary to shield the lamp at all times. This was accomplished with a metal box. When the lamp had to be run with the box removed (for lining up experiments) a pair of glasses opaque to u.v. were worn.

I^{131} is a weak beta emitter (0.61 and 0.33 Mev) with gamma energies of 0.35 and 0.64 Mev. The main danger to health is ingestion of active material, iodine being concentrated in the thyroid. Glass blowing onto the apparatus which had contained active iodine could not be avoided in this case and special precautions had to be taken. One of the following two methods was employed on each occasion: (depending on convenience).

(1) The apparatus was washed thoroughly with KI solution and distilled water

(2) Glass blowing was done through a cold trap.

All active iodine residues were collected in acetone and KI solutions and stored until they had decayed sufficiently to be disposed of down the drains.

CHAPTER III.

Light Emission Results.

Treatment of Results.

Let I_1 be the illuminating intensity in the central portion of the cell which is seen by the photomultiplier then

$$I_1 = \frac{1}{T} \quad (I_o + I_t)$$

where I_o and I_t are the intensities of the illumination incident on and transmitted by the cell respectively. T is a constant depending on the geometric properties of the cell. If the area viewed by the photomultiplier is around the centre of the cell then T would take a value of about 2 (i.e. approximately the average of I_o and I_t) but since it will be seen that the exact value of T is not important, provided that it remains constant, it is not necessary to derive a precise value for T

$$\text{then } I_e = K.i_m \qquad (1)$$

where I_e is the emission intensity, i_m is the current from the photomultiplier and K is a constant,

$$\text{and } I_t = K'.i_c \qquad (2)$$

Where i_c is the current from the photocell and K' is another constant.

No complication due to re-absorption of emitted light by acetone need be introduced as it is known that the emission and absorption spectra do not overlap.

The emission efficiency is given by

$$Q = \frac{{}_T I_e}{{}_T I_a} \qquad (3)$$

where ${}_T I_e$ is the total emission from the volume visible to the photomultiplier and ${}_T I_a$ is the total absorbed intensity in the same volume.

When the area seen by the photomultiplier is small enough for I_1 to be taken as constant over that region then

$$ {}_T I_a = I_1 - I_1 e^{-px} $$

$$ {}_T I_a \doteq I_1 \; (1-1+px) $$

$$ \therefore \quad {}_T I_a \doteq I_1 px \qquad (4) $$

where x is a cross section for absorption and p is the concentration of acetone.

Thus the emission efficiency, Q, is given by (3) and (4).

$$ Q = \frac{I_e}{I_1} \frac{1}{px} = \frac{K.im}{I_T px} = \frac{K.im}{\frac{1}{T} (I_o + I_t) \; px} $$

Introducing I_t from (2)

$$ \therefore \; Q = \frac{T.K.im \; I_t}{px \; K' i_c \; (I_t + I_o)} = \frac{T.K.im}{px \; K' i_c} \cdot \frac{\frac{I_t}{I_o}}{1 + \frac{I_t}{I_o}} $$

From the construction of the potentiometer

$$ \frac{i_m}{i_c} = \frac{r}{R} $$

$$ \therefore \; Q = \frac{T.K.r}{px. K'. R} \cdot \frac{\frac{I_t}{I_o}}{1 + \frac{I_t}{I_o}} $$

Collecting up the constants

$$ Q = \frac{C.r}{p \cdot \mathcal{E}} \left(\frac{\frac{I_t}{I_o}}{1 + \frac{I_t}{I_o}} \right) $$

where $\mathcal{E}$ = the extinction co-efficient ($x \propto \mathcal{E}$).

Extinction Co-efficient Measurements.

From the above theory the need for a knowledge of the value of $\mathcal{E}$ at each temperature is apparent. $\mathcal{E}$ for the lamp filter combination used in these experiments was measured on the apparatus in the following way:

With the photomultiplier disconnected the apparatus was switched on and allowed to warm up in the usual way. The cell was filled to a known pressure of acetone and the shutter was raised so that transmitted light gave an output current from the photocell. There being no balancing current from the photomultiplier, a deflection was recorded on the galvanometer. The potentiometer was adjusted until a large deflection was obtained on the galvanometer scale and a reading was quickly taken. The cell was rapidly evacuated and the galvanometer deflection with no acetone in the cell was taken. The ratio of the two readings gave $\frac{I_t}{I_o}$ for the pressure and temperature of acetone used. The need for haste between readings of I_t and I_o was because any change in lamp intensity in that time would introduce error into the result. Unlike measurements of emission efficiencies which involve a comparison of transmitted and emitted intensities, these transmission intensity measurements are not independent of the incident intensity.

TABLE I.

EXTINCTION CO-EFFICIENT MEASUREMENTS.

TEMPERATURE ^{o}C	$\frac{I_t}{I_o}$	ε $\frac{cm^2}{\text{molecules}}$
$20^{o}C$	0.771 ± 0.009	5.70×10^{-21}
$50^{o}C$	0.782 ± 0.01	5.95×10^{-21}
$70^{o}C$	Not available	6.25×10^{-21}
$100^{o}C$	0.790 ± 0.01	6.58×10^{-21}
$120^{o}C$	0.791 ± 0.01	6.92×10^{-21}
$150^{o}C$	0.801 ± 0.01	7.03×10^{-21}

All values of $\frac{I_t}{I_o}$ were measured at a pressure of 10 cms.Hg of acetone at $20^{o}C$.

Measurements of $\frac{I_t}{I_o}$ at various acetone pressures at the same temperature were taken and plots of log $\frac{I_t}{I_o}$ against pressure gave straight lines as expected (these results are not shown) ε could be calculated from the slopes of the lines but it was decided to take a series of readings at a constant acetone pressure for each temperature, so that an estimate of the error in the determination of $\frac{I_t}{I_o}$ could be easily made. The results at 20°C, 50°C, 100°C and 150°C are shown in Table I. The r.m.s. error is shown alongside the mean value for $\frac{I_t}{I_o}$. In the calculation of $\mathcal{E}$ (see below) log $\frac{I_t}{I_o}$ is used, thus reducing the effects of the error quoted for $\frac{I_t}{I_o}$.

<u>Typical Calculation of $\mathcal{E}$ (20°C).</u>

We have the Beer-Lambert Law $\frac{I_t}{I_o} = 10^{-\mathcal{E}.c.d}$ where c is the concentration and d is the path length. From Table (I) $\frac{I_t}{I_o} = 0.771$ for 10.0 cms. acetone measured at 20°C.

$$\therefore \log_{10} \frac{I_t}{I_o} = \bar{1}.8872 \quad \text{and} \quad -\log_{10} \frac{I_t}{I_o} = 0.1128$$

From the equation above

$$\mathcal{E} = \frac{-\log_{10} \frac{I_t}{I_o}}{d.c.}$$

if d is measured in cms. (6.0 cms. in this case) and c is in molecules/cc.

$$c = \frac{P}{76} \times \frac{273.2}{T} \times \frac{6.023 \times 10^{23}}{22414}$$

$$= \frac{P}{T} \times 9.663 \times 10^{19} \text{ molecules/cc}$$

when P = pressure in cms. and T = absolute temperature.

At 20°C and 10 cms. of acetone

$$c = 32.97 \times 10^{17} \text{ molecules/cm}^3$$

and $\mathcal{E} = \frac{0.1128}{6 \times 32.97 \times 10^{17}} = 5.702 \times 10^{-21} \frac{\text{cm}^2}{\text{molecules}}$

At all other temperatures $\mathcal{E}$ was calculated in the same way and the results are reported in Table I. The values of $\mathcal{E}$

calculated in this way were, within the limits of experimental error, consistent with values of ε derived from the slopes of the $\log_{10} \frac{I_t}{I_o}$ versus pressure graphs.

As reported previously by Luckey and Noyes (49) the extinction co-efficient increases with temperature but a precise comparison with their values is pointless since extinction co-efficients can only be compared exactly when the same lamp-filter combination is used. The effect of temperature on the measured value of ε in the apparatus used in this work is shown graphically in fig.(23).

OXYGEN-ACETONE LIGHT EMISSION RESULTS.

Preliminary experiments.

In testing and improving the apparatus the total emission from pure acetone at various acetone pressures and temperatures was studied. When the equipment was fully developed and refined results were obtained in substantial agreement with those published by Luckey and Noyes (39). These results are not recorded or discussed here but, if required, values of total emission efficiencies at varying acetone pressures and at several different temperatures can be extracted from the tabulated results for later experiments.

Calculation and tabulation of results.

The method of calculation and tabulation of the results can be illustrated by reference to Table 2 (p 74) which deals with results at 20°C for the acetone-oxygen system. The first four columns list the pressure and concentration of acetone and oxygen. The values of $\frac{I_t}{I_o}$ in column 5 were calculated from the previously obtained value for ε (see table 1). Column 6 is a combination of columns 5 and 2 with the previously determined value for ε. The corrected potentiometer reading was obtained as explained previously in the chapter on experimental techniques and multiplied by column 6 to give the total emission efficiency Q. Q' the fluorescence efficiency is the value of Q when excess oxygen is present. The assumption is made that oxygen in excess removes all the phosphorescence but does not modify the fluorescence. This assumption is justified by previous work on light emission in the presence of oxygen (39, 35). Q'' the phosphorescence efficiency can then be obtained as the difference

Fig. 12 Effect of acetone pressure on total phosphorescence efficiency

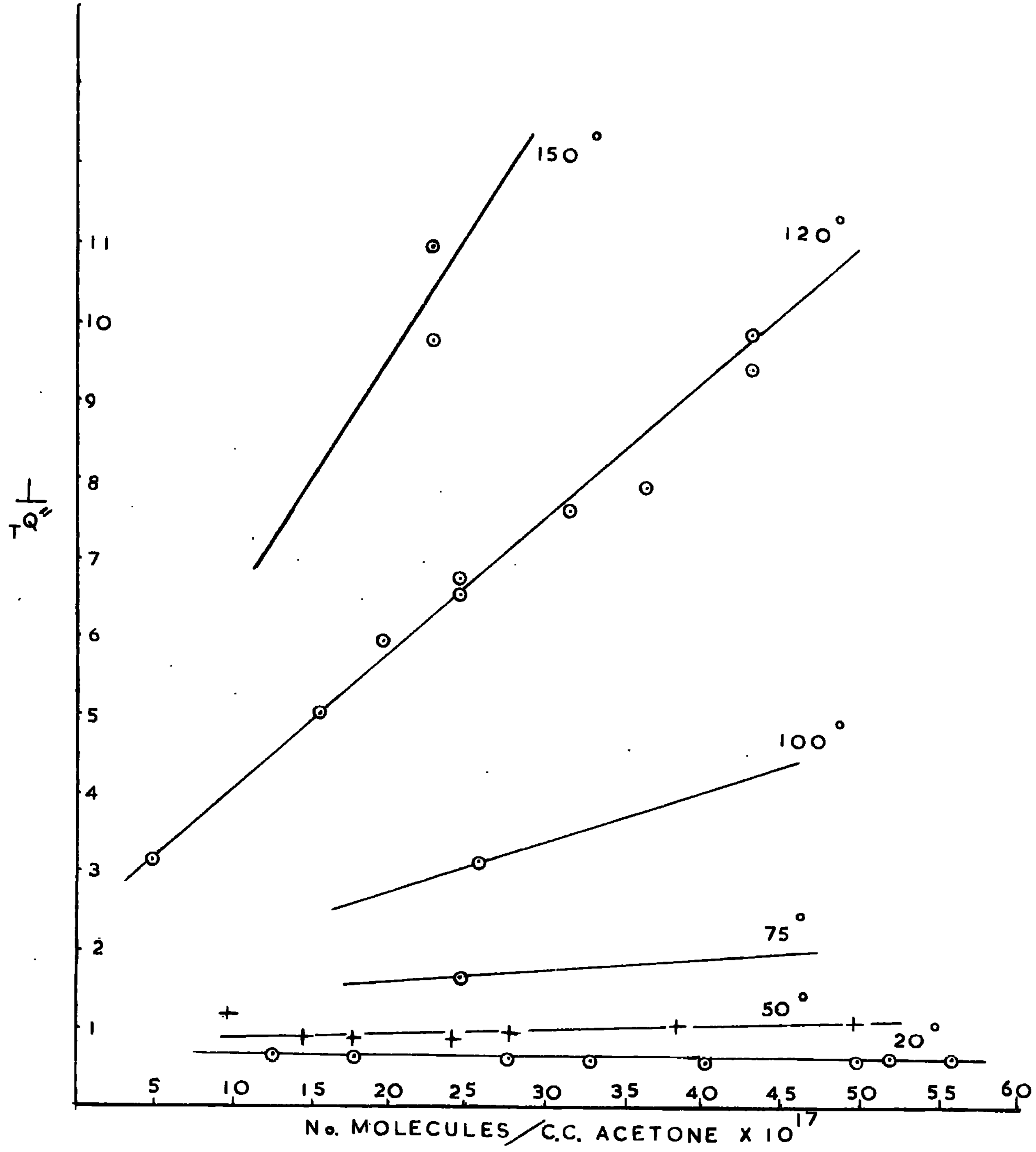


Fig. 13 Effect of acetone pressure on fluorescence efficiency

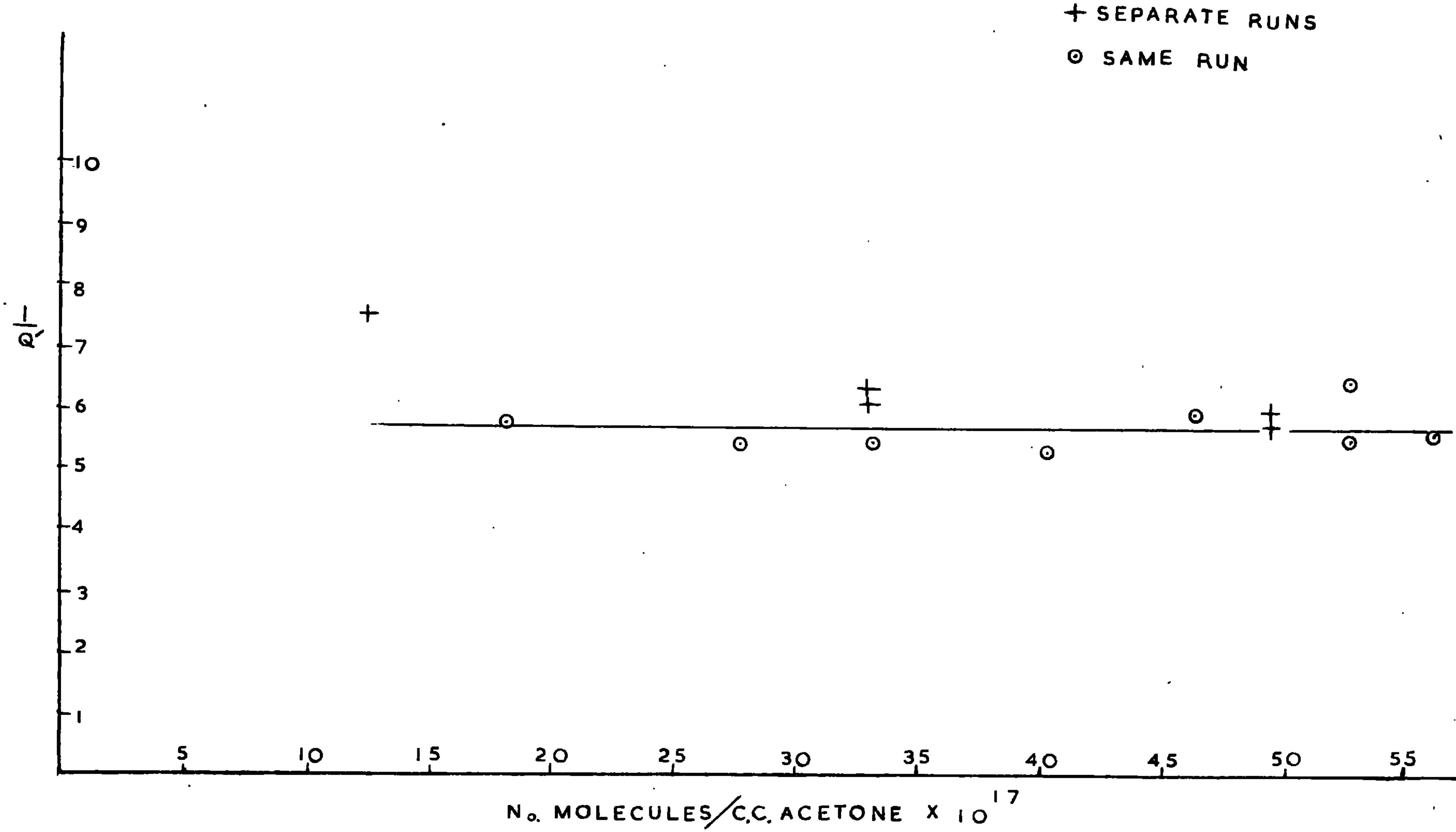
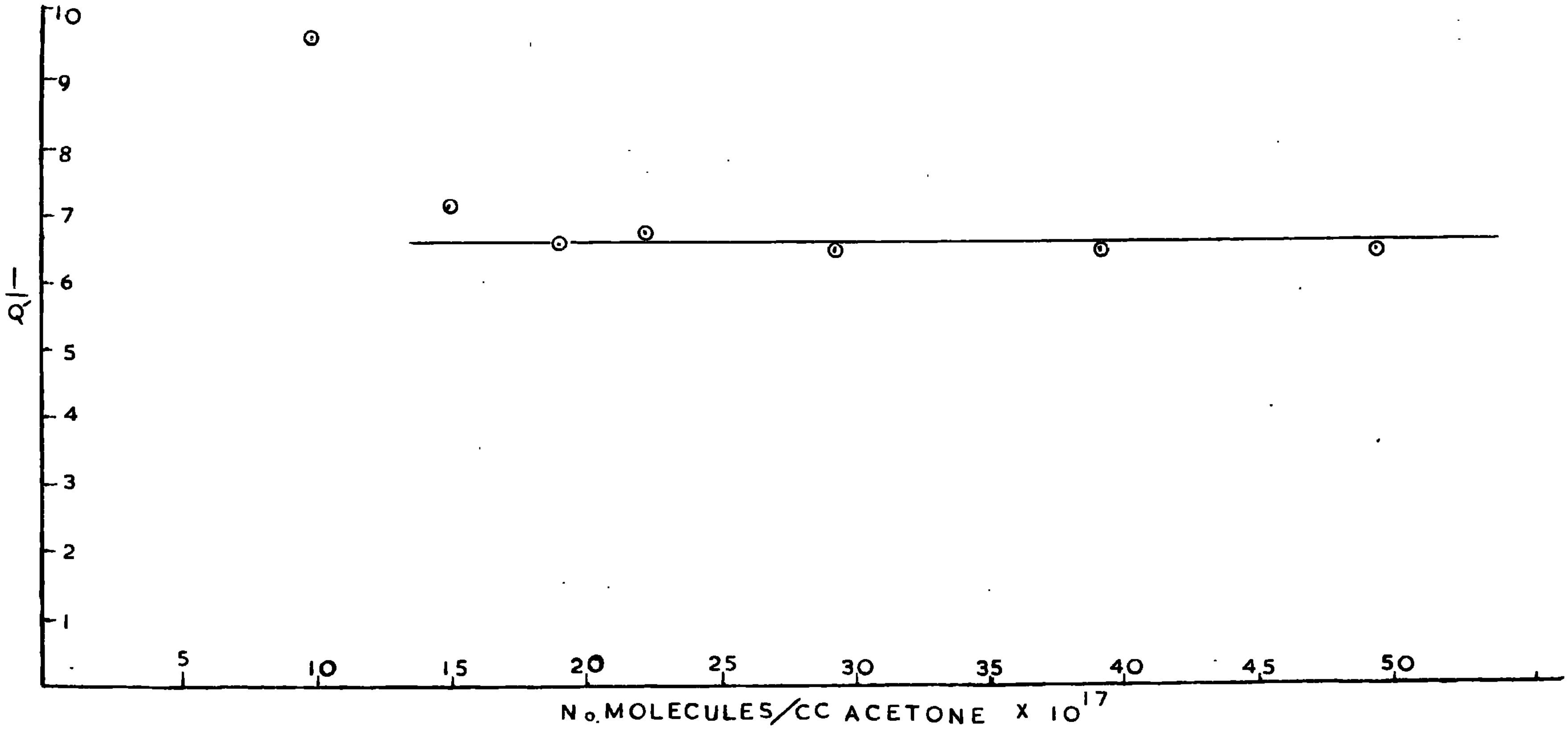


Fig. 14 Effect of acetone pressure on fluorescence efficiency 50°C



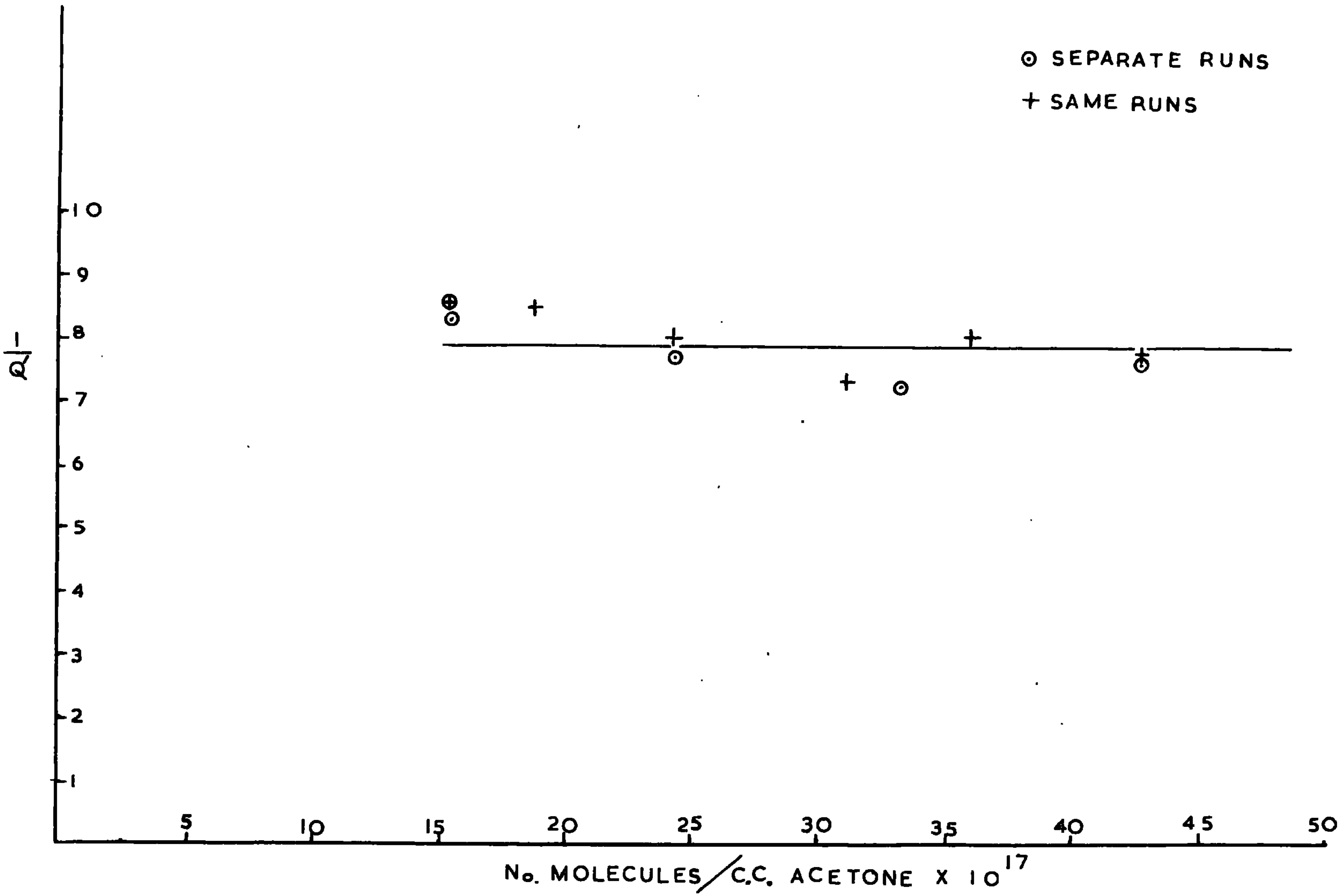


Fig. 15 Effect of acetone pressure on fluorescence efficiency 120°C

between Q and Q', $\frac{1}{Q'}$ and $\frac{1}{Q''}$ have been tabulated to allow Stern-Volmer type plots to be made; these graphs will be dealt with more fully in due course.

Tables 2 - 8 contain the light emission results for the acetone-oxygen system. The results are arranged according to the temperature at which they were obtained except for Table 8 where results obtained over a range of temperature are recorded. The temperature used covered the range 20°C up to 150°C.

The effect of acetone pressure on the total phosphorescence efficiency.

Fig.(12) contains data which has been extracted from Tables 2 - 8 to show the effect of temperature on the plot of $\frac{1}{Q''_T}$ against acetone concentration. Q''_T is the phosphorescence in the absence of any quenching by oxygen, iodine or other quenching agent. It can be seen from fig.(12) that at the lowest temperature used, change in acetone concentration has no detectable effect on the phosphorescence efficiency whereas at 120°C the effect is quite marked. It can also be seen from fig.(12) that at the three temperatures (20°C, 50°C and 120°C) where a range of acetone pressure was investigated a linear relationship applies between $\frac{1}{Q''_T}$ and acetone concentration. The lines drawn at 75°C, 100°C and 150°C have been estimated from the more extensive data at other temperatures.

The effect of acetone pressure on fluorescence efficiency.

The results relating the value of $\frac{1}{Q'}$ to acetone pressure are shown in figures (13, 14, 15). The points collected in a single set of readings are marked with circles, those marked by crosses are collected data from other runs. No tendency for $\frac{1}{Q'}$ to increase with acetone concentration is observed. When this result was first

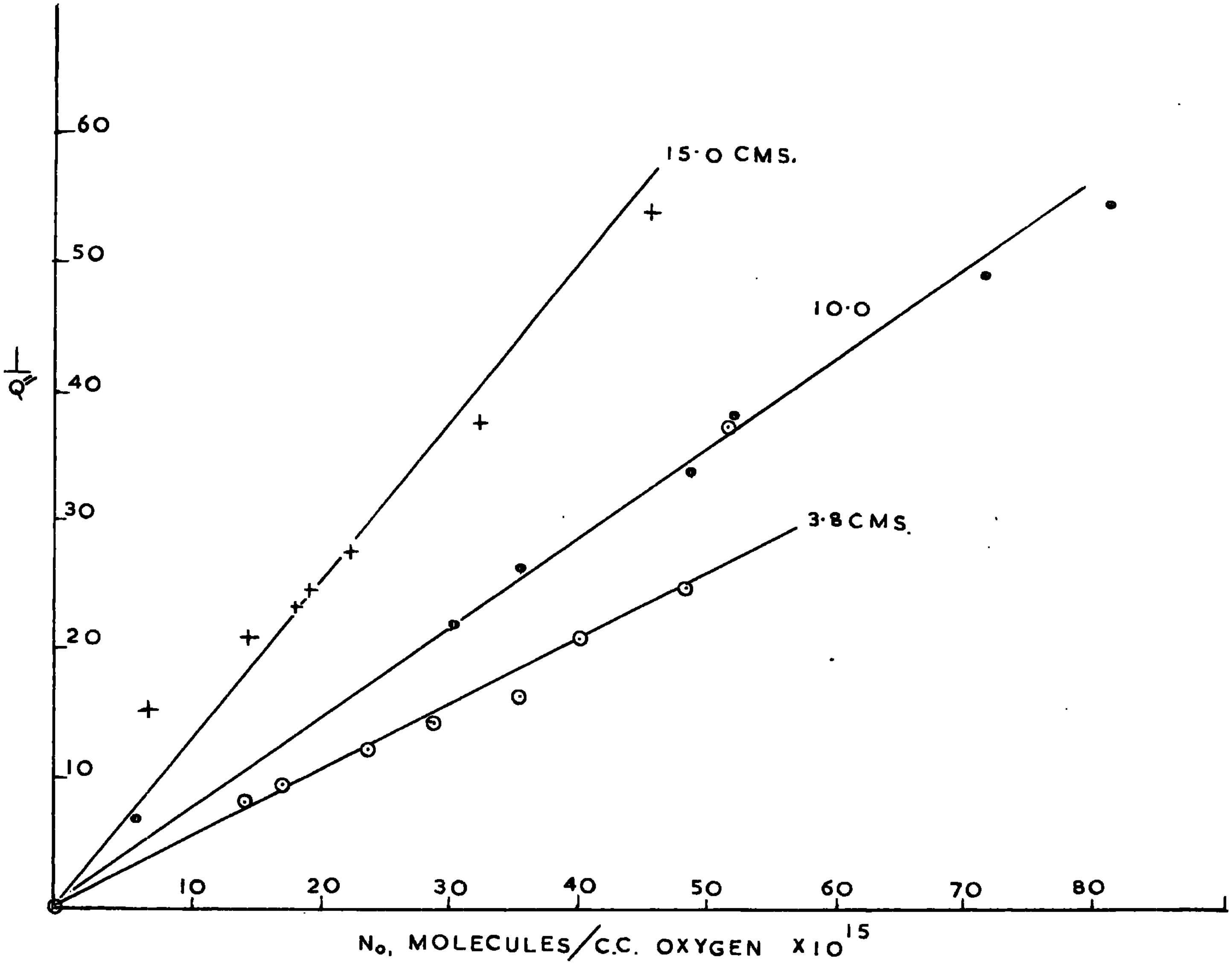


Fig. 16 Effect of oxygen on the phosphorescence efficiency 20°C

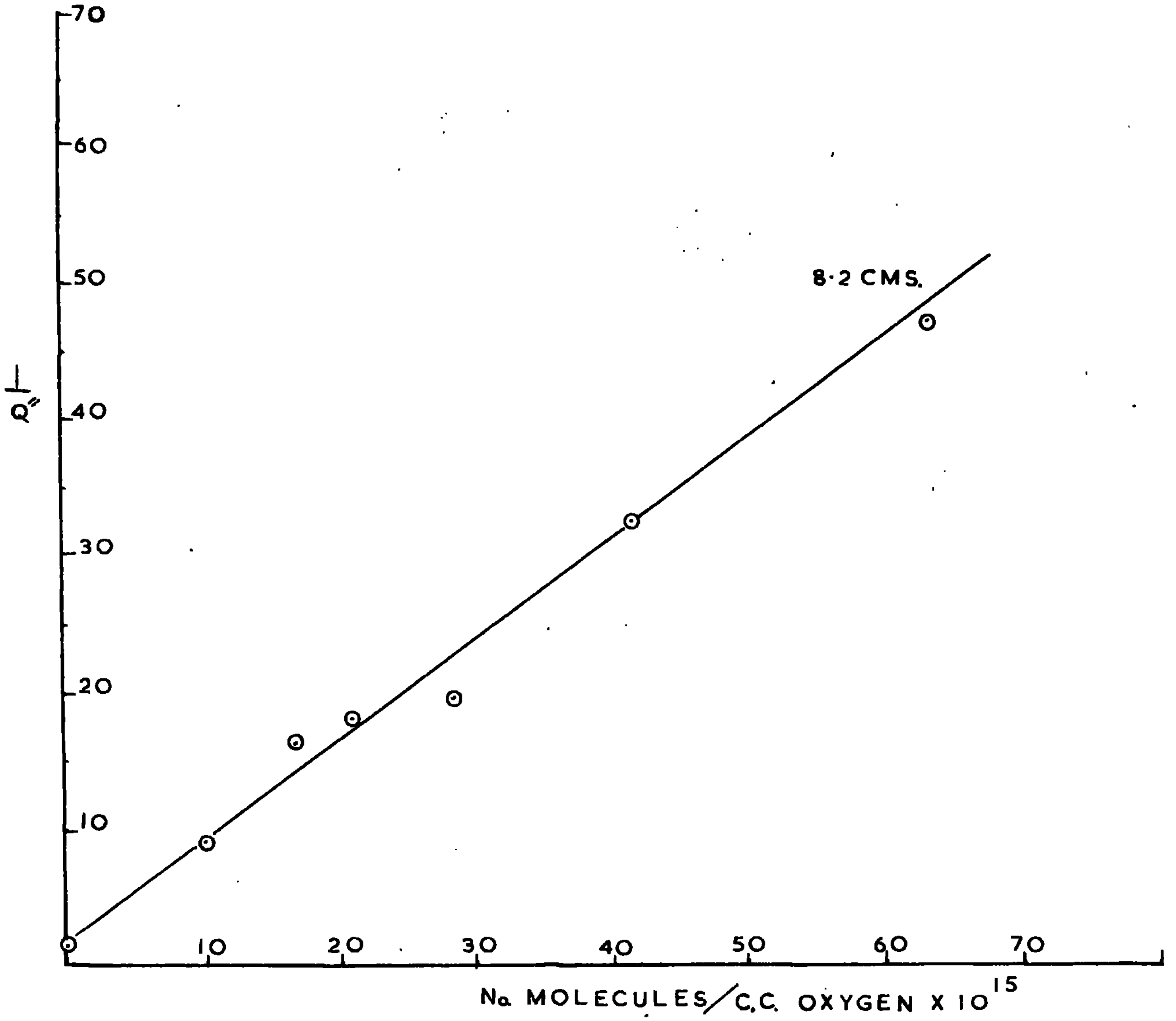


Fig. 17 Effect of oxygen on phosphorescence efficiency 50°C

Fig. 18 Effect of oxygen on phosphorescence efficiency 75°C

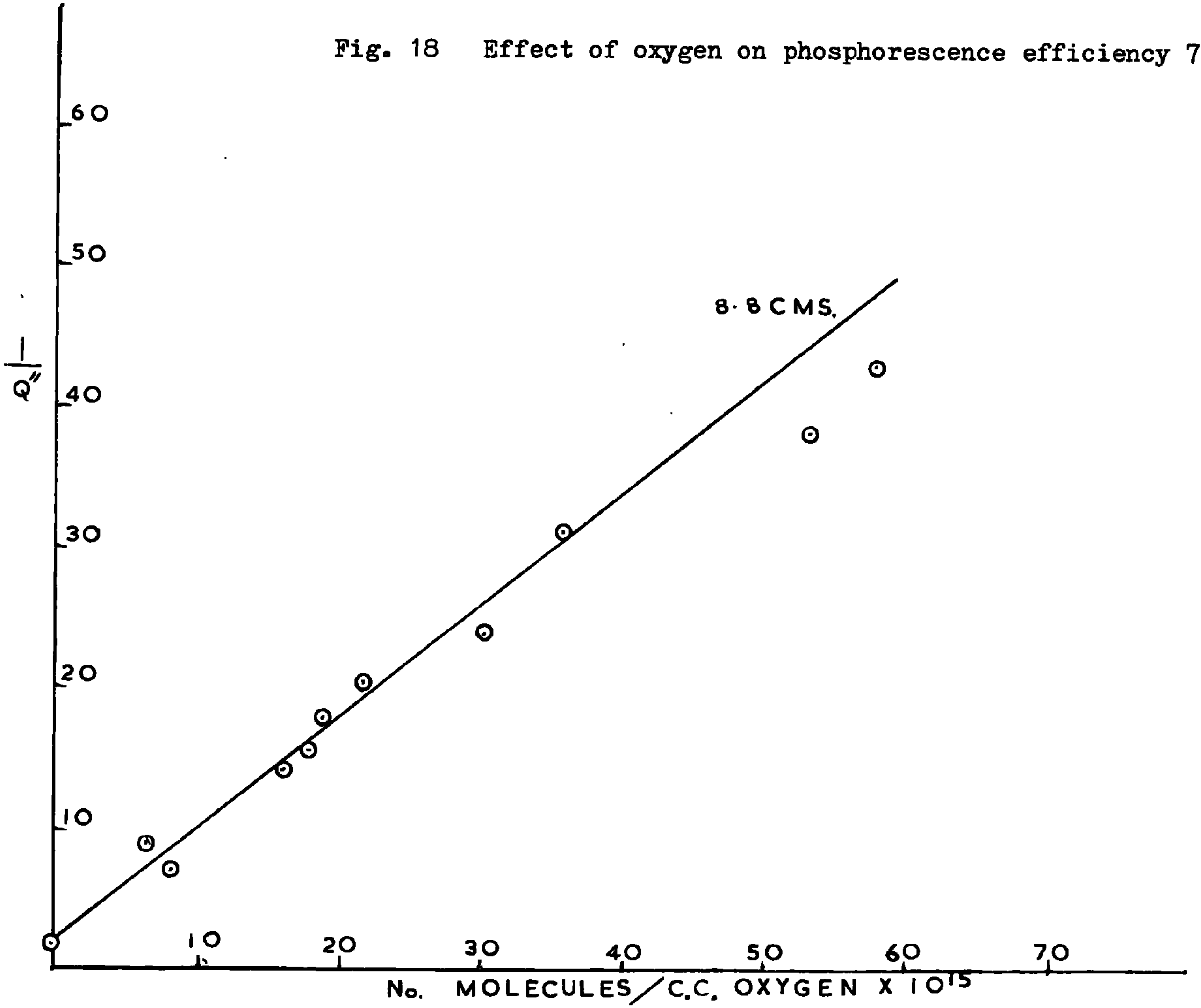
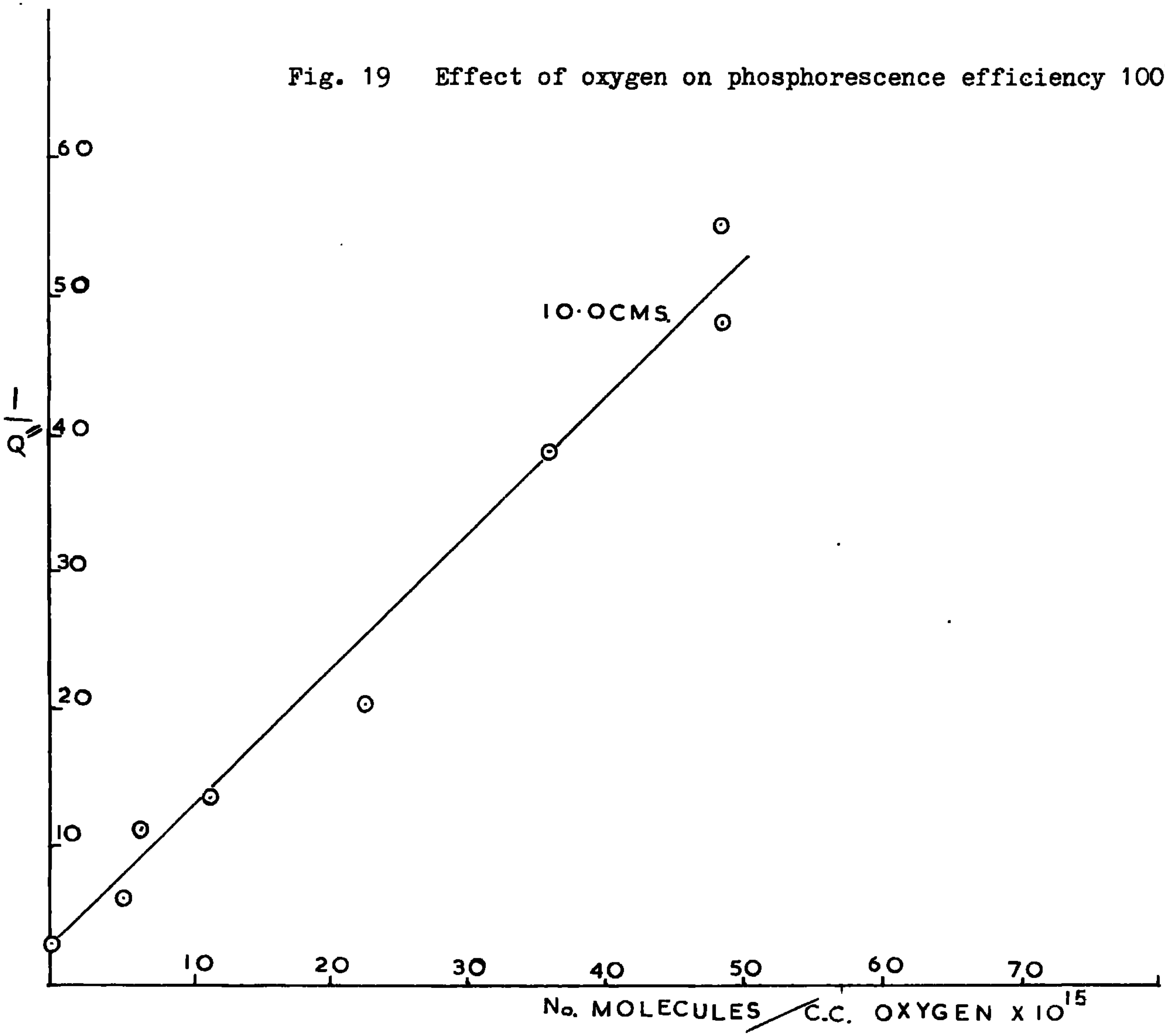


Fig. 19 Effect of oxygen on phosphorescence efficiency 100°C



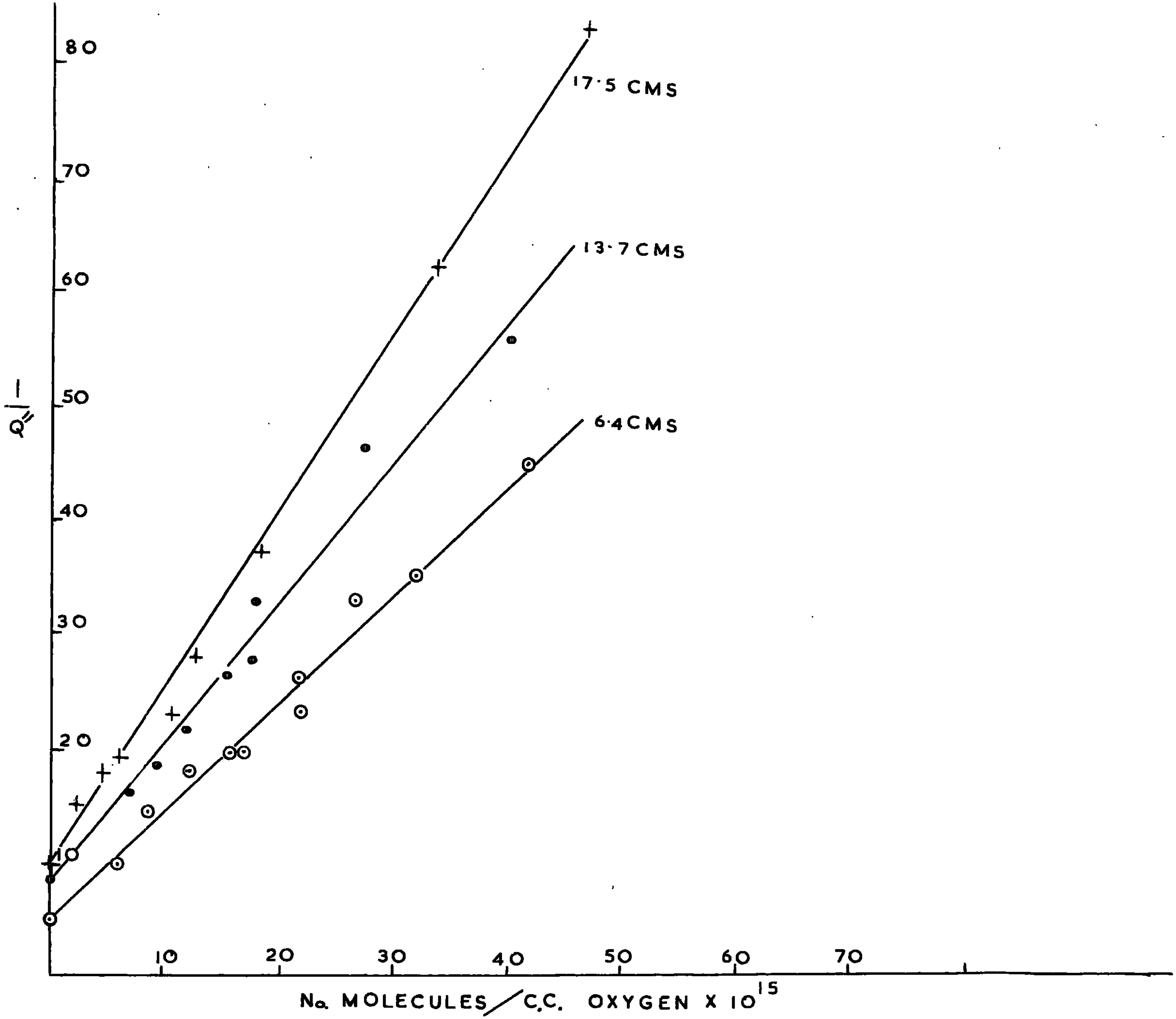


Fig. 20 Effect of oxygen on the phosphorescence efficiency 120°C

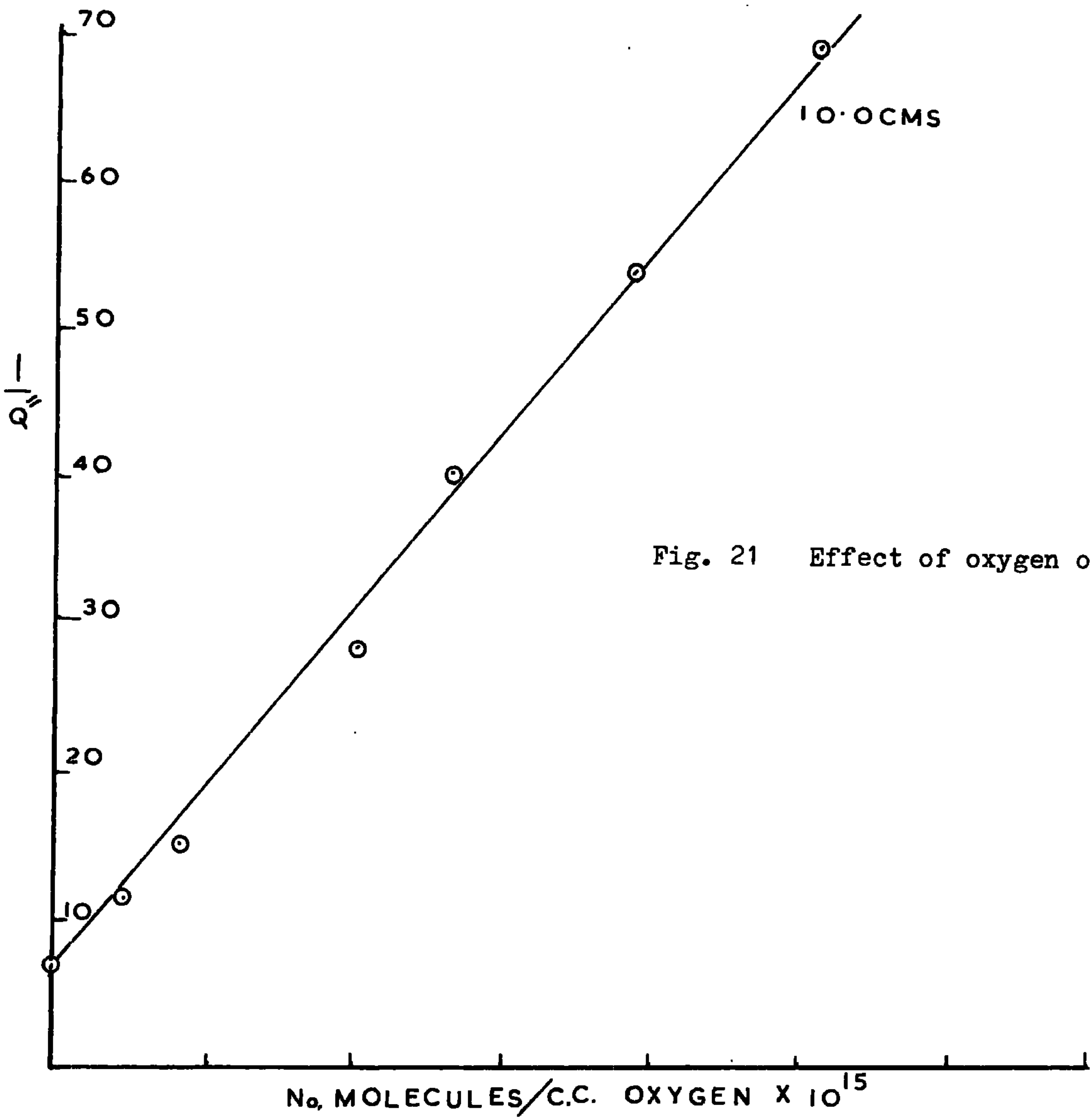
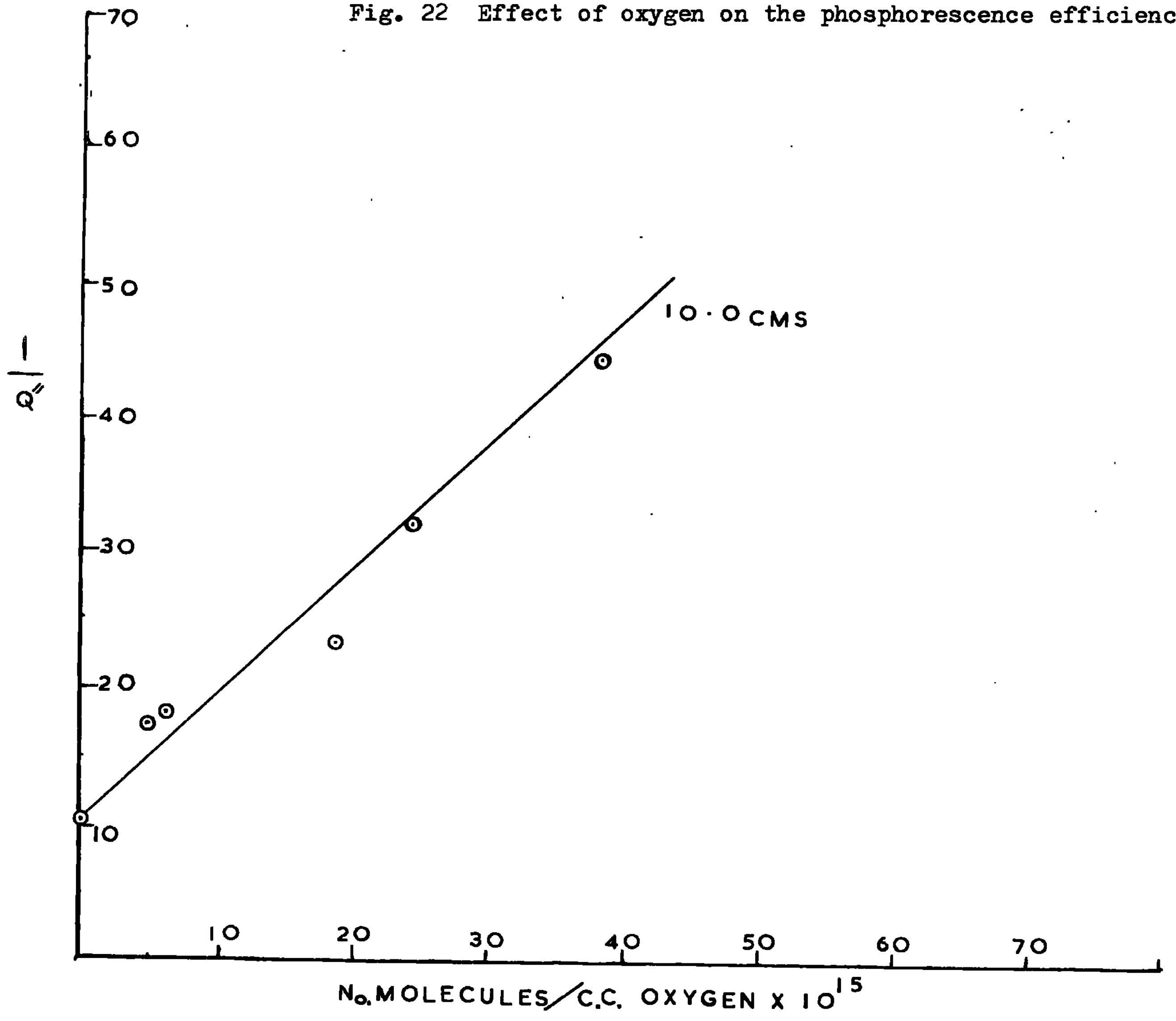


Fig. 21 Effect of oxygen on the phosphorescence efficiency 120°C

Fig. 22 Effect of oxygen on the phosphorescence efficiency 150°C



obtained it conflicted with what was then considered to be the most reliable data available (35). Later work by other authors (43) has confirmed that $\frac{1}{Q'}$ is independent of acetone pressure in the range studied here.

From Table (2) it can be seen that Q' is less than one tenth of the total emission efficiency at 20°C. At 150°C (Table 7) when phosphorescence efficiency is low, Q' represents about 60% of the total light emission. The marked effect of temperature is mainly due to the quenching of the phosphorescence by rise in temperature. It no doubt accounts for the absence of light emission data in the literature for temperatures above 50°C. A small but consistent temperature effect on the fluorescence efficiency can be seen by comparison of the results for $\frac{1}{Q'}$ at each of the temperatures investigated. Although the results support the view that $\frac{1}{Q'}$ is constant with varying acetone pressure the constant values of $\frac{1}{Q'}$ are slightly temperature dependent. $\frac{1}{Q'}$ is found to increase as the temperature increases. For temperatures 75°C, 100°C and 150°C extensive $\frac{1}{Q'}$ vs acetone pressure readings were not obtained but the trend is clear and will be dealt with more fully in the section "Results at various temperatures."

The effect of oxygen on the phosphorescence efficiency.

The results obtained for the quenching effect of oxygen on the phosphorescence are shown in Tables 2, 3, 4, 5, 6. The results are displayed over the range of temperature studied in graphs (16,17,18, 19, 20, 21, 22). Considering the results at 20°C fig.(16), it can be seen that at a fixed acetone concentration the plot of $\frac{1}{Q''}$ against oxygen pressure is a straight line, the slope of the line increasing with

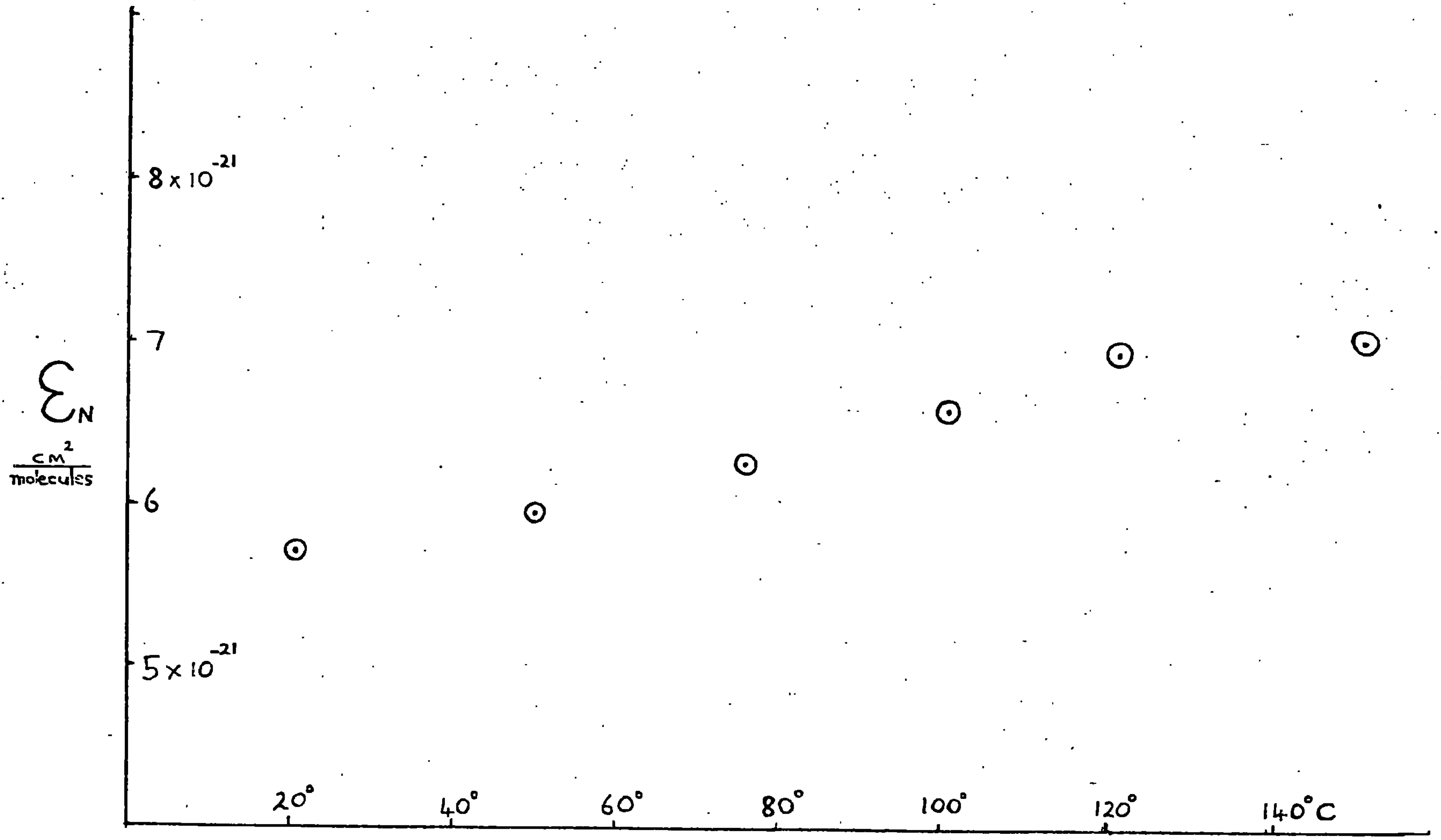


Fig. 23   Effect of temperature on the extinction coefficient

increasing acetone concentration (a 2.5 increase in slope resulting from a 4-fold increase in acetone pressure).

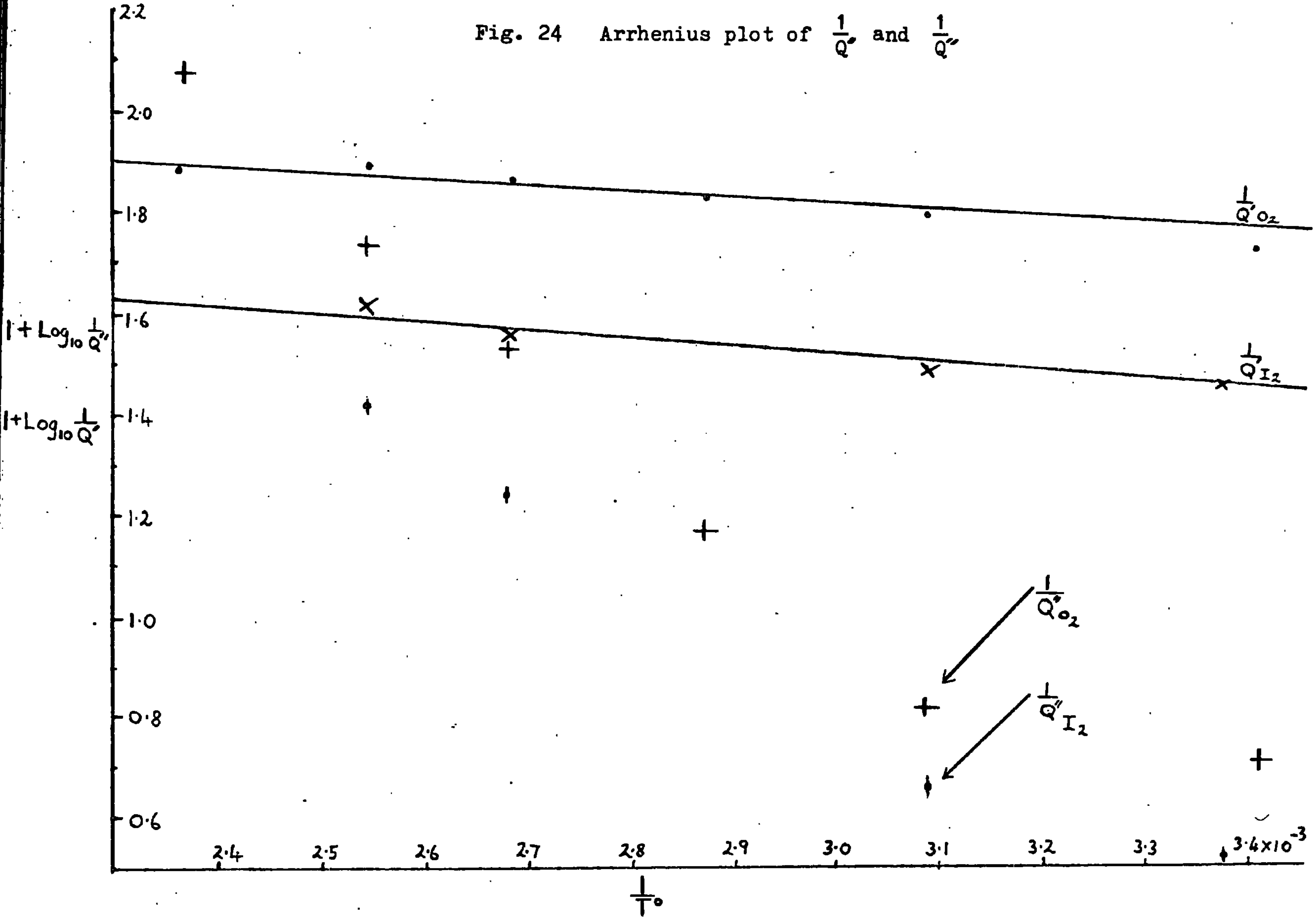
The plots of $\frac{1}{Q''}$ against oxygen concentration (figs.17,18, 19,20,21,22) show that a linear relationship is obtained at each temperature up to 150°C. Comparison of graphs at constant acetone concentration (24.5×10^{17} molecules/cc) shows that the effect of rise in temperature is to increase the slope of the $\frac{1}{Q''}$ against oxygen concentration plot.

RESULTS AT VARIOUS TEMPERATURES.

The effect of temperature change on $\mathcal{E}$ the extinction co-efficient is shown in fig.(23). The results used are those shown in Table 1. $\mathcal{E}$ shows a steady rise with temperature, as was observed by Luckey and Noyes.

The effect of temperature on the fluorescence efficiency and the total phosphorescence efficiency can be studied by selecting the relevant figures from those recorded previously for different temperatures. It was decided, however, to measure the required data in one run so that the results would be more self-consistent than those obtained over a long period of time. A series of readings was taken using approximately the same acetone concentration, the temperature being varied from 20°C to 150°C as shown in Table 8. Values of the unquenched and fully quenched emission efficiencies were taken at each temperature and the values of Q''_T and Q' were calculated in the usual way. It can be seen from Table 8 that both Q' and Q''_T are quenched by temperature but to a greatly different extent. At 150°C Q''_T is about one-twentieth of its value at 20°C. Q' is only reduced by about 30% over the same temperature range.

Fig. 24 Arrhenius plot of $\frac{1}{Q'}$ and $\frac{1}{Q''}$



An Arrhenius plot of $\log_{10} \frac{1}{Q''_T}$ against the inverse of the absolute temperature is shown in fig.(24). The points obtained could not be said to fall unequivocably on a straight line over the whole range of temperatures studied.

The graph of $\log_{10} \frac{1}{Q'}$ against inverse temperature is also shown in fig.(24). The effect of temperature is much less pronounced in this case.

The effect of temperature on the other variables which have been studied has been dealt with under the relevent heading in each case.

TABLE 2. RESULTS AT 20°C (OXYGEN)

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} "N"	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon} \times 10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q$'$	Q$''$	$\frac{1}{Q'}$	$\frac{1}{Q''}$
10.0	32.96×10^{17}	0.0	0	0.4354	2.317×10^{-2}	84.0	1.946		1.7808		0.5616
10.0	"	0.2	6.59×10^{15}	"	"	13.1	0.3030		0.1378		7.255
10.0	"	0.06	19.77 "	"	"	9.1	0.2111		0.0459		21.79
10.0	"	0.15	49.44 "	"	"	8.4	0.1946		0.0294		34.01
10.0	"	0.25	82.40 "	"	"	7.9	0.1836		0.0184		54.35
10.0	"	0.28	92.29 "	"	"	7.6	0.1762		0.0110		90.91
10.0	"	0.325	107.0 "	"	"	7.1	0.1652	0.1652		6.054	
10.0	"	0.415	136.0 "	"	"	7.1	0.1652	0.1652		6.054	
10.0	"	0.0	0 "	"	"	82.5	1.947		1.7767		0.5627
10.0	"	0.095	31.31 "	"	"	9.1	0.2152		0.0449		22.27
10.0	"	0.11	36.25 "	"	"	8.7	0.2077		0.0374		26.74
10.0	"	0.16	52.73 "	"	"	8.3	0.1965		0.0262		38.17
10.0	"	0.22	72.51 "	"	"	8.1	0.1909		0.0206		48.54
10.0	"	0.26	85.69 "	"	"	7.5	0.1778		0.0075		133.3
10.0	"	0.335	XS "	"	"	7.2	0.1703	0.1703		5.872	
10.0	"	0.42	XS "	"	"	7.2	0.1703	0.1703		5.872	
3.8	12.52×10^{17}	0.0	0 "	0.4753	6.658×10^{-2}	33.0	2.197		2.0638		0.4844
3.8	"	0.045	14.83 "	"	"	3.7	0.2463		0.1131		8.842
3.8	"	0.055	18.13 "	"	"	3.5	0.2330		0.0998		10.02
3.8	"	0.075	24.72 "	"	"	3.2	0.2130		0.0799		12.52
3.8	"	0.09	29.66 "	"	"	3.0	0.1997		0.0665		15.04
3.8	"	0.11	36.26 "	"	"	2.9	0.1931		0.0599		16.69
3.8	"	0.125	41.2 "	"	"	2.7	0.1789		0.0466		21.46
3.8	"	0.15	29.44 "	"	"	2.6	0.1731		0.0399		25.06
3.8	"	0.16	52.74 "	"	"	2.4	0.1598		0.0266		37.59
3.8	"	0.5	XS "	"	"	2.0	0.1332	0.1332		7.508	
10.0	32.96	0.0	0.0 "	0.4354	2.317×10^{-2}						
10.0	32.96	2.0	XS "	"	"	8.0	0.1854	0.1854		5.393	
16.0	52.74	0.0	0.0 "	0.3976	1.322×10^{-2}	151.0	1.996		1.835		0.5450

TABLE 2. RESULTS AT 20°C (OXYGEN) continued.

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} "N"	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\frac{I_T/I_o}{(1+I_T/I_o)}$	$\frac{I_T/I_o}{(1+I_T/I_o)N\mathcal{E}}\times10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q'	Q''	$\frac{1}{Q'}$	$\frac{1}{Q''}$
16.0	52.74 x 10^{17}	2.0	XS x10^{15}	0.3976	1.322 x 10^{-2}	12.2	0.1613	0.1613		6.200	
12.2	40.21 "	0.0	0.0 "	0.4215	1.838 "	118.0	2.169		1.976		0.5060
12.2	40.21 "	2.0	XS "	"	" "	10.5	0.1930	0.1930		5.181	
8.4	27.69 "	0.0	0.0 "	0.4456	2.822 "	76.5	2.159		1.9727		0.5068
8.4	27.69 "	2.0	XS "	"	" "	6.6	0.1863	0.1863		5.367	
5.5	18.13 "	0.0	0.0 "	0.4644	4.491 "	47.0	2.111		1.9359		0.5170
5.5	18.13 "	2.0	XS "	"	" "	3.9	0.1751	0.1751		5.711	
14.0	46.14 "	0.0	0.0 "	0.4101	1.559 "	-					
14.0	46.14 "	2.0	XS "	"	" "	11.0	0.1715	0.1715		5.832	
16.0	52.74 "	0.0	0.0 "	0.3976	1.322 "	154.0	2.036		1.8780		0.5325
16.0	52.74 "	2.0	XS "	"	" "	11.95	0.1580	0.1580		6.329	
17.0	56.03 "	0.0	0.0 "	0.3914	1.225 "						
17.0	56.03 "	2.0	XS "	"	" "	15.0	0.1838	0.1838		5.441	
15.0	49.44 "	0.0	0.0 "	0.4038	1.432 "	139.0	1.990		1.811		0.5522
15.0	" "	0.6	19.78 "	"	" "	12.5	0.1790				
15.0	" "	0.055	18.13 "	"	" "	15.5	0.2220		0.0432		23.15
15.0	" "	0.365	XS "	"	" "	13.1	0.1876		0.0086		116.3
15.0	" "	0.02	6.952 "	"	" "	17.0	0.2434		0.0644		15.3
15.0	" "	0.14	46.14 "	"	" "	13.8	0.1976		0.0186		53.76
15.0	" "	0.10	32.96 "	"	" "	14.8	0.2119		0.0329		30.40
3.8	" "	0.0	0.0 "	0.4753	6.658 "	33.0	2.197		2.0683		0.4844
15.0	49.44 "	0.0	0.0 "	0.4038	1.432 "	138.0	1.976		1.8034		0.5545
15.0	" "	2.0	XS "	"	" "	12.0	0.1718	0.1718		5.794	
15.0	" "	0.10	32.96 "	"	" "	13.9	0.1991		0.0265		37.74
15.0	" "	0.060	19.78 "	"	" "	14.9	0.2134	AVERAGE	0.0408		24.51
15.0	" "	0.069	22.74 "	"	" "	14.6	0.2091	0.1726	0.0365		27.40
15.0	" "	0.045	14.83 "	"	" "	15.4	0.2205		0.0479		20.88
15.0	" "	2.0	XS "	"	" "	12.1	0.1733	0.1733	5.794		
10.0	32.96 "	0.0	0.0 "	0.4354	2.317 "	84.0	1.946				

TABLE 3. RESULTS AT 50°C (OXYGEN).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	CORRECTED POTENTIOMETE READING	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon}$ x10^{-3}	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
8.2	24.52 x 10^{+17}	0.0	0.0	48.0	0.4499	3.084 x 10^{-2}	1.480		1.3566		0.7369
8.2	" "	0.35	10.46 x 10^{+15}	7.7	"	" "	0.2375		0.1141		8.764
8.2	" "	0.095	28.40 "	5.7	"	" "	0.1758		0.0524		19.08
8.2	" "	0.140	41.86 "	5.0	"	" "	0.1542		0.0308		32.47
8.2	" "	2.5	XS	4.0	"	" "	0.1234	0.1234		8.104	
8.2	" "	0.035	10.46 "	7.6	"	" "	0.2344		0.1110		2.009
8.2	" "	0.045	13.45 "	6.0	"	" "	0.1850		0.0616		16.23
8.2	" "	0.21	62.78 "	4.7	"	" "	0.1449		0.0215		46.51
8.2	" "	0.07	20.93 "	5.8	"	" "	0.1789		0.0555		18.02
16.45	49.18 "	0.0	0.0 "	90.2	0.4004	1.368 "	1.234		1.0767		0.9287
16.45	" "	2.0	XS "	11.5	"	" "	0.1573	0.1573		6.856	
12.90	38.57 "	0.0	0.0 "	67.2	0.4215	1.837 "	1.234		1.0760		0.9291
12.90	" "	2.0	XS "	8.6	"	" "	0.1580	0.1580		6.329	
9.6	28.70 "	0.0	0.0 "	51.0	0.4414	2.584 "	1.318		1.1604		0.8621
9.6	" "	2.0	XS "	6.1	"	" "	0.1576	0.1576		6.344	
7.45	22.27 "	0.0	0.0 "	39.3	0.4544	3.429 "	1.2234		1.0725		
7.45	22.27 "	2.0	XS "	4.4	"	" "	0.1509	0.1509		6.634	
6.06	18.12 "	0.0	0.0 "	32.2	0.4629	4.294 "	1.383		1.2284		0.8141
6.06	" "	2.0	XS "	3.6	"	" "	0.1546	0.1546		6.469	
5.05	15.10 "	0.0	0.0 "	26.6	0.4691	5.221 "	1.389		1.2480		0.8014
5.05	15.10 "	2.0	XS "	2.7	"	" "	0.1410	0.1410		7.092	
3.34	9.986 "	0.0	0.0 "	12.2	0.4795	8.070 "	0.9847		0.8798		1.137
3.34	9.986 "	2.0	XS "	1.3	"	" "	0.1049	0.1049		9.533	

TABLE 4. RESULTS AT 75°C (OXYGEN).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} "N"	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon}\times10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
8.8	24.42×10^{17}	0	0	0.4475	2.931×10^{-2}	26.0	0.7621		0.6449		1.551
8.8	"	0.03	8.325×10^{15}	"	"	9.0	0.2638		0.1466		6.821
8.8	"	0.067	18.59 "	"	"	6.2	0.1817		0.0645		15.50
8.8	"	0.13	36.08 "	"	"	5.1	0.1495		0.0323		30.96
8.8	"	0.21	58.27 "	"	"	4.8	0.1407		0.0235		42.55
8.8	"	0.06	16.65 "	"	"	6.4	0.1876		0.0704		14.20
8.8	"	0.07	19.42 "	"	"	5.9	0.1729		0.0557		17.95
8.8	"	0.025	6.938 "	"	"	8.0	0.2345		0.1173		8.525
8.8	"	0.08	22.20 "	"	"	5.7	0.1671		0.0499		20.04
8.8	"	0.195	54.11 "	"	"	4.9	0.1436		0.0264		37.88
8.8	"	3.0	XS	"	"	4.0	0.1172	0.1172		8.532	
8.8	"	0.11	30.53	"	"	5.4	0.1582		0.0411		24.33
8.8	"	1.0	XS	"	"	4.0	0.1172	0.1172		8.532	
16.0	44.4×10^{17}	2.0	XS	0.4053	1.460	11.5	0.1679	0.1679		5.955	
7.8	21.65×10^{17}	2.0	XS	0.4533	3.348	5.0	0.1674	0.1674		5.973	

TABLE 5. RESULTS AT 100°C (OXYGEN).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3}	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}\times10^{-3}}{(1+\frac{I_T}{I_o})N\varepsilon}$	CORRECTED POTENTIOMETER READING	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
10.0	25.89 x 10^{17}	0.0	0	0.4415	2.591 x 10^{-2}	18.8	0.4871		0.3290		3.040
10.0	"	0.02	5.178x10^{15}	"	"	12.0	0.3109		0.1528		6.546
10.0	"	0.045	11.65 "	"	"	8.9	0.2306		0.0725		13.79
10.0	"	0.088	22.78 "	"	"	8.0	0.2073		0.0492		20.33
10.0	"	0.14	36.25 "	"	"	7.1	0.1840		0.259		38.61
10.0	"	0.19	49.19 "	"	"	6.9	0.1788		0.0207		48.31
10.0	"	0.43	XS	"	"	6.1	0.1581	0.1581		6.325	
10.0	"	0.0	0	"	"	19.1	0.4923		0.3368		2.969
10.0	"	0.025	6.473 "	"	"	9.5	0.2461		0.0906		11.04
10.0	"	0.06	15.53 "	"	"	8.1	0.2099		0.0544		18.38
10.0	"	0.19	49.19 "	"	"	6.7	0.1736		0.0181		55.26
10.0	"	0.80	XS	"	"	6.0	0.1555	0.1555		6.431	

TABLE 6. RESULTS AT 120°C (OXYGEN).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	CORRECTED POTENTIOMETER READING	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon} x\ 10^{-3}$	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
10.0	24.58 x 10^{+17}	0.0	0.0 x 10^{+15}	10.7	0.4416	2.603 x 10^{-2}	0.2784		0.1481		6.734
"	24.58 "	0.2	4.915 "	8.3	"	"	0.2160		0.0859		11.65
"	"	0.035	8.601 "	7.5	"	"	0.1950		0.0649		15.41
"	"	0.085	20.89 "	6.25	"	"	0.1626		0.0325		30.8
"	"	0.11	27.03 "	5.95	"	"	0.1549		0.0248		40.15
"	"	0.16	39.32 "	5.7	"	"	0.1483		0.0182		54.9
"	"	0.21	51.16 "	5.55	"	"	0.1444		0.0143		69.9
"	"	2.2	XS	5.0	"	"	0.1301	0.1301		7.696	
17.5	43.01 "	0.0	0.0	17.2	0.3987	1.343 "	0.2310		0.1021		9.795
"	"	0.01	2.457 "	15.6	"	"	0.2095		0.0806		12.41
"	"	0.025	6.144 "	13.6	"	"	0.1826		0.0537		18.62
"	"	0.14	34.40 "	10.8	"	"	0.1450		0.0161		62.11
"	"	0.19	46.69 "	10.5	"	"	0.1410		0.0121		82.64
"	"	2.4	XS	9.6	"	"	0.1289	0.1289		7.755	
"	"	0.0	0.0	17.3	"	"	0.2323		0.1034		9.673
"	"	0.02	4.915 "	13.8	"	"	0.1853		0.0564		17.73
"	"	0.075	18.43 "	11.6	"	"	0.1558		0.0269		37.17
"	"	2.5	XS	9.6	"	"	0.1289	0.1289		8.532	
"	"	0.05	12.29 "	12.3	"	"	0.1652		0.0363		27.55
6.4	15.73 "	0.0	0.0 "	7.5	0.4625	4.260 "	0.3195		0.2011		4.973
"	"	0.025	6.144 "	5.2	"	"	0.2215		0.1031		9.700
"	"	0.05	12.29 "	4.1	"	"	0.1747		0.0561		17.76
"	"	0.09	22.12 "	3.7	"	"	0.1576		0.0392		25.51
"	"	0.11	27.03 "	3.5	"	"	0.1491		0.0307		32.57
"	"	4.0	XS	2.75	"	"	0.1172	0.1172		8.380	
"	"	0.035	8.601 "	4.4	"	"	0.1874		0.0690		14.49

TABLE 6. RESULTS AT 120°C (OXYGEN) Continued.

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	CORRECTED POTENTIOMETER READING	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\epsilon} \times 10^{-3}$	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
6.4	15.73 x 10^{+17}	0.065	15.97 x 10^{+15}	4.0	0.4625	4.260 x10^{-2}	0.1704		0.0520		19.23
"	" "	0.09	22.12 "	3.7			0.1576		0.0392		25.51
"	" "	0.14	34.40 "	3.5			0.1491		0.0307		32.57
"	" "	3.0	XS	2.8			0.1193	0.1193		8.380	
17.5	43.01 "	0.0	0.0	17.5	0.3987	1.343	0.2350		0.1074		9.310
17.5	43.01 "	2.0	XS	9.5	"	"	0.1277	0.1276		7.836	
6.4	15.73 "	0.0	0.0	7.5	0.4625	4.260	0.3195		0.2023		4.943
6.4	15.73 "	2.0	XS	2.75	"	"	0.1172	0.1172		8.532	
10.0	24.58 "	0.0	0.0	10.7	0.4416	2.603	0.2785		0.1536		6.511
10.0	24.58 "	2.0	XS	4.8	"	"	0.1249	0.1249		8.007	
12.8	31.46 "	0.0	0.0	13.8	0.4254	1.959	0.2703		0.1332		7.508
12.8	31.46 "	2.0	XS	7.0	"	"	0.1371	0.1371		7.294	
14.8	36.37 "	0.0	0.0	15.05	0.4139	1.649	0.2516		0.1279		7.816
14.8	36.37 "	2.0	XS	7.5	"	"	0.1237	0.1237		8.085	
7.8	19.17 "	0.0	0.0	8.3	0.4554	3.442	0.2857		0.1687		5.926
7.8	19.17 "	2.0	XS	3.4	"	"	0.1170	0.1170		8.547	
2.0	4.915 "	0.0	0.0	3.1	0.4883	14.39	0.4461		0.3246		3.087
2.0	4.915 "	2.0	XS	0.5—0.8	"	"	0.07195—0.1151	TAKE 0.1151		8.232	
13.7	33.67 "	0.0	0.0	15.0	0.4203	1.809	0.2714		0.1267		7.893
"	" "	0.045	11.06 "	10.4	"	"	0.1881		0.0434		23.04
"	" "	2.0	XS	8.0	"	"	0.1447	0.1447		6.911	
"	" "	0.04	9.850 "	11.2	"	"	0.2026		0.0597		17.27
"	" "	0.074	18.19 "	10.0	"	"	0.1809		0.0362		27.62
"	" "	0.03	7.373 "	11.5	"	"	0.2080		0.0633		15.80
"	" "	0.05	12.29 "	10.6	"	"	0.1918		0.0471		21.23
"	" "	2.0	XS	8.0	"	"	0.1447	0.1447		6.911	

TABLE 6. RESULTS AT 120°C (OXYGEN) Continued.

ACETONE PRESSURE CM.Hg AT 20°C	No. of MELECULES ACETONE x CM^{-3} N	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	CORRECTED POTENTIOMETER READING	$\frac{I_T/I_o}{(1+I_T/I_o)}$	$\frac{I_T/I_o}{(1+I_T/I_o)N\varepsilon} \times 10^{-3}$	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
13.7	$33.67 \times 10^{+17}$	0.0	0.0	15.1	0.4203	1.809×10^{-4}	0.2732		0.1357		7.369
"	" "	0.116	$28.51 \times 10^{+15}$	8.8	"	"	0.1592		0.0217		46.08
"	" "	0.075	18.43 "	9.3	"	"	0.1683		0.0308		32.47
"	" "	0.622	XS	7.6	"	"	0.1375	0.1375		7.273	
"	" "	0.165	40.55 "	8.6	"	"	0.1556		0.0181		55.25
"	" "	0.064	15.73 "	9.7	"	"	0.1755		0.0380		26.32
"	" "	1.0	XS	7.6	"	"	0.1375	0.1375		7.273	
"	" "	0.052	12.78 "	9.9	"	"	0.1791		0.413		24.21
"	" "	1.0	XS	7.62	"	"	0.1378	0.1378		7.257	
6.4	15.73 "	0.0	0.0	7.55	0.4625	4.260	0.3216		0.2045		4.890
"	" "	2.0	XS	2.7	"	"	0.1150			8.613	
"	" "	0.069	16.96 "	3.95	"	"	0.1683	TAKE MEAN VALUE OF 0.1161	0.0522		19.16
"	" "	0.09	22.12 "	3.75	"	"	0.1598		0.0437		22.88
"	" "	0.172	42.27 "	3.25	"	"	0.1385		0.0224		44.64
"	" "	2.0	XS	2.75	"	"	0.1172				
"	" "	0.132	32.44 "	3.4	"	"	0.1448		0.0287		34.84
"	" "	0.0	0.0	7.5	"	"	0.3195				

TABLE 7. RESULTS AT 150°C (OXYGEN).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o}) N \epsilon} \times 10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q$'$	Q$''$	$\frac{1}{Q'}$	$\frac{1}{Q''}$
10.0	22.88 x 10^{17}	0.0	0	0.4448	2.772 x 10^{-2}	9.3	0.2578		0.0915		10.93
10.0	"	0.03	6.85 x 10^{15}	"	"	7.9	0.2190		0.0527		18.98
10.0	"	0.11	25.12 "	"	"	7.1	0.1968		0.0305		32.79
10.0	"	0.17	38.82 "	"	"	6.8	0.1885		0.0222		45.05
10.0	"	0.45	XS	"	"	6.0	0.1663	0.1663		6.013	
10.0	"	0.0	0	"	"	9.2	0.2552		0.1025		9.659
10.0	"	0.025	5.71 "	"	"	7.5	0.2079		0.0554		18.05
10.0	"	0.085	19.41 "	"	"	7.0	0.1940		0.0415		24.10
10.0	"	0.17	38.82 "	"	"	6.3	0.1746		0.0221		45.25
10.0	"	1.5	XS	"	"	5.5	0.1525	0.1525		6.558	

TABLE 8. RESULTS AT VARIOUS TEMPERATURES (OXYGEN).

TEMPERATURE °C	ACETONE PRESSURE CM.Hg AT 20°C N	No. of MOLECULES ACETONE x CM^{-3}	OXYGEN PRESSURE CM.Hg AT 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon}$ $x10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q'	Q''	$\frac{1}{Q'}$	$\frac{1}{Q''}$
20	7.56	24.92 x 10^{+17}	0.0	0	0.4511	3.175 x 10^{-2}	67.6	2.146		1.952		0.5123
20	7.56	" "	2.0	XS	"	" "	6.1	0.1937	0.1937		5.163	
50	8.2	24.52 "	0.0	0	0.4499	3.084 x 10^{-2}	48.7	1.502		1.3416		0.7452
50	8.2	" "	2.0	XS	"	" "	5.2	0.1604	0.1604		6.235	
75	8.8	24.42 "	0.0	0	0.4475	2.931 "	28.5	0.8353		0.6844		1.461
75	8.8	" "	2.0	XS	"	" "	5.15	0.1509	0.1509		6.629	
100	9.45	24.46 "	0.0	0	0.4446	2.76 "	16.0	0.4419		0.2955		3.384
100	9.45	" "	2.0	XS	"	" "	5.3	0.1464	0.1464		6.830	
120	10.0	24.58 "	0.0	0	0.4416	2.59 "	11.9	0.3089		0.1877		5.505
120	10.0	" "	2.0	XS	"	" "	4.9	0.1272	0.1272		7.861	
150	10.8	24.66 "	0.0	0	0.4404	2.54 "	8.5	0.2159		0.0838		11.93
150	10.8	" "	2.0	XS	"	" "	5.2	0.1321	0.1321		7.571	
RESULTS ABSTRACTED FROM TABLES 2, 3, 4, 5, 6, 7.											7.508	0.4844
20	3.8	12.52 x 10^{+17}									5.711	0.517
"	5.5	18.13 "									5.367	0.507
"	8.4	27.69 "									5.77	0.562
"	10.0	32.96 "									5.181	0.506
"	12.2	40.21 "									5.832	
"	14.0	46.14 "									6.26	0.543
"	16.0	52.74 "									5.441	
"	17.0	56.03 "									9.533	1.137
50	3.34	9.986 "									7.092	0.8014
"	5.05	15.10 "									6.469	0.8146
"	6.06	18.12 "									6.634	
"	7.45	22.27 "									8.104	0.7369
"	8.2	24.52 "									6.344	0.8621
"	9.6	28.70 "									6.329	0.9291
"	12.9	38.57 "									6.352	0.928
"	16.45	49.18 "										

TABLE 8. RESULTS AT VARIOUS TEMPERATURES (OXYGEN) Continued.

TEMPER-ATURE °C	ACETONE PRESSURE CM.Hg AT 20°C N	No. of MOLECULES ACETONE x CM^{-3}	OXYGEN PRESSURE CM.Hg at 20°C	No. of MOLECULES OXYGEN x CM^{-3}	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon}$ xc^{-3}	CORRECTED POTENTIOMETER READING	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
75	7.8	21.65 x 10^{+17}									5.973	
75	8.8	24.42 "									8.532	1.552
"	16.0	44.40 "									5.955	
100	10.0	25.89 "									6.38	3.005
120	6.4	15.73 "									8.45	4.97
"	10.0	24.88 "									7.696	6.734
"	13.7	33.67 "									7.273	7.631
"	17.5	43.01 "									7.755	9.755

IODINE - ACETONE LIGHT EMISSION RESULTS.

Preliminary Experiments.

At the outset of these experiments the qualitative effects of iodine on the light emission were not known. Some preliminary experiments by Mitchell had suggested that iodine probably did quench the emission but he did not claim that the results were very reliable.

With the apparatus shown in fig.(1) and fig.(6), the qualitative effect of iodine could be easily investigated. The following facts emerged:

(1) The effect of iodine is to reduce the light emission at room temperature to about a tenth of its value in the absence of iodine.

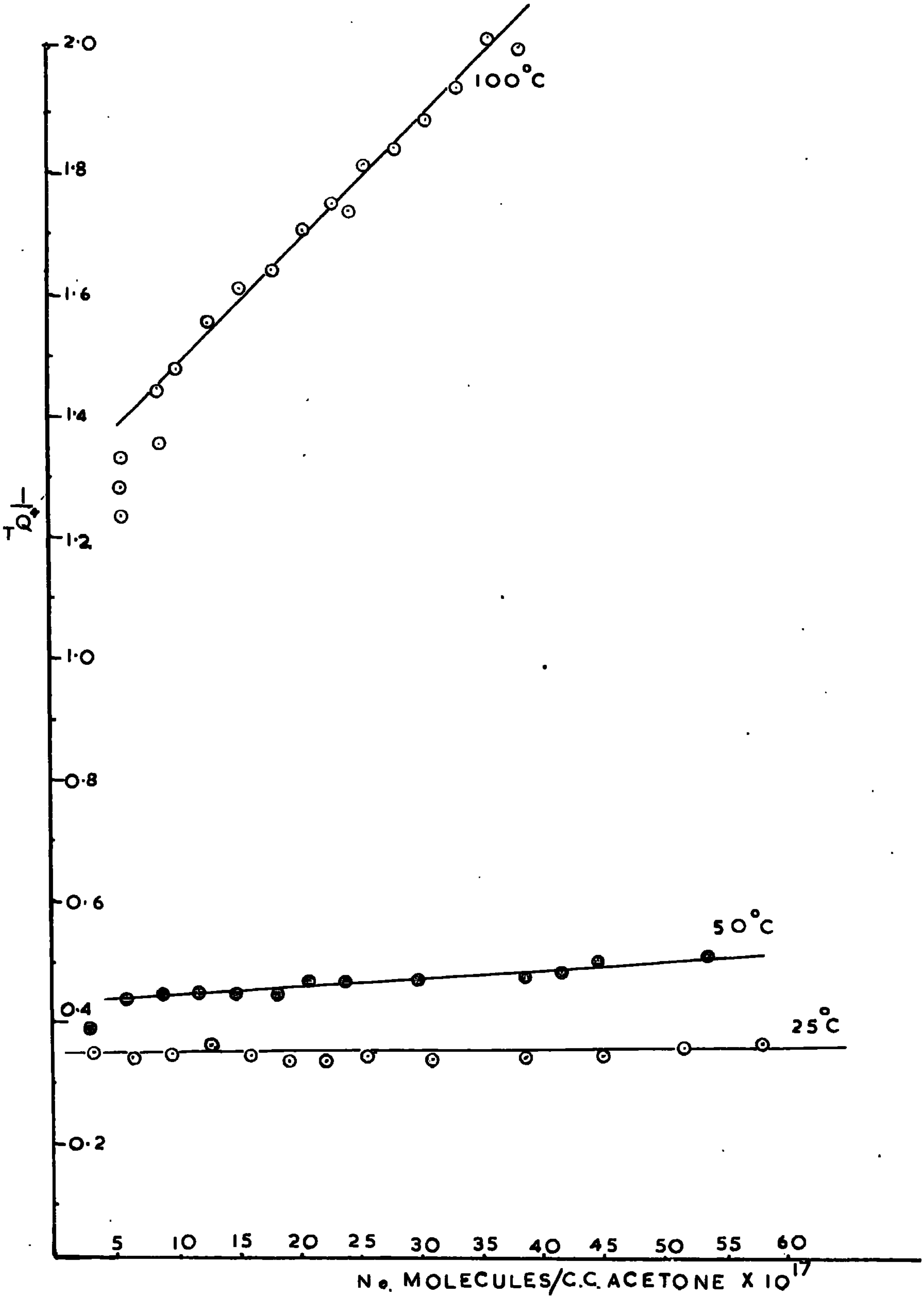
(2) A saturation effect is observed - the addition of iodine at pressures greater than about 5mm having no additional effect on the emission.

(3) The intensity of emission in the presence of excess iodine is the same as that in the presence of excess oxygen.

Point (2) above meant that the highest temperature required for the iodine reservoir was about 16°C (to provide the excess iodine pressure of 5mm) and the connecting tubes to the cell, and especially the taps, were required to be kept only a few degrees warmer than this. This observation was very important in preserving the silicone tap grease from attack by iodine.

On the basis of the preliminary results and the data collected in the acetone-oxygen system, an investigation was undertaken of the effect of temperature, acetone concentration

Fig. 25 Effect of acetone pressure on total phosphorescence efficiency



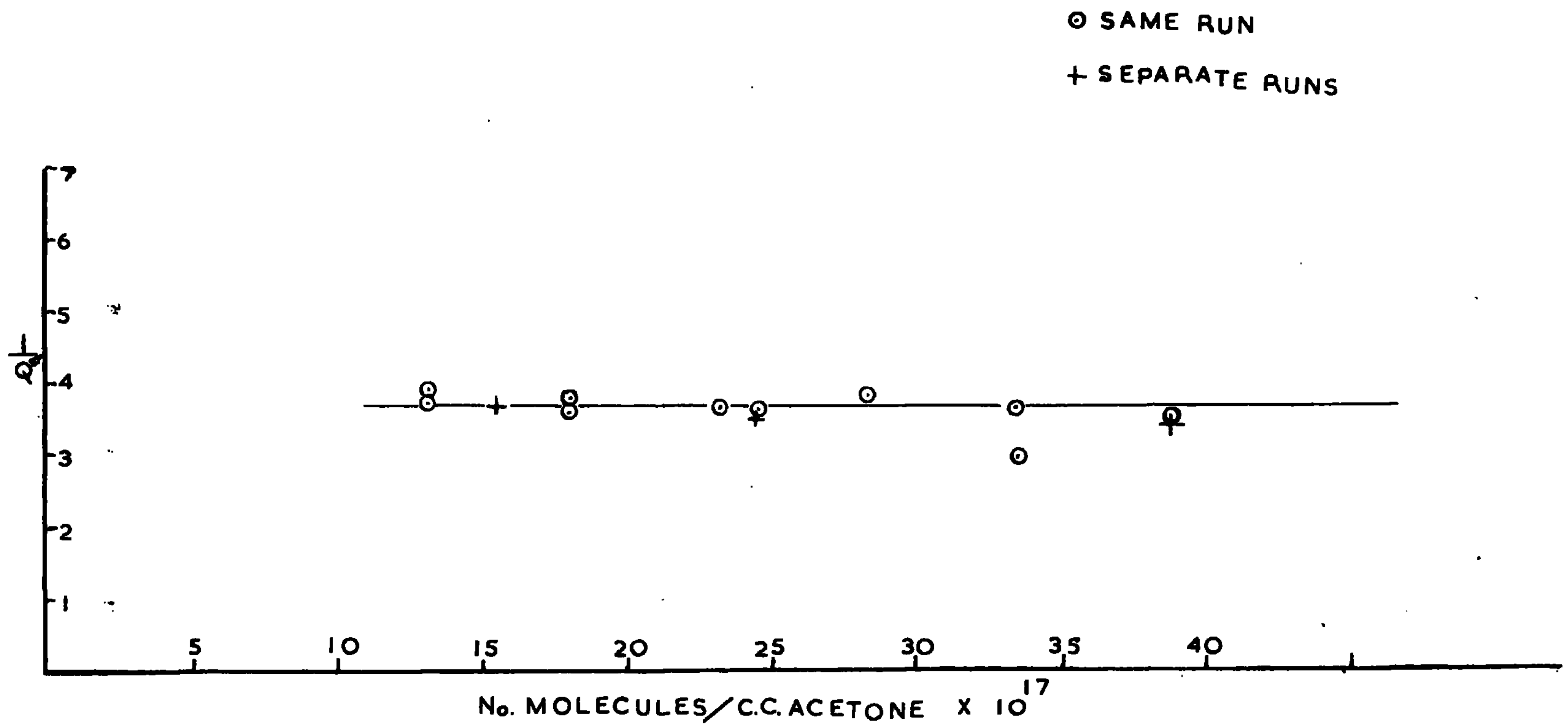


Fig. 26 Effect of acetone pressure on fluorescence efficiency 100°C

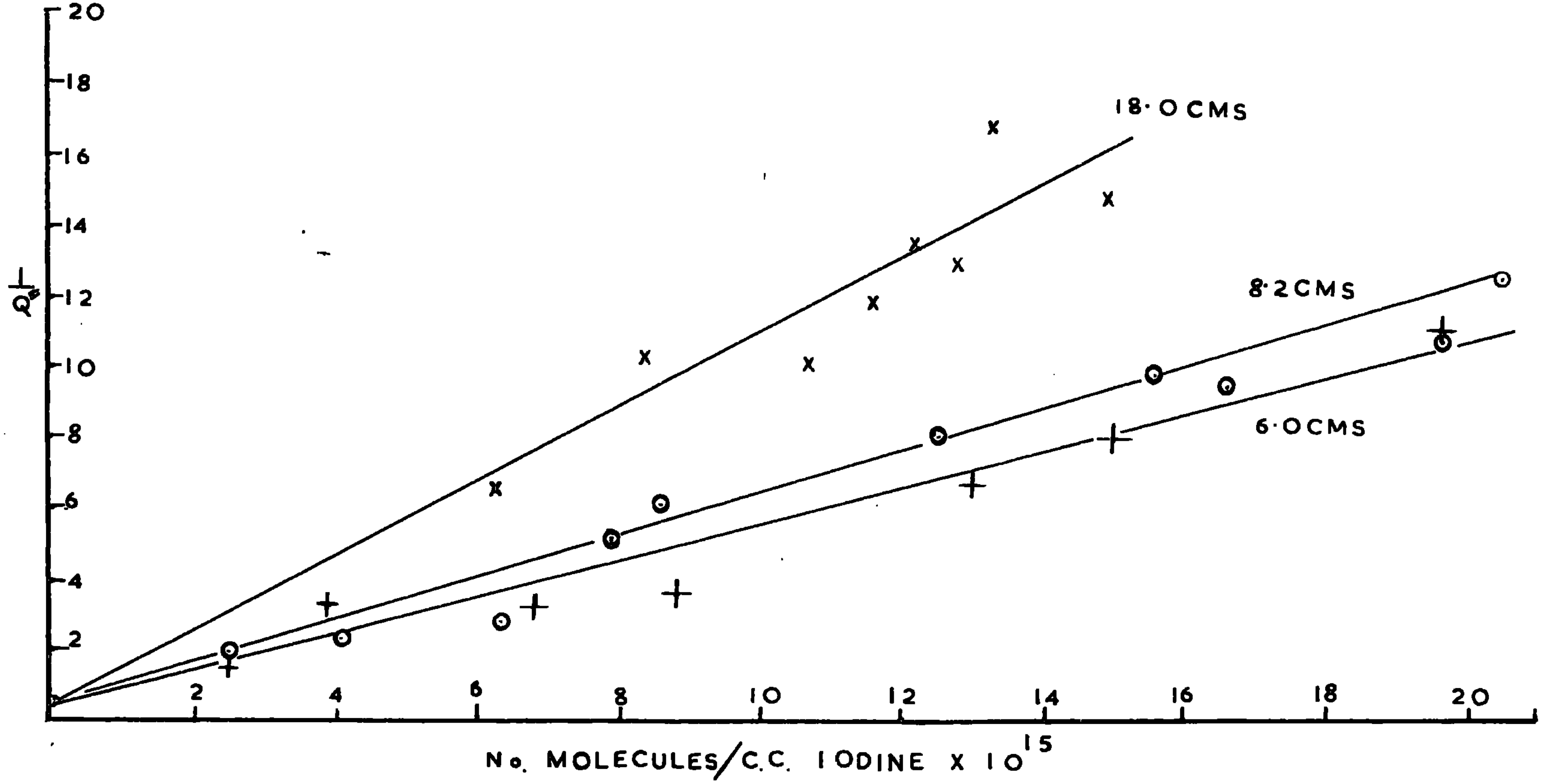
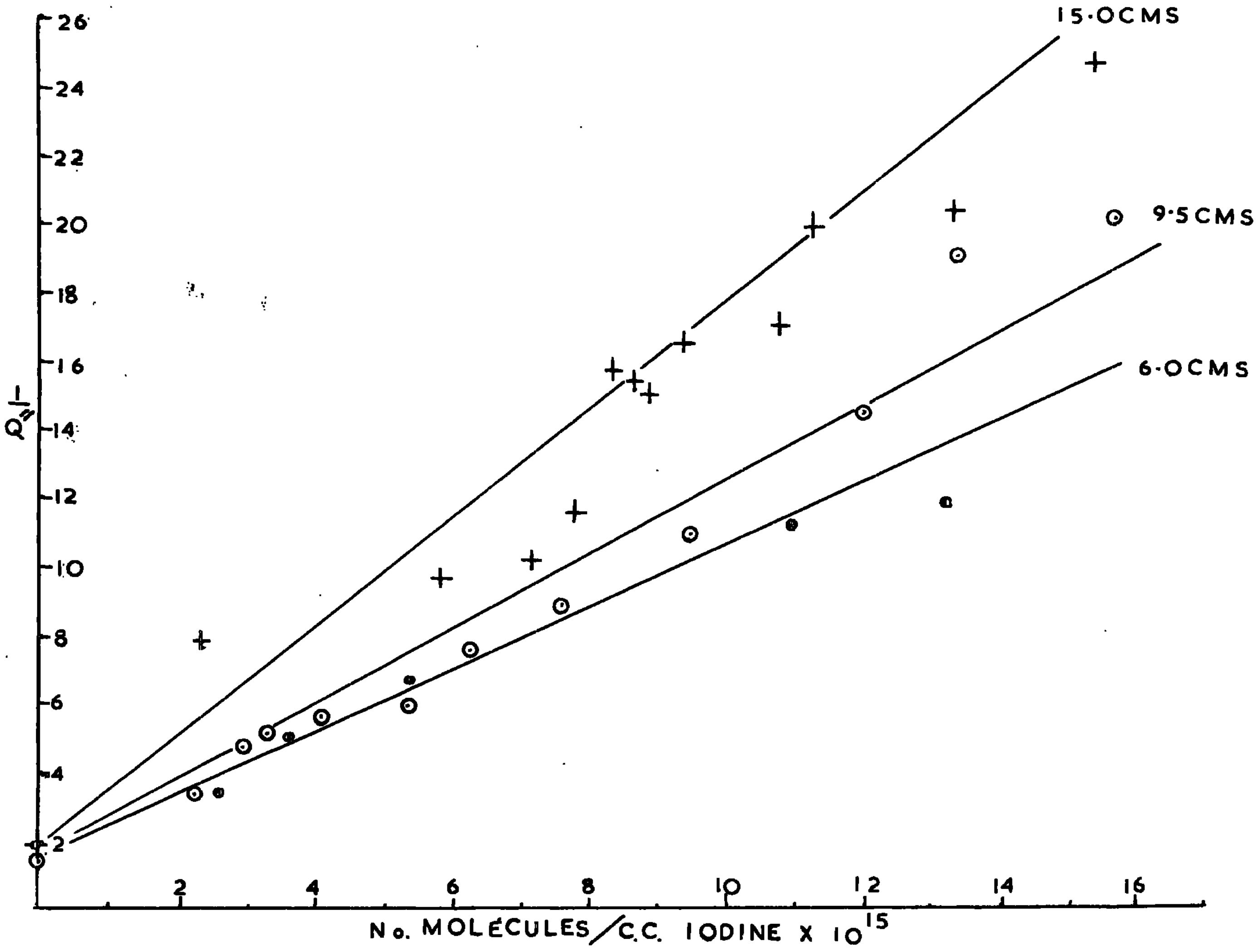


Fig. 27 Effect of iodine on the phosphorescence efficiency 50°C

Fig. 28 Effect of iodine on the phosphorescence efficiency 100°C



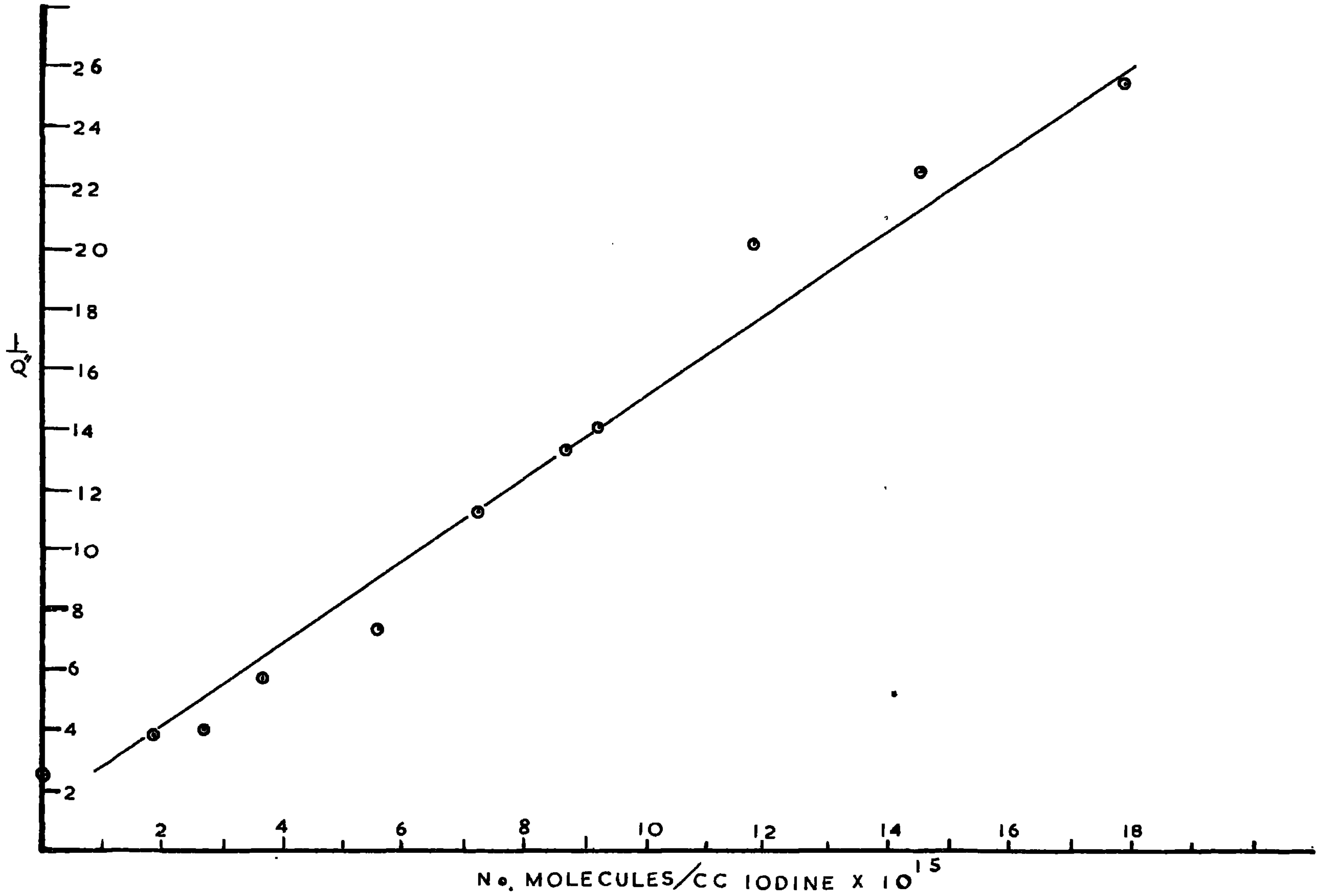


Fig. 29 Effect of iodine on the phosphorescence efficiency 120°C

and iodine concentration on the light emission.

More attention was paid in this system to the results at 100°C than at 120°C because most of the quantum yield data (especially for CH_3I) had been reported at the former temperature.

The rebuilding and realigning of the apparatus prior to the collection of iodine-oxygen emission data, improved the sensitivity (by a factor of about 1.8), and the accuracy considerably. This improvement can be seen reflected in, for instance, the better fit of the results of the plots for $\frac{1}{Q''_T}$ against acetone concentration. (fig.25).

Calculation and Tabulation of Results.

The method for taking readings and the calculation of the results was exactly the same as had been described previously in the oxygen-acetone system. The concentration of iodine was calculated from vapour pressure data as described previously in the section on experimental technique. The method for obtaining data for the calculation of the extinction co-efficient has been dealt with previously and the results at various temperatures are listed in Table I. For the results at 25°C in the iodine-acetone system the extinction co-efficient was not measured but its value was obtained from the graph showing the variation of $\mathcal{E}$ with temperature (fig.23).

The data collected and the calculated results for the iodine-acetone system are shown in tables 9 - 12, each table dealing with results at a different temperature. The graphs drawn from the results are shown in figs.(25,26,27,28,29).

The effect of acetone pressure on the total phosphorescence efficiency.

The results relating the effect of acetone concentration

on $\frac{1}{Q''_T}$ have been extracted from tables 9, 10 and 11 and are shown in fig.(25). The results at 100°C were obtained first and they showed a linear relationship with a slope comparable to that obtained in the oxygen-acetone system. At low acetone concentrations at 100°C the experimental results fall below the straight line through the points for higher concentrations. The high temperature and low acetone concentration used combine to produce low emission intensities and make the points at the lowest acetone concentration at 100°C rather suspect. Repeated measurements of the points in question did not establish a clear answer but rather served to illustrate the spread of results likely to be obtained under the different experimental conditions. It was then decided to measure $\frac{1}{Q''_T}$ at the lowest convenient temperature (25°C) where emission efficiencies are greater and the results at low acetone concentration are more reliable.
It can be seen from fig.(25) that, over the range of acetone pressures investigated at 100°C, all the results at 25°C fall on a straight line. The same can be said for the results at 50°C except for the result at the lowest acetone pressure (about 3×10^{17} molecules/cc).

The graphs of $\frac{1}{Q''_T}$ against acetone pressure show great similarity to the corresponding graphs obtained in the oxygen-acetone system (see fig.12). Thus in the iodine-acetone case the lowest temperature line is horizontal and the slope increases with temperature in the same way as in the oxygen-acetone result. Only one result for $\frac{1}{Q''_T}$ was obtained at 120°C and that is shown in table 12.

The effect of acetone pressure on the fluorescence efficiency.

At 50°C three results were obtained (see table 10) which show that Q' is independent of acetone concentration. The effect of acetone pressure on Q' was not investigated at 25°C or 120°C but at 100°C $\frac{1}{Q'}$ was determined over a wide range of acetone pressures. The results are contained in table 11 and are shown graphically in fig.(26). Most of the points (marked in circles) in fig.(26) were determined in a single series of measurements all performed on the same day so as to increase their mutual consistency. The points marked with crosses are for measurements taken at different times over a period of some weeks. The results show that, as in the oxygen-acetone system, $\frac{1}{Q'}$ is independent of acetone concentration.

The effect of iodine on the phopshorescence efficiency.

Measurements of the effect of iodine on Q'' were made at 50°C, 100°C and 120°C. The results and calculations are shown in tables 10, 11 and 12 and plots of $\frac{1}{Q''}$ against iodine concentration are shown in figs.(27,28,29). A linear relationship is again obeyed as in the oxygen-acetone system and at a fixed temperature the slope increases with acetone pressure. The effect of temperature can be seen by comparing the lines for the same acetone concentration, 24.5×10^{17} molecules/cc. This concentration corresponds to pressures of 8.2 cms, 9.5 cms and 10.0 cms at 50°C, 100°C and 120°C. As in the oxygen-acetone system the slope increases as the temperature is increased for a fixed acetone concentration.

Results at Various temperatures.

The effect of temperature on $\frac{1}{Q''_T}$ and $\frac{1}{Q''}$ has been dealt with above. Using data extracted from Tables 9, 10, 11 and 12 Arrhenius plots of $\frac{1}{Q''_T}$ and $\frac{1}{Q'}$ have been made and are shown on the same graph (fig.24) as those for the oxygen-acetone results. It can be seen that the graphs are very similar in each case except for a vertical difference in scale. This difference is due to the increase in sensitivity in the apparatus before the iodine-acetone investigation began.

The slight temperature dependence of the fluorescence efficiency and the marked temperature dependence of the Q_T'' is almost identical in both the iodine-acetone and oxygen-acetone cases.

Xenon - Acetone Light Emission Results.

With pressures up to 10 cms. of xenon and 15 cms. of acetone no appreciable effect on the intensity of the emission was detected at any temperature.

TABLE 9. RESULTS AT 25°C (IODINE).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	No. of MOLECULES IODINE x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})^{N\ell}}$ Nc^{-3}	CORRECTED POTENTIOMETER READING	Q	Q'	Q''	$\frac{1}{Q'}$	$\frac{1}{Q''}$
8.0	25.96 x 10^{+17}	0	0.4485	3.030 x 10^{-2}	111.0	3.363		3.013		0.332
10.0	32.4 "	"	0.4351	2.385 "	145.0	3.415		3.065		0.326
12.0	38.88 "	"	0.4231	1.906 "	177.5	3.383		3.033		0.329
14.0	45.36 "	"	0.4106	1.585 "	211.3	3.349		2.999		0.333
16.0	51.84 "	"	0.3981	1.344 "	255.9	3.439		2.889		0.346
18.0	58.32 "	"	0.3858	1.158 "	294.8	3.414		2.864		0.349
1.0	3.24 "	"	0.4935	26.67 "	13.1	3.493		2.943		0.340
2.0	6.48 "	"	0.4871	13.16 "	25.45	3.349		2.999		0.333
3.0	9.72 "	"	0.4806	8.658 "	38.5	3.333		2.983		0.335
4.0	12.96 "	"	0.4742	6.407 "	51.4	3.293		2.843		0.352
5.0	16.20 "	"	0.4657	5.034 "	66.7	3.357		3.007		0.333
6.0	19.44 "	"	0.4648	4.187 "	81.7	3.421		3.071		0.326
7.0	22.68 "	"	0.4549	3.512 "	98.0	3.442		3.092		0.323
8.0	25.92 "	"	0.4485	3.030 "	112.0	3.363		2.993		0.334
8.0	25.92 "	"	0.4485	3.030 "	111.0	3.363		3.013		0.332
8.0	25.92 "	) EXCESS OXYGEN	0.4485	3.030 "	11.6	0.3515	0.350		2.857	
10.0	32.40 "		0.4358	2.355 "	14.8	0.3485				
3.0	25.92 "		0.4485	3.030 "	11.7	0.3545				

TABLE 10. RESULTS AT 50°C (IODINE).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	No. of MOLECULES IODINE x CM^{-3}	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\mathcal{E}} \times 10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q'	Q"	$\frac{1}{Q'}$	$\frac{1}{Q''}$
8.2	24.52 x 10^{+17}	0	0.4498	3.084 x 10^{-2}	81.9	2.526		2.199		0.4546
8.2	" "	XS		" "	10.6	0.3269	0.3269		3.058	
8.2	" "	20.66 x 10^{+15}	"	" "	13.2	0.4071		0.0802		12.48
8.2	" "	19.80 "	"	" "	13.6	0.4194		0.0925		10.81
8.2	" "	15.77 "	"	" "	13.9	0.4287		0.1018		9.82
8.2	" "	16.76 "	"	" "	14.0	0.4318		0.1049		9.524
8.2	" "	12.66 "	"	" "	14.6	0.4503		0.1234		8.090
8.2	" "	8.064 "	"	" "	16.7	0.5150		0.1881		5.316
8.2	" "	8.736 "	"	" "	15.8	0.4873		0.1604		6.235
8.2	" "	6.508 "	"	" "	21.9	0.6754		0.3485		2.87
8.2	" "	4.174 "	"	" "	25.0	0.7710		0.4441		2.251
8.2	" "	2.688 "	"	" "	26.2	0.8080		0.4811		2.079
6.0	17.94 "	19.82 "	0.4632	4.339 "	9.6	0.4165		0.0911		10.98
6.0	" "	0	"	" "	62.1	2.695		2.370		0.4219
6.0	" "	13.16 "	"	" "	11.0	0.4773		0.1519		0.6590
6.0	" "	6.897 "	"	" "	14.45	0.6270		0.3016		0.3316
6.0	" "	3.926 "	"	" "	14.6	0.6335		0.3081		0.3246
6.0	" "	8.984 "	"	" "	13.7	0.5944		0.269		0.3717
6.0	" "	15.21 "	"	" "	10.4	0.4513		0.1259		0.7940
6.0	" "	2.617 "	"	" "	20.0	0.8678		0.5424		1.844
6.0	" "	XS	"	" "	7.5	0.3254	0.3254		3.073	
8.2	24.52 "	0	0.4498	3.084 "	82.0	2.529		2.203		0.4539
8.0	23.92 "	"	0.4510	3.162 "	80.0	2.530		2.204		0.4537
7.0	20.93 "	"	0.4572	3.671 "	68.4	2.511		2.185		0.4576
6.0	17.94 "	"	0.4632	4.339 "	59.3	2.573		2.247		0.4450
5.0	14.95 "	"	0.4694	5.277 "	48.9	2.580		2.254		0.4436
4.0	11.96 "	"	0.4755	6.682 "	39.3	2.626		2.300		0.4348
3.0	8.970 "	"	0.4816	9.024 "	29.2	2.635		2.309		0.4332
2.0	5.980 "	"	0.4877	13.70 "	19.5	2.672		2.346		0.4263
1.0	2.989 "	"	0.5550	31.21 "	9.5	2.965		2.639		0.3789

TABLE 10. RESULTS AT 50°C (IODINE) Continued.

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	No. of MOLECULES IODINE x CM^{-3}	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\epsilon}$ x10^{-3}	CORRECTED POTENTIOMETER READING	Q	Q'	Q''	$\frac{1}{Q'}$	$\frac{1}{Q''}$
1.0	2.989 x 10^{+17}	0	0.5550	31.21 x10^{-2}	9.7	3.027		2.701		0.3703
10.0	29.89 "	"	0.4389	2.468 "	100.9	2.490		2.164		0.4621
12.0	35.88 "	"	0.4269	1.999 "	121.9	2.437		2.147		0.4648
14.0	41.86 "	"	0.4149	1.666 "	145.0	2.416		2.090		0.4785
16.0	47.84 "	"	0.4030	1.416 "	166.0	2.350		2.024		0.4940
18.0	53.82 "	"	0.3912	1.222 "	190.0	2.322		1.996		0.5009
2.0	5.980 "	"	0.4877	13.70 "	19.3	2.644		2.318		0.4315
3.0	8.970 "	"	0.4816	9.024 "	28.8	2.599		2.273		0.4400
4.0	11.96 "	"	0.4755	6.682 "	39.0	2.606		2.280		0.4386
4.0	11.96 "	"	0.4755	6.682 "	38.8	2.593		2.267		0.4411
5.0	14.95 "	"	0.4694	5.277 "	50.0	2.638		2.312		0.4325
15.0	44.85 "	"	0.4089	1.536 "	155.7	2.392		2.066		0.4840
					TAKE Q =	0.3260	AVERAGE	3.067		
18.0	53.82 "	12.87 x 10^{+15}			33.0	0.4033		0.0783		12.77
18.0	" "	12.27 "	0.3912	1.222 "	32.7	0.3996		0.0746		13.4
18.0	" "	10.75 "	"	" "	34.6	0.4228		0.0978		10.22
18.0	" "	13.44 "	"	" "	31.5	0.3849		0.0599		16.69
18.0	" "	8.418 "	"	" "	34.5	0.4216		0.0966		10.35
18.0	" "	14.93 "	"	" "	32.2	0.3935		0.0685		14.60
18.0	" "	11.67 "	"	" "	33.6	0.4106		0.0856		11.68
18.0	" "	6.26 "	"	" "	39.0	0.4766		0.1516		6.600
18.0	" "	3.891 "	"	" "	50.0	0.6110		0.2860		3.497
18.0	" "	I8	"	" "	26.6	0.325	0.3250		3.077	

TABLE 11. RESULTS AT 100°C (IODINE).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	No. of MOLECULES IODINE x CM^{-3}	$\dfrac{I_T/I_o}{(1+\frac{I_T}{I_o})}$	$\dfrac{I_T/I_o}{(1+\frac{I_T}{I_o})N\varepsilon}$ x 10^{-3}	CORRECTED POTENTIOMETER READING	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
15.0	38.84 x 10^{+17}	XS	0.4127	0.1615 x 10^{-1}	16.9	0.2729			3.664	
15.0	" "	"	"	" "	16.9	0.2729			3.664	
13.0	33.66 "	"	0.4241	0.1915 "	14.4	0.3351			2.984	
13.0	" "	"	"	" "	14.3	0.2738			3.652	
5.0	12.95 "	"	0.4706	0.5521 "	4.7	0.2595			3.852	
5.0	" "	"	"	" "	4.9	0.2705			3.697	
7.0	18.12 "	"	0.4589	0.3841 "	7.3	0.2808			3.561	
7.0	" "	"	"	" "	6.9	0.2653			3.770	
9.5	24.60 "	"	0.4443	0.2744 "	9.9	0.2717			3.680	
9.5	" "	"	"	" "	9.9	0.2717			3.680	
9.0	23.30 "	"	0.4472	0.2915 "	9.4	0.2740			3.650	
9.0	" "		"	" "	9.5	0.2769			3.611	
11.0	28.48 "	"	0.4357	0.2324 "	11.3	0.2626			3.809	
11.0	" "	"	"	" "	11.2	0.2603			3.842	
					MEAN	0.2750				
10.0	25.89 x 10^{+17}	0	0.4414	0.2590 "	31.9	0.8262		0.5512		1.814
9.0	23.30 "	0	0.4472	0.2915 "	29.1	0.8483		0.5733		1.744
9.5	24.60 "	0	0.4443	0.2744 "	31.0	0.8506		0.5756		1.737
12.0	31.07 "	0	0.4299	0.2102 "	38.4	0.8072		0.5322		1.879
11.0	28.48 "	0	0.1875	0.2324 "	35.3	0.8204		0.5454		1.834
13.0	33.66 "	0	0.4241	0.1915 "	41.4	0.7928		0.5178		1.931
14.0	36.25 "	0	0.4184	0.1754 "	44.0	0.7718		0.4968		2.013
15.0	38.84 "	0	0.4127	0.1615 "	48.1	0.7768		0.5018		1.993
8.0	20.71 "	0	0.9530	0.3324 "	26.0	0.8642		0.5892		1.697
7.0	18.12 "	0	0.4589	0.3846 "	23.1	0.8884		0.6134		1.630
6.0	15.53 "	0	0.4684	0.4547 "	19.8	0.9003		0.6253		1.599
5.0	12.95 "	0	0.4706	0.5521 "	16.7	0.9220		0.6470		1.546
4.0	10.36 "	0	0.4764	0.6986 "	13.7	0.9571		0.6821		1.466
3.0	7.767 "	0	0.4823	0.9434 "	10.8	1.019		0.7440		1.344

TABLE 11. RESULTS AT 100°C (IODINE). Continued.

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	No. of MOLECULES IODINE x CM^{-3}	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\frac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\epsilon}\times10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q'	Q''	$\frac{1}{Q'}$	$\frac{1}{Q''}$
3.0	7.767 x 10^{+17}	0	0.4823	0.9434 x 10^{-1}	10.3	0.9717		0.6967		1.435
2.0	5.178 "	0	0.4883	1.433 "	7.2	1.032		7.7570		1.321
2.0	" "	0	0.4883	" "	7.4	1.060		0.7850		1.274
2.0	" "	0	0.4883	" "	7.6	1.089		0.8140		1.229
2.0	" "	0	0.4883	" "	7.2	1.032		0.7570		1.321
							0.276			
9.5	24.6 x 10^{+17}	0	0.4443	0.2744 "	31.0	0.8506		0.5789		1.727
9.5	" "	XS	"	" "	9.9	0.2717	0.2717		3.609	
9.5	" "	20.16 x 10^{+15}	"	" "	11.3	0.3100		0.0383		26.11
9.5	" "	13.44 "	"	" "	11.8	0.3238		0.0521		19.19
9.5	" "	9.585 "	"	" "	13.2	0.3622		0.0905		11.05
9.5	" "	12.10 "	"	" "	12.4	0.3403		0.0686		14.58
9.5	" "	7.64 "	"	" "	13.9	0.3814		0.1124		8.89
9.5	" "	6.331 "	"	" "	15.2	0.4171		0.1454		6.883
9.5	" "	5.447 "	"	" "	15.9	0.4363		0.1646		6.076
9.5	" "	4.174 "	"	" "	16.3	0.4473		0.1756		5.694
9.5	" "	15.77 "	"	" "	11.7	0.3210		0.0493		20.28
9.5	" "	3.360 "	"	" "	16.9	0.4637		0.1920		5.208
9.5	" "	2.299 "	"	" "	20.3	0.5570		0.2853		3.505
9.5	" "	3.042 "	"	" "	17.5	0.4802		0.2085		4.796
9.5	" "	7.923 "	"	" "	13.0	0.3567		0.0850		11.76
15.0	38.84 "	0	0.4127	0.1615 "	48.0	0.7752		0.523		1.991
15.0	" "	10.89 x 10^{+15}	"	" "	20.5	0.3311		0.0582		17.18
15.0	" "	8.807 "	"	" "	20.9	0.3392		0.0646		15.48
15.0	" "	9.055 "	"	" "	21.0	0.3343		0.0663		15.08
15.0	" "	9.550 "	"	" "	20.7	0.3230		0.0614		16.29
15.0	" "	11.39 "	"	" "	20.0	0.3133		0.0501		19.96
15.0	" "	15.39 "	"	" "	19.4	0.3359		0.0404		24.75
15.0	" "	8.489 "	"	" "	20.8	0.3763		0.0630		15.87
15.0	" "	5.977	"	" "	23.3	0.3765		0.1034		9.650

TABLE 11. RESULTS AT 100°C (IODINE). Continued.

ACETONE PRESSURE CM.Hg AT 20°C N	No. of MOLECULES ACETONE x CM^{-3}	No. of MOLECULES IODINE x CM^{-3}	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})}$	$\dfrac{\frac{I_T}{I_o}}{(1+\frac{I_T}{I_o})N\varepsilon} \times 10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
15.0	$38.84 \times 10^{+17}$	$5.447 \times 10^{+15}$	0.4127	0.1615×10^{-1}	23.5	0.3795		0.1066		9.390
15.0	" "	4.138 "	"	" "	23.6	0.3810		0.1081		9.254
15.0	" "	2.440 "	"	" "	24.7	0.3989		0.1269		7.939
15.0	" "	13.44 "	"	" "	20.3	0.3278		0.0549		18.21
15.0	" "	XS	"	" "	16.9	0.2729	0.2729		3.664	
6.0	$15.53 \times 10^{+17}$	0	0.4648	0.4547 "	20.0	0.9094		0.6344		1.576
6.0	" "	$7.286 \times 10^{+15}$	"	" "	8.2	0.3728		0.0978		10.22
6.0	" "	11.07 "	"	" "	8.0	0.3638		0.0888		11.26
6.0	" "	5.447 "	"	" "	9.3	0.4229		0.1479		6.760
6.0	" "	2.688 "	"	" "	12.4	0.5638		0.2888		3.462
6.0	" "	3.714 "	"	" "	10.3	0.4683		0.1933		5.173
6.0	" "	13.44 "	"	" "	7.9	0.3592		0.0844		11.88
						MEAN	0.2750		3.636	

TABLE 12. RESULTS AT 120°C (IODINE).

ACETONE PRESSURE CM.Hg AT 20°C	No. of MOLECULES ACETONE x CM^{-3} N	No. of MOLECULES IODINE x CM^{-3}	$\dfrac{I_T/I_o}{(1+\frac{I_T}{I_o})}$	$\dfrac{I_T/I_o}{(1+\frac{I_T}{I_o})N\epsilon} \times 10^{-3}$	CORRECTED POTENTIOMETER READING	Q	Q′	Q″	$\frac{1}{Q'}$	$\frac{1}{Q''}$
10.0	24.58 x 10^{+17}	0	0.4416	2.603 x 10^{-2}	24.0	0.6247		0.3826		2.164
10.0	" "	17.69 x 10^{+15}	"	" "	19.2	0.4998		0.2557		3.911
10.0	" "	XS	"	" "	9.3	0.2421	0.2421			
10.0	" "	24.26 x 10^{+15}	"	" "	10.2	0.2655		0.0234		42.74
10.0	" "	17.90 "	"	" "	10.8	0.2811		0.0390		25.64
10.0	" "	11.74 "	"	" "	11.2	0.2915		0.0494		20.24
10.0	" "	9.196 "	"	" "	12.0	0.3124		0.0703		14.22
10.0	" "	8.666 "	"	" "	12.2	0.3176		0.0755		13.25
10.0	" "	5.518 "	"	" "	14.4	0.3748		0.1327		7.530
10.0	" "	3.608 "	"	" "	16.0	0.4165		0.1744		5.734
10.0	" "	2.688 "	"	" "	18.7	0.4868		0.2447		4.086
10.0	" "	XS	"	" "	9.5	0.2473	0.2473			
10.0	" "	7.18 x 10^{+15}	"	" "	12.7	0.3306		0.0885		11.30
10.0	" "	14.50 "	"	" "	11.0	0.2863		0.0442		22.62

CHAPTER IV.

RESULTS OF METHYL IODIDE QUANTUM YIELD MEASUREMENTS.

The results for $\Phi\,CH_3I$, obtained as described previously, are tabulated in Table 13 and displayed graphically in figs.(30)and (31). In fig.(30) the results obtained for $\Phi\,CH_3I$ at 100°C are plotted along with data previously reported by other workers. Points measured at the same acetone pressure are joined by lines, other acetone pressures are indicated on the graph. In fig.(31) the results for $\Phi\,CH_3I$ at 120°C are plotted in a similar way.

In table 13 the iodine runs are numbered with "1" e.g. $A1_1$, $B1_2$, etc; the pure acetone runs with a letter and number subscript only e.g. A_1, B_2. Most of the data was obtained at 100°C so that a comparison with Martin and Sutton's work (4) could be made. The new analytical technique for CH_3I allowed rather more sensitive determinations of $\Phi\,CH_3I$ to be made and lower pressures of iodine could be investigated than had previously been possible. This meant that a great deal of supporting evidence, by an independent analytical technique, could be obtained for the effect of both acetone pressure and iodine pressure on $\Phi\,CH_3I$.

While they were in good agreement with all of the previously reported data, the results obtained in this work showed that iodine is rather more effective at relatively low concentration than had been previously predicted by the Martin and Su~~dd~~tton mechanism. Consequently attention was focussed on the low iodine pressure region to confirm this. The temperature effect noted by Pitts and Blacet (8) was confirmed by this work although lack of time prevented as much evidence as would have been desirable from being collected on this

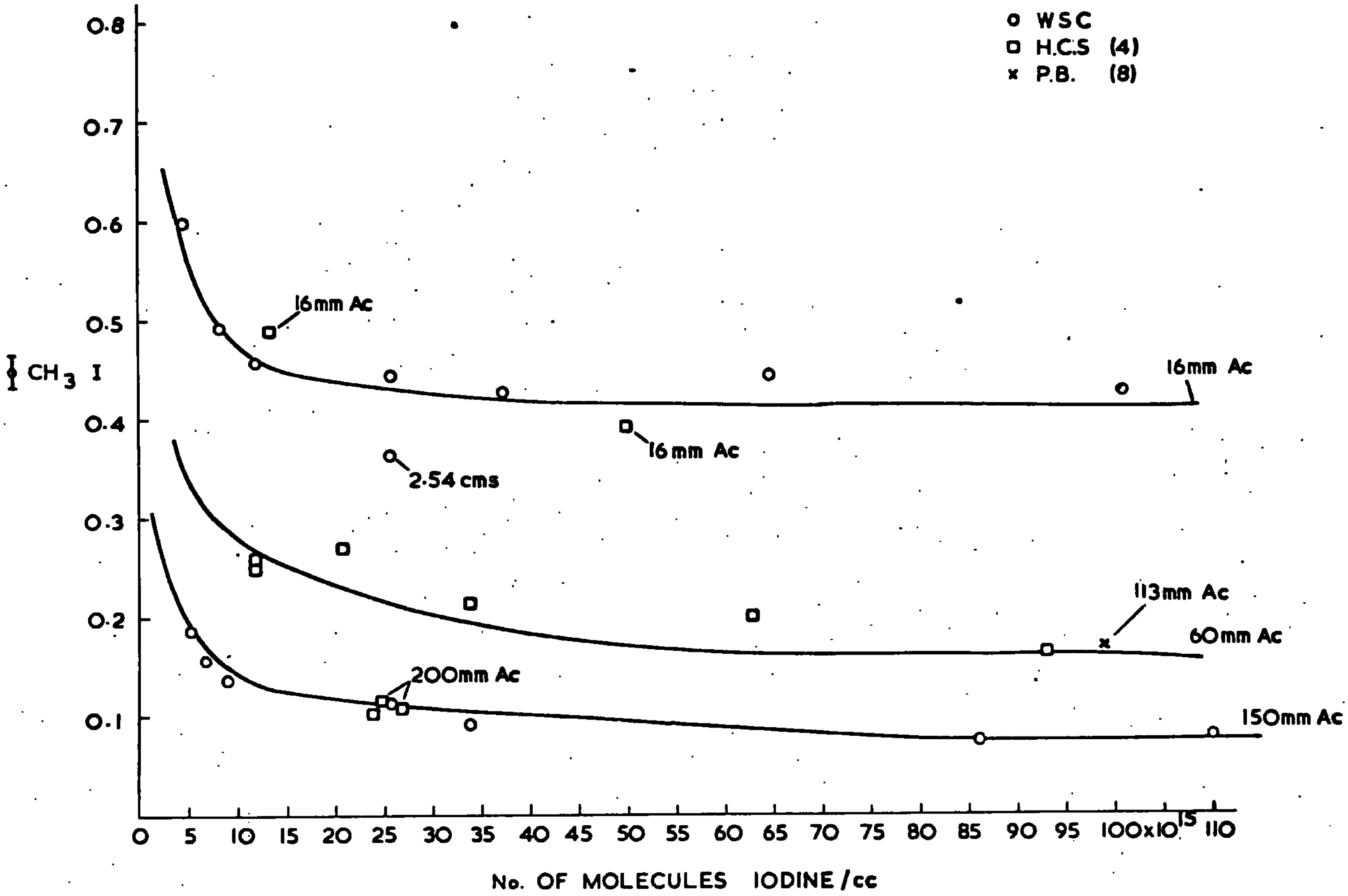


Fig. 30 Methyl iodide quantum yields 100°C

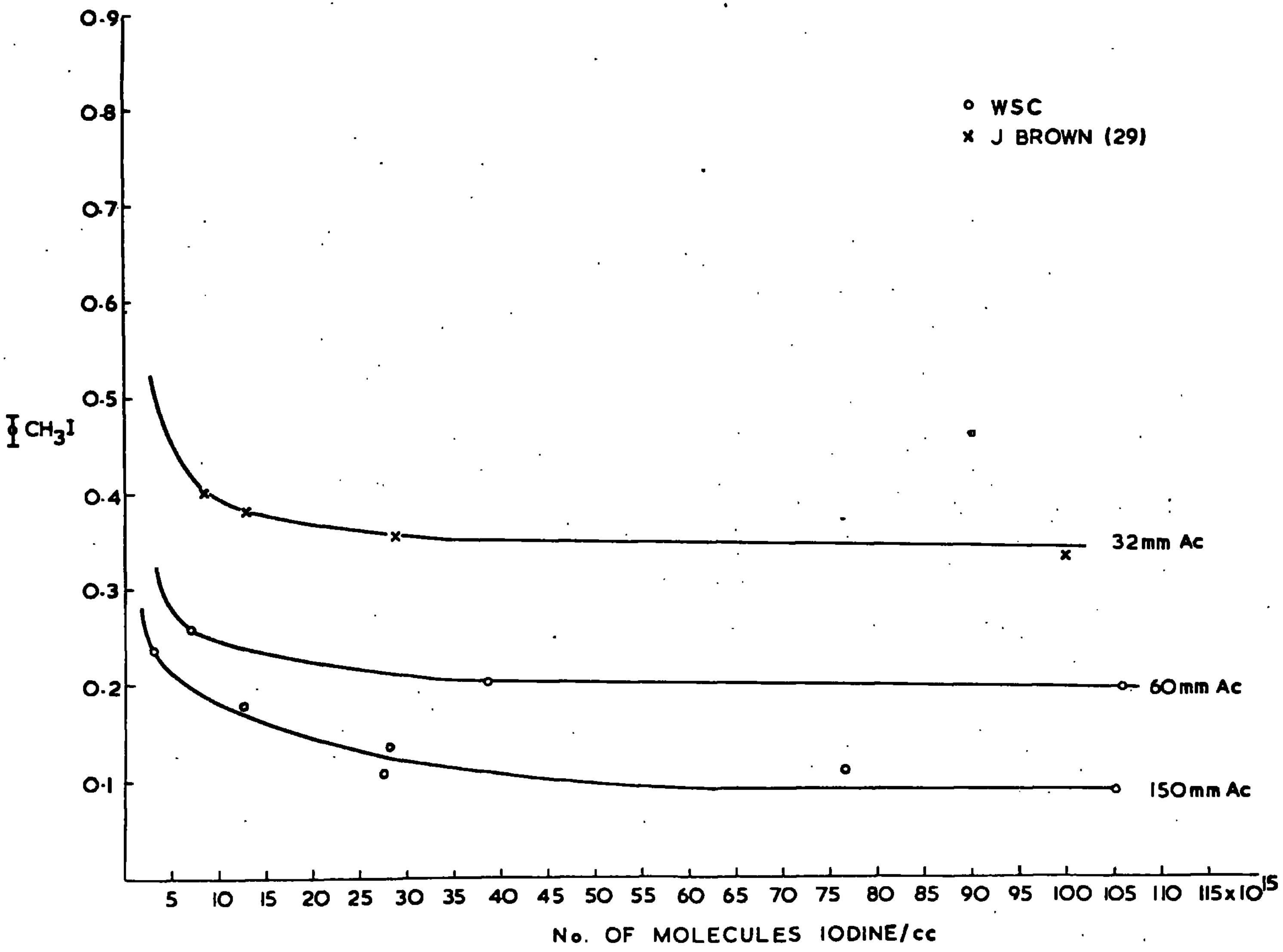


Fig. 31 Methyl iodide quantum yields 120°C

aspect of the measurements. The results will be discussed further and used in the derivation of the mechanism in chapter (V).

TABLE 13. QUANTUM YIELD OF METHYL IODIDE.

RUN No.	PRESSURE Ac MEASURED AT 100°C CMS	PRESSURE CO IN CALIBRATED VOLUME III (0·756 cc.) AT 21°C CMS	TEMPERATURE OF RUN °C		μ MOLES CO	CH_3I μ MOLES	Φ CH_3I	IODINE CONCENTRATION/CC molecules
A_1	2.535	2.828	120	)	1.174			
A_2	2.535	2.682	120	)				
A_3	2.535	2.940	120	)				
A_4	2.535	2.900	120	)				
A_5	2.535	2.898	120	)				
AI_1	2.535		100			0.427	0.364	$25.59 \times 10^{+15}$
B_1	15.0	8·90 ~~3.5616×2.5~~	120	)	3.64			
B_2	15.0	8·93 ~~3.577×2.5~~	120	)				
B_3	15.0	8·74 ~~3.493×2.5~~	120	)				
BI_1	15.0		120			0.494	0.1358	$28.18 \times 10^{+15}$
BI_2	15.0		120			0.654	0.179	$11.97 \times 10^{+15}$
C_1	1.60	3.372	120	)	1.376			
C_2	1.60	3.358	120	)				
C_3	1.60	3.362	120	)				
C_4	1.60	3.262	120	)				
CI_1	1.60		100			0.616	0.448	$25.67 \times 10^{+15}$
CI_2	1.60		100			0.630	0.458	$11.71 \times 10^{+15}$
D_1	1.60	3.624	120	)	1.471			
D_2	1.60	3.531	120	)				
D_3	1.60	3.648	120	)				

.TABLE 13. QUANTUM YIELD OF METHYL IODIDE. (Continued)

RUN No.	PRESSURE Ac MEASURED AT 100°C CMS	PRESSURE CO IN CALIBRATED VOLUME III(0.756cc) AT 21°C CMS	TEMPERATURE °C	µ MOLES CO	CH_3I µ MOLES	Φ CH_3I	IODINE CONCENTRATION/CC molecules
DI_0	1.60		100		0.725	0.493	$8.028 \times 10^{+15}$
DI_1	1.60		100		0.8835	0.601	4.656 "
DI_2	1.60		100		0.655	0.445	64.68 "
DI_3	1.60		100		0.628	0.428	37.02 "
DI_4	1.60		100		0.625	0.426	101.0 "
EI_0	15.0		100		0.8294	0.139	8.860 "
EI_1	15.0		100		0.640	0.0795	109.97 "
EI_2	15.0		100		0.451	0.0756	86.07 "
EI_3	15.0		100		0.548	0.0917	33.72 "
EI_4	15.0		120		0.648	0.1085	27.56 "
EI_5	15.0		100		0.6834	0.1145	25.42 "
EI_6	15.0		100		1.127	0.188	5.06 "
EI_7	15.0		120		1.403	0.235	2.97 "
EI_8	15.0		100		0.9482	0.1589	6.54 "
EI_9	15.0		120		0.6592	0.1106	76.75 "
EI_{10}	15.0		120		0.5326	0.0893	105.2 "
E_1	15.0	14.37	120	5.97			
E_2	15.0	14.70	120				
E_3	15.0	14.50	120				
FI_1	6.0		120		0.833	0.202	38.75 "

TABLE 13. QUANTUM YIELD OF METHYL IODIDE. (Continued)

RUN No.	PRESSURE* Ac MEASURED AT 100°C CMS	PRESSURE CO IN CALIBRATED VOLUME III(0.75cc) AT 21°C CMS	TEMPERATURE °C		μ MOLES CO	CH_3I μ MOLES	Φ CH_3I	IODINE CONCENTRATION/CC molecules
FI_2	6.0		120			1.064	0.257	$7.04 \times 10^{+15}$
FI_3	6.0		120			0.8007	0.195	106.2 "
F_1	6.0	9.986	120	)				
F_2	6.0	9.900	120	)	4.134			
F_3	6.0	10.304	120	)				

CHAPTER V.

Discussion of Results.

From the results in this work and those of other investigators which have been summarised in chapter I, some general conclusions and consequent limitations on allowable mechanisms can now be taken as established. These are:

(a) The fluorescence efficiency from the singlet state is little or not at all modified by acetone, oxygen or iodine pressures or by temperature, whereas the phosphorescence efficiency from the triplet state is greatly affected by these parameters. The same parameters also have a great effect on the quantum yield of decomposition in pure acetone, acetone/oxygen and acetone/iodine mixtures. Hence it seems probable that the decomposition products must come predominantly from the triplet state and that the singlet and triplet states cannot be in equilibrium.

(b) At temperatures below 100°C the observed quantum yields of decomposition in pure acetone fall appreciably below unity but the phosphorescence yield does not show a corresponding rise to 40-50% as would occur if phosphorescence were the only alternative means of deactivation of the triplet. The back reaction, $CH_3' + CH_3CO' \longrightarrow CH_3COCH_3$, usually regarded as a secondary reaction, may be the reason for this low quantum yield but it is necessary that any acceptable mechanism must, either by primary or secondary steps account for the fractional quantum yield of decomposition.

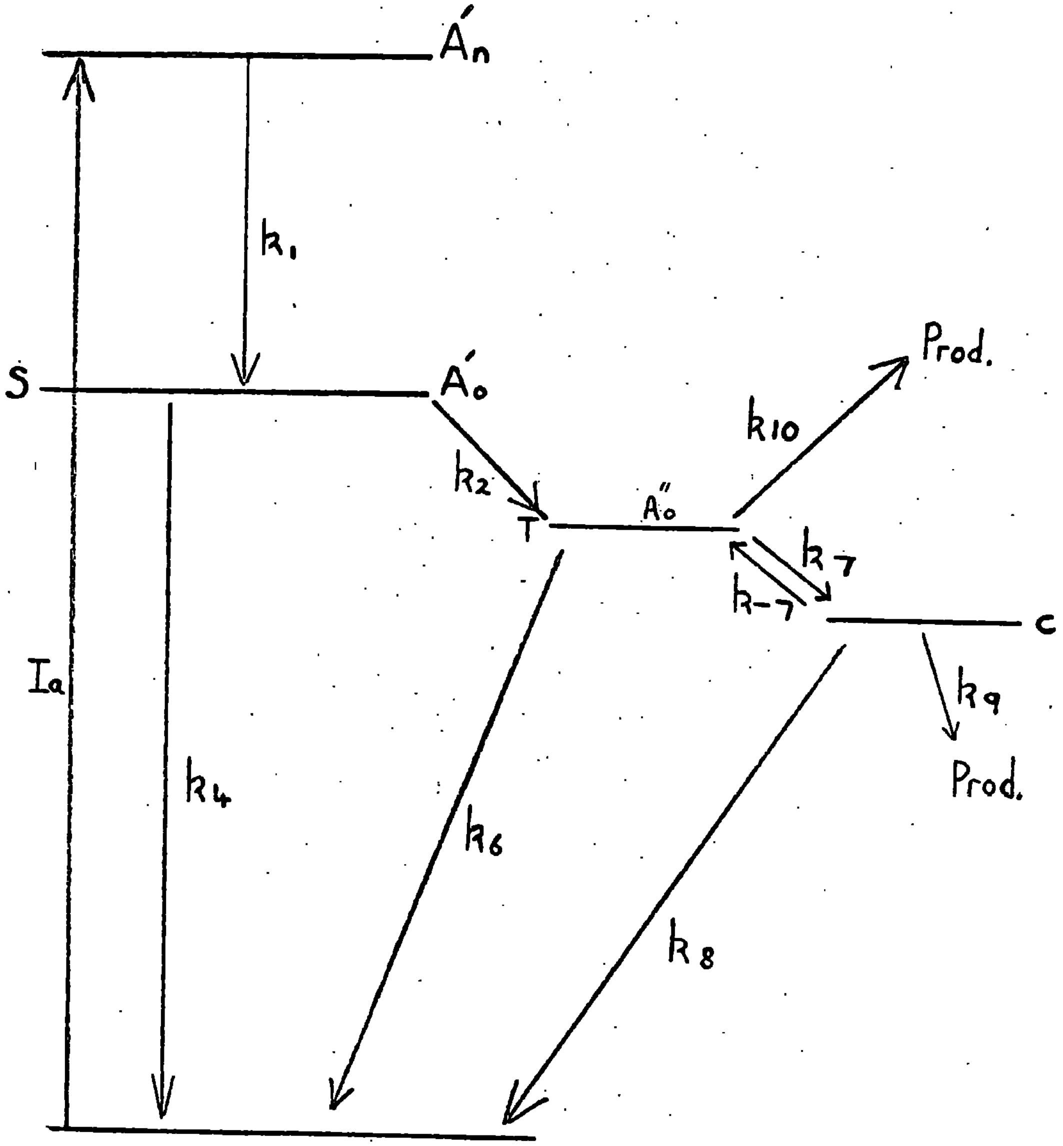


Fig. 32 Mechanism

(c) At temperatures of 120°C, where the quantum yield of acetone decomposition is near unity and is independent of the acetone pressure, acetone is, nevertheless, still exerting a considerable quenching effect on the triplet state (see figures 12, 25). The phosphorescence yield under these conditions is less than 1% and the quantum yield of decomposition must differ from unity by at least this amount, although such a small difference is concealed by the experimental error in the measurement of the quantum yield of decomposition. However, although acetone has been shown to exert a specific effect on the phosphorescence at this temperature, it cannot be determined whether the acetone quenches the triplet by producing a decomposition or a deactivation alternative to triplet emission.

(d) The fact that iodine or oxygen acts in co-operation with acetone to quench the phosphorescence and also in depressing the quantum yield can most simply by accounted for by postulating a complex between the triplet and the iodine or oxygen which is deactivated by acetone rather than by invoking a three body collision process.

To explain the above general conclusions and as a basis for a more detailed and quantitative discussion of the results in this work, the mechanism shown in figure 32 is proposed. The electronically excited states S(singlet) and T(triplet) are shown by horizontal lines. S is formed directly from the ground state by absorption of a quantum of energy. T is formed <u>irreversibly</u> from the excited singlet and C, which is a complex between the triplet and iodine or oxygen, is formed by a <u>reversible</u> step shown. The inclusion of the various steps may be justified qualitatively as follows:

(1) k_1 takes account of the fact that the absorbed radiation (3130Å) is at a shorter wavelength than the shortest observed fluoresdence wavelength (i.e. about 3700Å). k_1 does not appear in the kinetic equations as all the molecules which absorb quanta are assumed to form S without loss by other processes so that the reaction rate for $A'_n \longrightarrow A'_o$ is equal to the rate of absorption of quanta (Ia).

(2) $k_{\cancel{2}4}$ and $k_{\cancel{4}2}$ are essentially transition probabilities (to the triplet and for fluorescence respectively) and as such would not be expected to be greatly affected by temperature change or by the pres~~sure~~ence of other molecules. This allows $\frac{1}{Q}$ to be more or less independent of these parameters.

(3) The step k_6 is included to account for the triplet phosphoresence which is in fact observed and k_{10} is needed to represent the decomposition which is found in the photolysis of pure acetone. The reasons for associating k_{10} with the triplet rather than the singlet have been outlined under (a) above.

(4) The formationsof the complex C by the reversible step k_7 and k_{-7} have also been dealt with above (see (d))

(5) The deactivation of the complex by step k_8 must be included because under conditions where the phosphorescence is completely quenched (i.e. deactivation by step k_6 is completely supressed by addition of, say, iodine) then the quantum yield of acetone decomposition is nevertheless far below unity. The effect of high iodine concentrations in reducing the quantum yield of decomposition is most clearly seen in figures (30) and (31).

(6) k_9 must be included because, in the region where the phosphorescence is fully quenched by oxygen or iodine, there are, nevertheless, some products formed. Alternatively these products could be formed from C via k_{-7} and k_{10} but only if $k_{10} \gg k_{-7}$ so that A_o'' is maintained at a low enough concentration for there to be no appreciable phosphorescence via k_6. If this latter is the case quantitative treatment of the mechanism could be expected to yield the value $k_9 = o$.

(7) The observed effect of acetone pressure on the phosphorescence (noted in (c) above) indicates that either k_6 or k_{10} must have a concurrent bimolecular mechanism involving acetone.

The kinetic treatment of the proposed mechanism is shown in full in Appendix (3). The mechanism can now be shown to fit the experimental facts kinetically and in the process of doing this the significance of the various experimental observations will become apparent.

In Appendix (3) equation (5) it is shown that the inverse fluorescence efficiency is given by

$$\frac{1}{Q'} = \frac{k_2 + k_4}{k_2} \doteq \frac{k_4}{k_2}$$

As discussed above, these rate constants would be expected to be fairly insensitive to change of temperature or the presence of added reagents. The experimental results confirm that this is indeed the case with respect to added reagents and the effect of temperature on $\frac{1}{Q'}$ is very small. (fig.24). Furthermore the temperature effect variation of $\frac{1}{Q'}$ is the same when either oxygen or iodine is used as the quenching reagent as can be seen from figure (24) where the results are plotted in the Arrhenius form and where it can be seen that, within the limits of experimental error, both series of results conform to the same slope. The slope of the line corresponds to an activation energy (calculated from E act. = 2.303 x 1.986 x slope) of 780 cals/mole ($= E_4 - E_2$) - although temperature coefficients of transition probabilities are not usually discussed in terms of activation energies.

It has also been shown (Appensix (3) equation 4) that the primary quantum yield of acetone decomposition in the photolysis of pure acetone is given by

$$\Phi_d = \frac{k_{10}}{k_6 + k_{10}}$$

To account for the reported values of less than unity for the quantum yield for decomposition of acetone below 100°C, the above expression must be less than unity at these temperatures. This is only possible if k_6 is comparable with k_{10}. However the rate of decomposition under these conditions is determined by k_{10} and if k_{10} and k_6 are to be of the same magnitude then the phosphorescence efficiency (i.e. the quantum yield of phosphorescence) must be comparable with the quantum yield of decomposition. This is not so - the quantum yield of phosphorescence is much smaller - but the impasse can be avoided if k_6 is taken to have the form $k_6 = l_6 + h_6$ (A), that is if there also exists a bimolecular (non-radiative) mode of deactivation by ordinary acetone molecules. The condition that $k_6 = k_{10}$ can now be met since now l_6 is the rate constant associated with the phosphorescence and there is no restraint on the value of h_6 (A).

Furthermore, this argument is not invalidated if k_{10} also has the form $l_{10} + h_{10}(A)$, as will be postulated later. Therefore the quantum yield for acetone composition is given by either

$$\Phi d = \frac{k_{10}}{k_{10}+l_6+h_6(A)} \quad \text{or} \quad \Phi d = \frac{l_{10}+h_{10}(A)}{l_{10}+l_6+(h_{10}+h_6)(A)}$$

either of which forms predict that the primary quantum yield of acetone decomposition should be a partial inverse function of the acetone pressure at the low temperatures where $k_6 = k_{10}$ as is required. At temperatures above 100°C the above expressions predict the observed quantum yield of unity if k_{10} is assumed to have a significantly greater activation energy than k_6 so that at these temperatures $k_{10} \gg k_6$. This assumption is entirely reasonable since k_6 is the rate constant for a deactivation process which is not likely to have an activation energy whereas the decomp~~se~~osition step k_{10}, <u>may</u> have an activation energy even if the triplet state lies at an energy level above that of the products. If the energy level of the triplet lies below the level of the products then the decomposition process <u>must</u> have an activation energy.

The expression for the inverse phosphorescence yield from the postulated mechanism can be shown to be (Appendix (3) equation 7)

$$\frac{1}{Q''} = \frac{1}{l_6}\left\{k_{10} + h_6(A) + j_7(I)\frac{\left(1+\frac{h_8(A)}{k_9}\right)}{1+\frac{h_8(A)}{k_9}+\frac{k_{-7}}{k_9}}\right\}$$

and in pure acetone this simplifies to the expression

$$\frac{1}{Q''_T} = \frac{k_{10} + h_6(A)}{l_6}$$

since in pure acetone (I) = o and the last term in the bracket becomes zero. This has the linear form (viz: $\frac{1}{Q''} = K + K'(A)$ necessary to fit the results which have been obtained (see, for example figures (12), (25)). However, as demonstrated in figure (25) the slopes of these graphs have an appreciable temperature coefficient. Using the expression derived above from the mechanism proposed, the slopes of the $\frac{1}{Q''_T}$ against (A) graphs are given by h_6/l_6 and since both h_6 and l_6 are deactivation processes neither can be expected to have sufficiently large activation energy.

If, however, k_{10} is replaced by $l_{10} + h_{10}(A)$ in the same way as was done for k_6 above, the expression for the inverse phosphorescence efficiency becomes

$$\frac{1}{Q''_T} = \frac{l_{10}}{l_6} + \frac{(h_6 + h_{10})(A)}{l_6}$$

and the temperature coefficient of both the intercepts and the slopes of graphs such as figure (25) can now be accounted for by the variation with temperature of l_{10} and h_{10} respectively. The requirement and the probability that l_{10} and h_{10} have significant activation energies has been discussed above and needs no further justification. If the above treatment is accepted then the intercepts of the plot of $\frac{1}{Q''_T}$ against (A) at $(I_2) = (O_2) = (O)$ are proportioned to $\frac{l_{10}}{l_6}$

TABLE 14 : Oxygen series

TEMP. °C	GRAPHS $\frac{1}{T^{Q''}}$ vs (A)		GRAPHS $\frac{1}{Q''}$ vs (O_2)	
	$\frac{1}{T^{Q''}}$ AT (A) = 0	SLOPE cc Mol^{-1}	(A) Mol.cc^{-1}	SLOPE cc Mol^{-1}
	x a	x 10^{-20} a	x 10^{17} a	x $10\,a^{-16}$
20	0.480	1.10	49.44	11.8
			32.97	7.03
			12.52	4.96
50	0.734	4.30	24.52	7.54
75			24.42	7.70
100			25.89	9.64
120	2.58	1.88	43.01	14.9
			33.67	13.4
			24.58	11.5
			15.73	9.10
150			22.83	8.83

TABLE 15 : Iodine Series

TEMP. °C	GRAPHS $\frac{1}{TQ''}$ vs (A)		GRAPHS $\frac{1}{Q''}$ vs (I)	
	$\frac{1}{TQ''}$ AT (A) =10	SLOPE cc Mol^{-1}	(A) Mol.cc^{-1}	SLOPE cc Mol^{-1}
	x a	x 10^{-20}a	x 10^{17}a	x 10^{-16}a
25	0.333	0.06		
50	0.422	1.38	53.82	9.41
			24.52	5.89
			17.94	4.80
100	1.277	19.3	38.84	15.0
			24.60	9.93
			15.53	8.77
120			24.58	12.1

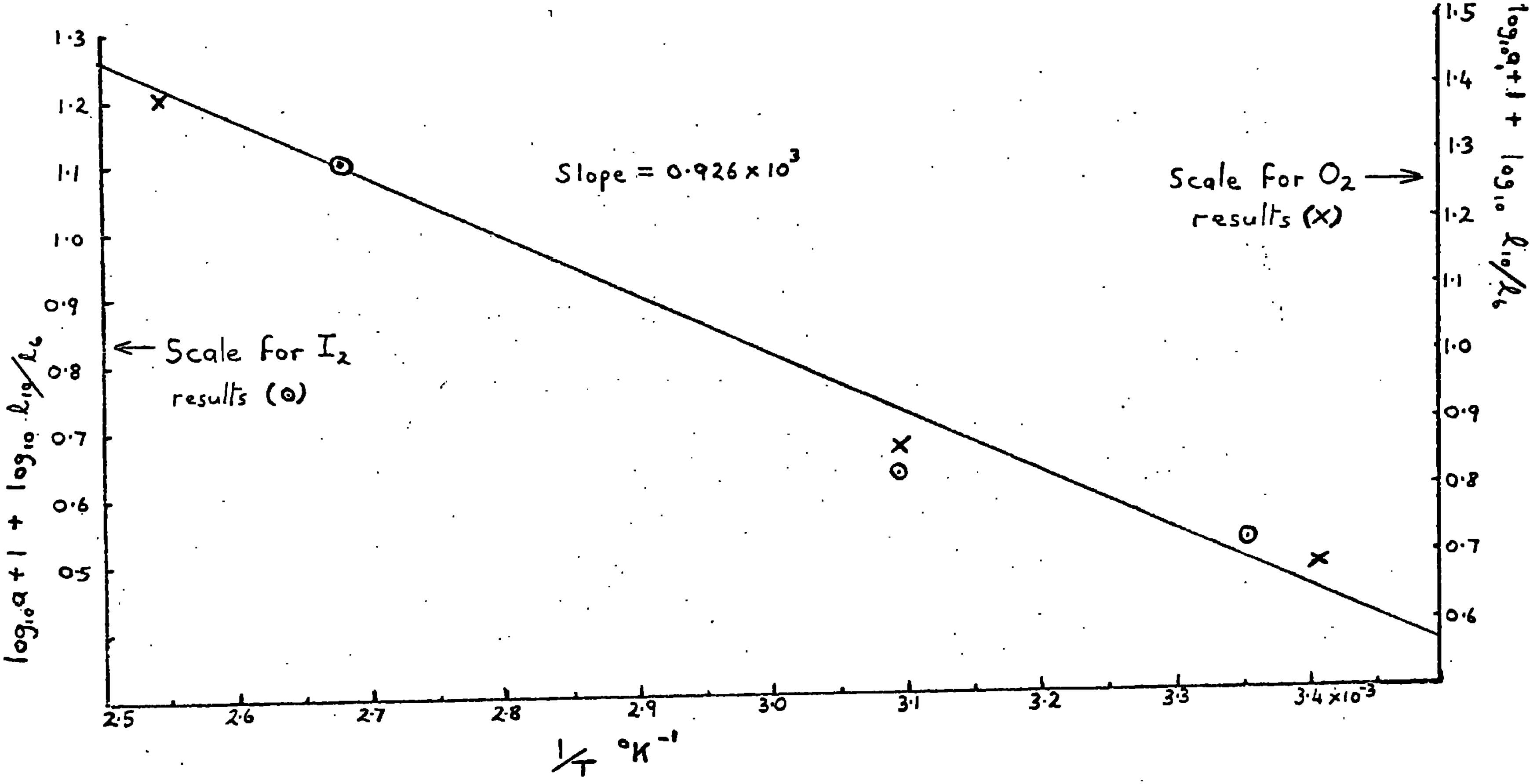


Fig. 33 Arrhenius plot for l_{10}/l_6

and the slopes are proportional to $(h_6 + h_{10})/l_6$. Values of these ratios obtained from the graphs have been tabulated in columns 2 and 3 of Tables 14 and 15. It will be seen that a proportionality constant, a, has been included in these Tables. The reason for "a" is as follows. The light emission results have been presented in terms of arbitary units (consistent within the oxygen and the iodine series, but differing in the two series). Thus it can only be said (for example) that the intercept of the $\frac{1}{Q_T''}$ versus (A) plot is <u>proportional</u> to l_{10}/l_6 It is true that the intercept is equal to l_{10}/l_6 only if the phosphorescence efficiencies Q_T'' were expressed in absolute units. Now it is known that the phosphorescence efficiency at 50°C is <u>about</u> 0.2% (39) so that $\frac{1}{Q_T''}$ at this temperature should be of magnitude about 500 whereas the intercept at (A)=0 and 50°C from figure 25 gives $\frac{1}{Q_T''} = 0.422$ in the arbitary units used. Clearly a proportionality constant, a, of the order 1250 is required to yield absolute values of l_{10}/l_6 and $(h_6 + h_{10})/l_6$. It will, however, transpire that this same factor, a, appears elsewhere in the results for rate constant ratios like l_{10}/l_6 but is removed by cancellation when these rate constant ratios are combined with others in the development and testing of the mechanism. Consequently many of the matters yet to be discussed are in no way invalidated by having no very accurate value for this constant. Where necessary special mention will be made of matters which are affected by the precise value of a.

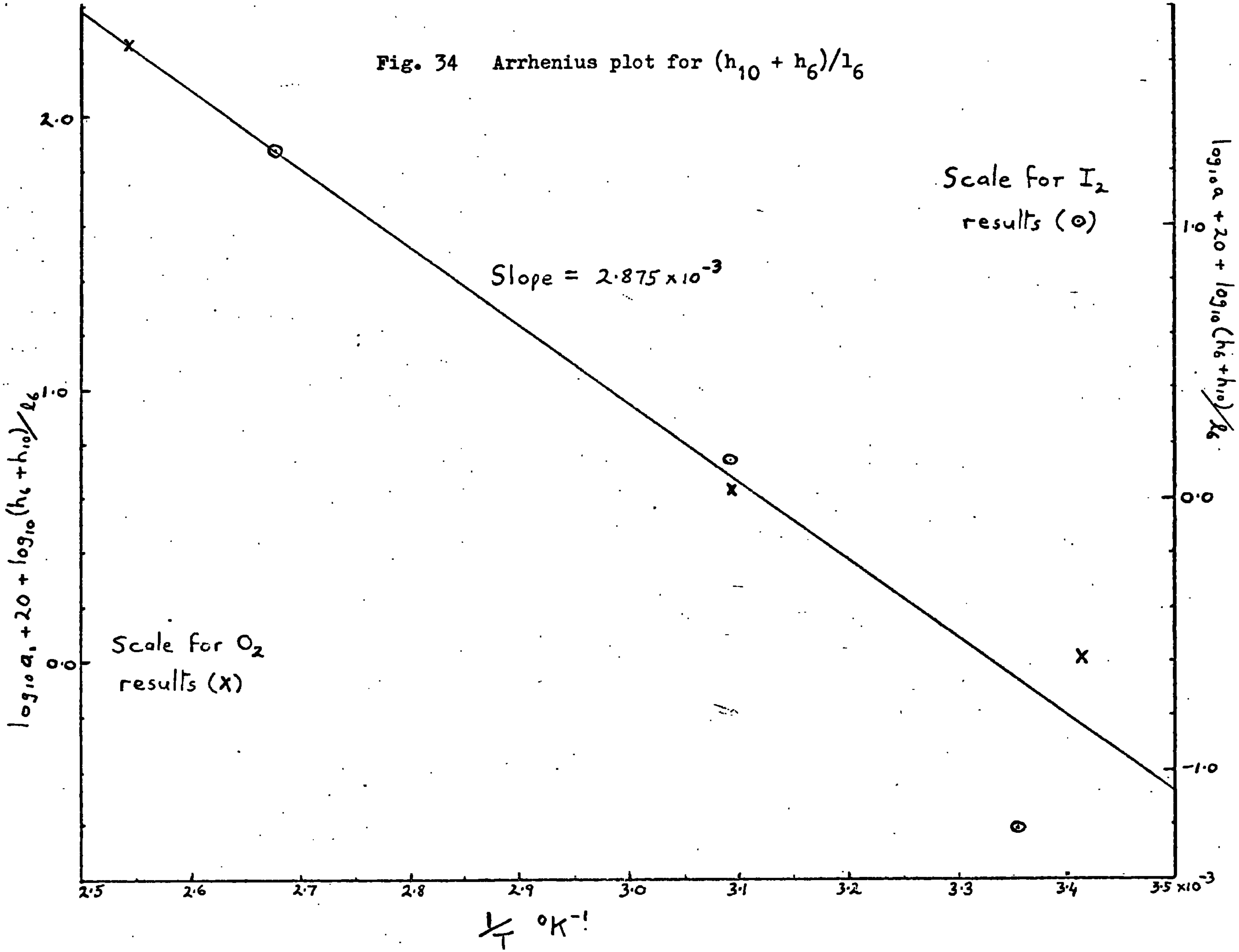


Fig. 34 Arrhenius plot for $(h_{10} + h_6)/l_6$

The results of the intercepts and the slopes of $\frac{1}{T^{Q}}$ vs (Ac) graphs (i.e. l_{10}/l_6 and $(h_6 + h_{10})/l_6$) are tabulated in columns 2 and 3 of Tables 14 and 15. They can be treated in the Arrhenius manner as is shown in figures (33) and (34). From the figures it can be seen that:

(1) The results from the oxygen and from the iodine experiments are concordant as required by the mechanism

(2) in so far as the points in figure (34) can be taken to describe a straight line it follows that either h_6 or h_{10} has a negligible temperature coefficient. Reasons have been outlined above to suggest that the temperature coefficient of h_6 should be small and the activation energy from this graph may be ascribed (see below) to $E_{h_{10}} - E_{l_6}$.

(3) From the slopes of the figures, and applying the above simplification, it can be calculated that Eact = $E_{l_{10}} - E_{l_6}$ = $2.303 \times 1.986 \times 0926 \times 10^3$ = 4.2 kcal/mole and similarly $E_{h_{10}} - E_{l_6}$ = 13 kcal/mole.

The extraction of the ratio h_8/k_9 from ΦCH_3I data.

It is generally accepted that the primary products of reaction k_{10} are one $CH_3^{\cdot}$ radical and one $CH_3\dot{C}O$ radical. It has been shown by Martin and Sutton (4) that in the presence of an excess of iodine CH_3 CO I is formed and, although the quantitative determination proved to be impossible due to difficulties in analysis, there is no reason to suppose that it is decomposed under the conditions of the irradiation. This conclusion is reinforced by the absence of carbon monoxide from the products of the photolysis in the presence of an excess of iodine. Provided then that the reaction of methyl radicals with iodine to form methyl iodide is sufficiently fast to exclude the formation of other products from methyl radicals, then each molecule of acetone decomposing by reaction 10 will yield one molecule of methyl iodide. The absence of such products as methane and ethane indicates that, in fact, the reaction of iodine with the methyl radical is fast enough to preferentially remove all methyl radicals. Assuming that each molecule of the complex C decomposing by reaction 9 also gives rise to one molecule of CH_3I (regardless of whether the decomposition is molecular or into radicals with subsequent capture as above) it follows that the primary quantum yield of acetone decomposition is equivalent to the quantum yield of CH_3I and hence, from Appendix (3) equation 9, it follows that

$$\Phi_{MeI} = \Phi_d = \frac{\dfrac{k_{10}}{j_7(I)} + \dfrac{1}{1 + \dfrac{h_8(A)}{k_9} + \dfrac{k_{-7}}{k_9}}}{\dfrac{k_{10} + h_6(A)}{j_7(I)} + \dfrac{1 + \dfrac{h_8(A)}{k_9}}{1 + \dfrac{h_8(A)}{k_9} + \dfrac{k_{-7}}{k_9}}}$$

When the iodine concentration is sufficiently high the first terms in both the numerator and denominator become negligible and under those conditions (i.e. excess of iodine) the above equation simplifies to

$$\underset{(I)\to\infty}{\Phi_{MeI}} = \underset{(I)\to\infty}{\Phi_d} = \frac{1}{1 + h_8(A)/k_9}$$

Inversion of the expression would allow a graphical treatment of the data but, as the limiting quantum yields were only measured at two acetone concentrations at each temperature, the ratio h_8/k_9 has been obtained by calculation and the results are given in Table (16).

Table 16. The calculation of h_8/k_9

TEMP. °C	ACETONE CONCENTRATION (molecules cc^{-1})	h_8/k_9 (cc. molecules $^{-1}$)	h_8/k_9 mean
100	4.142×10^{17}	3.159×10^{-18}	3.041×10^{-18}
100	38.84×10^{17}	2.922×10^{-18}	
120	15.53×10^{17}	2.576×10^{-18}	2.409×10^{-18}
120	38.84×10^{-17}	2.242×10^{-18}	

It can be seen that the two values of h_8/h_9 calculated at 100°C differ by about 8%. This difference may be due to errors in the experimental data, especially at the lower acetone concentrations used, which would prevent the value of ΦCH_3I from being determined with sufficient accuracy. However, it is more probable that the error is inherent in the mechanism where it is taken that k_8 can be replaced by $h_8(A)$. Reaction 8 is the deactivation of the complex, and it might be expected that this deactivation could also be brought about by collision with iodine molecules although with a much lower efficiency than is ascribed to acetone molecules. If the deactivation by iodine in reaction 8 is included, the mechanism is modified by writing $k_8 = h_8(A) + j_8(I)$ when necessary. Provided that $h_8 \gg j_8$ the importance of $j_8(I)$ will normally be small since it always occurs as an addition term to $h_8(A)$ and generally (A) is much greater than (I). However, for the calculations here in question which concern experiments in which deliberately high iodine concentrations were used (about 1×10^{17} molecules cc^{-1}) the iodine can amount to about 25% of the acetone concentration (4.14×10^{17} molecules cc^{-1}). Allowance for this effect would lower the calculated values of h_8/k_9 and, since the correction would be proportionately greater at the lower acetone concentration, a suitable choice for j_8 would allow the discrepency to be eliminated. However, a reasonable explanation of the discrepancy having been found, the quantitative determination of the value of j_8 has not been pursued because the data for its calculation is so limited as to make the number which would emerge of doubtful quantitative significance. Accepting the mechanism to be in accord with the experimental findings the mean values of h_8/k_9 at the two temperatures can be used to calculate that $Eh_8 - Ek_9 = -3.4$ kcal/mole by the usual Arrhenius treatment.

The values calculated for h_8/k_9 can now be used to treat the slopes of the Stern-Volmer plots of $\frac{1}{Q''}$ against (I). From the expression quoted above (page 87) for $\frac{1}{Q''}$ it can be seen that the slope, S, of these graphs is given by

$$S \cdot \cancel{\alpha} = \frac{j_7 \left(1 + \frac{h_8(A)}{k_9}\right)}{I_6 \left(1 + h_8(A)/k_9 + \frac{k_{-7}}{k_9}\right)}$$

~~where a is the constant introduced previously to convert light emission results to absolute units~~ and therefore

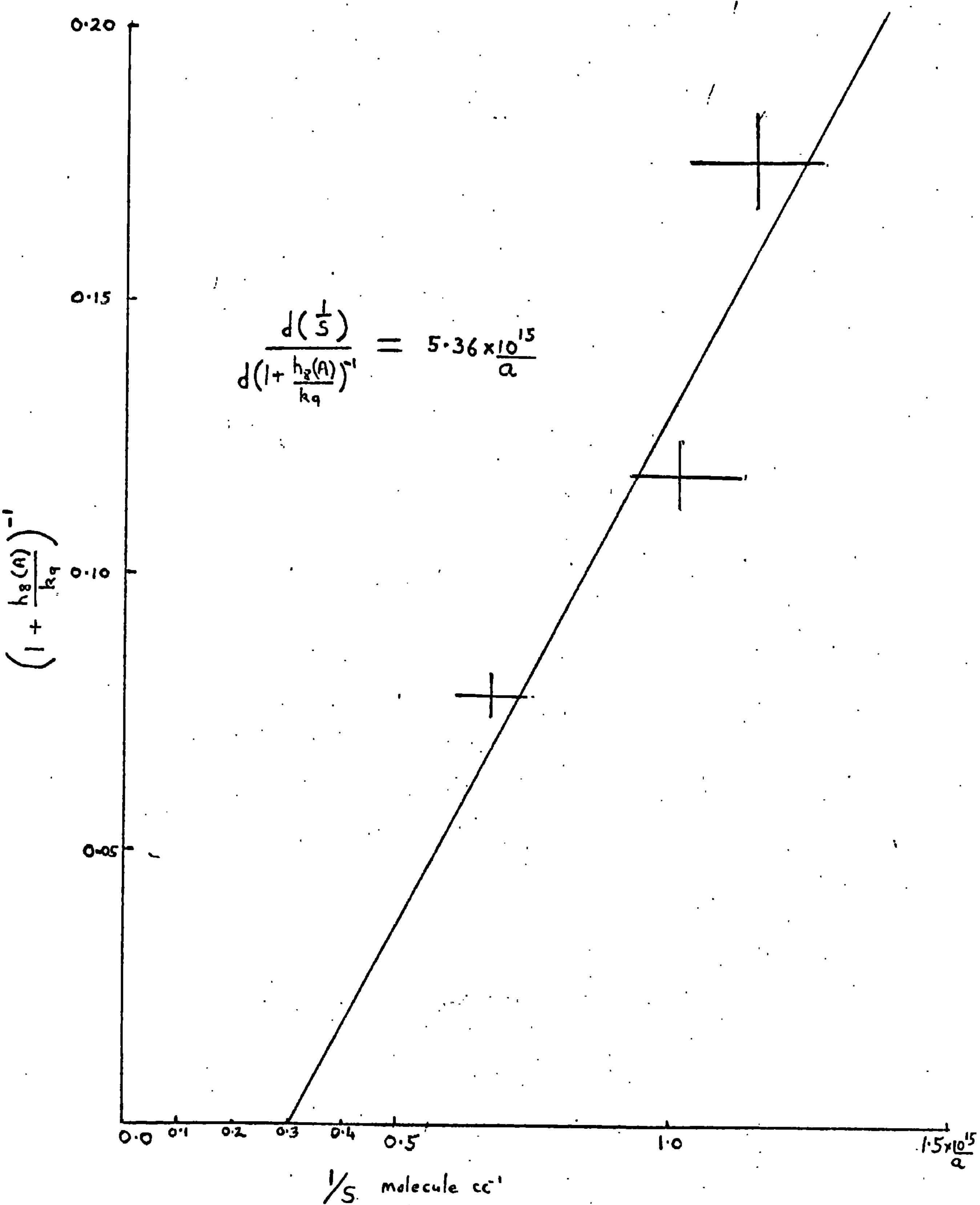


Fig. 35 Determination of l_6/j_7 and $\frac{k_7}{k_9}$ at 100°C

$$\frac{1}{Sa} = \frac{l_6}{j_7} + \frac{l_6 k_{-7}}{j_7 k_9} \left(\frac{1}{1+h_8(A)/k_9}\right)$$

The expression in the bracket can be calculated and plotting this against $\frac{1}{Sa}$ should give a straight line from the intercept and slope of which $\frac{l_6}{j_7}$ and $\frac{k_{-7}}{k_9}$ can be obtained. The Stern-Volmer plots obtained for iodine quenching at 100°C have been previously included as figures 27, 28 and 29, and the slopes of these lines are listed in Table (15 column 5). Using these slopes and the method outlined above the results shown in Table 17 and plotted in figure (35) are obtained.

<u>TABLE 17</u>. The calculation of l_6/j_7 and k_{-7}/k_9 at 100°C.

(A) Concentration molecule cc^{-1}	$1 + \frac{h_8(A)}{k_9}$	$(1 + \frac{h_8(A)}{k_9})^{-1}$	S cc molecule^{-1}	$\frac{1}{S}$ molecule cc^{-1}
3.882×10^{18}	12.81	0.07807	$15\times10^{-16}a$	$0.667\times10^{15}/a$
2.459×10^{18}	8.478	0.1181	$9.93\times10^{-16}a$	$1.007\times10^{15}/a$
1.553×10^{18}	5.722	0.1747	$8.77\times10^{-16}a$	$1.140\times10^{15}/a$

In figure (35) the points have been marked with a vertical uncertainty computed assuming ± 6% indeterminancy in the values of h_8/k_9 and a horizontal uncertainty by assuming ± 10% in the slopes. This degree of indeterminancy is not felt to be excessive in view of the formidible experimental difficulties which had to be overcome to obtain the emission results at the higher temperature (see chapter 2).

From figure (35) it can be calculated from the intercept that $l_6/j_7 = \frac{3.00}{a} \times 10^{14}$ molecules cc^{-1} and from the ratio slope/intercept $k_{-7}/k_9 = 17.9$.

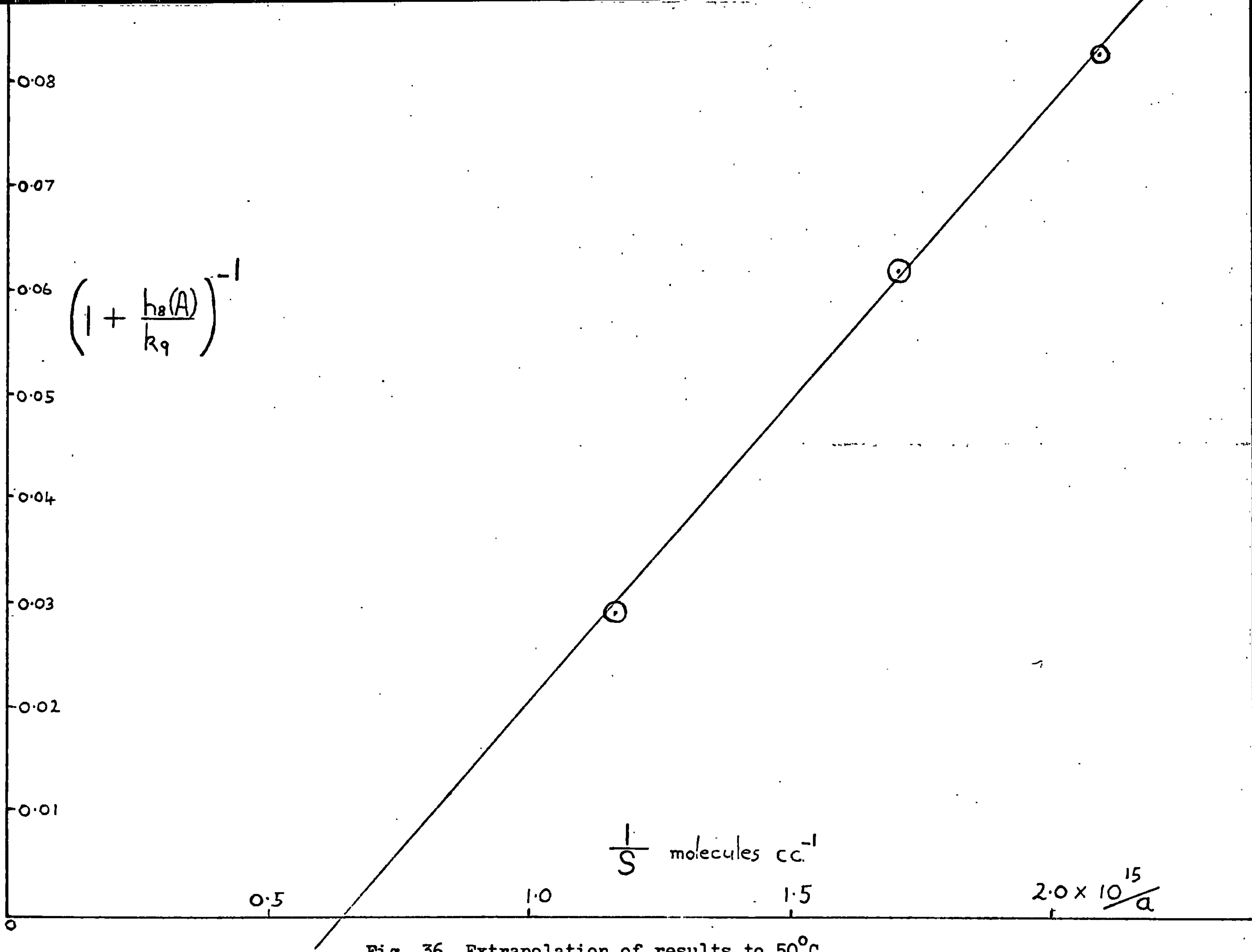


Fig. 36 Extrapolation of results to 50°C

The prediction of results at 50°C from results at higher temperatures.

Some assurance that the above manipulations do not stretch the experimental evidence too far may be obtained as follows. Using the values of h_{8}/h_{9} at 100°C and 120°C the Arrhenius E-factor has been calculated to be $E_{h_8} - E_{k_9} = -3.4$ kcal/mole (page 95) and this may be used to calculate $h_{8}/k_{9} = 6.19\times10^{-18}$ at 50°C. This value of $\frac{h_8(A)}{k_9}$ may then be used to generate $(1 + \frac{h_8(A)}{k_9})^{-1}$ at 50°C as shown in table 18, and this has been plotted in figure (36) against the slopes of the family of Stern-Volmer curves (figure 27) available at this temperature.

Table 18. Data for figure 35.

Acetone Concentration molecule cc^{-1}	$1 + \frac{h_8(A)}{k_9}$	$(1 + \frac{h_8(A)}{k_9})^{-1}$	S cc molecule^{-1}	$\frac{1}{S}$ molecule cc^{-1}
53.82×10^{17}	34.32	0.02913	$9.41\times10^{-16}a$	$1.063\times\frac{10^{15}}{a}$
24.52×10^{17}	16.18	0.06182	5.89 "	1.698 "
17.94×10^{17}	12.11	0.08258	4.80 "	2.083 "

It can be seen that in figure (36) the fit to the required linear relationship is almost perfect. The experimental determinations of the slopes are, for the reasons outlined in chapter 2, more reliable at 50°C, and the excellence of the fit, even after an extrapolation of over 50°C, of figures derived from a 20°C temperature interval, is regarded as giving a high measure of confidence that the proposed mechanism is acceptable and that the derived values for h_8/k_9 are not in serious error. From the intercept at $(1 + \frac{h_8(A)}{k_9})^{-1} = 0$ in figure (36) it can be calculated that at 50°C $l_6/j_7 = \frac{6.45 \times 10^{14}}{a}$ molecules cc^{-1} and from the slope and the intercept $k_{-7}/k_9 = 19.41$. The temperature coefficients of these ratios over the range 50°C - 100°C give $E_{l_6} - E_{j_7} = -3.66$ kcal/mole and $E_{k_{-7}} - E_{k_9} = -398$ cals/mole.

<u>The final harmonisation of light emission and quantum yield data.</u>

The ratios of rate constants which have been evaluated above at 100°C are sufficient to allow a fairly rigorous test of the proposed mechanism to be made by calculating values of $\Phi\,CH_3I$ using the determined rate constants and comparing the results with the experimental values which have been measured in this work (figure 30). The ratios of rate constants which have been established from light emission and chemical yield data may be listed as follows

At 100°C $\quad h_8/k_9 = 3.041 \times 10^{-18}$ cc molecules $^{-1}$

$$l_6/j_7 = \frac{3.00}{a} \times 10^{14} \text{ molecules cc}^{-1}$$

$$k_{-7}/k_9 = 17.86$$

$$l_{10}/l_6 = 1.277a$$

$$\frac{h_6 + h_{10}}{l_6} = 19.3a \times 10^{-20} \text{ cc molecules}^{-1}$$

and it is necessary to form

$$\Phi_{CH_3I} = \frac{\dfrac{l_{10} + h_{10}(A)}{j_7(I)} + \dfrac{1}{1 + \frac{h_8(A)}{k_9} + \frac{k_{-7}}{k_9}}}{\dfrac{l_{10} + (h_6 + h_{10})A}{j_7(I)} + \dfrac{1 + \frac{h_8(A)}{k_9}}{1 + \frac{h_8(A)}{k_9} + \frac{k_{-7}}{k_9}}}$$

All the required ratios can be obtained except h_{10}/j_7 but we know that at this temperature the primary quantum yield of acetone decomposition is near unity (12).

$$\text{i.e. } \Phi_d = \frac{k_{10}}{k_6 + k_{10}} \doteqdot 1 \quad \text{or} \quad k_6 \ll k_{10}$$

$$\therefore \quad l_6 + h_6(A) \ll l_{10} + h_{10}(A)$$

Now $l_6 \ll l_{10}$ since $\frac{l_{10}}{l_6} = 1.277a$ and $a \doteqdot 1000$ (see previously)

$$\therefore \quad \overset{h}{k}_6(A) \ll l_{10} \cancel{+} \cancel{l_{10}} + h_{10}(A)$$

Now $h_{10}(A)$ is not negligible compared to l_{10}; if it were then the argument above (page 88) for replacing k_{10} with $l_{10} + k_{10}(A)$ would be irrelevant. It will be assumed (for the present) that $h_{10}(A) \doteqdot l_{10}$ and therefore $h_6(A) \ll l_{10}$ <u>and</u> $h_6(A) \ll h_{10}(A)$. Since $h_6(A) \ll h_{10}(A)$ the function $\frac{h_{10}(A)}{j_7(I)}$ in the numerator will be calculated as

$$\frac{(h_6 + h_{10})(A)}{j_7(I)}$$

The other ratios of constants can be obtained from those listed previously as follows

$$\frac{l_{10}}{j_7} = \frac{l_{10}}{l_6} \cdot x \ \frac{l_6}{j_7} = 1.277a \times \frac{3.00 \times 10^{-1}}{a} = 3.831 \times 10^{14} \text{ molecules cc}^{-1}$$

$$\frac{h_6 + h_{10}}{j_7} = \frac{h_6 + h_{10}}{l_6} \ \frac{l_6}{j_7} = 19.3a \times 10^{-20} \times \frac{3.0 \times 10^{14}}{a} = 5.79 \times 10^{-5}$$

Having evaluated all the necessary ratios the value of $\Phi\, CH_3I$ can now be calculated at any given acetone concentration. The calculation at $(A) = 38.84 \times 10^{17}$ molecules cc^{-1} is included below as an example

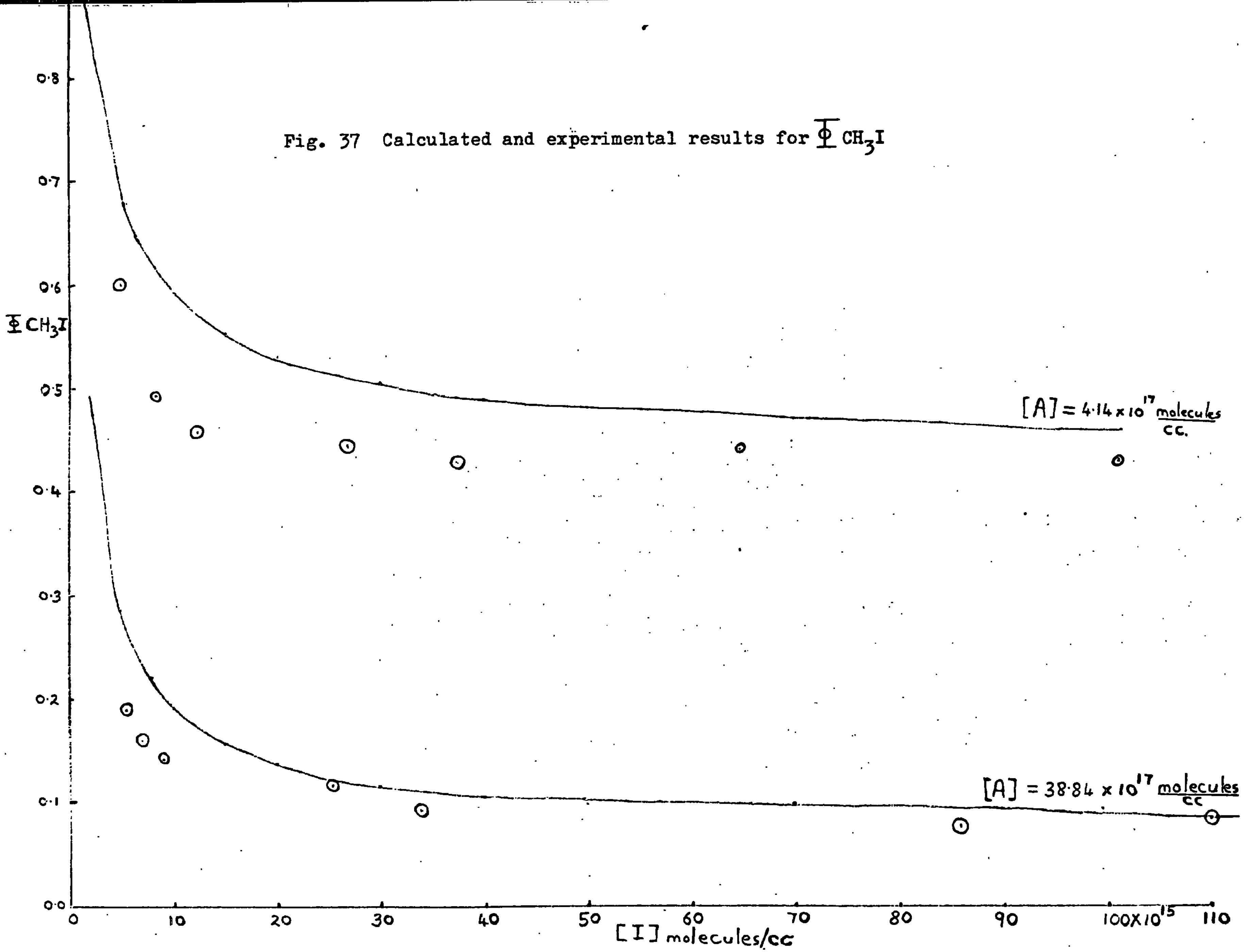


Fig. 37 Calculated and experimental results for $\Phi\ CH_3I$

$$\frac{(h_6+h_{10})(A)}{j_7} = 5.79\times10^{-5} \times 38.89\times10^{17} = 2.249\times10^{-14}$$

$$\frac{l_{10}}{j_7} = 3.831\times10^{14} \text{ cc molecules}^{-1}$$

$$\frac{k_8(A)}{k_9} = 3.041\times10^{-18} \times 38.84\times10^{17} = 11.81$$

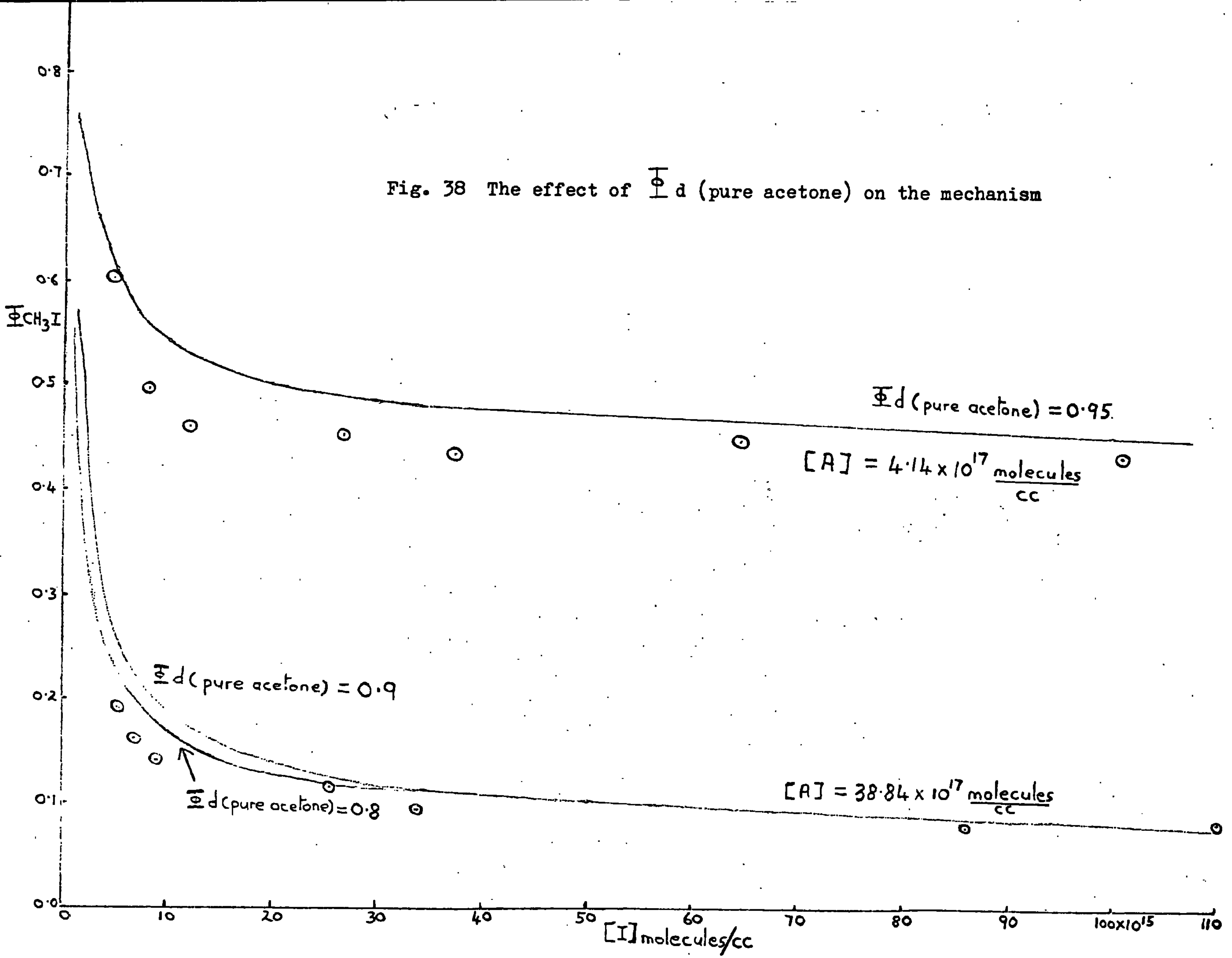
$$1 + \frac{k_8(A)}{k_9} = 12.81 \quad ; \quad 1 + \frac{k_8(A)}{k_9} + \frac{k_{-7}}{k_9} = 30.67$$

$$\left(1 + \frac{k_8(A)}{k_9} + \frac{k_{-7}}{k_9}\right)^{-1} = 0.03261 \quad ; \quad \left(1 + \frac{h_8(A)}{k_9}\right)\left(1+\frac{h_8(A)}{k_9} + \frac{k_{-7}}{k_9}\right)^{-1} = 0.4177$$

A	B	C	D	
(I_2) Molecule cc^{-1}	$\frac{l_{10}+(h_6+h_{10})(A)}{j_7(I)}$	Numerator (B + 0.0326)	Denominator (B + 0.4177)	$\Phi_d = C/D$
1×10^{15}	0.6080	0.6406	1.0257	0.6245
3 "	0.2027	0.2353	0.6204	0.3793
5 "	0.1216	0.1542	0.5393	0.2859
7 "	0.0896	0.1195	0.5046	0.2368
10 "	0.0608	0.0934	0.4785	0.1952
20 "	0.0304	0.0630	0.4481	0.1406
30 "	0.0203	0.0529	0.4380	0.1208
50 "	0.0122	0.0448	0.4299	0.1042
100 "	0.0061	0.0387	0.4238	0.0913

A similar calculation at (A) = 4.142 gave calculated results which are plotted with those above in figure (37) as the continuous lines. The experimental points for $\Phi\, CH_3I$ marked on figure (37) can be compared to the predicted values. The agreement is good over most of the range and the correct trend with iodine pressure is predicted throughout.

Fig. 38 The effect of Φ d (pure acetone) on the mechanism



At the lowest iodine pressures the agreement is not perfect but it is believed to be close enough to indicate that the mechanism is probably sound. The small discrepency could be ascribed to a combination of errors in the determination of Φ CH_3I and errors in one or more of the rate constants derived from the light emission results. However, an explanation which is not in conflict with the results of the thesis emerges from a re-examination of the inequality $h_6(A) \ll h_{10}(A) + l_{10}$ which was used in the calculation of Φ CH_3I above. The inequality is based on the experimental determination that Φ d = 1 in pure acetone at 100°C. (12) (see below). However, examination of the reported values for quantum yields in pure acetone (12, 42, 51, 52) reveals considerable discrepencies in both the value of Φ d determined at various temperatures and the effect of acetone pressure on Φ d. At 100°C Φ d (pure acetone) appears to be critically dependent on both incident light intensity and wavelength. The most recent measurements using carefully selected wavelength and low intensity (52) indicate that at 100°C Φ d can be less than 0.8 in conditions similar to those used in this work.

The effect on the proposed mechanism of allowing Φ d (pure acetone) to take values of less than unity can be investigated as follows:

In pure acetone the mechanism gives

$$\Phi\, d = \frac{k_{10}}{k_6+k_{10}} = \frac{l_{10} + h_{10}A}{h_6A + l_6 + h_{10}A}$$

and at a selected value of Φ d (e.g. 0.8, 0.9, 0.95) and (A) the ratios of rate constants determined previously can be used to calculate the ratio h_6/h_{10}. The calculation of ΦCH_3I, described in detail previously, can then be repeated using the calculated value of h_6/h_{10} in place of the assumption $(h_6 + h_{10}) \doteq h_{10}$. The results obtained by re-calculating ΦCH_3I in this way are shown in figure (38) where the calculated lines corresponding to a range of possible values of Φd (pure acetone) are shown with the experimental results for ΦCH_3I. It can be seen from figure (38) that the fit of the experimental points and the calculated line is even better than was obtained previously (figure 37) if Φd (pure acetone) is allowed to take a value slightly less than unity. The extent to which the above correction is allowable cannot be determined from data presently available. Accurate determinations of Φd (pure acetone) at 100°C do not exist and neither are there any data on the extent (if any) of the secondary reaction $\dot{C}H_3 + CH_3CO \rightarrow CH_3COCH_3$ at this temperature. However, the correction is small, does not contradict established experimental evidence and its use produces almost perfect agreement between the calculated and experimental results of figure (37).

Activation energy differences at 100°C.

In the above treatment of the mechanism of figure 32 activation energy differences between the various steps have emerged. They are summarised below.

At 100°C

1) $Ek_4 - Ek_2 = 0.78$ kcal/mole

2) $El_{10} - El_6 = 4.2$ kcal/mole

3) $Eh_{10} - El_6 = 13$ kcal/mole

4) $Eh_8 - Ek_9 = -3.4$ kcal/mole

5) $El_6 - Ej_7 = -3.66$ kcal/mole

6) $Ek_{-7} - Ek_9 = -3\ 98$ kcal/mole

If the deactivation step l_6 can be taken to have a small activation energy then the activation energy for the formation of products in pure acetone is about 13 kcal/mole for the bimolecular step and 4.2 kcal/mole for the unimolecular decomposition (l_{10}). Similarly if El_6 is small compared to Ej_7 then Ej_7, the activation energy for the formation of the acetone-iodine complex, is about 3.6 kcal/mole. If Eh_8 is also assumed to be small compared to Ek_9 then, from (4) and (6) above, both the formation of products from the complex and the re-formation of the triplet from the complex are associated with activation energies of about 3 kcal/mole.

General conclusions.

The data which has been obtained from measurements of the light emission from acetone and the primary decomposition yield have been combined to produce a mechanism which encompasses both sets of data. The photolysis of acetone has been shown to be more complex than previously supposed but the mechanism and the rate constants which have been derived from the experimental data give a complete account of the effect of pressure, temperature, and the presence of de-exciting species in the primary photolysis at 3130Å.

BIBLIOGRAPHY.

1. STEACIE "ATOMIC AND FREE RADICAL REACTIONS" 2nd ED. REINHOLD PUBLISHING CO. (1954).
2. DAVIS, CHEM. REV. 40. 201. (1947).
3. NOYES, PORTER AND JOLLEY, CHEM. REV. 56. 49. (1956).
4. MARTIN AND SUTTON, TRANS. FARADAY SOC. 48. 812. (1952).
5. BENSON AND FORBES, J. AM. CHEM. SOC. 14. 70. (1943).
6. MARTIN AND SUTTON, TRANS. FARADAY SOC. 48. 823. (1952).
7. CORIN, J. CHEM. PHYS. 7. 256. (1939).
8. PITTS AND BLACET, J. AM. CHEM. SOC. 74. 455. (1952).
9. LEEMAKERS, J. AM. CHEM. SOC. 56. 1899. (1934).
10. WINKLER, TRANS. FARADAY SOC. 31. 765. (1935).
11. FERRIS AND HAYNES, J. AM. CHEM. SOC. 72. 893. (1950).
12. HERR AND NOYES, J. AM. CHEM. SOC. 62. 2052. (1940).
13. SPONER, REV. MOD. PHYS. 16. 224. (1944).
14. SPONER AND STUCKLEN, J. CHEM. PHYS. 14. 101. (1946).
15. DUNCAN AND HARRISON, PHYS. REV. 49. 221. (1936).
16. SPONER, J. CHEM. PHYS. 8. 705. (1940).
17. SPONER, ET AL. J. CHEM. PHYS. 7. 207. (1939).
18. DIEKE AND KISTIAKOWSKY, PHYS. REV. 45. 4. (1934).
19. DUNCAN AND HARRISON, PHYS. REV. 49. 211. (1936).
20. CRONE AND NORRISH, NATURE, 132. 241. (1933).
21. DUNCAN, J. CHEM. PHYS. 8. 444. (1940).
22. DUNCAN, ELLS AND NOYES, J. AM. CHEM. SOC. 58. 1454. (1936).
23. NOYES, DUNCAN AND MANNING, J. CHEM. PHYS. 2. 717.
24. BOWEN AND THOMPSON, NATURE, 133. 571. (1934).

25. PORTER AND IDDINGS, J. AM. CHEM. SOC. 48. 40. (1926).

26. FISK AND NOYES, J. CHEM. PHYS. 2. 654. (1934).

27. MATHESON AND NOYES, J. AM. CHEM. SOC. 60. 1857. (1938).

28. LUCKEY, DUNCAN AND NOYES, J. CHEM. PHYS. 16. 407. (1948).

29. BROWN, Ph.D. THESIS, UNIVERSITY OF DURHAM, 1954.

30. NOYES AND MARCOTTE, DISC. FARADAY SOC. 10. 235. (1951).

31. MARCOTTE AND NOYES, J. AM. CHEM. SOC. 74. 783. (1952).

32. MITCHELL, Ph.D. THESIS, UNIVERSITY OF DURHAM, 1960.

33. OKABE AND NOYES, J. AM. CHEM. SOC. 79. 801. (1957).

34. DAMON AND DANIELS, J. AM. CHEM. SOC. 56. 2370. (1933).

35. GROH, LUCKEY AND NOYES, J. CHEM. PHYS. 21. 115. (1953).

36. HUNT AND NOYES, J. AM. CHEM. SOC. 70. 467. (1948).

37. LASKAN AND DUNCAN, J. CHEM. PHYS. 18. 427. (1950).

38. KASKAN AND DUNCAN, J. CHEM. PHYS. 16. 223. (1948).

39. LUCKEY AND NOYES, J. CHEM. PHYS. 19. 227 (1951).

40. MATHESON AND ZABOR, J. CHEM. PHYS. 7. 236. (1939).

41. ALMY AND ANDERSON, J. CHEM. PHYS. 8. 805. (1940).

42. HEICKLEN AND NOYES, J. AM. CHEM. 81. 3858. (1959).

43. HEICKLEN, J. AM. CHEM. SOC. 81. 3863. (1959).

44. AUSLOOS AND MURAD, J. CHEM. PHYS. 65. 1519. (1961).

45. WEIR, J. CHEM. PHYS. 83. 2629. (1961).

46. BAXTER, J. AM. CHEM. SOC. 37. 1061. (1915).

47. ELLIOT AND RADLEY, LABORATORY PRACTICE, 371. (1961).

48. LOVELOCK, J. OF CHROMATOGRAPHY, 1. 35. (1958)

49. McLURE, J. CHEM. PHYS. 17. 905. (1949).

50. G. M. BARROW, MOLECULAR SPECTROSCOPY. McGRAW-HILL. (1962).

51. SPENCE AND WILD, J. CHEM. SOC. 352. (1937).

52. LARSON AND O'NEAL, J. PHYS. CHEM. 70. 2475. (1966).

APPENDIX 1

The Synchronous Detector.

The synchronous detector, the function of which was described in chapter II is shown in detail in fig.(I1). It was triggered by a signal derived from a Mullard CV90 photocell which received light from the u.v. lamp by a six bladed sector disc on the same shaft as the main chopper disc. This signal was fed via the pre-amplifier (A.E.R.E. type 200) to a scale-of-two circuit (the first stage of an A.E.R.E. 200 scaler). Outputs were taken from the two anodes of the scale-of-two circuit, providing two stepped wave forms in antiphase which were used to actuate the synchronous amplifier. Thus self-synchronism was achieved with none of the troubles associated with mechanical rectification and the band width of the signal could be made as narrow as desired without any danger of the signal wandering out of the pass band of the detector. Any phase differences along the two signal paths could, of course, be balanced out by adjusting the relative orientation of the discs which were fixed to the common spindle by means of grub screws.

The signal from the main amplifier, fig.(1) came in at PL1, harmonics having already been removed by the filter at the input of the amplifier. V1 is a phase-splitter, producing outputs from anode and cathode in anti-phase, their amplitudes being made equal by suitable adjustment of RV1. These two signals are fed to the grids of V2a and V3b respectively, each of which forms one half of a 'long-tailed pair' circuit. V2b and V3a are fed, through a

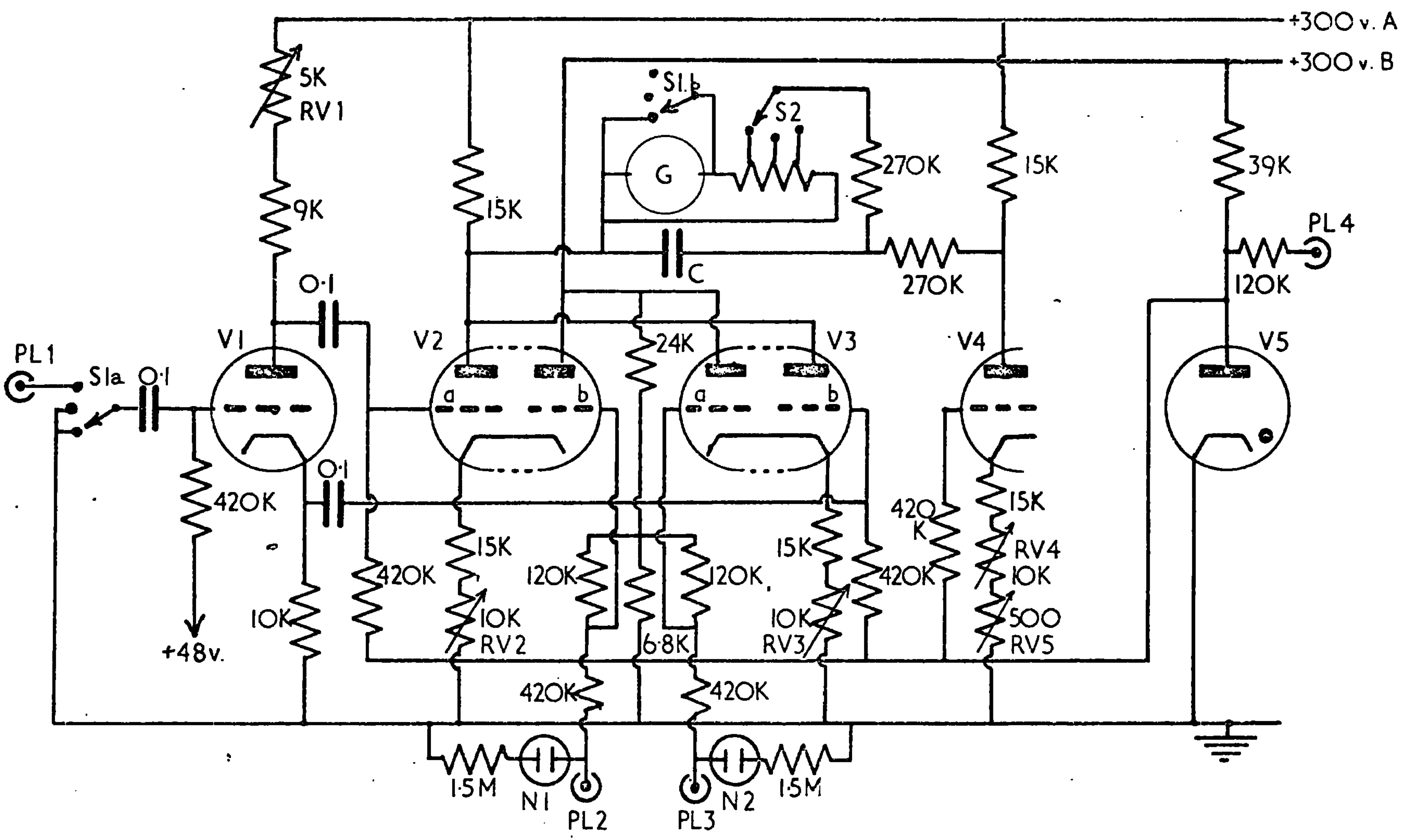


Fig. I$_1$ The synchronous detector

potential divider network, with anti-phased square waves from a 'scale-of-two' circuit, so that V2a and V3b are turned on in alternate half-cycles of the reference signal. Neons N1 and N2 indicate which section is 'on' at any moment, and are useful during the setting-up stage. PL2 and PL3 are taken directly to the anodes of the 'scale-of-two' stage already mentioned.

RV2 and RV3 are used to adjust the currents through V2a and V3b so that, without any input signal (i.e. S1a in the anti-clockwise position) the two anode currents are equal (determined by observing the waveform at the common anode point with an oscilloscope whilst the reference signal is being fed to PL2 and PL3.) With S1 in the centre position (still no input signal but galvo no longer shorted) the current through V4 is adjusted (by means of RV4 and RV5, coarse and fine potentiometers respectively) until the current through the galvo is just zero, i.e. until V4 anode and the common V2a and V3b anodes are at the same potential. If a signal is now applied (S1 in clockwise position) which is synchronous with the reference signal, then V2a + V3b anodes will no longer, on average, be at the same potential as V4 anode, and the extent of this imbalance can be read on the galvo. In practice, the circuit was used as a null instrument, and the input adjusted until the synchronous signal had disappeared. V5 provides a reference voltage to which long-tailed pair grids can be returned, and also provides HT for the photocell which gives the reference signal. S2 provides sensitivity

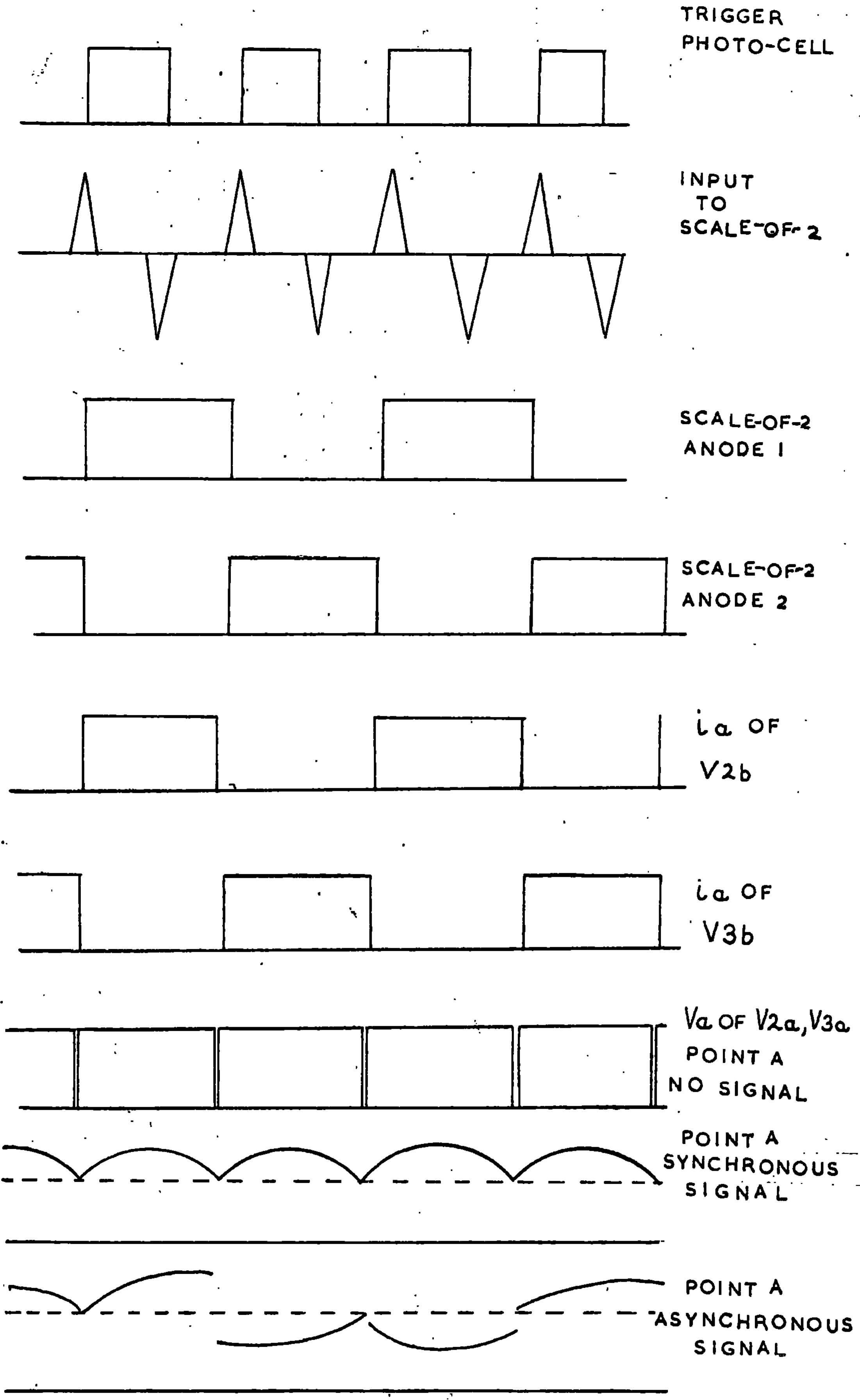


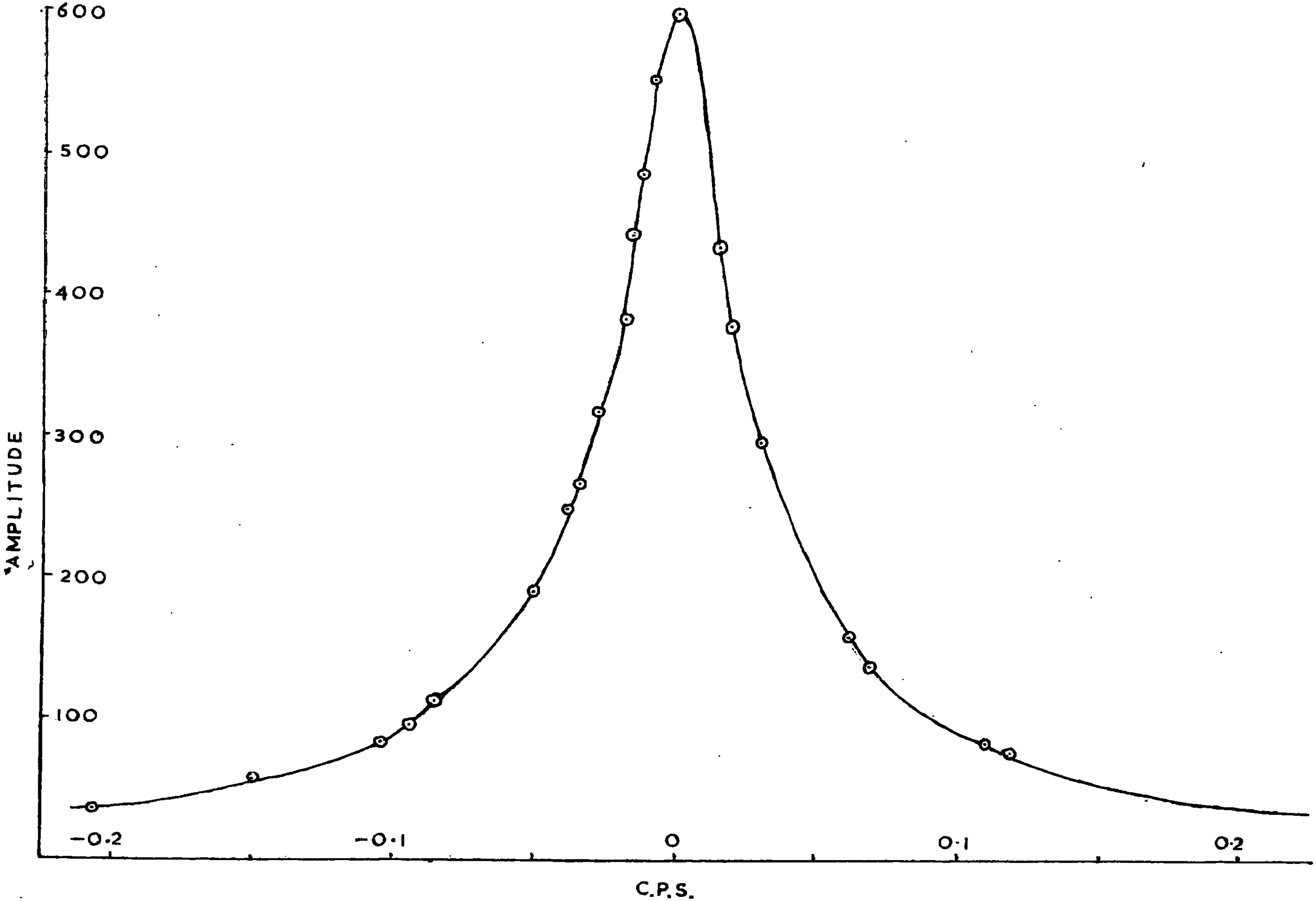
Fig. I 2 Wave forms in synchronous detector control of the galvo, through a universal shunt circuit. Two HT lines were provided, one rather carefully stabilised and free from ripple, the other somewhat cruder.

The typical wave forms at key points in the synchronous detector are shown in fig.(I_2).

Any odd harmonic of the chopping frequency will not be eliminated by this detector and will produce a resultant change on G. Odd harmonics were largely eliminated by the frequency selective filter inserted after the head amplifier. The required signal had therefore to be detected against a background of random noise in a band centered on the synchronous frequency, and with a width determined by the effective number of cycles over which the galv~~o~~anometer circuit integrates.

Trouble from random noise was a major difficulty only when the photomultiplier tube potential was raised to the point (over 1000volts) where the amplified noise output was sufficient to exceed the bias applied to V2a and V3a, during the half cycles when V2b and V3b respectively should have been conducting. Cooling of the photomultiplier below room temperature was not found to be necessary under the conditions used. It was necessary, however, to include cooling coils on the box containing the photomultiplier to prevent it from becoming warm due to its proximity to the oven containing the irradiation cell. Scattered daylight entering the photomultiplier was also a source of random noise and great care was taken to ensure that no daylight entered the reaction vessel or the aluminium block containing it. The tubes leading into the

Fig. I_3 Pass band of the detector



quartz cell were coated with "A" dag colloidal graphite along 15 cms. of their length where they emerged from the oven, in order to prevent the passage of light up the tubes into the photomultiplier.

The results of some data collected to measure the pass-band of the synchronous amplifier are shown in fig.(I_3).

The required frequency of about 300 c.p.s. (to simulate experimental conditions) was obtained from a quartz crystal oscillator through a divide-by-twenty stage of a 200 scaler. The fundamental frequency was used both as control and input to the synchronous amplifier.

An extra random frequency, obtained from a scintillation counter and source, through a 200 scaler as before, could be added onto either the control or input frequency. Thus the maximum amplitude of the galv~~o~~anometer could be measured in terms of a fixed frequency difference. The results are shown graphically in fig.(I_3). It can be seen that the pass band is symmetrical and quite sharp (with a $\frac{1}{2}$ peak width equal to 0.05 c.p.s.).

The phase sensitivity of the synchronous amplifier was also investigated using a synthetic signal as input and control. The signal from the quartz oscillator was again passed through the divide-by-twenty units on two scalers before being applied to the synchronous detector, one as the input and one as the control. The steady deflection of the galvonometer when the two signals were in phase was noted, then the input signal was moved 18° (i.e. $\frac{360^\circ}{20}$) out of phase relative to the control signal by adding an extra pulse to

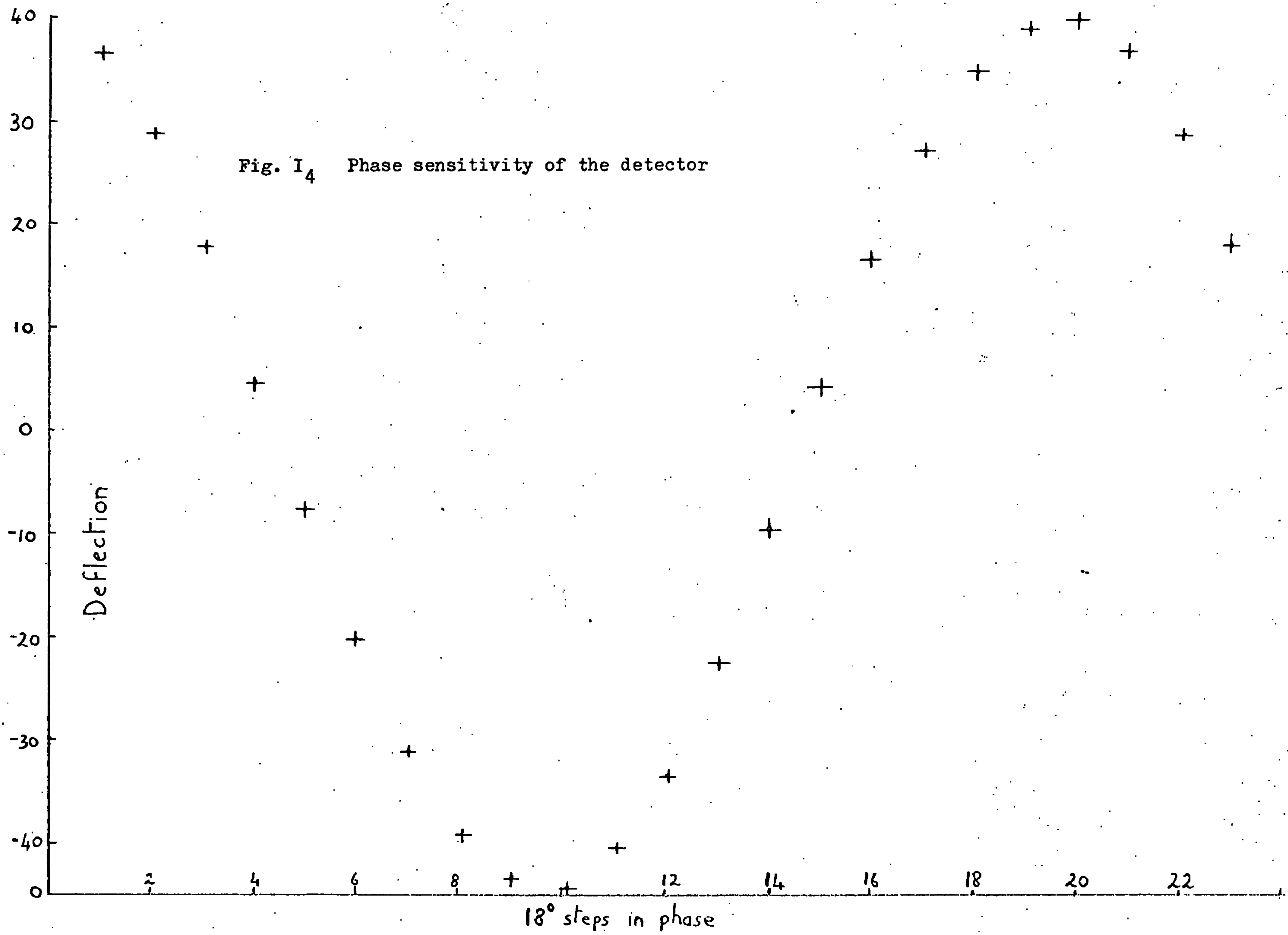


Fig. I_4 Phase sensitivity of the detector

the divide-by-twenty stage in the input supply line. The steady deflection of the galvonometer was again measured and this manoeuvre was repeated in 18° steps until a whole cycle had been investigated (i.e. at least 20 steps). The results are shown graphically in fig. (I_4). It can be seen that the phase sensitivity of the synchronous amplifier is an almost perfect sine wave.

APPENDIX 2.

THE CONSTRUCTION OF A GAS CHROMATOGRAPHY APPARATUS.

At the beginning of the work reported in this thesis a gas chromatography apparatus was constructed with the intention of separating products of the photolysis of acetone-oxygen mixtures with a view to identifying them and determining the quantum yields. This branch of the work was never in fact investigated because the light emission and ΦCH_3I determinations were given preference over it.

The chromatography apparatus was used, however, in the development of a technique for determining ΦCH_3I (see chapter II), and its construction will be described briefly.

It was decided that the apparatus should be mobile (for convenience when used by other workers in the department) and so it was mounted in a box-shaped framework of Handy Angle Steel. The whole framework was mounted on four wheels and was easily movable.

Argon (welding grade) was used as a carrier gas and the detector device was based on the idea proposed by Lovelock (48) and is similar to that produced commercially by Pye. A beta particle source in the detection chamber excites Argon atoms in the carrier gas to a meta stable state (11.6ev). When the carrier gas contains organic molocules with an ionisation potential lower than this, ionisation occurs and the resultant current passing between the two electrodes, maintained at different potentials in the gas, is used to record a peak.

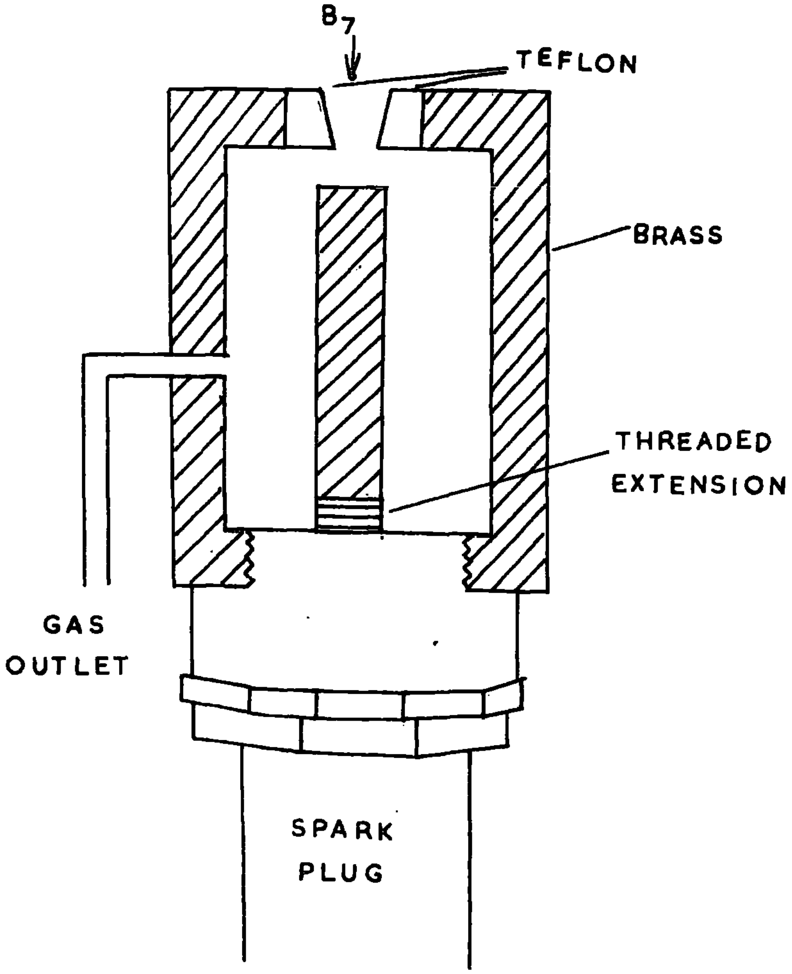


Fig. II$_1$ Gas chromatography detector head

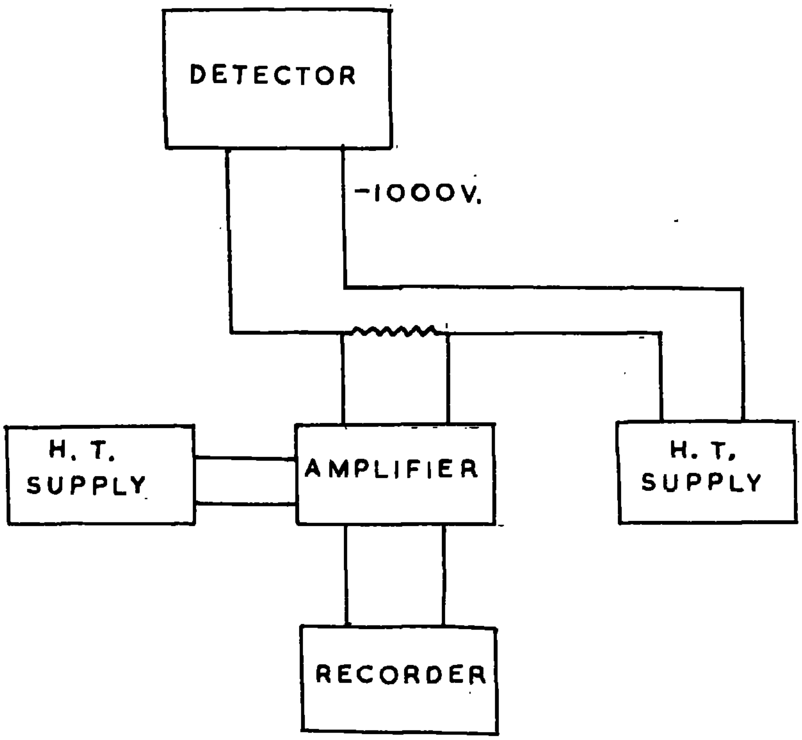


Fig. II_2 Schematic diagram of chromatography apparatus

The detection chamber fig.(II_1) was constructed from a normal car spark-plug. The piece of metal which, combined with the central electrode formed the spark gap, was completely removed. The central electrode was extended by means of a brass rod one tenth of an inch in diameter threaded onto it. The outer brass cylinder was constructed so that it screwed onto the thread of the spark plug as shown in the diagram. The outer cylinder had a hole in one wall with a brass pipe soldered onto it to act as the gas outlet. The top of the cylinder had a teflon plug in it into which a cone had been machined so that a B7 glass joint was a good fit. This acted as the gas inlet.

The radio-active source consisted of a piece of foil containing RaD-E-F with activity 37μ curies/mm. length. It was provided in a strip 2-5cms. wide. About 3cms. length of the strip (about 111μ curies) was coiled inside the cylinder - a gap being left for the gas outlet. The volume of the detection chamber was kept to a minimum, an earlier chamber of larger dimensions having achieved no separation.

The electrical set-up is shown in fig.(II_2). E.H.T. (up to 2000v) was applied to the outer cylinder of the detection chamber from a standard power pack (1007).

The central electrode was connected to the DC amplifier whose output was used to control a Phillips Recorder. The amplifier feed back gain could be attenuated by factors of 1, 3, or 20 and the output by factors of 1, 3, and 10. Thus the maximum gain (of about 10^6) could be attenuated over quite a large range. The resistances used in the dividers to give the attenuations above were specially selected high stability grade. The amplifier had its own power pack to supply high stability HT.

The detection cell was supported on an insulating column of plaster of Paris with holes in it for the electrical leads and the gas outlet.

The cylindrical oven 1 metre in length and 8 cms. internal diameter rested on the plaster of Paris block with a detection cell in the lower end and the column containing the stationary phase standing vertically inside it. The column, which consisted of three limbs of 1 cm. tubing with a B7 pyrex cone on the lower end, and a ball socket on the upper end, protruded out of the top of the oven which was sealed by a removable insulating lid with holes bored in it to accommodate the column and a thermometer.

The flow rate was determined by measuring the time taken by a soap bubble in travelling between two set marks in a glass tube on the outlet end of the detection chamber.

The argon supply was obtained directly from a cylinder and connected to the column via the ball joint on the top of it. This ball joint could be disconnected to put a sample on the column. The small samples required were delivered from a capillary dropper purchased from Pye and said to deliver 0.1 micro-litres of liquid.

The temperature of the oven was controlled by means of a "variac" which controlled the power dissipation in the heating coils.

Firebrick grade 30-60 was used as the supporting medium and dinonyl phthalate, silicone grease and P.E.G. 400 were investigated as stationary phases.

It was found that separating of acetone, ether, methyl iodide, ethyl iodide, methanol and ethanol were possible and the best conditions for separations of particular mixtures were investigated. With the columns used water gave a very poorly defined peak.

Attempts to obtain quantitative results from the apparatus by cutting out the peaks on the recorder paper, and weighing them, gave results varying up to 20%. Much of this variation was no doubt due to errors in the volume of liquid put onto the column. Drying of the carrier gas, a constant head device for the input pressure of the argon and the use of constant weight paper in the recorder would also improve the reproducibility. A device to deliver a constant amount of organic vapour into the argon stream was designed but it had not been built when results from the light emission apparatus caused attention to be focussed on that section of the work.

APPENDIX 3.

Kinetic Treatment of Mechanism of figure 32.

The symbols in figure 32 have the following meanings,

$\overset{\prime}{\mathrm{An}}$ = vibrationally excited levels of the singlet state. $\overset{\prime}{\mathrm{Ao}}$ = zero vibrational level of the singlet state. $\overset{\prime\prime}{\mathrm{Ao}}$ = zero vibrational level of the triplet state. C = complex between $\overset{\prime\prime}{\mathrm{Ao}}$ and iodine or oxygen. The products arising from $\overset{\prime\prime}{\mathrm{Ao}}$ and C are not necessarily identical. (A) and (I) will be used for acetone and iodine (or oxygen) concentrations respectively.

To simplify the algebra, the equations will be handled in terms of k's treated as first order rate constants. These will be replaced in the final equations by $k_i = (l_i + h_i(A) + j_i(I))$ as necessary and shown to be justified in the discussion of results. Care must be exercised in replacing the rate constants for light emission (k_2 and k_6) by this procedure since if it proves necessary to expand, for example, k_6 as $l_6 + h_6(A)$ the phosphorescence, Ip, will be associated only with the first order process l_6.

The following relationships are obtained from the usual steady state treatment.

$$(\overset{\prime}{\mathrm{Ao}}) = \frac{\mathrm{Ia}}{k_2 + k_4} \qquad (1)$$

$$(\overset{\prime\prime}{\mathrm{Ao}}) = \frac{\dfrac{k_4\,\mathrm{Ia}}{k_2 + k_4} + k_{-7}\,(\mathrm{C})}{k_6 + k_7 + k_{10}} \qquad (2)$$

$$(\mathrm{C}) = \frac{k_7\,(\overset{\prime\prime}{\mathrm{Ao}})}{k_{-7} + k_8 + k_9} \qquad (3)$$

and since fluorescence is a minor process under all conditions it is justifiable to take $k_2 \ll k_4$ hence the numerator of (2) reduces to $\mathrm{Ia} + k_{-7}\,(\mathrm{C})$.

The Primary Quantum Yield in Pure Acetone.

For the system containing only acetone then $k_7 = k_{-7} = k_8 = k_9 = 0$ and now $(A''o) = Ia\ (k_6 + k_{10})^{-1}$

hence $\Phi d = k_{10}\ (A''o)/Ia = k_{10}\ (k_6 + k_{10})^{-1}$ (4)

Inverse Fluorescence Yield.

By definition the fluorescence yield is given by

$$Q' = {}^{If'}/Ia$$

$$\therefore \quad \frac{1}{Q'} = \frac{Ia}{k_2(A'o)} = \frac{k_2 + k_4}{k_2} \doteqdot \frac{k_4}{k_2} \qquad (5)$$

Inverse Phosphorescence Yield.

It has been shown in the discussion of the mechanism that k_6 must be replaced in the form $l_6 + h_6(A)$.

We now have

$$(A''o) = \frac{Ia + k_{-7}\ (C)}{l_6 + h_6(A) + k_7 + k_{10}} \qquad (6)$$

and since the phosphorescence is under all conditions a minor process l_6 must be negligible compared with one or all of the other terms in the denominator. Hence substituting (3) into (6) with the omission of l_6 from the denominator, and then using the expression

$$Q'' = l_6(A''o)/_{Ia}$$

it follows that

$$\frac{1}{Q''} = \frac{1}{l_6}\left\{k_{10} + h_6(A) + k_7 \cdot \frac{1 + {}^{k_8}/k_9}{1 + {}^{k_8}/k_9 + {}^{k_{-7}}/k_9}\right\}$$

Since a molecule of iodine is required to form the complex, k_7 must take the form $j_7(I)$. Further the process k_8 involves the dissipation of considerable energy and is therefore likely to require a 'third body' which will probably be acetone which is present in large excess; hence $k_8 = h_8(A)$ is probable.

This leads to

$$\frac{1}{Q''} = \frac{1}{l_6}\left\{k_{10} + h_6(A) + j_7(I)\,\frac{1 + \dfrac{h_8(A)}{k_9}}{1 + \dfrac{h_8(A)}{k_9} + \dfrac{k_{-7}}{k_9}}\right\} \tag{7}$$

The above equation applies to acetone - iodine mixtures. For acetone alone, (I) = 0 hence the last term in the bracket is zero and

$$\frac{1}{Q''} = \frac{k_{10}}{l_6} + \frac{h_6(A)}{l_6} \tag{8}$$

The Primary Quantum Yield in Acetone/Iodine Mixtures.

The primary quantum yield is given by

$$\Phi_d = \frac{k_{10}(A_o'') + k_9(C)}{Ia}$$

$$= \frac{\left(k_{10} + \dfrac{k_7\,k_9}{k_{-7} + k_8 + k_9}\right)(A_o'')}{Ia}$$

and, substituting the value for (A_o'') obtained in (6) (with the exclusion of l_6) and substituting as before for k_7 and k_8 we obtain

$$\Phi_d = \frac{\dfrac{k_{10}}{j_7(I)} + \dfrac{1}{1 + \dfrac{h_8(A)}{k_9} + \dfrac{k_{-7}}{k_9}}}{\dfrac{k_{10} + h_6(A)}{j_7(I)} + \dfrac{1 + \dfrac{h_8(A)}{k_9}}{1 + \dfrac{h_8(A)}{k_9} + \dfrac{k_{-7}}{k_9}}} \tag{9}$$

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