PHOTO-REACTIONS IN THE SOLID STATE;

TITANIUM DIOXIDE AND RELATED SYSTEMS.

## THESIS

presented for the degree of Doctor of Philosophy

by

JOHN MACKENZIE, B.Sc.

University of Edinburgh.                    1952.

# CONTENTS

A wide range of photo-degradations and photo-syntheses has been observed as occuring naturally but all have not yet been worked out in detail in the laboratory. This is mainly due to the difficulties of reproducing in the laboratory the conditions under which the natural reactions occur. The work described below is concerned, in the main, with the sensitised degradation aspect and in particular with the sensitising action of various compounds upon substances in contact or in proximity to them. Regarding the naturally occuring degradations, there

## INTRODUCTION

is available a large volume of information mainly observed without any attempt to control experimental conditions rigidly, and also a smaller although rapidly increasing volume of experiments performed in idealised conditions. So far these two aspects of what is fundamentally the same problem have not been completely and successfully married. The initial step of light absorption and the change of this energy into chemical action, however, has been considered in some detail, both experimentally and theoretically.

### Action of Light

When light is absorbed by an atom or a molecule, the potential energy of the absorber is raised by the excitation of an electron to an orbital of higher

# INTRODUCTION

A wide range of photo-degradations and photo-syntheses has been observed as occurring naturally but all have not yet been worked out in detail in the laboratory. This is mainly due to the difficulties of reproducing in the laboratory the conditions under which the natural reactions occur. The work described below is concerned, in the main, with the sensitised degradation aspect and in particular with the sensitising action of various compounds upon substances in contact or in proximity to them. Regarding the naturally occurring degradations, there is available a large volume of information mainly observed without any attempt to control experimental conditions rigidly, and also a smaller although rapidly increasing volume of experiments performed in idealised conditions. So far these two aspects of what is fundamentally the same problem have not been completely and successfully married. The initial step of light absorption and the change of this energy into chemical action, however, has been considered in some detail, both experimentally and theoretically.

## Action of Light

When light is absorbed by an atom or a molecule, the potential energy of the absorber is raised by the excitation of an electron to an orbital of higher

energy[1]. This excited state is normally extremely
unstable and the energy is re-emitted within a very
short period, accompanied by a reversion to the initial
energy level by the electron. In certain cases a
lifetime of approximately $10^{-8}$ sec. is normally
associated with the emission of light as fluorescence.
Where a triplet state, i.e. a system with two unpaired
electrons, is formed this lifetime may extend to
1 sec. because of the forbidden and difficult energy
translations entailed.[1,2]

While in the excited state the atom or molecule is
potentially highly reactive and may lose its energy,
apart from the manner described above, to other
substances present. If the excited state of the
substance (S) is represented by an asterisk, then

$$S + h\nu \rightarrow S^*$$
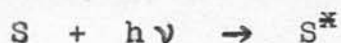
By collision with another molecule (M) a transfer of
energy may occur

$$S^* + M \rightarrow S + M^*$$

In this case the initial light absorber (S) returns
to its original state but it is possible for the
process to proceed directly by the oxidation or
reduction of S. The excited electron may have
sufficiently high energy content to leave the molecule
and as a result S is oxidised -

$$S^* + M \rightarrow S^+ + M^-$$

It is not essential that this electron enter M, but as
it has left a vacant energy level in S, this may lead
to reduction of the latter by transfer of an electron
from M -

$$S^* + M \rightarrow S^- + M^+$$

Electron emission from dyes has been shown to be
significant only when high energy radiation is used,

FIG. 1

exist in equilibrium and C is the outermost of the
normally full or partially filled bands (valence bands).
For photo-conductivity it is necessary for an electron
to pass between C and A on illumination. This may be
difficult, or even impossible, and in such cases the
substances are known as insulators. In contrast, with
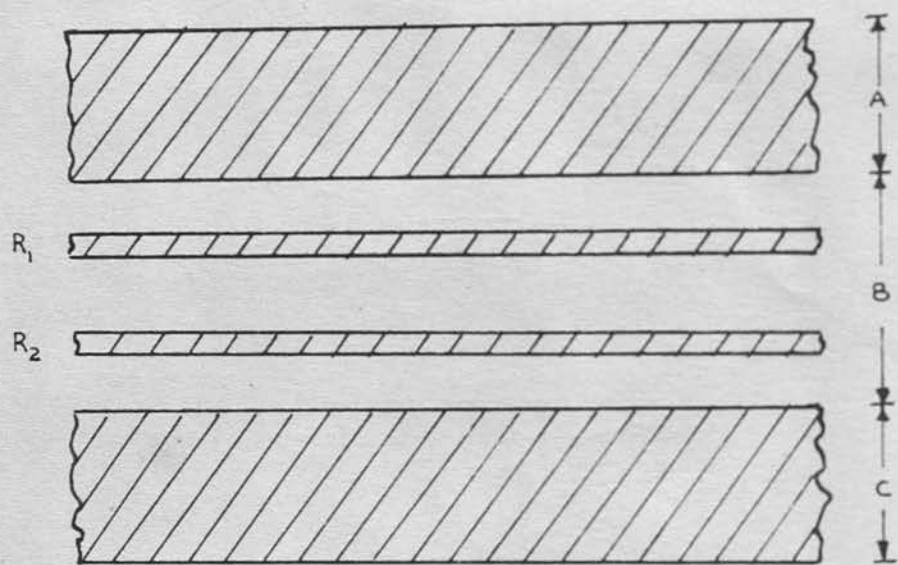metals these tw. bands are very near and may overlap.

FIG 1.

It is not essential that this electron enter M, but as
it has left a vacant energy level in S, this may lead
to reduction of the latter by transfer of an electron
from M -

$$S^{x} + M \rightarrow S^{-} + M^{+}$$

Electron emission from dyes has been shown to be
significant only when high energy radiation is used[3],
but with other types of light absorbent materials, such
as $TiO_2$, ZnO etc, this electron transfer is more likely.
In the case of the crystalline solids, it is necessary
to consider the theories of their structure proposed
inter alia by Bloch[4] and Gurney & Mott[5].   In these
materials, owing to their compact nature, the normal
electronic distribution around the nuclei is disturbed
and, in the  proposed models, it is re-arranged into
discrete bands of energy levels common to the whole crys-
tal.    Of these bands, the main interest lies in the two
outermost, shown diagramatically in FIG.1 (opposite)
where A is the conductivity band which is normally
empty, B is a forbidden band where no electron can
exist in equilibrium and C is the outermost of the
normally full or partially filled bands (valence bands).
For photo-conductivity it is necessary for an electron
to pass between C and A on  illumination.   This may be
difficult, or even impossible, and in such cases the
substances are known as insulators.   In contrast, with
metals these two bands are very near and may overlap,

thus permitting the easy conduction of electrons which is characteristic of this class. The ionic compounds which show photoconductivity, would normally belong to the first class as insulators but owing to various defects in the crystal lattice, such as substitutional impurities, interstitial ions etc, a re-arrangements of the possible energy levels occurs and this may be represented by a new band R. This may lie either just below A or above C and as a result electrons may easily pass between these bands R and either A or C.

There is little data on the energy required for this step in the case of $TiO_2$ and similar compounds but the photo-emission of electrons from alkali oxides and metallic semi-conductors indicates a possible energy of 1 - 3.5 e.V's respectively[6]. - within the range of the visible spectrum.

Sensitisers

There are known systems which are not reactive when illuminated per se but which undergo change on the addition of a substance which can absorb light and apparently transfer the energy to the reactants. This added substance is then referred to as a photo-sensitiser. The nature of these photo-sensitisers is as widespread as the types of reaction which they activate but at present three classes may be considered as important in the study of reactions in the solid state. These are the white (or near white) pigments, dyes and thallous halides.

Although the sensitising action of the pigments was
not discovered until many years after that of the
dyes, there is now considerable information on their
action. Eibner[7] published his original results in
1911 when he demonstrated the role of ZnO, ZnS and
$ZnSO_4$ in the fading of paintings. Since then many
workers have studied the action of ZnO and the reac-
tions sensitised by it; these were summarised by
Dhar[8]. In later years other pigments with similar
properties have been found and Goodeve[9] has listed
eight such oxides as sensitising the bleaching of
dyes but of these, only in cases of $TiO_2$, ZnO and
$Sb_2 O_3$ is the action appreciable. Many of the
reactions investigated appeared to be sensitive only
to specific oxides.[10,11].

The presence of dyes has enabled systems - such as a
photographic plate - to utilise light of a longer wave
length than that required for the direct action. This
was in fact the first sensitising action to be shown by
dyes.[12]. Later they were shown to activate the oxida-
tion of substances by molecular oxygen[13] and a very
detailed study has been undertaken since their role in
the degradation of textile fibres has been realised.
This work has shown that a wide range of acetate, acid,
basic, direct, sulphur and vat dyes[14] can act as
sensitisers but attempts to correlate the degree of

activity with substituent groups have not met with any real success.[15,16] It was also found that, in the degradation of textiles, varying results were obtained with the same dye on different fibres.[14]

The activation of oxidation reactions by the thallous halides was demonstrated by Lonie and Ritchie[17,18] for the autoxidation of a copper treated chlorophyll and related substances and by Reid[19] for the degradation of the dyestuff, Malachite Green oxalate as well as of oxalic acid.

## White Pigments as Sensitisers

In the reactions cited above, it was found that the activating light lay within the lower end of the visible spectrum and part of the U.V. range, i.e. down to, and including $3650\,\mathrm{\mathring{A}}$. To establish that this light was being absorbed by the pigments, Goodeve[10] measured their diffuse reflecting power as powders. He found, as was expected, that the active sensitisers absorbed light of longer wavelength than the less active ones, while inert materials, such as $BaSO_4$, did not absorb down to the limit investigated $2500\mathrm{\mathring{A}}$. The absorption bands of the various oxides were found to have sharp threshold values in the region of $4000\mathrm{\mathring{A}}$ for $TiO_2$, $3850\mathrm{\mathring{A}}$ for $ZnO$[10] and $3750\mathrm{\mathring{A}}$ for $Sb_2O_3$[20]. These bands correspond to the regions of maximum sensitising efficiency.

As the scope of this review is limited to a survey
of reaction schemes proposed for solid reactions,
those occuring in solution will not be discussed except
where a parallel or a significant point may be drawn.
In the solid state, the overall reactions sensitised
by these pigments would appear to be oxidations; in
the degradation of fibres for example Egerton has shown
that an appreciable effect is obtained only in the
presence of oxygen.[14] There are examples in the
literature, however, of substances apparently being
oxidised when illumination was made of evacuated
systems. Goodeve gave an illustration of this in the
fading of Chlorazol Sky Blue adsorbed on $TiO_2$.[21]

This suggested that some of the lattice oxygen
atoms were being split off and this theory has been
proposed, with modifications, on numerous occasions.

Goodeve has attempted to measure the oxygen
evolved from illuminated $TiO_2$[21] and $Sb_2O_3$[20] but was
unsuccessful. He proposed therefore, in the case of
$Sb_2O_3$ that the normal crystal lattice was disrupted
and the oxygen so released was retained in a neighbour-
ing position. Apparently the presence of oxidisable
matter on the crystal surface allows further disruption
with the transfer of the oxygen atom. Some samples
of these oxides showed a darkening of the surface
during illumination and this was attributed to the
formation of either the free metal or a lower oxide.

Jacobsen[22] adopting the suggestion put forward by Renz[23]
investigated the end products of the illuminated system,
$TiO_2$ (rutile) - mandelic acid, in air and claims to have
detected therein $\alpha$- $Ti_2O_3$, identified by X-ray analysis.
The deepening of the color of the oxide, due to the postu-
lated presence of $\alpha$- $Ti_2O_3$, was a reversible process
with the recovery of a white surface on ceasing
illumination or in the presence of excess oxygen.
Weyl and Forland[24] have remarked that this re-oxidation
should be a comparatively easy process due to the
so-called "memory effect." They have also suggested
that the assymetry of the bonds around surface atoms
should, on illumination, result in the production of
small amounts of atomic oxygen from any oxide. This
has been demonstrated for $SiO_2$.

Most workers are agreed however that in the
absence of oxygen only a limited reaction occurs.
Egerton has demonstrated this frequently while investi-
gating the degradation of textile fibres.[14] In the
presence of oxygen there was conclusive evidence that
a highly reactive oxidising agent was produced.
Winther[25] originally suggested the formation of ozone
but this theory has been shown to entail a direct
refutation of Stokes Law. McMorris and Dickinson[26]
following the suggestion by Jung and Kanau[27] that the
oxidising agent was zinc oxynitrate, claimed to have
detected $NO_2$ when zinc oxide was illuminated by U.V.
light in the presence of oxygen. This claim has

not been substantiated for other samples tested.

The observation that $TiO_2$ darkened on exposure to light has prompted suggestions that a higher oxide was being formed - perhaps a true peroxide. Ruben[28] suggested the formation of pertitanic acid which was then decomposed by exposure to further light. However Yamafuzi, Nishioeda and Imagawa[29] stated that in the case of ZnO, no oxygen was taken up from the atmosphere. Williamson[30] has proposed that this darkening was due to the phototropic effect of small quantities of impurity iron present. This effect was discussed in greater detail by Weyl and Forland[24] who have observed it also with Ce, Zr and Th oxides.

The only oxidising agent, formed in the presence of illuminated pigments, which has definitely been identified was $H_2O_2$. It was originally detected by Baur and Neuweiler[31] in suspensions of zinc oxide in water illuminated by sunlight and was proved to be $H_2O_2$ conclusively by the action of catalase[29,32]. The reaction was not specific for ZnO as ZnS, CdO, $SnO_2$ and $ThO_2$ have been shown to act in a similar manner[14,33]. The case of $TiO_2$ is more complex however, as, in solution, Egerton[14] and Hamilton[33] have found only traces of an unidentified oxidising agent which Goodeve[21] could not detect at all. The illumination of $Sb_2O_3$ in similar circumstances has not been accompanied by the formation of any peroxide[20]. Hamilton has suggested that the

case of $TiO_2$ may be explained by the discovery of
O. and A. Deny-Henault[34] that $TiO_2$ retained $H_2O_2$
tenaciously as an additive complex. In the solid
state Egerton[14] has shown that a volatile peroxide has
been produced in the vicinity of ZnO, ZnS and $TiO_2$
illuminated in humid atmospheres containing oxygen.
At zero humidity, however, no volatile oxidising agent
was produced and no effect was observed on an oxidisable
material unless it was in intimate contact with the
sensitiser.

## Dyes as Sensitisers

The overall reactions with dyes were strikingly sim-
ilar to those with the pigments and Egerton[14] amongst
others, has attempted to correlate the two systems.
The formation of organic peroxides by uptake of
molecular oxygen, altho' reported for several organic
compounds, has not been considered seriously as a
possible reaction scheme.[35] Since Kautsky's[36,37]
experiments indicated the formation of a volatile
oxidising agent with an appreciable mean free path,
it has been generally agreed that with dyes this has
been a cause of degradation in their vicinity. The
controversy has been over the formation and nature of
this substance.

Various workers,[31,38,39] around 1930, demonstrat-
ed the formation of a peroxide when aqueous solutions

of fluorescent dyes were illuminated. It was left
to Blum and Spealman[35] to analyse in more detail the
nature of this substance and they concluded that no
organic dye peroxide was formed and that the reaction
was the autoxidation of the solvent to hydrogen
peroxide, the process being sensitised by the dye.
Since then various other workers have in similar work
arrived at the same conclusion.[10.40.]

When the experimental conditions are changed
from the liquid to the solid-gaseous phase, there is
again strong evidence[14.41.42] that hydrogen peroxide
is formed when water and oxygen are present. In the
absence of water, however, Kautsky[36] demonstrated that
under suitable conditions (i.e. a specific pressure
range) a volatile oxidising agent was formed, which was
capable of acting on a material reasonably remote in
space from the sensitising dye. This required
acceptance of the theory that the energy transfer was
from the dye to the oxygen molecules and not directly
to the acceptor as other workers had suggested.[9.43.]
Kautsky proposed that this activated form of oxygen was
a metastable form of the molecule with possible energy
values of 22.5 - 37.3 kg. cal. per mole. This agreed
with the observation that no oxidation occurred with
oxygen pressures $> 24 \times 10^{-4}$ m.m. (Hg.) unless the acceptor
and sensitising dye were in very close proximity.

Kautsky's theory has been answered by various
other suggestions as to the nature of the activated

oxygen. Weiss[44] has suggested that the substance in question was $HO_2$ and Livingstone[2] has accepted this in proposing the reaction to be

$$DH' \; + \; O_2 \; \rightarrow \; D \; + \; HO_2$$
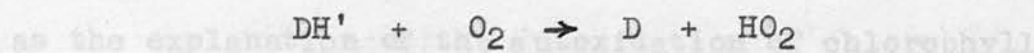
where DH'was the triplet state of the active dye. The direct rupture of the dye in such a manner was kinetically impossible[45] unless a tautomeric change occurred. A further objection may be raised that the action of $HO_2$ on an acceptor[46,] or by its own decomposition[47,] would result in the formation of $H_2O_2$. No evidence has been found that this peroxide was present in such circumstances. The formation of $HO_2$ is also inconceivable in the presence of the illuminated oxides but this objection does not hold for $O_2^-$. In an earlier part of this introduction the photo-emission of the oxides has been discussed. The photo-emission of electrons from dyes[3] and the acceptance of free electrons by oxygen molecules[48,49] have both been demonstrated. There have, however, been serious omissions from the range of dyes[14,50] which have shown this phenomenon when the illumination was conducted with light in the visible spectrum and kinetically it should be easier to accomplish with light in the U.V. range.[51] Egerton has shown that the sensitisation by dyes does not occur with light of wavelength $< 3400\mathring{A}$.[14.]

## Thallous Halides as Sensitisers

Electronic transfer from the sensitising substrate to the oxygen has been adopted by Lonie and Ritchie[17] as the explanation of the autoxidation of chlorophyll adsorbed on thallous halides. On absorption of light the halide ion (say $Br^-$) expelled an electron to the conduction band.
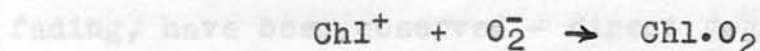
$$Br^- + h\nu \rightarrow Br + e_1$$

Although directly reversible, this electron may also be trapped by an oxygen molecule with the formation of the adsorbed negative ion, $O_2^-$.

$$O_2 + e_1 \rightarrow O_2^-$$
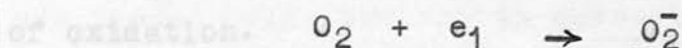
The bromine atom then reverted to its original state by accepting an electron from the chlorophyll

$$Chl \rightarrow Chl^+ + e_2$$
$$Br + e_2 \rightarrow Br^-$$

and finally

$$Chl^+ + O_2^- \rightarrow Chl \cdot O_2$$
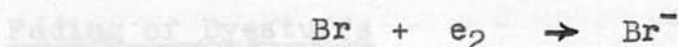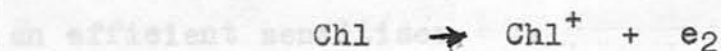
More recently Laurie[55] has suggested that the production of the excited chlorophyll may be explained in terms of the structure of crystals. By reference to Fig. 1 (page 3), where band A now is the conductivity level of TlBr and band C constitutes a source of electrons by emission from activated bromine atoms and with $R_1$ and $R_2$ representing upper and lower energy levels of the adsorbed chlorophyll molecule, the reaction can be shown graphically.

On illumination, the energy was adsorbed by a bromine atom which expelled an electron from band C to band A leaving behind it a positive hole which can be regarded as mobile. An electron then passed from the lower energy level of the chlorophyll molecule $(R_2)$ to this positive hole thereby regenerating the bromine atom while the upper energy level $(R_1)$ gained an electron from the conductivity band, (A). The result was therefore effectively to raise an electron in the chlorophyll molecule to a higher energy level and thus produce an excited molecule which was capable of oxidation.

i.e. $Chl + h\nu \rightarrow Chl^x$

For this reaction it was found that ZnO was not an efficient sensitiser.

## Fading of Dyestuffs

Two types of degradation of dyes, resulting in their fading, have been observed - direct degradation on illumination and sensitised degradation in the presence of compounds, such as described above. This latter reaction has been shown to be dependent on the presence of oxygen but there is still division of opinion as to whether direct degradation is an oxidation or reduction process.

Harrison[52] has shown, for example, that the change of color on illumination of flavanthrone may be assumed to be the formation of dihydro-flavanthrone. Similar

reductions of azo-dyes in solution has been reported
by Blaisdell.[53]  It has also been suggested[54] that
the final oxidation of dyes is preceeded by an initial
reduction of the dye.  Landolt[15], accepting this
theory, visualised the reaction scheme as an initial
reduction of the dye photochemically, followed by
thermal oxidation with molecular oxygen.  Atherton
and Seltzer[16] have pointed out, however, that no
reduced form was detected by spectral analysis during
the oxidation of mono-azo dyes.

Oxidation products of faded dyes have been demon-
strated as being present in several cases[56,57] and
the necessity of oxygen in the surrounding atmosphere
during marked fading has also been noted by several
workers.[58,59]  Konig[60] goes further in stating that
the presence of oxygen and water was required before
the majority of dyes were attacked and degraded.

The photosensitised bleaching of dyes has been
shown to be an oxidation process, either with activated
oxygen or hydrogen peroxide.  Blum and Spealman[35] have
shown that the oxidation of eosin with $H_2O_2$ is again a
photo-sensitive reaction.  A parallel point may be found
in Egerton's demonstration[14] that the degradation of
cellulose by $H_2O_2$ vapor is light induced.  This he
has suggested may be due to the necessity of the
photo-decomposition of the peroxide into the reactive

and degrading hydroxyl radicals.

The following experimental work was conceived as an investigation into the reactions of various substances when illuminated by themselves in various atmospheres and also into their action upon other substances adsorbed upon them. In particular the semi-conducting oxide type of sensitiser was investigated and compared with inert substances; the detailed investigation was made with $TiO_2$ as the sensitising material owing to its high reactivity compared with ZnO etc. It was foreseen that any reaction occuring might be small and it was therefore decided to follow it by measurement of the pressure changes above the solid film. This experimental technique had been successfully used in following the oxidation of solid dye and pigment films. Two dyes - Chlorazol Sky Blue and Malachite Green oxalate, about the degradation of which some previous information was recorded - were chosen as the substances which would most easily reflect the action of the sensitisers. It was also intended to study the fading mechanism of these dyes by measurement of the possible pressure changes occuring on degradation.
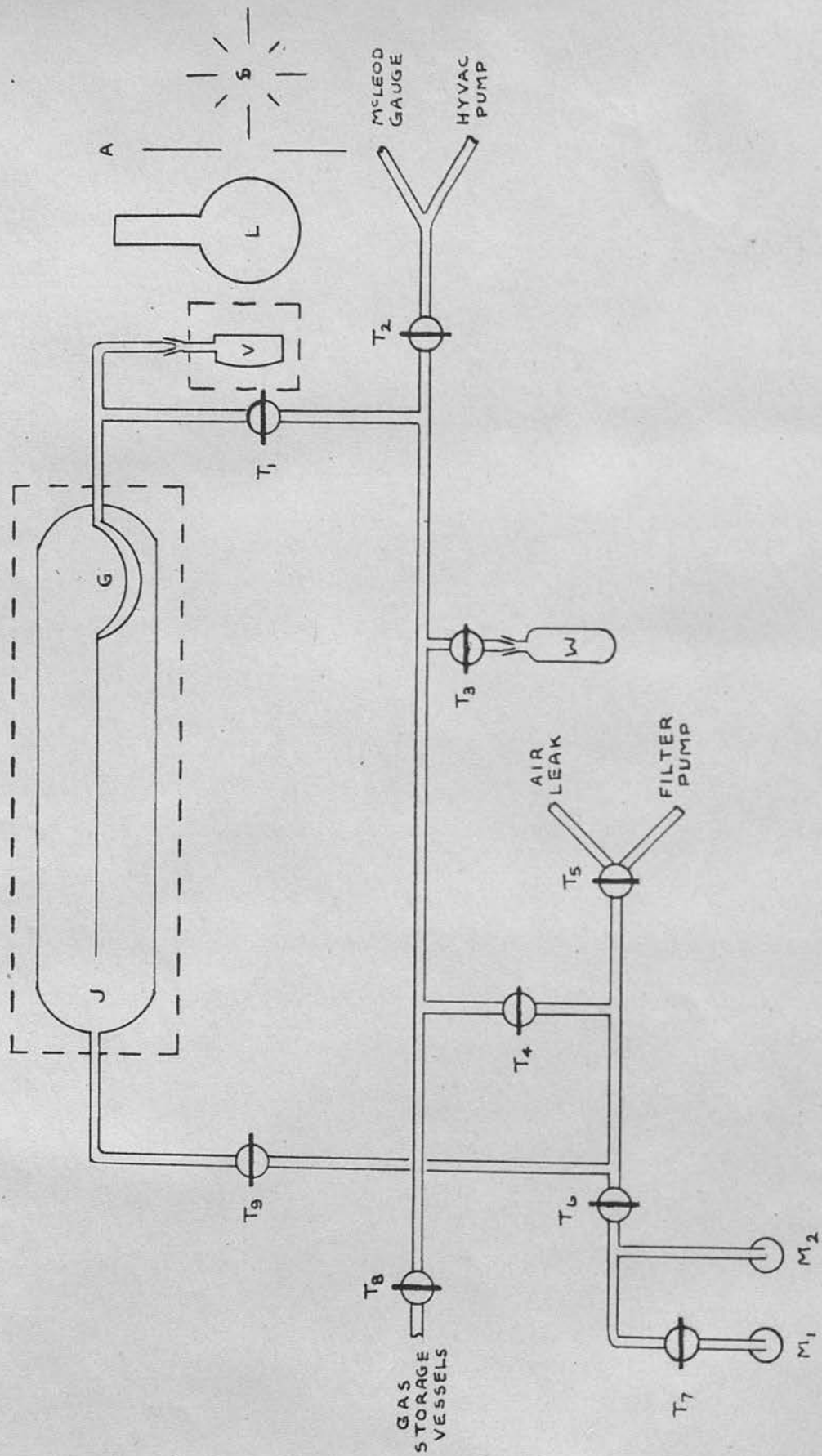
# EXPERIMENTAL DETAILS.

FIG. 2.

[- - - - INDICATES POSITION OF THERMOSTAT JACKETS.]

## EXPERIMENTAL DETAILS.

The apparatus, shown in Fig. 2, consisted, in its
essentials, of an accurate pressure recording system
(Bourdon gauge) connected directly to a reaction vessel
illuminated by high intensity light.   As the pressure
changes were small, accurate thermostating of the
pressure sensitive sections was essential.   In
addition, adequate service for evacuation, admission
of gases etc. were added.

As far as was practicable, the apparatus was
blown as an entity from soda glass tubing.   It was
however necessary to  use ground glass joints for some
parts and these were kept airtight by smearing with
Apiezon L grease.   The few parts made from Pyrex
glass are detailed below.

### Bourdon Gauge.

In order to follow accurately the pressure
changes in the reaction vessel (V) during the course
of a run, use was made of a glass Bourdon gauge (G).
As this gauge will only record pressure changes in
comparison with the constant pressure of its
compensating jacket (J), two manometers ($M_1$, $M_2$) of
which $M_1$ indicated the barometric pressure, were used
to obtain the absolute pressure of the gas in the
apparatus.   For the measurement of very low pressures,

and to ensure that effective evacuation was being attained, the McLeod gauge was used in place of the manometers.

The Bourdon gauge was blown from soft glass tubing and the measure of its contraction or expansion was increased by the addition of a long glass arm to its free end. This pointer was viewed thro' a telescope with a calibrated eye-piece and thus accurate pressure readings were obtained. It was found advantageous to add a small tip of fine diameter Platinum wire to the end of the pointer, as this gave a sharper image in the telescope.

Previous work by Lonie has shown that the sensitivity of these gauges was constant over a reasonably wide range of pressure (0-200 mm. Hg) and therefore in the present work the sensitivity was determined at a pressure of 50 mm. (Hg) and the value obtained used for other pressures.

To calibrate the gauge approximately 50 mm. (Hg) of dry air were admitted to the apparatus and allowed to attain thermostatic conditions. Tap $T_4$ was then closed and accurate readings were made of manometers $M_1$ and $M_2$ and of the gauge. Some of the air in the jacket was then removed by the filter pump thro' $T_5$ and as a result of the pressure change the pointer

moved downwards, as seen thro' the telescope. The
final gauge position was noted. By means of the
Hyvac pump, air was taken from the vessel and gauge
until the pointer rose to the top of the scale and the
reading was again noted. This procedure of removing
air alternately from either side was repeated until a
reasonable pressure change was recorded on the
manometer, when the pointer was brought back to its
initial position by evacuation of the appropriate side
of the gauge. At this point, the pressure difference
recorded by the manometer was equal to the number of
scale divisions traversed by the pointer in one
direction (either up or down) and thus the pressure
change equivalent to one scale division could be
calculated.

For the calibration of one gauge, 282.4 scale
divisions were found to be the equivalent of a pressure
change of 11.7 mm. (Hg).

∴ 1 scale division = 0.0414 mm. (Hg).
Repetition gave the result

1 scale division = 0.0420 mm. (Hg).
The mean of these two values, correct to the second
significant figure, was used and the sensitivity was
therefore taken as 0.042 mm. (Hg)/scale division.
Other gauges used had sensitivities of 0.033 mm. (Hg)/

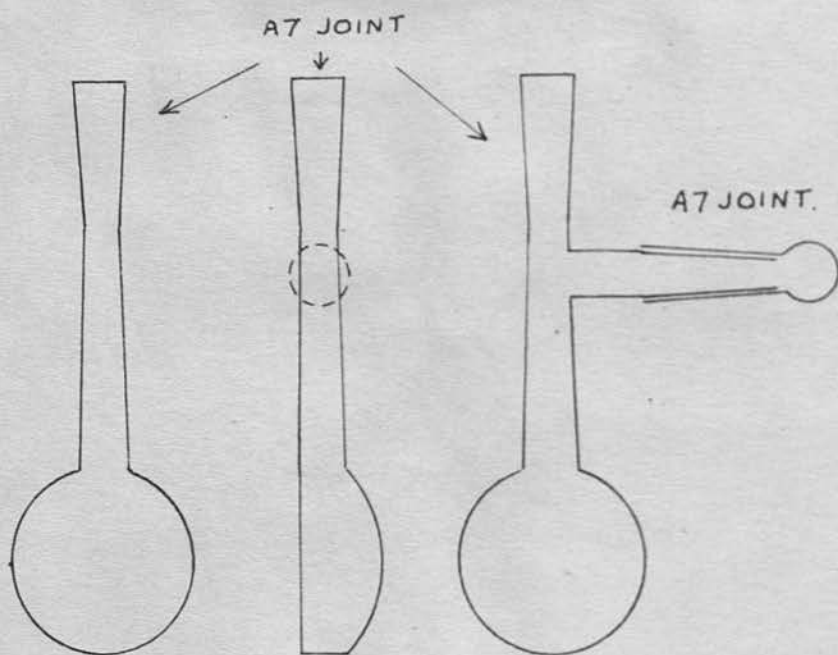FIGS 3 & 3A.

A7 JOINT

A7 JOINT.

FIG 3          FIG 3A

REACTION VESSELS.

(SCALE: 2/3 ACTUAL SIZE)

allowed to expand thro' $T_1$ into the leads while the compensating jacket was evacuated thro' $T_5$ by the filter pump to the same pressure. When the air was fully expanded, the manometer reading gave the final pressure. This procedure was then repeated, allowing the air to expand into vessel W in this case and a third equilibrium pressure was recorded.

The results obtained during one determination were

Volume of vessel V $= V_1$

"    "    leads $= V_2$

"    "    vessel W $= V_3$      = 144.88 ml.

Pressure in vessel V $= P_1 = 304.2$ mm. (Hg)

"    "    "    " + leads $= P_2 = 147.6$ "    "

"    "    "    " "   " + vessel W $= P_3 = 40.7$ "    "

Therefore, as temperature is constant, by Gas Laws

$$P_2 (V_1 + V_2) = P_3 (V_1 + V_2 + V_3)$$

$$\therefore (P_2 - P_3)(V_1 + V_2) = P_3 V_3$$

$$\therefore (V_1 + V_2) = \frac{P_3 V_3}{(P_2 - P_3)}$$

and $$P_1 V_1 = P_2 (V_1 + V_2)$$

$$\therefore V_1 = \frac{P_2}{P_1}(V_1 + V_2)$$

$$= \frac{P_2}{P_1} \frac{P_3 V_3}{(P_2 - P_3)}$$

Substituting the values obtained, we have

$$V_1 = \frac{147.6 \times 40.7 \times 144.9}{304.2 \times 106.9}$$

$$= 26.8 \text{ ml.}$$

Repetition gave values within $\pm$ 0.1 ml of this figure.

All the vessels used were of approximately 30 ml. volume.

## Illumination.

The illumination unit consisted of a light source and a shutter, and the light passing thro' a round bottom flask filled with distilled water was thus focussed as a parallel beam on to the film in the reaction vessel. This interposition of a water filled flask served also to eliminate heat effects.

Two sources of light were used; a 230v. 125w high pressure Osira mercury vapor lamp (in a pearl soft glass envelope) and a 230v. 250w Osram projector lamp (in a clear glass envelope). Both were connected to the mains thro' a voltage stabilizer. The Osram lamp was kept cool by a continuous air blast playing on it.

Owing to the nature of the system, the light reaching the film did not contain any illumination of wavelength less than 3500 Å. Thus with the Osira lamp the characteristic wavelengths of its emission spectrum - 3650Å, 4047Å, 4358Å and 5780Å were all

transmitted. The projector lamp, on the other hand, is characterised by a continuous spectrum which is more intense towards the red end of the spectrum viz.

| Wavelength of emitted light Å | Relative Energy (arbritary units) |
|---|---|
| 3400 | 0 |
| 4000 | 1 |
| 5000 | 3 |
| 6000 | 6 |

## Temperature Control.

To obtain the steady temperature conditions required a closed circuit circulating water system was used. A main tank of large capacity was maintained at constant temperature by a heating element regulated thro' a large chloroform (+1% alcohol) - mercury switch in circuit with a Sunvic control. The water was raised by a centrifugal pump to a small constant head reservoir above the level of the apparatus. By gravity flow this water then passed thro' the thermostat jackets surrounding the gauge, compensating jacket and reaction vessel and thence to the main tank. Such a system was found to maintain a steady temperature ($\pm$ 0.01$^\circ$C) in the apparatus. Should the main tank temperature change by a small amount, the effect on the gauge is nullified by the twin-flow system; any variation in the reaction vessel is counterbalanced by a similar variation, acting

in the reverse direction, in the compensating jacket.

Procedure during an Experiment.

Each experiment may be divided into three parts:-
(a) preparation of the film;  (b) evacuation of apparatus
and addition of the required gas phase;  and (c) the
recording of the pressure under fixed experimental
conditions.

(a) It was found during preliminary work that
approximately 0.12g of the oxides was sufficient to
give a complete film on the rear face of the reaction
vessel.   Approximately this quantity was therefore
weighed to the nearest milligram and was added, thro'
a small funnel, to the reaction vessel.   To bind this
solid to the rear face, a small known quantity (0.2 ml.)
of liquid, either water or acetone, or, in the case of
dyed films, of dye solution, was added and a slurry was
obtained.   The vessel was gently rotated to spread this
over the rear face and then evacuated slowly by the
Hyvac pump over $P_2O_5$ and required traps.   Occasional
rotation of the vessel sufficed to ensure an even film.
When the film was dry, evacuation was continued for a
further period after which the reaction vessel was
removed and attached to the gauge.

(b) With the reaction vessel firmly in position,
the apparatus was evacuated by a Hyvac rotary oil pump,

thro' a liquid oxygen trap, to a pressure of approximately $10^{-3}$ mm. (Hg) as measured by a McLeod gauge.    While there was still an appreciable gas pressure indicated on the manometer $M_2$, tap $T_6$ was closed to prevent the evaporation of mercury vapor into the apparatus.    Having stood overnight evacuated, the system was pumped out for a further 30 minutes before adding the required gas.    The gauge, compensating jacket, reaction vessel and leads were then washed out by a small quantity of the gas being added, which was removed by the Hyvac pump.    The quantity of gas required for the experiment was then added.

Gases such as oxygen, nitrogen and carbon dioxide were added, from reservoirs, thro' tap $T_8$;  dry air was admitted thro' tap $T_5$;  and water vapor was added from vessel W which contained a small quantity of water.

(c) When the apparatus appeared to have reached temperature equilibrium, taps $T_4$, $T_9$ and $T_1$ were closed and the gauge reading, estimated to the nearest 0.1 of a scale division, was noted at 15 minute intervals. When this reading had remained constant over a period of 30 - 60 minutes, the shutter on the light house was opened allowing the light to fall on the film.    Readings of the gauge were then made at intervals and were plotted against time.    At the end of a run or part

of a run the taps $T_4$, and $T_1$ were opened and the system either evacuated or left at the prevailing gas pressure.

## Colorimetric Determination of Dyestuffs.

Quantitative results on the fading of the dyestuffs examined were obtained by measurement of the light absorption by the dye solutions or extracts with the aid of a Spekker colorimeter. By means of a previously calibrated concentration curve the residual dye on the film could be determined.

## Preparation of Chemicals.

Gases: Oxygen and nitrogen were obtained from cylinders (B.O.C.) and after passing over $P_2O_5$ and thro' a trap cooled by a solid $CO_2$/ acetone mixture were stored in bulbs of approximately 2 litre capacity. Carbon dioxide was obtained by sublimation of solid $CO_2$ and was thereafter dried over $P_2O_5$. The water in vessel W was distilled water which had been boiled out at reduced pressure.

## Solid Substrates:

Powdered glass:- A sample of ground Winchester glass was used - the analysis being given as $SiO_2$ 73.3% $Fe_2O_3$ 0.5%, CaO 20.9%, PbO 0.3% and $H_2O$ 0.5%.

Thallous Bromide (TlBr):- 50 ml of Thallous nitrate solution (5.32g in 100 ml solution were added to 25 ml

of Potassium Bromide solution (5.00g in 100 ml. solution)
in a brown glass bottle, a few mls. at a time, with
constant shaking.    The precipated TlBr was washed six
times with distilled water by decantation, before being
filtered off and dried in a desiccator over $CaCl_2$ and
$P_2O_5$.

Zinc Oxide (ZnO):-  A sample of zinc oxide (A.R.)
prepared by British Drug House was used.

Zinc dust (Zn):-

Antimony Oxide ($Sb_2O_3$):-

Bismuth Oxide ($Bi_2O_3$):-

Calcium Hydroxide ($Ca(OH)_2$):-

The samples used were
those held in stock
in the department.
(Hopkin and Williams).

Titanium Dioxide ($TiO_2$):-  Six samples of titanium
dioxide were -

> Sample A:- This was the technical grade of $TiO_2$
> produced by Hopkin and Williams.    It
> was used as supplied.
>
> Sample B:- This was the purified grade of $TiO_2$
> produced by Hopkin and Williams.    It
> was used as supplied.
>
> Samples C and D:- These were prepared at different
> times but  by exactly the same method.
> A small quantity of $TiCl_4$, from a
> sample in the  Chemistry Museum, Edinburgh
> University, was added to many times

its bulk of water and was boiled for 30 minutes. The free acid formed was neutralised (tested by litmus) at $100^{\circ}C$ with dilute ammonia and the coagulated $TiO_2$ was filtered off and washed with hot water until it was free from $Cl^-$ ions, (tested with $AgNO_3$). The washed precipitate was then dried at $100-110^{\circ}C$ for a period of 44 hours. The resultant finely ground powder was white.

Sample E:-   A fresh sample of $TiCl_4$ (B.D.H.) was distilled at reduced pressure, in an all glass apparatus, to remove non-volatile impurities and was then hydrolysed as detailed for the previous sample. The free acid was, in this case, neutralised by NaOH (A.R.). The coagulated precipitate was dried over $P_2O_5$ at $100^{\circ}$ in a pistol drier connected to a Hyvac pump. The powder obtained was white.

Sample F:-   In this preparation, the $TiCl_4$ (B.D.H.) used was distilled four times under reduced pressure and the middle fraction of the last distillate was used for

hydrolysis. It was then treated as
detailed for Sample E. The product
was a white powder.

Dyes:- Two dyes were used during the experimental work -

(a) Chlorazol Sky Blue was purified by precipitation
from an aqueous solution by the addition of
alcohol. The precipitated dye was filtered
off and dried over $P_2O_5$ in a vacuum desiccator.
The formula
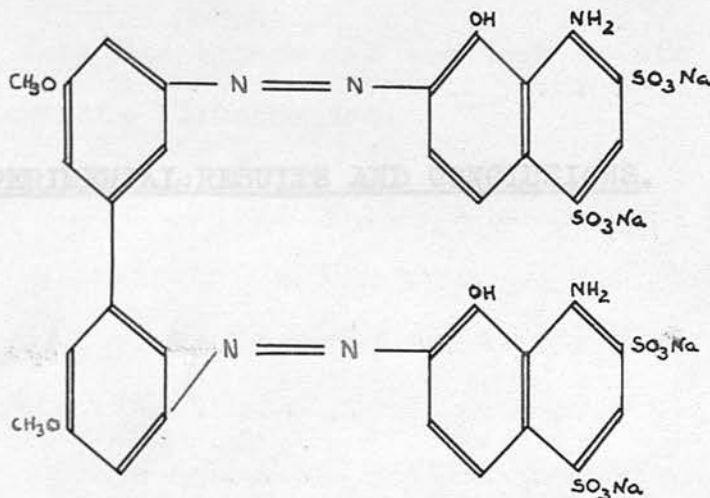


corresponds to a molecular weight of 992.

(b) The Malachite Green used was a purified
sample of the oxalate salt prepared by Reid[19]
who gave the formula as $(D.Ox) D'Ox_2$ where
$D' = DOH$ carbinol and $Ox = $ oxalic acid. The
molecular weight was taken as 944.

EXPERIMENTAL: RESULTS AND CONCLUSIONS.

NOTE:- In the tables of results below, the following
symbols are used :-

B, indicating that the film was evacuated to
approximately $10^{-3}$ m.m. Hg at this point and stood
for several hours at this pressure in the dark
before the oxygen pressure was restored to
50 m.m. Hg. and illumination resumed.

S, indicating that the film stood for several hours
in 50 m.m. Hg. oxygen in the dark before
recommencing illumination.

## EXPERIMENTAL:RESULTS AND CONCLUSIONS.

## EXPERIMENTAL: RESULTS AND CONCLUSIONS.

NOTE:- In the tables of results below, the following
symbols are used :-

E, indicating that the film was evacuated to
approximately $10^{-3}$ m.m. Hg. at this point and stood
for several hours at this pressure in the dark
before the oxygen pressure was restored to
50 m.m. Hg. and illumination resumed.

S, indicating that the film stood for several hours
in 50 m.m. Hg. oxygen in the dark before
recommencing illumination.

## I. PHOTO REACTIONS OF VARIOUS SOLIDS.

### A. Sensitised Degradation of Chlorazol Sky Blue.

In his investigation into the fading of Chlorazol
Sky Blue, sensitised by $TiO_2$, Goodeve suggested that
the degradation was due to oxidation.   This proposition
was based on the observed formation of a reddish inter-
mediate compound during the fading experiments and
during the chemical oxidation of aqueous solutions of the
dye.

These observations have been repeated with some
experimental modifications.   To 1 ml. of a 0.1%
solution of the dye, 10 ml. of 20 volume hydrogen
peroxide were added and the mixture was subjected to
the illumination (and heat) of an Osira lamp.   During
the fading the formation  of a purplish solution, which
eventually passed to pink, was observed.   If the
illumination was cut off at this point and the solution
passed through a chromatographic column (chromatographic
alumina, developed by dilute $HCl$) a reddish band
separated out below the blue one of the unattacked dye.
This lower  band was also obtained from illuminated
films of the dye adsorbed on ZnO but was not present on
any extract from an un-illuminated film.   With
illuminated films of $TiO_2$ this reddish substance could
be detected as a ring encircling those blue parts of
the film as were yet unattacked.

The sensitising action of ZnO and TiO$_2$ has been already mentioned and various other solids were tested for this activity. The dyestuff, Chlorazol Sky Blue, is useful for this purpose as it is almost completely light fast by itself.

Six compounds were chosen to exemplify the three following classes:-

(a) photo-inactive materials - glass and Ca(OH)$_2$;

(b) non-oxide sensitiser - TlBr; and (c) oxide sensitisers - ZnO, TiO$_2$ and Sb$_2$O$_3$. Dyed films of these substances were made as described above and were illuminated in vacuum ($\sim 10^{-3}$m.m. Hg.) and in 50 m.m. oxygen, with the Osira lamp for periods of 180 minutes. At the end of this period, the degree of fading was estimated visually, and the following results were observed.

| SUBSTRATE | DEGREE OF FADING[x] | |
|---|---|---|
| (0.12g.) | VACUUM | OXYGEN |
| Powdered Winchester Glass | 0 | 0 |
| Calcium Hydroxide | - | 0 |
| Thallous Bromide | 0 | 0 |
| Zinc Oxide | +? | + |
| Titanium Dioxide | + | ++ |
| Antimony Oxide | - | + |

(x; 0: no fading, +: slight fading, ++: marked fading, -: no result.)

Only the oxide preparations show photofading, this being particularly obvious with titanium oxide in the presence of oxygen. In the absence of oxygen gas a reduced body action was also to be observed in such cases, doubtfully so with ZnO and $Sb_2O_3$ but definitely present with $TiO_2$.

To distinguish, if possible, any oxygen absorption during illumination, by the solid substrate from that directly absorbed by the dyestuff, it was necessary to examine possible reactions of the solids alone under corresponding conditions.

## B. Illumination of the Solids in Vacuum.

(i) 0.12g. of powdered Winchester glass was illuminated at $\sim 10^{-3}$ m.m. Hg. for 90 minutes by Osira lamp and for 40 minutes by Osram lamp. No pressure change was recorded over these periods.

(ii) 0.12g of Thallous Bromide was illuminated at $\sim 10^{-3}$ m.m. Hg. for 100 minutes by Osira lamp and for 280 minutes by Osram lamp. No pressure change was observed.

(iii) 0.12g of Zinc Oxide was illuminated at $\sim 10^{-3}$ m.m. Hg. for 100 minutes by Osira lamp and for 120 minutes by Osram lamp. No pressure change was observed.

(iv) 0.12g of Titanium Dioxide was illuminated at $\sim 10^{-3}$ m.m. Hg. for 90 minutes by Osira lamp and for 40 minutes by Osram lamp. No pressure change was recorded.

(v) 0.12g. of Antimony Oxide was illuminated at $\sim 10^{-3}$ m.m. Hg. for 240 minutes by Osira lamp. No pressure change was recorded.

## C. Pressure Changes in the Dark.

The apparatus did not allow of easy detection of any rapid oxygen uptake by the solid while the gas was being admitted to the reaction vessel but with those solids examined in section ID, no pressure change was observed on standing in the dark over periods of up to 120 minutes on any occasion.

## D. Illumination of the Solids in Oxygen.

(i) 0.12g. of Winchester glass was illuminated in 50 m.m. oxygen for 140 minutes by Osira lamp and for 360 minutes by Osram lamp. In neither case was there a change in pressure.

(ii) 0.12g. of Calcium Hydroxide was illuminated in 50 m.m. oxygen for 800 minutes by Osira lamp. There was a small pressure increase (0.08 m.m. Hg.) recorded over this period.

(iii) 0.12g. of Thallous Bromide was illuminated in 50 m.m. oxygen for 130 minutes by Osira lamp and for 120 minutes by Osram. No pressure change was recorded over these periods.

(iv) 0.29g. of Zinc Oxide was illuminated in 50 m.m. oxygen by the Osira lamp and a steady but slow pressure decrease was observed. The observed results were :-

FIG. 4

ZINC OXIDE IN O₂.

FIG 5

TITANIUM DIOXIDE IN O₂.
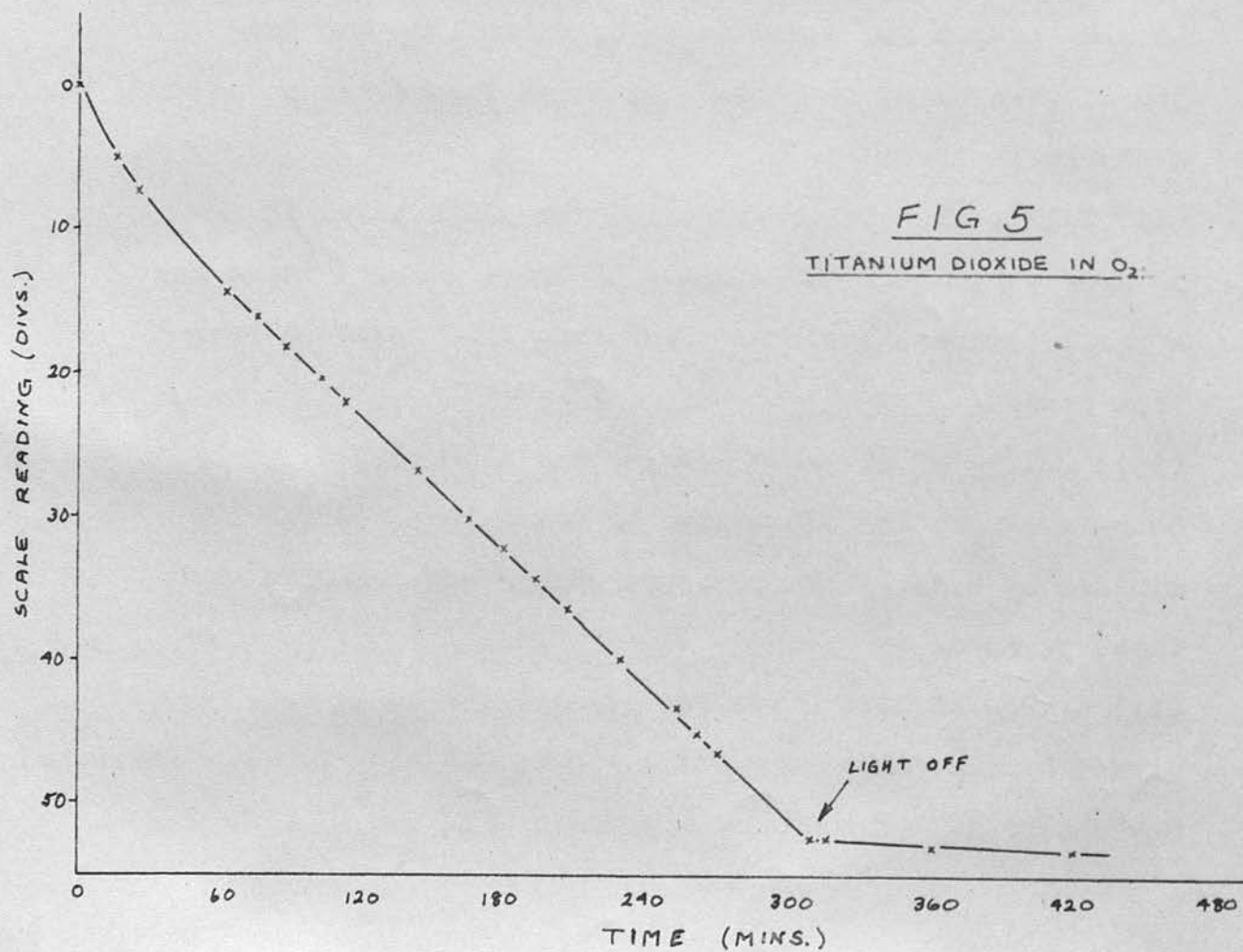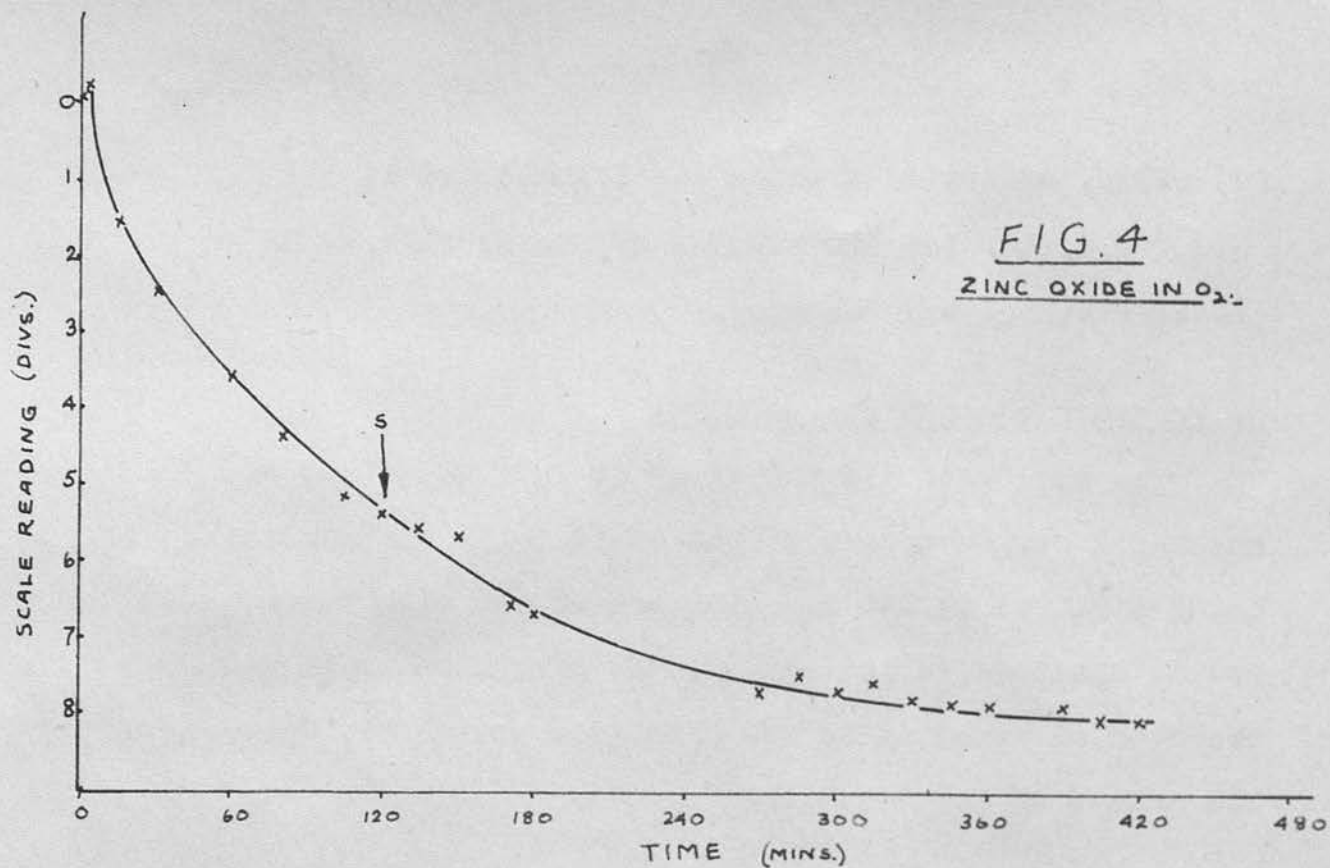
| Time (Mins.) | Scale Reading | Time (Mins.) | Scale Reading |
|:---:|:---:|:---:|:---:|
| 0 | 0.0 | 180 | 6.7 |
| 2 | (-0.2) | 270 | 7.7 |
| 15 | +1.6 | 285 | 7.5 |
| 30 | 2.5 | 300 | 7.7 |
| 60 | 3.6 | 315 | 7.6 |
| 80 | 4.4 | 330 | 7.8 |
| 105 | 5.2 | 345 | 7.9 |
| 120 | 5.4 | 360 | 7.9 |
| S | 5.4 | 390 | 7.9 |
| 135 | 5.6 | 405 | 8.1 |
| 150 | 5.7 | 420 | 8.1 |
| 170 | 6.6 | | |

The above results are plotted in Fig. 4 and show an appreciable uptake of oxygen at a rate which falls off with time to practically negligible values. If the Osram lamp were substituted for the Osira, the reaction virtually ceased.

(v) 0.40g. of Titanium Dioxide (sample B) was illuminated in 50 m.m. oxygen by the Osira lamp. A rapid pressure decrease was recorded, the figures being -

FIG. 6.
ANTIMONY OXIDE IN $O_2$.

FIG. 7.
BISMUTH OXIDE IN $O_2$.
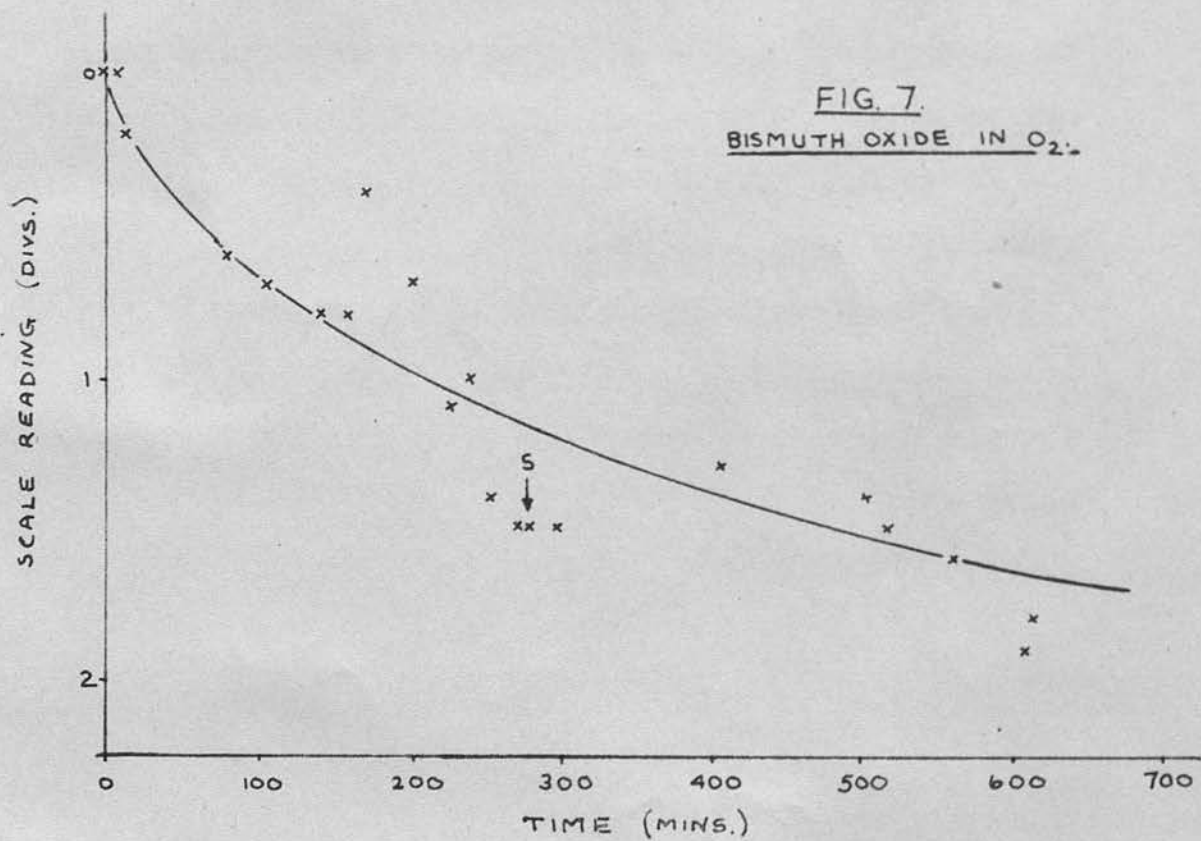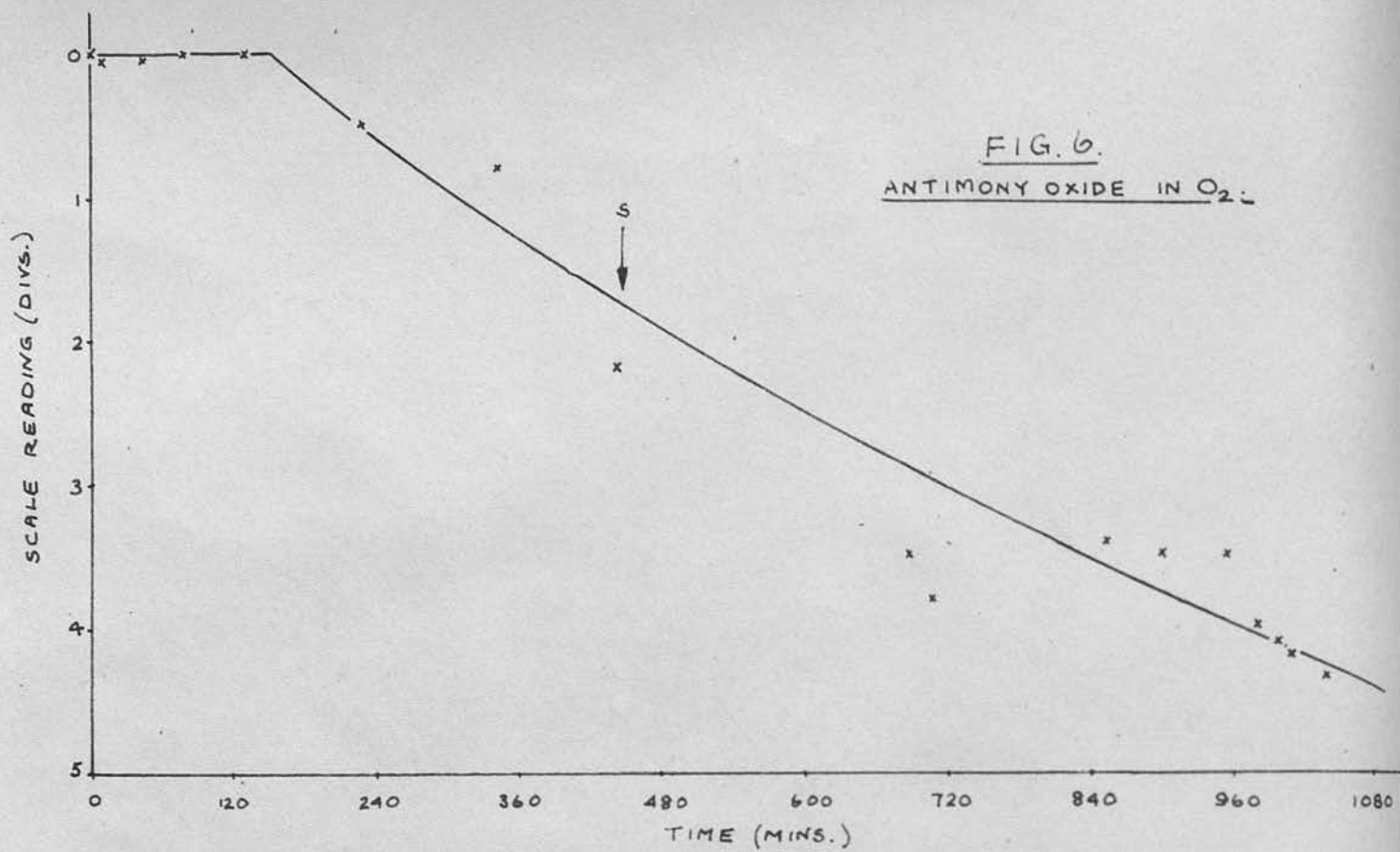
| Time (Mins.) | Scale Reading | Time (Mins.) | Scale Reading |
|---|---|---|---|
| 0 | 0.0 | 180 | 32.3 |
| 15 | 5.1 | 193 | 34.3 |
| 25 | 7.3 | 206 | 36.5 |
| 63 | 14.4 | 229 | 40.0 |
| 65 | 14.6 | 253 | 43.4 |
| 76 | 16.2 | 262 | 45.1 |
| 88 | 18.1 | 270 | 46.5 |
| 103 | 20.4 | 309[x] | 52.4 |
| 113 | 22.2 | 315 | 52.6 |
| 144 | 26.7 | 360 | 53.1 |
| 165 | 30.1 | 420 | 53.3 |

[x] at this point the light was switched off.

These readings are plotted in Fig. 5.

(vi) 0.12g. of Antimony Oxide were illuminated in 50 m.m. oxygen and the following pressure changes recorded – see Fig. 6.

| Time (Mins.) | Scale Reading | Time (Mins.) | Scale Reading |
|---|---|---|---|
| 0 | 0.0 | 688 | 3.5 |
| 10 | 0.1 | 708 | 3.8 |
| 45 | 0.1 | 856 | 3.4 |
| 80 | 0.0 | 905 | 3.5 |
| 130 | 0.0 | 954 | 3.5 |
| 227 | 0.5 | 979 | 4.0 |
| 342 | 0.8 | 996 | 4.1 |
| 351 | 1.1 | 1008 | 4.2 |
| 443 | 2.2 | 1038 | 4.3 |
| S | 2.2 | | |

(vii) 0.12g. of Bismuth Oxide were illuminated by Osira lamp in 50 m.m. oxygen and the following results, which are plotted in Fig. 7, were recorded.

| Time (Mins.) | Scale Reading | Time (Mins.) | Scale Reading |
|---|---|---|---|
| 0 | 0.0 | 253 | 1.4 |
| 10 | 0.0 | 275 | 1.5 |
| 16 | 0.2 | 282 | 1.5 |
| 83 | 0.6 | S | 1.5 |
| 110 | 0.7 | 300 | 1.5 |
| 146 | 0.8 | 412 | 1.3 |
| 163 | 0.8 | 507 | 1.4 |
| 176 | 0.4 | 522 | 1.5 |
| 207 | 0.7 | 563 | 1.6 |
| 229 | 1.1 | 609 | 1.9 |
| 243 | 1.0 | 616 | 1.8 |

## E. Discussion

All the oxides examined above thus show oxygen uptake on illumination by the Osira lamp, with rates under the given conditions increasing in the order $Bi_2O_3$, $Sb_2O_3$, $ZnO$, $TiO_2$. It is thus a distinct possibility that the degradation of Chlorazol Sky Blue adsorbed on such oxides is an oxidation in which the oxygen taken up by the substrate is largely responsible for the oxidation of the dyestuff. Comparison of such oxygen uptakes with the general fading results of section IA. supports this conclusion; a stronger argument may be

made out if one of the sensitisers could be made to show

corresponding changes in these phenomena by suitable

treatment.

For this purpose, titanium dioxide was chosen for
the experimental material owing to the ease of obtaining
various samples, to the fact that it had been studied
before in some detail and to the more rapid reactions
to be expected with it in comparison with the other
oxides.

## II. TITANIUM DIOXIDE: ACTIVITY OF VARIOUS PREPARATIONS

The study of the relationship between the apparent
oxygen uptake by the substrates and their sensitising
activity was extended in this section to various samples
of $TiO_2$. The most convenient manner in which such a
series of samples could be obtained was by modification
of the method of preparation and subsequent treatment.
The results obtained with such controlled variations

would also, possibly, give an insight into the nature

of the reaction, as various possibilities could be
eliminated during preparation from $TiCl_4$ (Page 28) -
e.g. by substitution of NaOH (samples E and F) for
$NH_4OH$ (samples C and D) as the neutralising agent for
the acid liberated during hydrolysis, by the removal
of iron by fractional distillation (sample E and to a
greater extent sample F) and by the vigorous drying
methods - ignition and heating at $100^{\circ}C$ at low pressure-
to remove a possible water content built into the
lattice.

The scope of the reaction, with respect to gaseous
atmospheres other than dry oxygen, would also indicate
the type of reaction being studied. The results with
four such possibilities were evaluated.

In examining the results of experiments described
in this section it was sometimes found more useful to
construct a rate vs. total pressure change curve (than)

than to use the pressure change vs.time curve for com-
parison.    This rate curve was calculated from the
smoothed pressure change vs. time curve and was plotted
in units of scale divisions of pressure change over
30 minutes ($R_{30}$) vs. scale divisions of total pressure
change at the middle of each rate section ($\Sigma p. ch.$).
From such a curve it was hoped that the total pressure
change could be extrapolated when $R_{30}= 0$.

## A. Pressure Changes over Various Samples Illuminated in Oxygen.

Throughout the series of experiments described in
this section, no pressure change was recorded while the
films stood in 50 m.m. oxygen in the dark.    They were
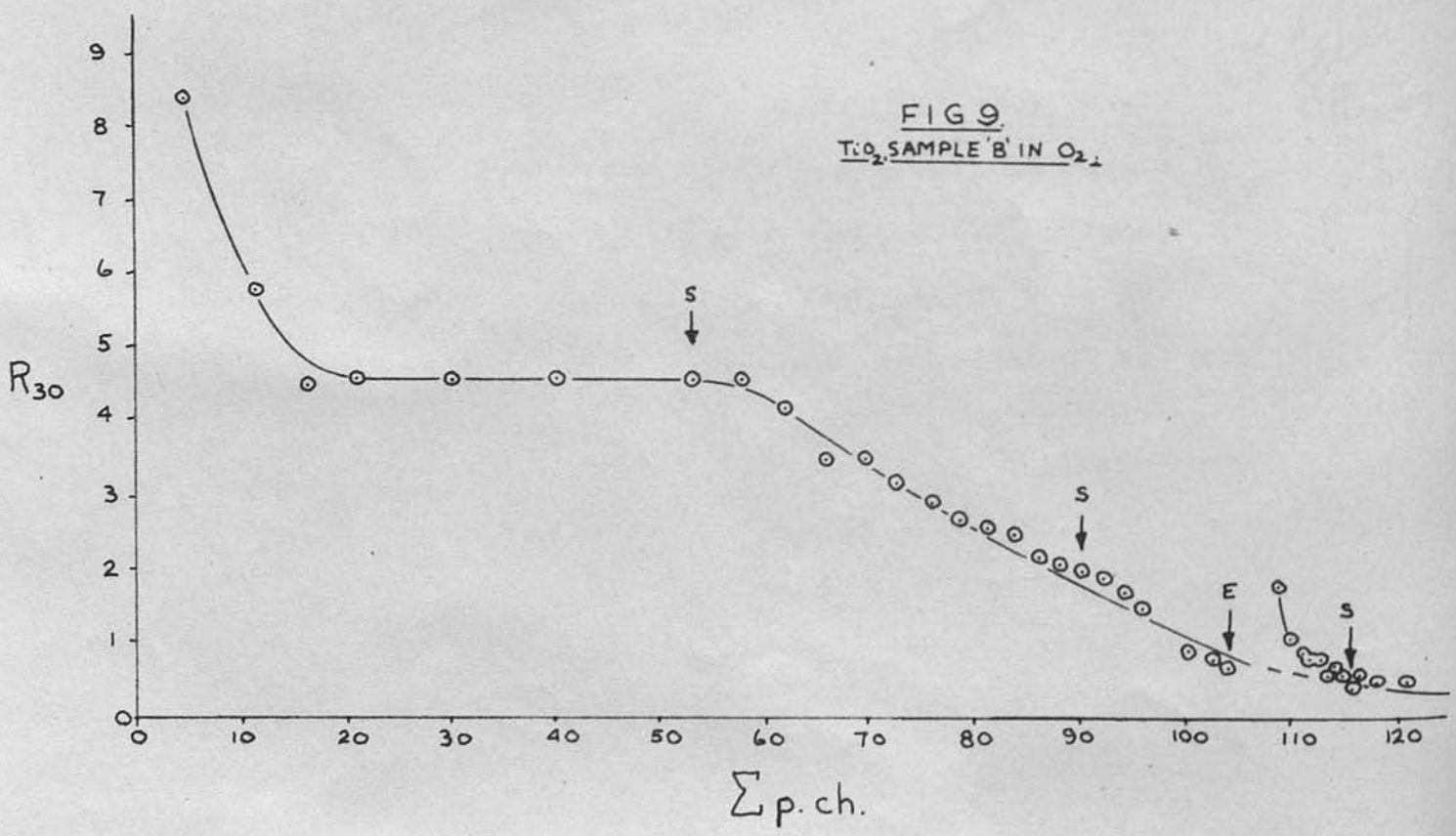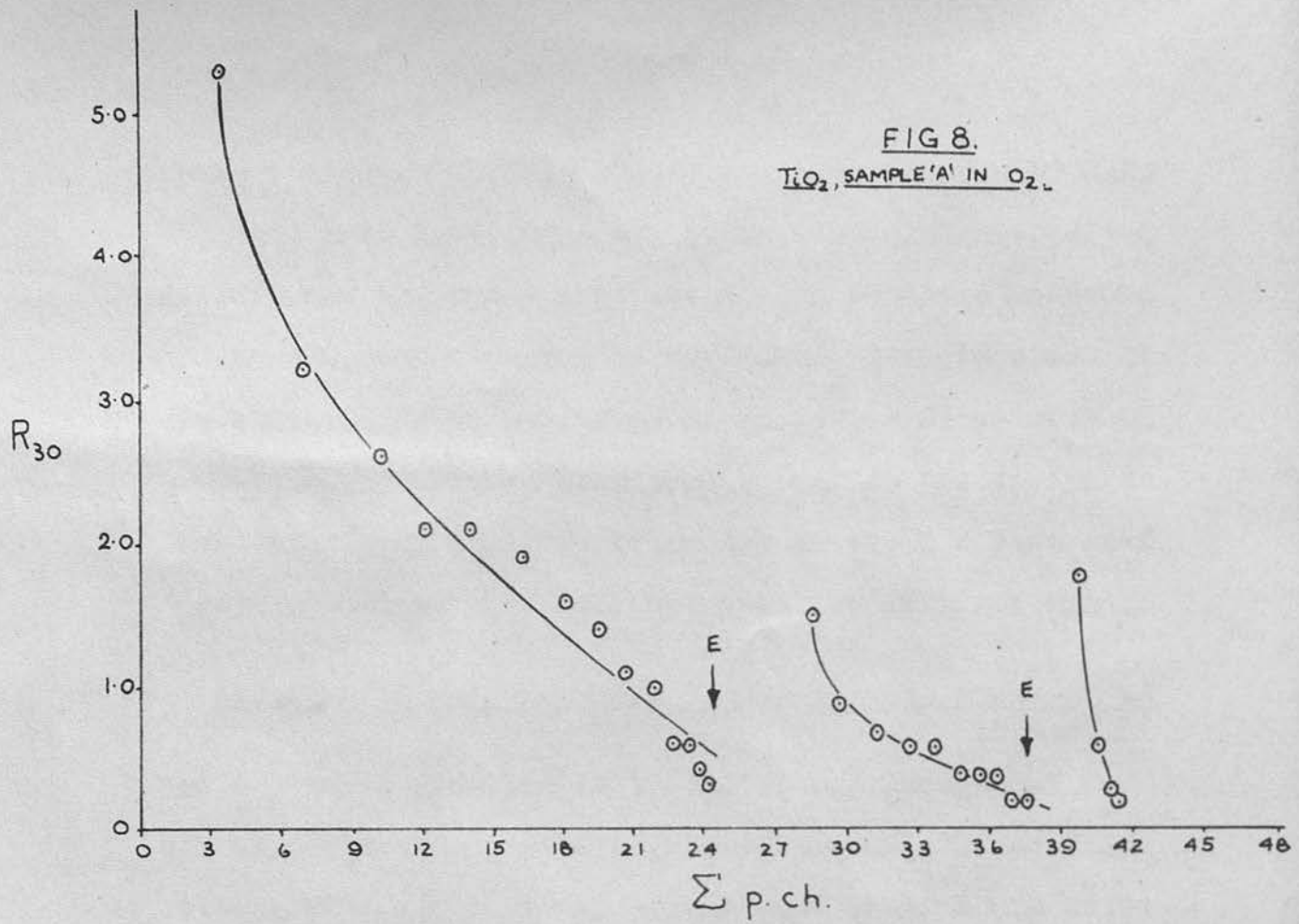all illuminated by the Osira Lamp in 50 m.m. oxygen at
25°C.

(i) Sample A (p. 27).

Wt. of $TiO_2$ - 0.13g.

Volume of reaction vessel - 26.90 ml.

Sensitivity of gauge - 0.033 m.m./scale div.

The rate curve, shown in Fig. 8, was constructed
from the following results :-

FIG 8.
$TiO_2$, SAMPLE 'A' IN $O_2$.

FIG 9.
$TiO_2$, SAMPLE 'B' IN $O_2$.

41.

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|---|---|---|---|---|---|
| 5.3 | 3.5 | 0.6 | 22.7 | 0.4 | 34.7 |
| 3.2 | 7.0 | 0.6 | 23.3 | 0.4 | 35.6 |
| 2.6 | 10.2 | 0.4 | 23.7 | 0.4 | 36.3 |
| 2.1 | 12.1 | 0.3 | 24.0 | 0.2 | 36.9 |
| 2.1 | 14.3 | E | E | 0.2 | 37.5 |
| 1.9 | 16.3 | 1.5 | 28.5 | E | E |
| 1.6 | 18.1 | 0.9 | 29.6 | 1.8 | 39.7 |
| 1.4 | 19.5 | 0.7 | 31.2 | 0.6 | 40.5 |
| 1.1. | 20.8 | 0.6 | 32.6 | 0.3 | 41.0 |
| 1.0 | 21.8 | 0.6 | 33.7 | 0.2 | 41.2 |

(ii) Sample B (p. 27)

Wt. of $TiO_2$ - 0.40g.

Volume of reaction vessel - 26.90 ml.

Sensitivity of gauge - 0.033 m.m./scale division.

Fig. 9 is plotted from the following results.

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|---|---|---|---|---|---|
| 8.4 | 4.5 | 2.6 | 81.3 | 0.9 | 111.1 |
| 5.8 | 11.5 | 2.5 | 83.8 | 0.8 | 111.9 |
| 4.5 | 16.2 | 2.2 | 86.1 | 0.8 | 112.7 |
| 4.6 | 21.0 | 2.1 | 88.3 | 0.6 | 113.4 |
| 4.6 | 30.0 | 2.0 | 90.3 | 0.7 | 114.1 |
| 4.6 | 40.0 | S | S | 0.6 | 114.7 |
| 4.6 | 53.3 | 1.9 | 92.5 | 0.5 | 115.3 |
| S | S | 1.7 | 94.3 | 0.4 | 115.7 |
| 4.6 | 57.8 | 1.5 | 95.8 | S | S |
| 4.2 | 62.1 | 0.9 | 100.4 | 0.6 | 116.3 |
| 3.5 | 65.9 | 0.8 | 102.8 | 0.5 | 116.9 |
| 3.5 | 69.5 | 0.7 | 104.3 | 0.5 | 117.8 |
| 3.2 | 72.7 | E | E | 0.5 | 119.9 |
| 2.9 | 76.0 | 1.8 | 108.8 | 0.5 | 120.9 |
| 2.7 | 78.7 | 1.1 | 110.1 | | |

FIG 10.
$TiO_2$, SAMPLE 'D' IN $O_2$.

$R_{30}$

$\Sigma$ p. ch.

FIG 11.
$TiO_2$, SAMPLE 'E' IN $O_2$.

$R_{30}$

$\Sigma$ p. ch.
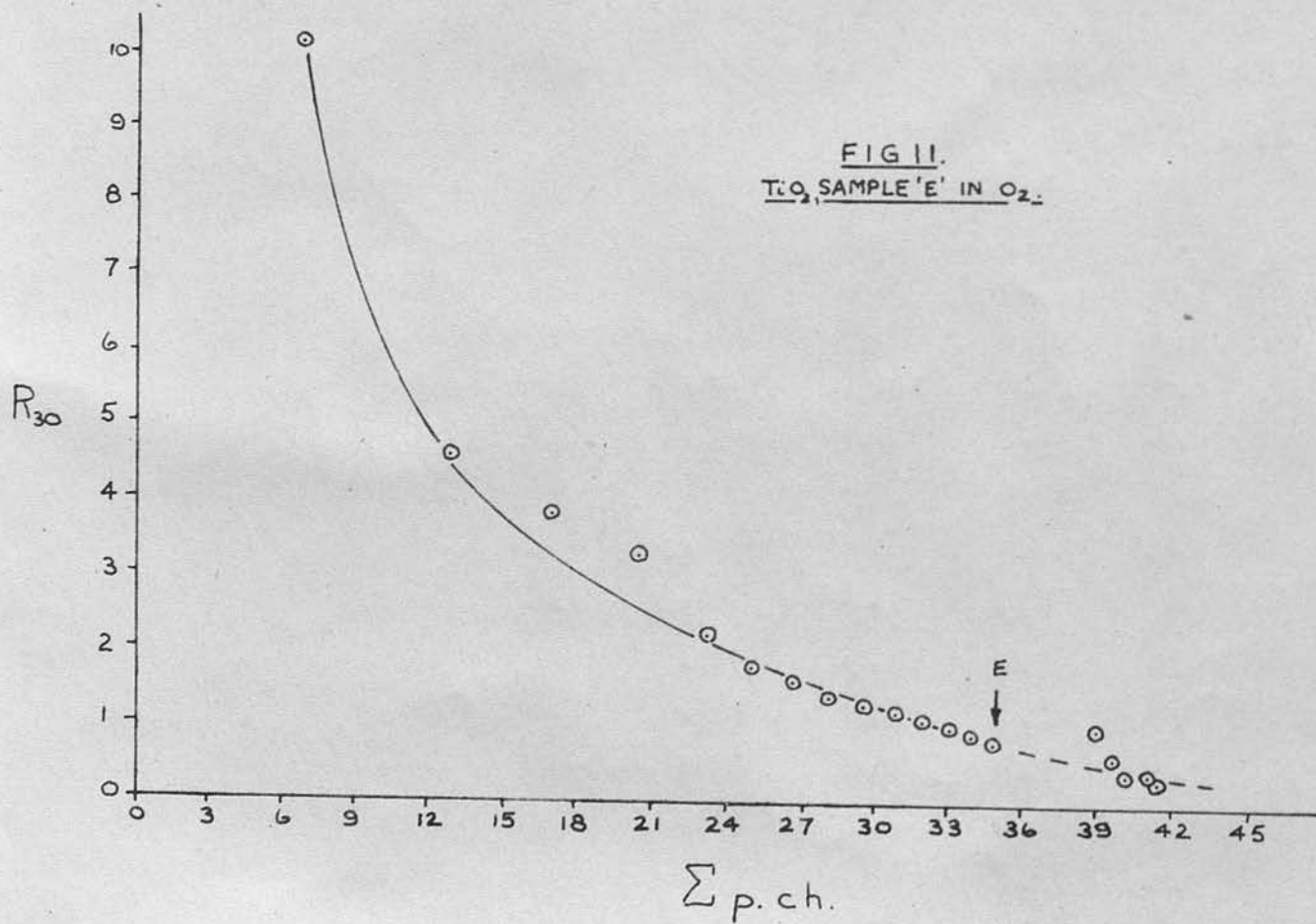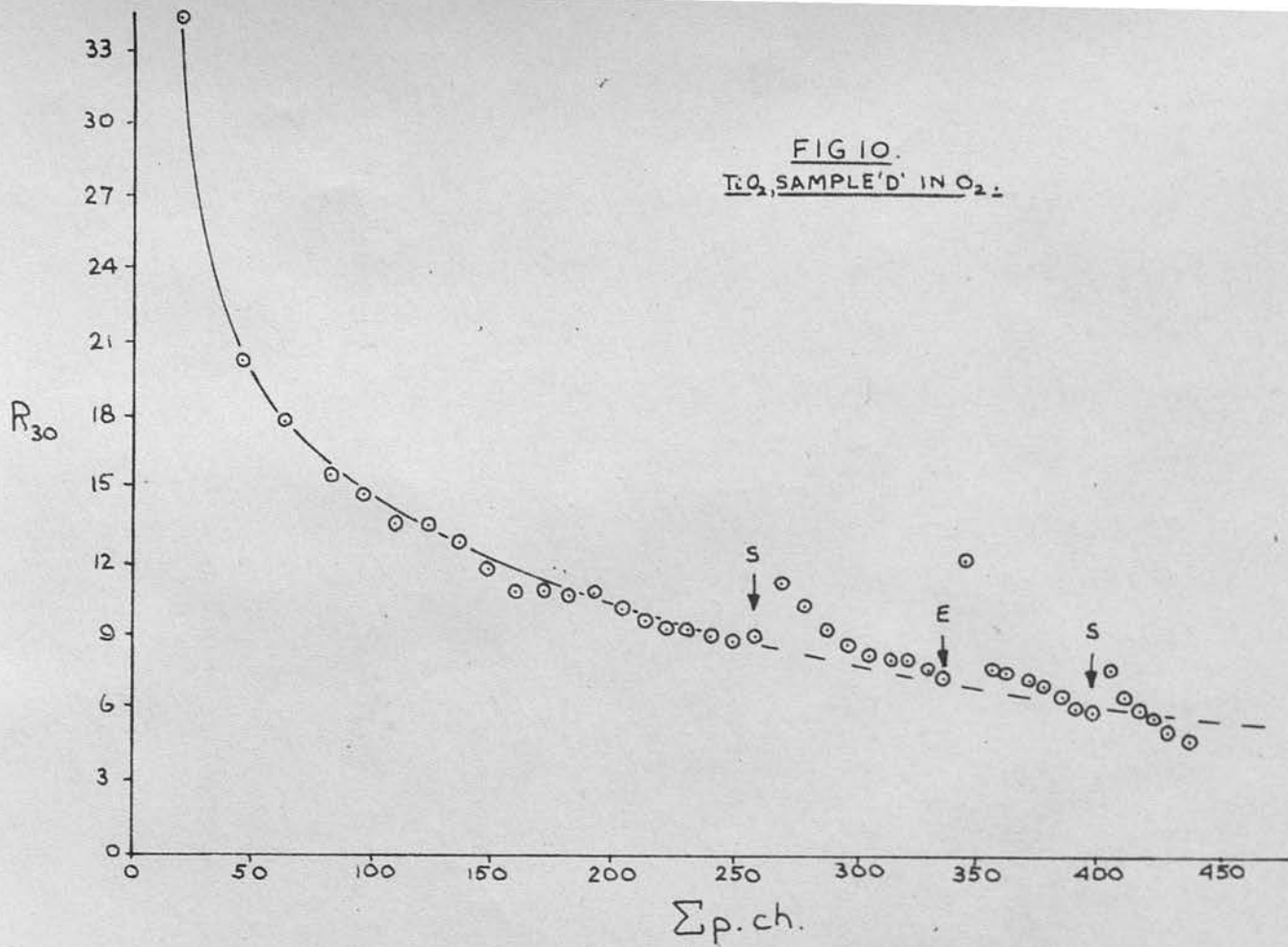
(iii) Sample C and D (p.27).

These two samples prepared in the same manner gave comparable results although no two rate curves could be superimposed. The following results were obtained using sample D.

Wt. of $TiO_2$ - 0.12g.

Volume of reaction vessel  -  26.75 ml.

Sensitivity of gauge  -  0.042 m.m/scale division.

The rate curve, Fig.10, was plotted from the results given below :-

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|---|---|---|---|---|---|
| 34.3 | 20.5 | 9.3 | 231.4 | 7.9 | 356.3 |
| 20.2 | 45.0 | 9.0 | 240.7 | 7.6 | 363.8 |
| 17.7 | 63.1 | 8.7 | 249.5 | 7.2 | 371.2 |
| 15.6 | 80.5 | 8.9 | 258.0 | 7.0 | 378.4 |
| 14.8 | 95.5 | S | S | 6.6 | 385.0 |
| 13.6 | 109.4 | 11.0 | 268.5 | 6.1 | 391.5 |
| 13.5 | 123.0 | 10.3 | 278.6 | 5.9 | 397.5 |
| 12.8 | 136.0 | 9.3 | 288.4 | S | S |
| 11.6 | 148.0 | 8.6 | 297.2 | 7.6 | 404.3 |
| 10.7 | 159.0 | 8.2 | 305.7 | 6.5 | 411.4 |
| 10.8 | 170.0 | 7.9 | 314.0 | 6.1 | 417.7 |
| 10.6 | 181.0 | 7.8 | 322.0 | 5.6 | 423.5 |
| 10.8 | 192.3 | 7.7 | 329.7 | 5.1 | 428.6 |
| 10.1 | 202.4 | 7.4 | 337.0 | 4.7 | 433.6 |
| 9.7 | 212.7 | E | E | 4.7 | 438.3 |
| 9.3 | 222.3 | 12.1 | 346.8 | | |

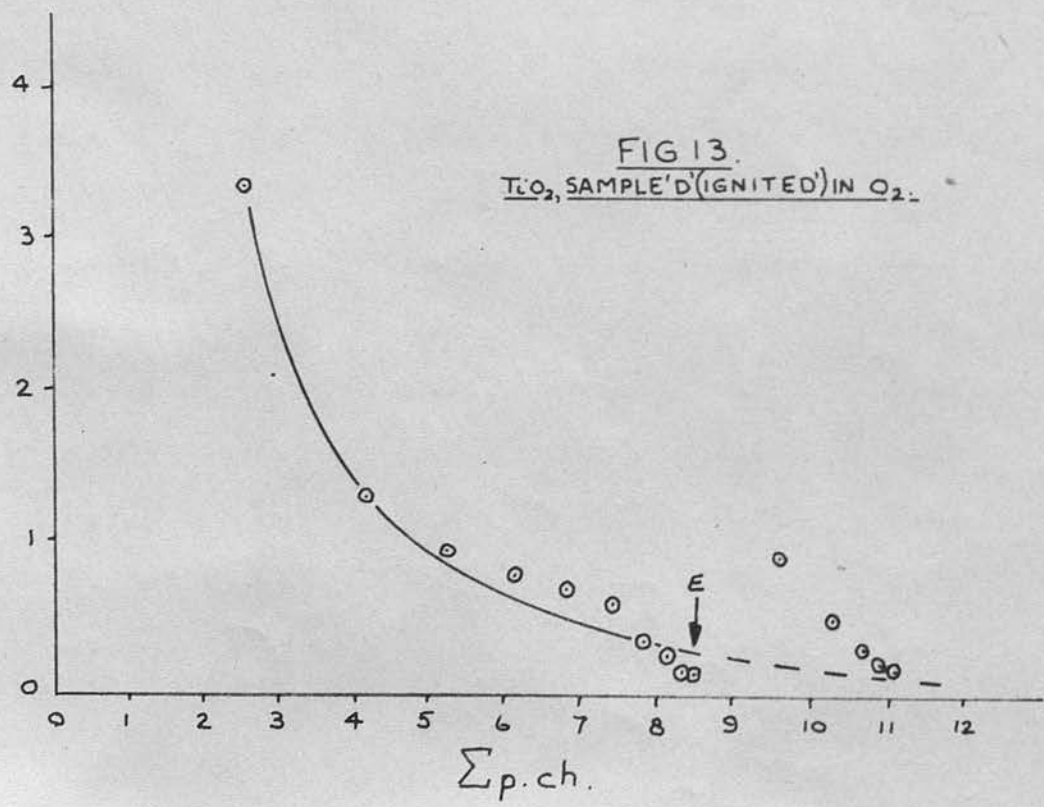FIG 12.
$TiO_2$, SAMPLE 'F' IN $O_2$.
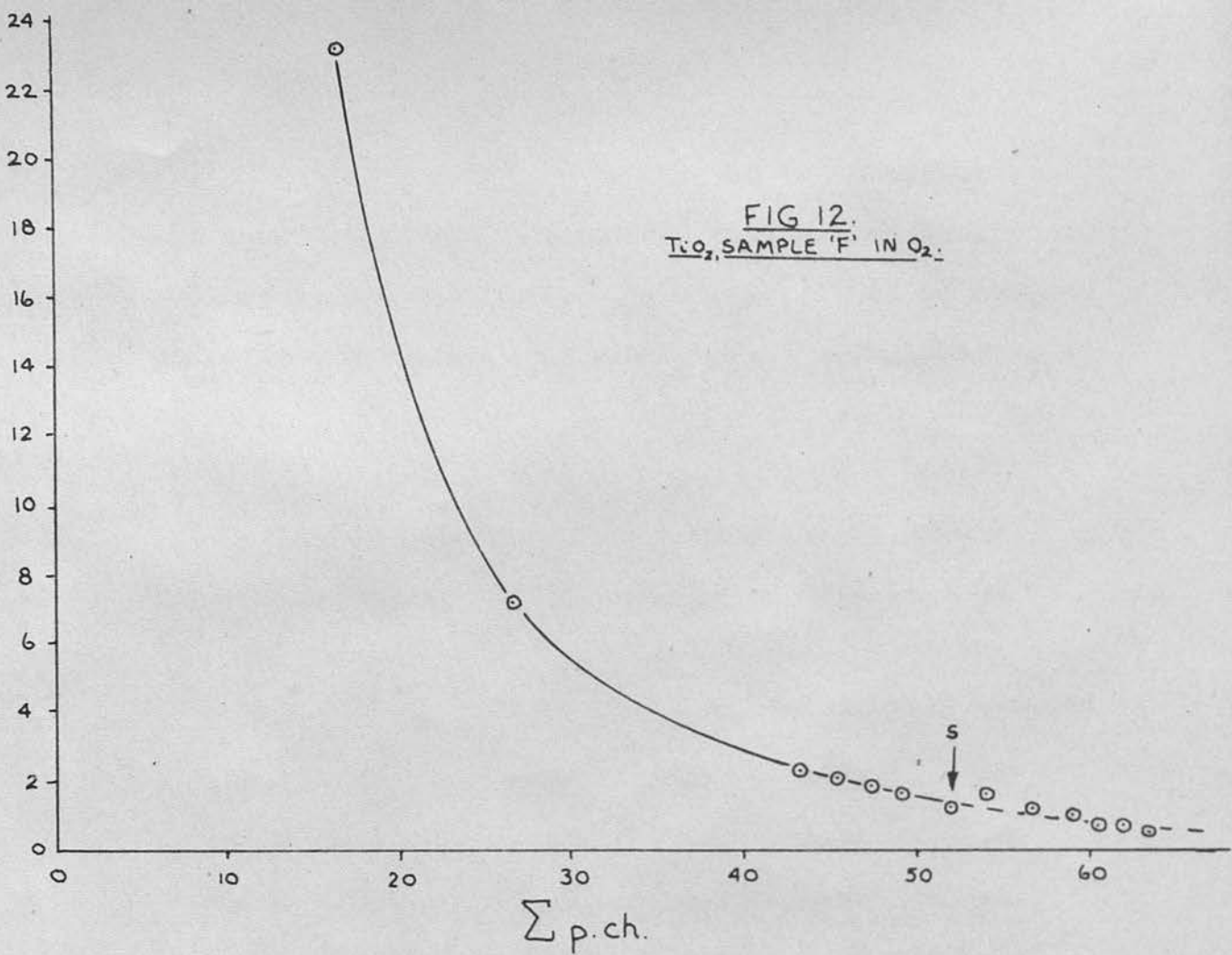


FIG 13.
$TiO_2$, SAMPLE 'D' (IGNITED) IN $O_2$.

(iv) Sample E (p.28).

Wt. of $TiO_2$ - 0.12g.

Volume of reaction vessel - 26.75 ml.

Sensitivity of gauge - 0.042 m.m./scale division.

The following results, plotted in Fig.11., were calculated from the pressure change vs. time curve :-

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|------|------|------|------|------|------|
| 10.1 | 6.7 | 1.4 | 28.1 | E | E |
| 4.6 | 12.7 | 1.3 | 29.5 | 2.9 | 37.5 |
| 3.8 | 16.7 | 1.2 | 30.8 | 1.0 | 38.9 |
| 3.3 | 20.3 | 1.1 | 31.9 | 0.6 | 39.6 |
| 2.2 | 23.0 | 1.0 | 33.0 | 0.4 | 40.1 |
| 1.8 | 24.9 | 0.9 | 33.9 | 0.4 | 40.9 |
| 1.6 | 26.6 | 0.8 | 34.8 | 0.3 | 41.3 |

(v) Sample F (p.28).

Wt. of $TiO_2$ - 0.12g.

Volume of reaction vessel - 26.75 ml.

Sensitivity of gauge - 0.042 m.m./scale division

Fig.12 is constructed from the following values:-

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{50}$ | $\Sigma$p.ch. |
|------|------|------|------|------|------|
| 23.2 | 16.5 | 1.6 | 49.1 | 1.0 | 59.0 |
| 7.2 | 26.6 | 1.2 | 52.0 | 0.7 | 60.5 |
| 2.3 | 43.2 | S | S | 0.7 | 61.9 |
| 2.1 | 45.4 | 1.6 | 54.1 | 0.5 | 63.3 |
| 1.9 | 47.4 | 1.2 | 56.7 | | |

(vi) Sample D, ignited.

A quantity of sample D of the prepared dioxide was ignited in a silica crucible while protected from the reducing gases of the Meker. The heating was continued for six hours, after which the powder had assumed a fawnish colour.

Wt. of $TiO_2$ - 0.12g

Volume of reaction vessel - 26.90 ml.

Sensitivity of gauge - 0.033 m.m./scale division.

In the results given below, and plotted in Fig.13, $R_{60}$ is used in place of $R_{30}$ owing to the slow rate obtained.

| $R_{60}$ | $\Sigma$p.ch. | $R_{60}$ | $\Sigma$p.ch. | $R_{60}$ | $\Sigma$p.ch. |
|---|---|---|---|---|---|
| 3.35 | 2.50 | 0.35 | 7.80 | 0.50 | 10.30 |
| 1.30 | 4.10 | 0.25 | 8.10 | 0.30 | 10.70 |
| 0.95 | 5.20 | 0.15 | 8.30 | 0.20 | 10.90 |
| 0.80 | 6.10 | 0.15 | 8.45 | 0.15 | 11.10 |
| 0.70 | 6.80 | E | E | | |
| 0.60 | 7.40 | 0.90 | 9.60 | | |

(vii) Sample E - dried at $100^{\circ}$C.

A quantity of preparation E was dried, in a pistol drier connected to a Hyvac pump, over $P_2O_5$ at $100^{\circ}$C for a period of 36 hours. Two films were prepared using acetone (A.R.) as the binding agent - one from this dried sample and another from the bulk sample E.

Although the rate curves were not identical, they were
sufficiently comparable, as judged from other repetitive
experiments, to justify the assumption that the above
treatment did not materially affect the reaction
resulting in a pressure change.

Consideration of the rate curves for the various
samples given above indicated that although the course
of the reaction was similar in each case, the method
of preparation greatly influenced the reactivity.   On
the results obtained, especially with those for the more
reactive samples, it was not generally possible to
extrapolate directly a definite value for the final total
pressure change, owing to the lack of any considerable
linear portion to the curves.   It was possible however
to place the samples in their order of reactivity as
judged from the magnitude of the pressure change.   In
decreasing activity, this order was

Sample D(C): Sample F: Sample E: Sample B:
Sample A.

With these samples it was further shown that
extensive drying at 100°C did not alter the results but
that ignition to red heat resulted in the virtual
inactivation of the sample.   Further conclusions
drawn from these results have been left to the next
section where they could be more completely dealt with.

The similarity in the shape of the rate curves for
all the samples examined enabled a general picture of

the reaction with $TiO_2$ to be drawn. This showed a
rapid initial reaction falling away until it merged
smoothly with a steadier but much slower reaction.
At any point during the reaction, cessation of illumina-
tion coupled with standing in oxygen, or, to a greater
extent, with standing in a vacuum, was attended on
re-illumination in oxygen by a rise in the rate of the
pressure change when compared with the rate in the
period immediately preceeding the break. This new curve
fell rapidly and eventually merged with the original
curve extended.

## B. Sensitising Action of Various Samples Illuminated in Oxygen.

To obtain comparative results for the efficiency of
sensitisation of various samples, a known volume of
0.1% solution of Chlorazol Sky Blue was precipitated,
by the removal of the solvent, on 0.12g. of each sample
and the resultant dyed film was illuminated by the
Osira for 3 hours in 50 m.m. oxygen. The dye was then
extracted with 2N NaOH, the suspension centrifuged clear
and 10 ml. of this clear solution neutralised exactly
by 2N HCl. The absorption of light by these neutral
samples was then obtained on a Spekker colorimeter,
using Spectrum Orange 607 filters to eliminate the
effect of the red oxidation product.

The calibration curve of dye concentration vs. drum

reading for this particular dye was found to be a
straight line over the regions of concentration
(measured) $(5-50 \times 10^{-6} g./ml.)$ and therefore the drum
reading for the neutral extracts was taken as a measure
of the dye remaining.    A control experiment was
carried out with a sample of $TiO_2$, dyed as above but un-
illuminated.    The results obtained were :-

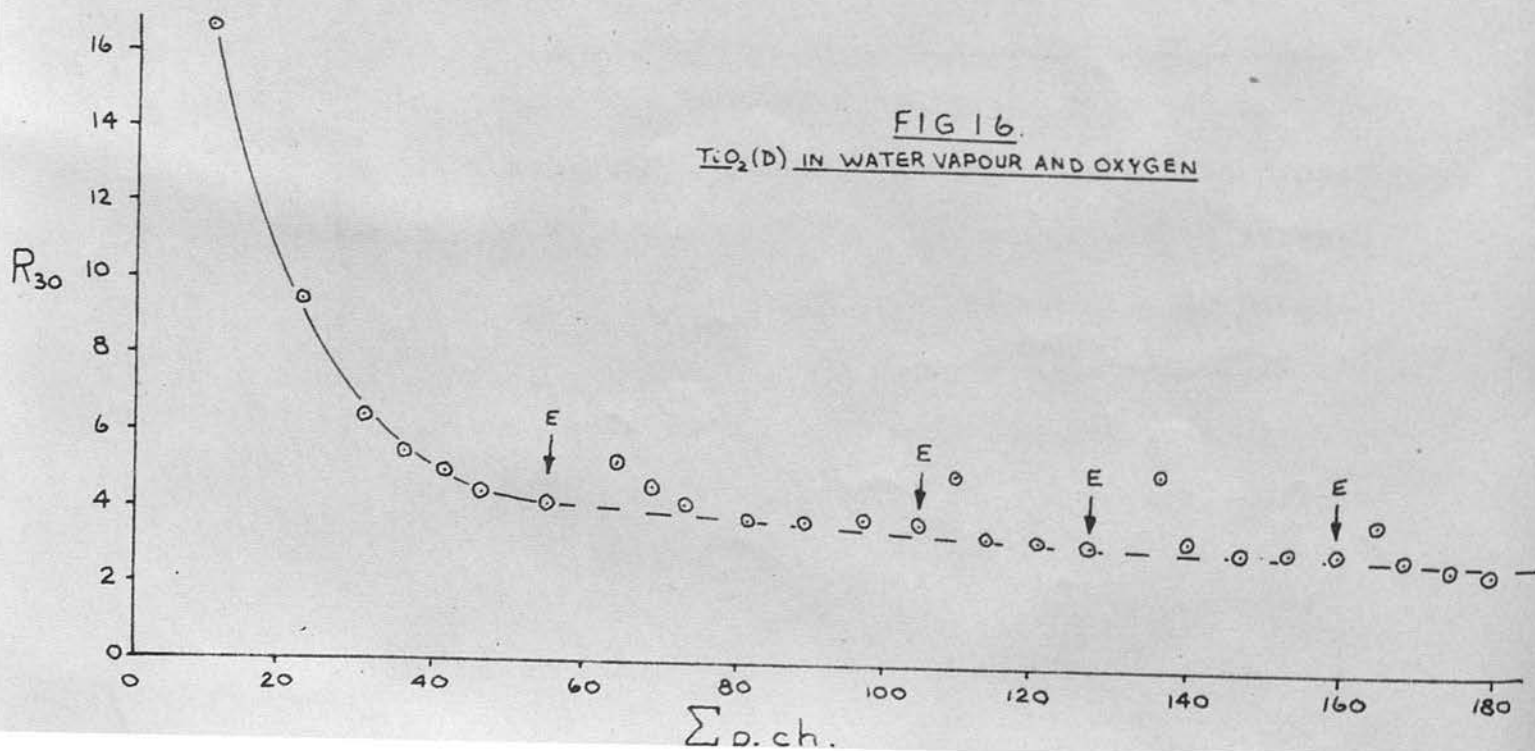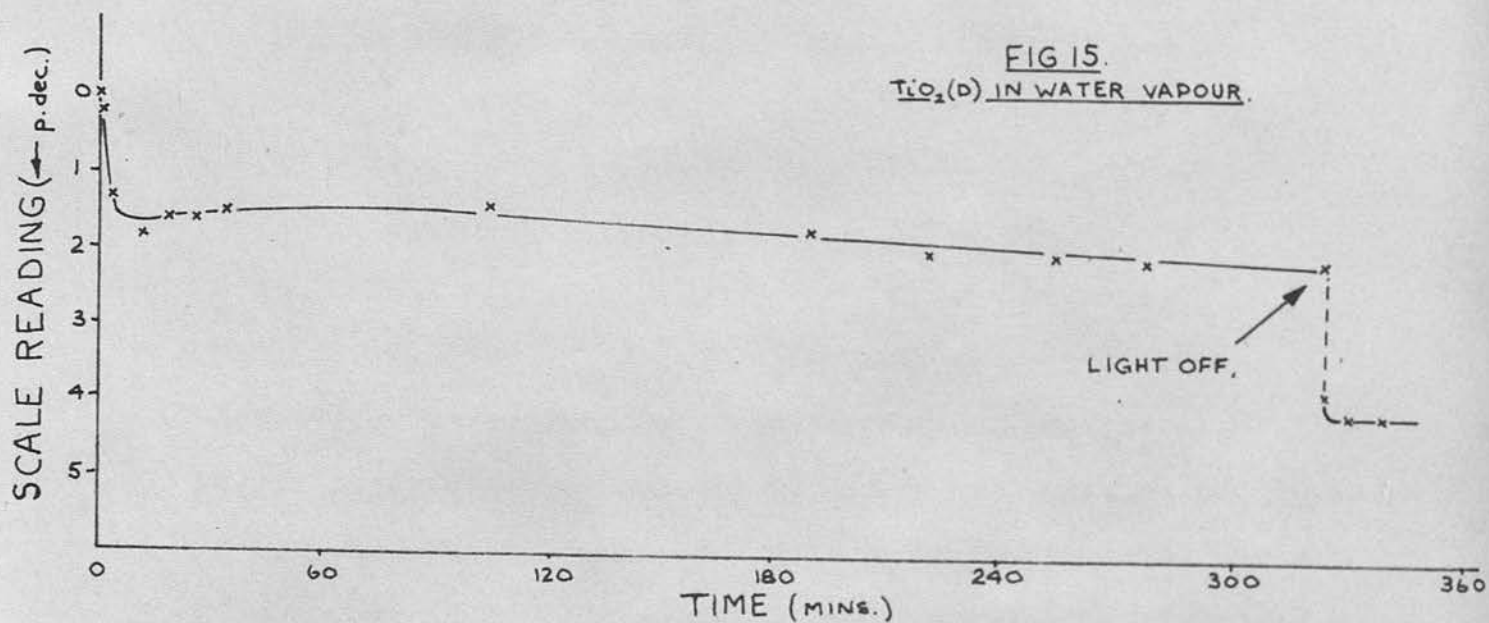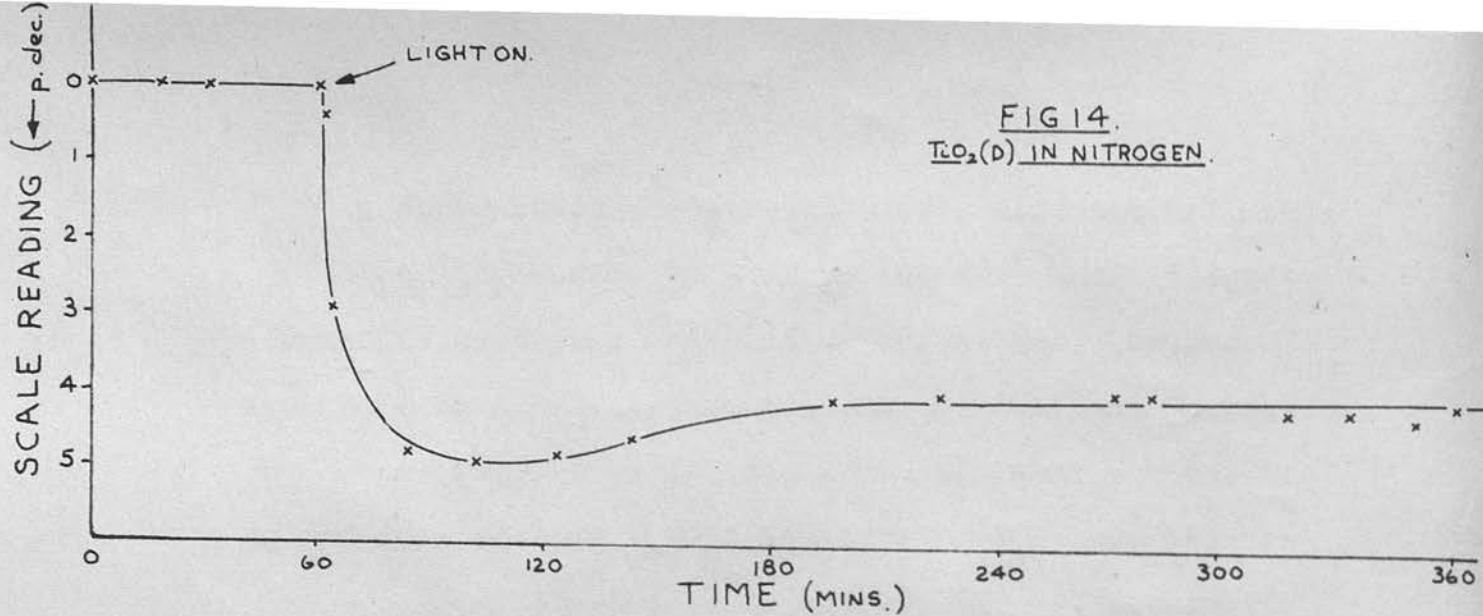| SAMPLE | DRUM READING | DYE LOST | % DYE LOSS |
|--------|--------------|----------|------------|
| Control | 0.498 | - | - |
| A | 0.479 | 0.019 | 3.8 |
| D | 0.251 | 0.247 | 49.6 |
| D(ignited) | 0.475 | 0.023 | 4.6 |
| F | 0.314 | 0.164 | 32.9 |

These results showed that the sensitising activities
of the samples tested lay in the same order as that listed
above for their reactivity as measured by the decrease
in oxygen pressure on illumination.

## C. Pressure Changes in Various Atmospheres.

So far only the illumination of substances in
vacuum or oxygen has been studied;    therefore various
samples were illuminated in nitrogen, water vapour and a
mixture of oxygen and water vapour.

(i) Nitrogen.

50 m.m. dry nitrogen were illuminated over 0.12g.
of $TiO_2$ (sample D). by the Osira lamp at $25^\circ C$.

FIG 14.
TiO₂(D) IN NITROGEN.



FIG 15.
TiO₂(D) IN WATER VAPOUR.



FIG 16.
TiO₂(D) IN WATER VAPOUR AND OXYGEN

Volume of reaction vessel - 26.75 ml.

Sensitivity of gauge - 0.042 m.m./scale division.

The following results were obtained and plotted in Fig.14:-

| Time (Mins.) | Scale Reading | Time (Mins.) | Scale Reading |
|---|---|---|---|
| 0 | 0.0 | 143 | 4.6 |
| 18 | 0.0 | 196 | 4.1 |
| 31 | 0.0 | 224 | 4.0 |
| 60* | 0.0 | 270 | 4.0 |
| 61 | 0.4 | 280 | 4.0 |
| 64 | 2.9 | 315 | 4.2 |
| 84 | 4.8 | 332 | 4.2 |
| 102 | 4.9 | 349 | 4.3 |
| 123 | 4.8 | 360 | 4.1 |

* at this point the lamp was switched on.

(ii) Water Vapour.

On the addition of water vapour to the evacuated oxide, there occurred an immediate rapid adsorption of the vapour which was not examined quantitatively. Following this, there was a slower adsorption from the atmosphere above the film - in the following case of 1.34 m.m. in 40 minutes. There after the pressure change was negligible over a period of 50 minutes and this was taken as the steady state before commencement of illumination by the Osira lamp.

Wt. of $TiO_2$ (sample D) – 0.12g.

Volume of reaction vessel – 25.74 ml.

Sensitivity of gauge – 0.042 m.m./scale division.

Pressure of water vapour over film at steady state –

0.55 m.m.

| Time (Mins.) | Scale Reading | Time(Mins) | Scale Reading |
|---|---|---|---|
| 0 | 0.0 | 205 | 1.9 |
| 1 | 0.2 | 220 | 2.0 |
| 4 | 1.3 | 254 | 2.0 |
| 12 | 1.8 | 278 | 2.1 |
| 19 | 1.6 | 325 | 2.1 |
| 26 | 1.6 | LIGHT OFF | |
| 34 | 1.5 | 325 | 3.8 |
| 104 | 1.4 | 331 | 4.1 |
| 189 | 1.7 | 340 | 4.1 |

These results are plotted in Fig. 15.

(iii) Oxygen and Water Vapour.

Water Vapour was added to the reaction vessel as described in the previous experiment. Oxygen was then added under sufficient pressure to prevent any back-flow of the water vapour. At the end of each section of the run the apparatus was evacuated and fresh gases admitted the next day.

Wt. of $TiO_2$ (sample D) – 0.12g.

Volume of reaction vessel – 26.75 ml.

Sensitivity of gauge – 0.042 m.m/scale division

Approximate oxygen pressure at commencement of each run – 50 m.m.

" water vapour " " " – 1 m.m.

As there was a reaction of some magnitude the results are given and plotted (Fig. 16) as rates:-

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|------|------|------|------|------|------|
| 16.7 | 10.0 | 3.8 | 81.3 | 3.5 | 139.8 |
| 9.5 | 22.2 | 3.8 | 88.8 | 3.2 | 146.7 |
| 6.4 | 30.3 | 3.9 | 96.6 | 3.2 | 153.0 |
| 5.5 | 36.0 | 3.8 | 104.3 | 3.2 | 159.4 |
| 5.0 | 41.3 | E | E | E | E |
| 4.5 | 46.0 | 5.1 | 109.1 | 4.0 | 164.7 |
| 4.2 | 54.5 | 3.4 | 113.2 | 3.1 | 168.1 |
| E | E | 3.4 | 120.0 | 2.8 | 174.0 |
| 5.2 | 63.7 | 3.3 | 126.7 | 2.7 | 179.4 |
| 4.6 | 68.6 | E | E | 2.6 | 194.0 |
| 4.2 | 73.0 | 5.2 | 136.2 | | |

(iv) Carbon Dioxide.

When carbon dioxide, which had been purified by passing over yellow phosphorus to remove any oxygen, was illuminated over $TiO_2$ (sample D) by the Osira lamp there was no appreciable pressure change over a period of one hour.

With nitrogen, water vapour and carbon dioxide there was no reaction comparable to that obtained with oxygen and indeed such small reaction as exists is most probably due to oxygen traces.    In the case of the first two gases, there was a slight pressure decrease which showed an abrupt cessation (unlike the oxygen

reaction), followed by a long steady period.    A more

detailed analysis of these results, based on further

information, is made in the General Discussion.

When oxygen and water vapour were added to the

reaction vessel simultaneously the rate curve varied

from that obtained with dry oxygen in that the initial

fast portion was considerably reduced.    In other

respects it was similar.

## D. Conclusion

In this section the close relationship between the

extent of the pressure change on illumination in oxygen

and the photo-sensitising activity of various samples

of $TiO_2$ with respect to an oxidation reaction has been

established.

By demonstrating that the former reaction was con-

fined to oxygen and that it was not dependant on the

presence of various impurities (shown by elimination in

the preparation of samples) some further evidence has

been obtained with respect to the nature of the reaction.

However it was yet too soon to build a theory upon such

indirect evidence and the next section of work was

devoted to a study of various possible reactions - by

direct and detailed analysis of the reaction products

and the residual gas, if any.

## III TITANIUM DIOXIDE: NATURE OF REACTION

Having established that all the tested samples of
$TiO_2$ showed a pressure change when illuminated in oxygen,
it remained to locate the chemical or physico-chemical
cause of the pressure change.   This was investigated
from three approaches, as detailed below.

### A. Impurities Present in Samples.

The expected impurities may have entered the vari-
ous samples in two ways - being present in the
tetrachloride from which samples C to F were prepared
or being built into or on the structure during
preparation.

The most common example of the former type of
impurity was iron which is often present in samples
of $TiCl_4$.   It was for this reason that, previous to
hydrolysis, the tetrachloride was distilled in the case
of samples E and F.   The iron content of the samples
was estimated by boiling a quantity of the oxide with
concentrated HCl (A.R.) and testing the diluted filtrate
with potassium thiocyanate.   In the case of sample D
the characteristic red coloration was observed, but no
trace of any reddish tinge was apparent when sample F
was so treated.   It was concluded therefore that iron
was not an essential factor in the reaction.

During illumination it was noted that some samples

tended to darken;  this was especially noticeable with
samples C and D but was not observed with samples A
and B.   Further investigation showed that sample D
became tinged to this yellow-brown on light exposure
in vacuum, water vapour and nitrogen.  When these
darkened samples were kept in the dark for a period
they did not  appear to have regained much,  if any, of
their original white colour.   No pressure changes were
recorded during any such darkening in vacuo.

If the method of preparation of samples C to F is
studied, it can be seen that there are obvious con-
taminants which could be present:-  chlorides or
oxychlorides due to incomplete hydrolysis and washing
of the precipitate, nitride due to nitrogen uptake on
drying in air and water built into the lattice.

By oxidation, the first impurity would liberate
chlorine into the atmosphere and it should be possible
to detect this gas in the usual way.   0.12g of $TiO_2$
(sample D) was therefore illuminated in 50 m.m. oxygen
for 270 minutes at the end of which the gases were
pumped out over water contained in a trap cooled by
liquid oxygen.   The contents of the trap were then
brought to room temperature and tested for chlorine by
potassium iodide and starch.   A negative result was
obtained.

The presence of a nitride was suspected when a quantity of $TiO_2$ (sample D) was boiled with water and appreciable amounts of ammonia were evolved. Various samples were tested for the evolution of ammonia, therefore, by boiling with water and collecting the distillate in approximately $^N/100$ HCl. By back titration of this acid and distillate with approximately $^N/100$ NaOH, the quantity of ammonia evolved per gram of oxide sample tested could be calculated.

| SAMPLE | WT. OF SAMPLE | AMMONIA EVOLVED |
|--------|---------------|-----------------|
| D | (i) 0.204 | $2.09 \times 10^{-4}$ g. mol/g. $TiO_2$ |
| | (ii) 0.207 | $1.99 \times 10^{-4}$ g. mol/g. $TiO_2$ |
| | Mean | $2.04 \times 10^{-4}$ g. mol/g. $TiO_2$ |
| D(ignited) | 0.165 | $5 \times 10^{-7}$ g. mol * |
| F | 0.307 | $5 \times 10^{-7}$ g. mol * |

(* These values define the limit of experimental

sensitivity of the method used.)

Sample F, which showed a considerable pressure decrease on illumination in oxygen, did not appear to contain any source of ammonia which could be liberated on boiling. It was unlikely therefore that the oxidation of a nitride was the reaction resulting in a pressure change in this case.

With sample D, the results above merited further consideration on more detailed lines. On illumination, 0.014g of the sample showed a pressure decrease of

166 scale divisions in a reaction vessel of volume
26.75 ml, and with a gauge sensitivity of 0.042 m.m./scale
division. This pressure decrease corresponds therefore
to a material decrease in the gaseous phase of

$$\frac{166}{0.014} \times \frac{0.042}{760} \times \frac{26.75}{22400} \times \frac{273}{298} \text{ g.mol./g.TiO}_2.$$

$$= 7.17 \times 10^{-4} \text{g.mol/g.TiO}_2$$

By proposing a theoretical nitride of formula
$Ti_xNy$ the following relationships can be demonstrated;
on hydrolysis

$$Ti_xNy \rightarrow y NH_3.$$

i.e. 1 mol. of nitride gives y mols. ammonia.

∴ g.mols of nitride/g.TiO$_2$ = (g.mols. NH$_3$ evolved)/y — (1)

and on photo-oxidation

$$Ti_xNy + xO_2 \rightarrow x TiO_2 + y/2.N_2$$

i.e. 1 mol. of nitride gives rise to a pressure decrease

equivalent to $x - y/2$ g.mols.

∴ g.mols. of nitride/g.TiO$_2$ = (g.mols pressure decrease)/

$(x - y/2)$ — (2)

Then, assuming that the reaction proceeds to
completion in both cases, i.e. that all the nitride be
decomposed, the right hand sides of equations (1) and
(2) may be equated -

$$\frac{(g.mols\ NH_3\ evolved)}{y} = \frac{(g.mols.\ pressure\ decrease)}{(x - y/2)} \quad - (3)$$

Substituting the experimental results in (3) and
rearranging the equation becomes

$$(x - y/2) \times 2.04 \times 10^{-4} = y \times 7.17 \times 10^{-4}$$
$$\therefore \quad 2.04 \ x = 8.19 \ y.$$

$\therefore$ By approximation

$$x = 4y.$$

The theoretical nitride required to satisfy these
results would therefore be $Ti_4N$, which is far removed
from the only common stable nitride known for titanium
i.e. TiN.   Further, the oxidation of such a compound
to the dioxide as follows

$$Ti_4N + 4O_2 \rightarrow 4TiO_2 + \tfrac{1}{2}N_2$$

would result in a pressure decrease of $\tfrac{7}{8}$ (=0.875) of
the total oxygen present, provided that there was excess
$Ti_4N$ present.   This point is further investigated in
section IIIB, below.

On boiling a quantity of $TiO_2$ (sample D) with water
until no more evolved ammonia was detectable, drying
this material as for the bulk sample D and exposing
to light and oxygen in the usual way, the pressure time
curve was found to be of the same form and extent as
before although the initial rates were somewhat greater.
This, at first sight, seems to dispose of nitride as an
explanation of the decrease in pressure, but it is
possible that both light exposure in oxygen and boiling
in water affect only the outermost layers, probably to

different    extents such that no stoichiometric $N_2:O_2$
ratio would be obtained.    On the basis of this
explanation, it is necessary to assume that  boiling
with water 'opens up' the surface to oxygen on subse-
quent  illumination while not opening it up sufficiently
to permit further ammonia evolution on longer boiling.

While attempts to demonstrate the  production  of
$N_2$ were considered it was decided that the results detailed
in the next section (IIIB) provide an answer to this
question.

## B.  Illumination at Low Pressures

By defining the low pressures as of the range
0 - 2 m.m.(Hg) in volumes of circa 30 ml., it was
necessary to analyse accurately the oxygen content of
the cylinder oxygen used.    The method chosen was to
oxidise white phosphorus contained in a side tube on the
apparatus and to measure the pressure change with the
Bourdon gauge.    The phosphorus was contained in a tube
to replace vessel W (see Fig. 2, page 17), and the tap
$T_3$ was closed after evacuating this side arm.    The
remainder of the  apparatus was evacuated to $10^{-3}$ m.m.
and then taps $T_2$ and $T_9$ were cbsed.    Oxygen or air was
added through the appropriate taps and the pressure
increase was recorded by the gauge.    The tap $T_3$ was then
opened and the oxygen uptake measured by the travel of
the gauge pointer.

The method was tested by measuring the oxygen content of dry air and the results obtained, 0.211 and 0.208, (total sample of air being taken as 1.000) were in agreement with the literature[61], 0.210. Two samples of oxygen were used during these experiments - sample X which contained approximately 50% oxygen and sample Z (direct from the cylinder) which contained approximately 100% oxygen. By analysis as detailed above the accurate oxygen contents of these samples were -

Sample X, oxygen content = 0.472, 0.507, 0.500, 0.492

Mean = 0.495

Sample Z, oxygen content = 0.953, 0.963, 0.995, 0.989

Mean = 0.975

When working at these low oxygen pressures over illuminated $TiO_2$, the oxygen added was measured in the manner described above. A typical example of the pressure change vs time curves (which were similar for oxygen samples Z and X) is shown in Fig. 17. These results were obtained on illuminating 1.08 m.m. (25.8 scale dividions) oxygen, sample X, over 0.12g $TiO_2$ sample D by the Osira lamp.

FIG 17

T.O₂(D) IN O₂ : LOW PRESSURES.



FIG 18

CONTINUOUS FLOW APPARATUS.
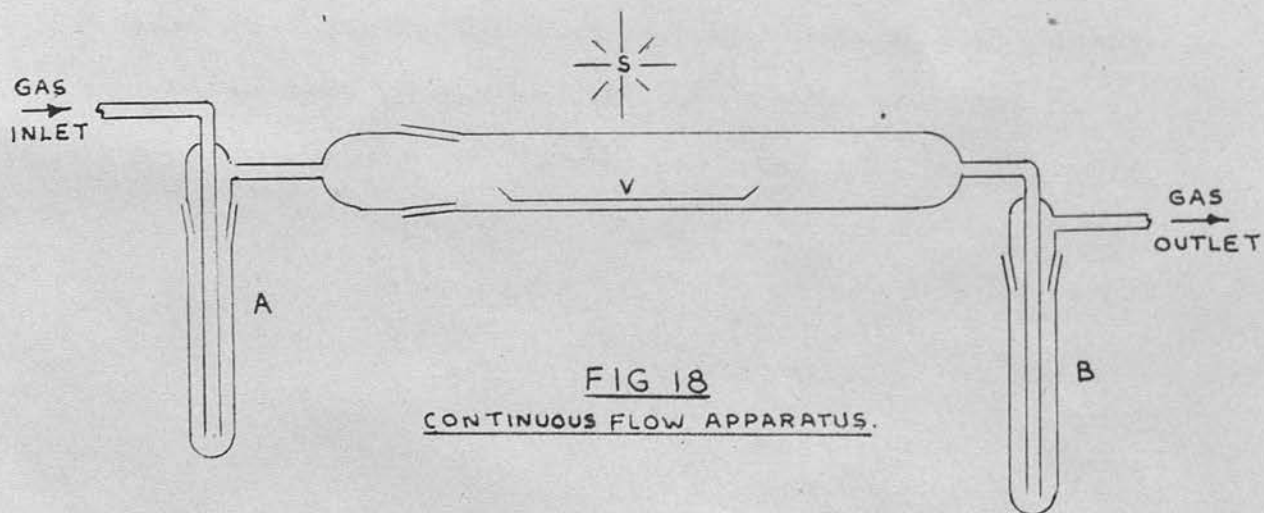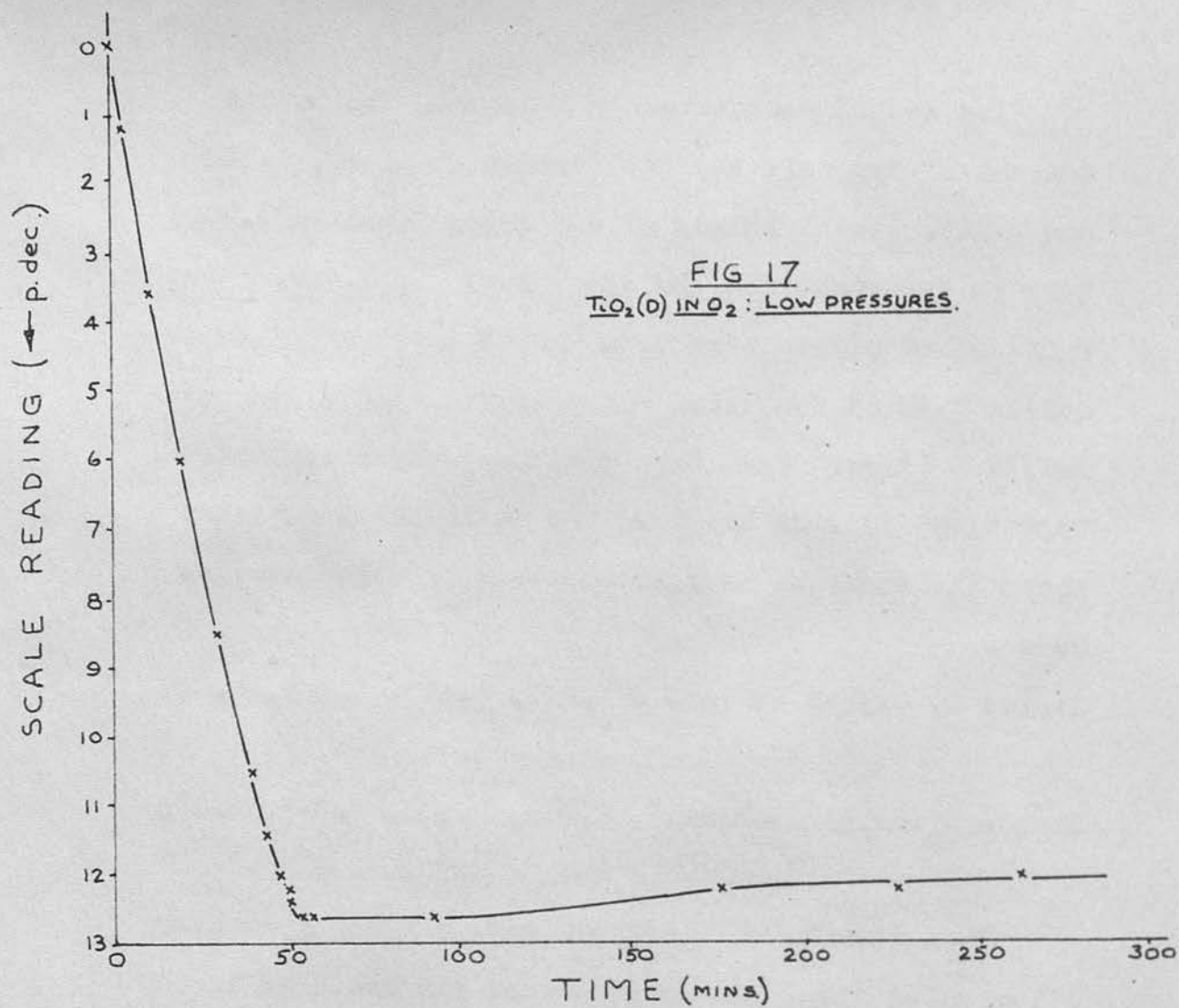
| Time (Mins.) | Scale Reading | Time (Mins.) | Scale Reading |
|---|---|---|---|
| 0 | 0.0 | 51 | 12.2 |
| 3 | 1.2 | 53 | 12.4 |
| 11 | 3.6 | 55 | 12.6 |
| 20 | 6.0 | 58 | 12.6 |
| 30 | 8.5 | 93 | 12.6 |
| 40 | 10.5 | 177 | 12.2 |
| 44 | 11.4 | 228 | 12.2 |
| 48 | 12.0 | 264 | 12.0 |

If a further quantity of oxygen was now added,
there was an immediate pressure decrease on re-illumination.

On examining these results, the following relation-
ship was established viz. that on illumination the
maximum pressure change (i.e. before the final small
increase in pressure occurred) was equal to the oxygen
content of the gas examined.   This is shown in the
results below

(a) Oxygen sample X;  $TiO_2$, sample D, 0.12g.

(b) Oxygen sample Z;  $TiO_2$, sample D, 0.12g.

| | TOTAL PRESSURE Before Illum[n.] (m.m.Hg) | GAS ADDED (m.m.Hg) (A) | PRESSURE CHANGE (m.m.Hg) (B) | RATIO B/A |
|---|---|---|---|---|
| (a) | 1.083 | 1.083 | 0.528 | 0.487 |
| | 1.810 | 1.810 | 0.898 | 0.497 |
| | 1.417 | 0.505 | 0.253 | 0.502 |
| | 1.579 | 0.415 | 0.201 | 0.484 |
| | | | Mean | 0.493 |
| (b) | 0.898 | 0.898 | 0.869 | 0.968 |
| | 0.892 | 0.873 | 0.848 | 0.970 |
| | | | Mean | 0.969 |

The relationship was checked for various other samples and the following results show that it is valid in all cases. i.e. ratio of pressure change (p.ch.) to initial oxygen pressure (p.$O_2$.) approaches unity.

| SAMPLE OF $TiO_2$ (0.12g) | RATIO p.ch/p.$O_2$. |
|---|---|
| D(water bound) | 0.997 |
| D(boiled in water to remove $NH_3$) | 1.012 |
| E(acetone bound) | 1.006 |
| E(water bound | 1.010 |
| F(water bound) | 1.048 |

This ratio was also tested over a wide range of the reaction and was found to remain constant throughout.

| SAMPLE OF $TiO_2$ (0.12g) | PREVIOUS ILLUM[n]. (mins) | RATIO p.ch/p.$O_2$. |
|---|---|---|
| D | NIL | 0.997 |
| E | 380 | 0.997 |
| E | 787 | 1.013 |

The effect of adsorbents in a side-arm attached to the reaction vessel was also investigated with 0.12g $TiO_2$ sample D illuminated in oxygen sample X.

| ABSORBENT | RATIO p.ch./p.$O_2$ |
|---|---|
| Soda lime | 0.972, 1.011, 0.993 Mean = 0.992 |
| Phosphorus pentoxide | 0.972, 0.963 Mean = 0.968 |

The presence of these absorbents did not alter the ratio obtained.

It may here be noted that such a method affords a reliable determination of the oxygen content of an otherwise inert gas such as $N_2$, with a sensitivity only limited by the sensitivity of the gauge.

## C. Production of an Oxidising Agent by Illuminated $TiO_2$.

A further impurity which may have been present was water trapped within the crystal lattice and which may be oxidised to $H_2O_2$, thus explaining the sensitising properties. This view was consistent with the effect of 'drying' (by ignition) samples of the oxide. However as is shown below, no direct evidence of the presence of $H_2O_2$ was obtained.

Several of the films of $TiO_2$ illuminated by the Osira lamp in 50 m.m. oxygen were extracted with water and filtered. These filtrates were tested for hydrogen peroxide by the perchromic acid [62] and Beningis tests. [63] Although this latter test, which depends on the formation of $Ag_4 Fe(CN)_6$ is sensitive to 1 m.g. $H_2O_2$ per litre, in no case was any positive result obtained.

Illumination of a suspension of ZnO in water, through which air is bubbled, gives appreciable quantities of hydrogen peroxide within a few minutes. The experiment was repeated with $TiO_2$ (sample C) replacing the ZnO and the liquid was tested for hydrogen peroxide. It was found difficult to remove all the traces of the oxide from the test sample but when tested with $FeSO_4$

and KCNS in methyl alcohol, no positive reaction was observed.

A series of experiments was made, using the apparatus shown in Fig. 18 which permitted study of the oxidising agent formed under continuous flow conditions. In each case the small silica vessel (v) was filled with $TiO_2$ (sample B) and illuminated from above by an Osira lamp. The oxygen used was passed directly in tube A from a B.O.C. cylinder. The following results were observed :-

(i) Oxygen passed over damp starch-iodide paper replacing the $TiO_2$ in vessel V. This test paper showed a slight blue coloration after 3 hours.

(ii) Oxygen was passed over dampened $TiO_2$ which was in contact with a piece of starch iodide paper. Illumination for 1 hour gave a dark blue stain on those portions of the test paper uncovered by the oxide.

(iii) Oxygen was again passed over dampened $TiO_2$ but in this case the test paper was removed to a distance (near edge) of 2 - 3 cms. from the vessel V on the gas outlet side. After 1.5 hours illumination only a faint blue tinge was apparent on the starch iodide paper.

(iv) Although the sample of $TiO_2$ was not treated in any special manner care was taken to dry the gas passing over it. This was achieved by passing it through conc. $H_2SO_4$ contained in tube A and then over $P_2O_5$ before reaching

the vessel V.   The test paper which was again in direct
contact with the oxide showed a yellow coloration on
the uncovered portions after a run of 3 hours.   These
yellow stains became blue on dampening.

(v) The same experimental conditions used for run (iv)
were repeated except that the outlet gas was passed
through a solution of $FeSO_4$ and KCNS in methyl alcohol
contained in tube B.   A run of 10 hours saw the con-
tents of this tube become yellowish orange - only
slightly deeper in color than a control tube which stood
exposed to air for the same period.

## D. Conclusion

The work described above has eliminated iron,
chlorine (as oxychloride) and nitrogen (as nitride or
ammonia) as being essential to the reaction resulting
in a decrease in oxygen pressure.   No direct evidence
has been obtained in the case of water however and it
is left for consideration in the General Discussion.
In the low pressure experiments, the absence of any
considerable residual pressure after illumination has
been shown for a variety of samples and thus there was
no possibility of any gaseous reaction product.   These
results have also shown that there was a dependance of
the reaction velocity on the oxygen pressure at the
lower pressures used.   The rate curves for such
experiments showed such a similarity (in the sharp

cessation of the reaction) to those obtained with nitrogen (page 47) and water vapour (page 48), that they suggest the presence of traces of oxygen as the cause of the pressure decrease in these two cases.

It has already been shown that there were no gaseous reaction products but the identification of any product in the solid phase was not conclusive. A darkening of the surface of the samples on illumination suggested the formation of a peroxide (by reference to the well known test for $H_2O_2$) but treatment such as ignition and illumination in vacuum also produced a darkened product. Further to this, no peroxide was detected with any sample of $TiO_2$ when tested in any of three ways – (a) by extraction of illuminated films, (b) illumination of aqueous suspensions and (c) by the passage of oxygen over wet or dry oxide samples. The latter method gave ample evidence of the formation of a short life, very active, oxidising agent produced in the vicinity of $TiO_2$ on illumination.

The evidence presented to date suggested that the most likely reaction appeared to be between the oxygen and the oxide. On this basis further investigation of the various parameters is given in the following sections.

## IV TITANIUM DIOXIDE: PHYSICAL VARIABLES.

### A. Variation of Oxygen Pressure.

A film of 0.12g $TiO_2$ (sample C) using acetone
(A.R.) as the binding liquid was illuminated in approxi-
mately 50 m.m. oxygen for a period of 20 minutes.
The illumination (Osira lamp) was then cut off and part
of the oxygen removed by the Hyvac pump, the remainder
being re-illuminated for a similar period. This cycle
was repeated until the oxygen pressure was reduced to
4 m.m. when the gauge and compensating jackets were
evacuated to approximately $10^{-3}$ m.m. Oxygen was then
added to the reaction vessel only. This caused
the pointer to move over 12.4 scale divisions which
with a gauge sensitivity of 0.033 m.m/scale division
is equivalent to 0.41 m.m. The film was then
re-illuminated as above.

FIG 19.

TiO_2(b), VARIATION IN OXYGEN PRESSURE.

[BROKEN CURVE INDICATES COMPARABLE
READINGS FOR REACTION AT 49±1 m.m.]
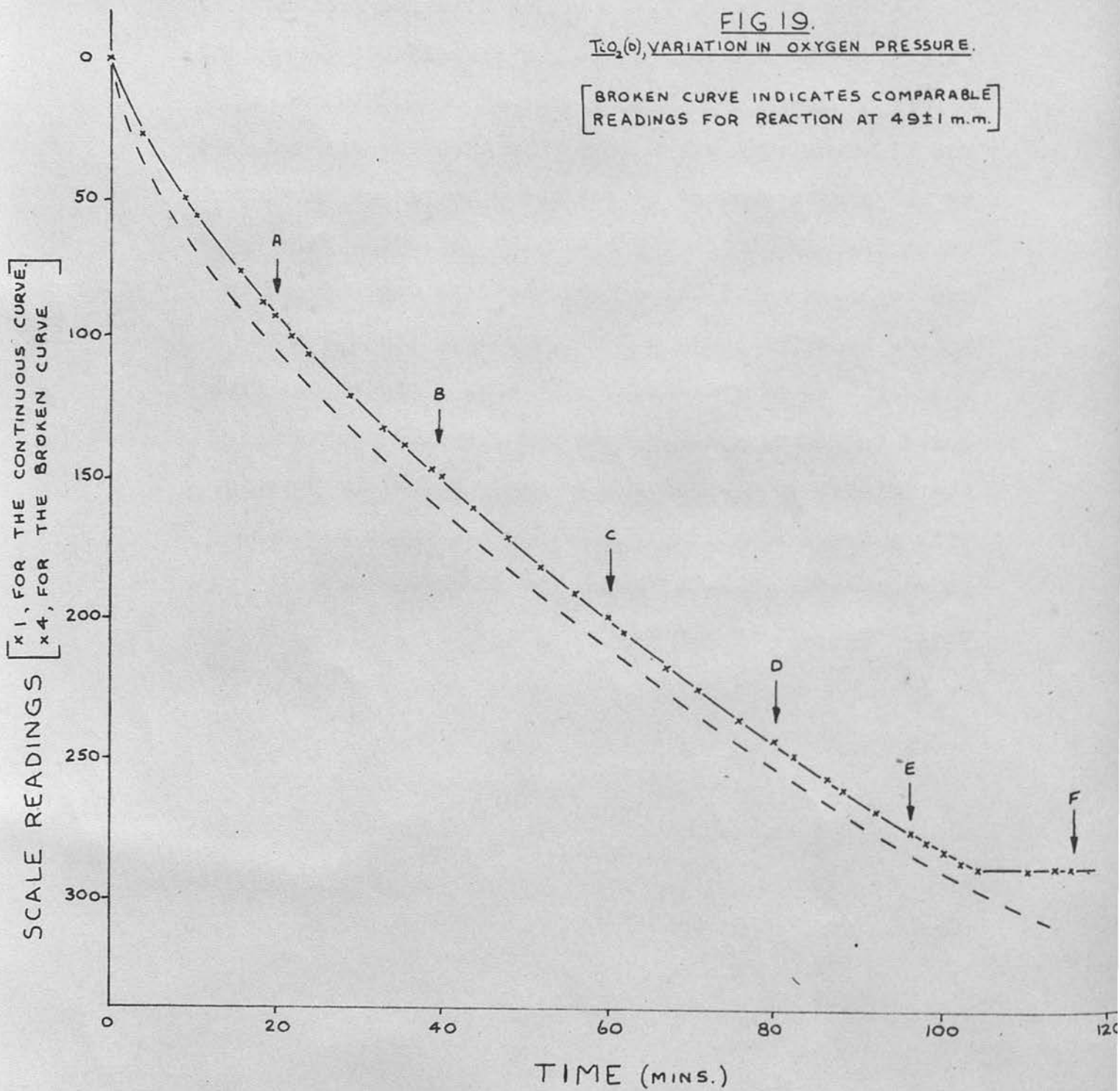
The results obtained were –

| Time (mins.) | Scale Reading | $O_2$ Press. m.m. | Time (mins.) | Scale Reading | $O_2$ Press. m.m. |
|---|---|---|---|---|---|
| 0 | 0 | | 62 | 204.9 | |
| 4 | 27.3 | | 67 | 216.8 | 8.0 |
| 9 | 49.8 | 49.1 | 71 | 225.6 | (CD) |
| 10.5 | 56.5 | (OA) | 76 | 236.2 | |
| 15.5 | 76.0 | | 80 | 244.4 | |
| 18.5 | 87.0 | | 82 | 249.2 | |
| 20 | 92.0 | | 86 | 256.3 | 4.0 |
| 22 | 99.6 | | 88 | 260.4 | (DE) |
| 24 | 105.8 | | 92 | 268.5 | |
| 29 | 121.0 | 25.6 | 96 | 276.6 | |
| 33 | 132.4 | (AB) | 98 | 279.8 | |
| 35.5 | 138.6 | | 100 | 283.0 | |
| 39 | 147.8 | | 102 | 286.7 | 0.41 |
| 40 | 150.0 | | 104 | 288.6 | (EF) |
| 44 | 161.7 | | 110 | 289.0 | |
| 48 | 172.2 | 16.3 | 113 | 289.0 | |
| 52 | 182.2 | (BC) | 115 | 289.0 | |
| 56 | 191.5 | | | | |
| 60 | 200.1 | | | | |

These results are plotted in Fig. 19 along with a
curve constructed from the readings obtained from a
similar film illuminated at a pressure maintained at
$49\pm 1$ m.m. oxygen (broken line). From the similarity
of the two curves it was concluded that the rate of pressure

change was independent of the oxygen pressure over the range 50 m.m. to the break in section E.F. which occurred at a pressure $<0.1$ m.m.

## B. Variation of Light Source.

The light sources available were an Osram Tungsten filament lamp and an Osira mercury vapour lamp. Their characterisitcs have been discussed previously (page 22).

0.12 g of $TiO_2$ (sample C) was made into a film and was illuminated by the two lamps in turn. The following rates were observed in 50 m.m. oxygen.

| LAMP | $R_{30.}$ | $\Sigma p.ch.$ |
|---|---|---|
| Osira | 54.0 | 35.0 |
| Osram | 2.8 | 55.8 |
| " | 2.3 | 58.0 |
| " | 2.3 | 60.2 |
| " | 2.3 | 62.6 |
| " | 2.3 | 64.9 |
| " | 2.2 | 67.1 |
| " | 2.3 | 69.3 |
| Osira | 42.0 | 95.0 |

These results indicated that the effective light was of wavelength less than 4000 Å, i.e. those wavelengths absorbed by $TiO_2$.

## C. Variation of Light Intensity

As there is no part of the reaction where the rate

remains constant or follows a straight line the
following method of ascertaining the effect of this
variable was adopted.    A wooden frame was inserted
between the light source and the reaction vessel.    It
was so constructed that it held the filters directly
in the light path but did not interfere with the latter
itself.    During the experiment the rate without any
interposed filters was obtained over a period.    A
filter was inserted and the rate again calculated.
This alternate exposure, with and without the filter,
was repeated until results had been obtained for each
filter.

The usual rate curve was drawn from the results
obtained with the frame only in position, the missing
portions being filled in by extrapolation.    For each
filter, the rate $(R_{30})$ and the total pressure change
at the midpoint of the period of illumination were
calculated.    From the rate curve the equivalent rates
for 100% transmission were obtained and thus the relative
rates determined.

Goodeve's results on the absorption limits of $TiO_2$
and the results given directly above indicate that only
light of wavelength less than 4000 Å was active.    As
the Osira lamp was used in these experiments, by far the
greatest light absorption by the oxide  will be of the
3650 Å Mercury line.    The percentage transmission was
therefore calculated for this line, for the following
Chance Neutral Filters, from previous calibrations.[64]

FIG 20.
$TiO_2$(D), VARIATION IN LIGHT INTENSITY.

FIG 21.
$TiO_2$(D), VARIATION IN FILM SIZE.
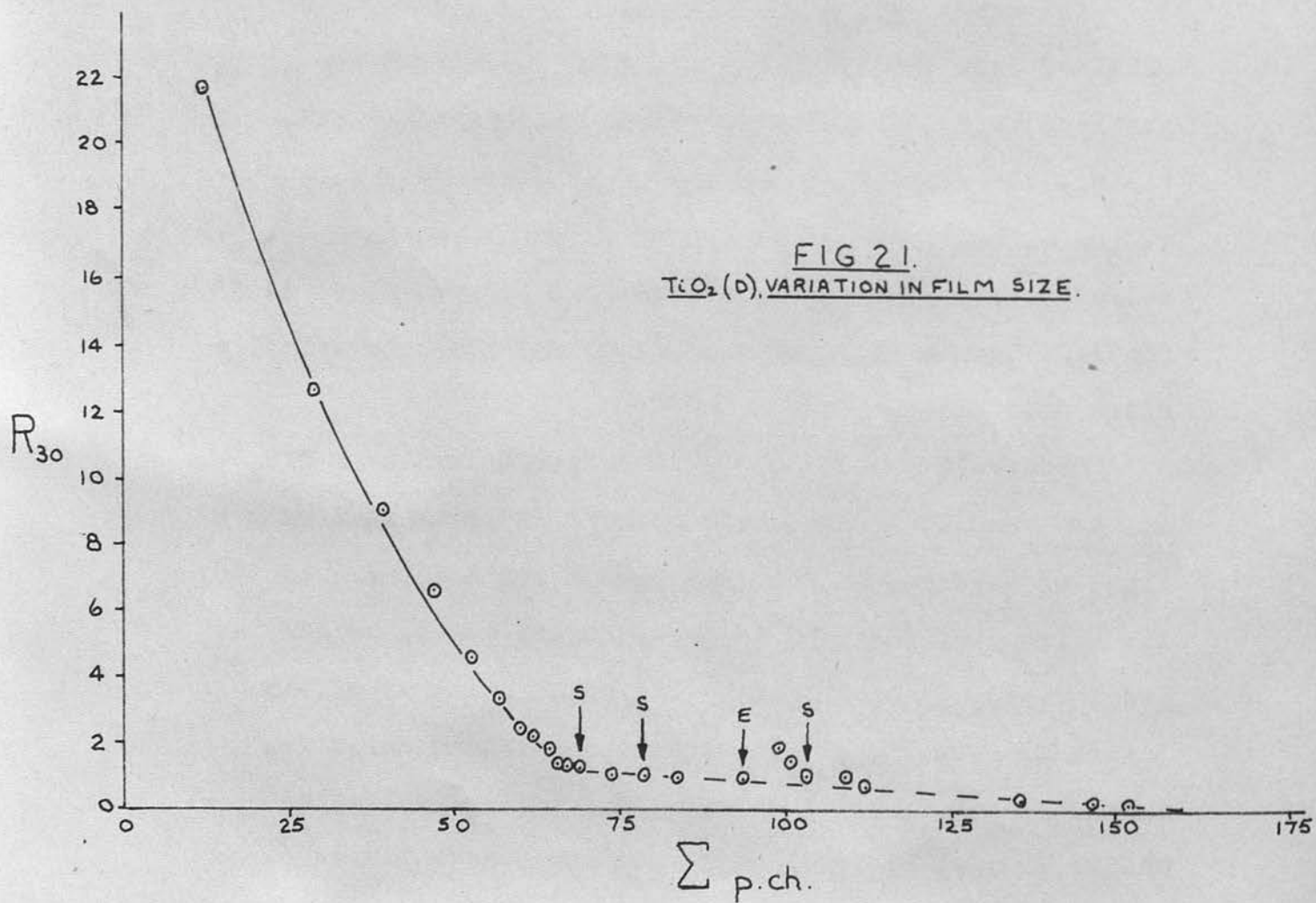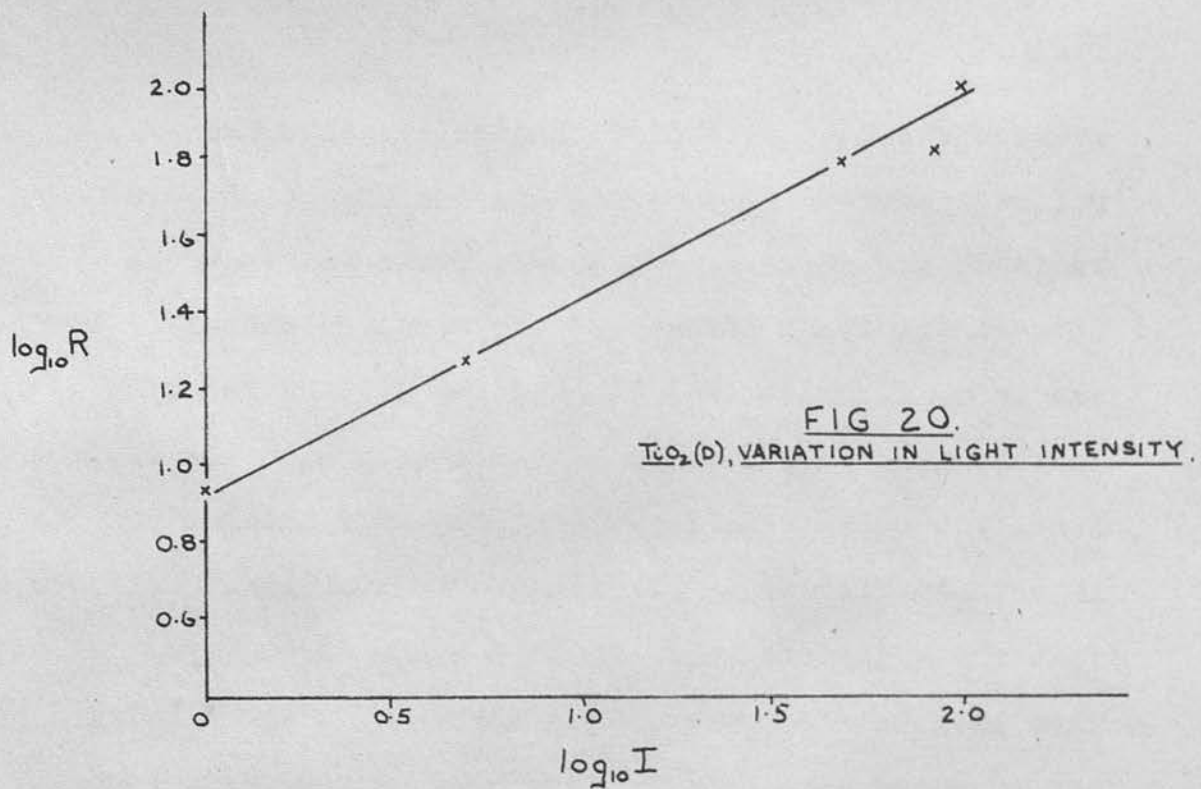
| FILTER | % TRANSMISSION (3650 $\overset{\circ}{A}$) |
|--------|------------------------------------------|
| Chance ON 10 | 1.0 |
| " ON 30 | 5.0 |
| " ON 33 | 50.0 |
| " ON 19 | 88.0 |

The results obtained on illumination were :-
(where I = incident light intensity.)

| % TRANSMISSION (I) | % RELATIVE RATE (R) | $LOG_{10}$ I | $LOG_{10}$ R |
|--------------------|---------------------|--------------|--------------|
| 1.0 | 8.7 | 0.00 | 0.94 |
| 5.0 | 19.0 | 0.70 | 1.28 |
| 50.0 | 63.7 | 1.70 | 1.80 |
| 88.0 | 85.7 | 1.94 | 1.93 |
| 100.0 | 100.0 | 2.00 | 2.00 |

When the $\log_{10}$I is plotted against $\log_{10}$R (Fig. 20) the following relationship is obtained from the resulting straight line.

$$\log_{10}R = 0.52 \ \log_{10}I + const.$$
$$\therefore \ R = K.I^{0.52}$$

where k is a constant.

Since the reaction is a slow one which can involve only the outer layers of the $TiO_2$ lattice, with a low absorption coefficient, the light energy absorbed will be proportional approximately to the incident light intensity; accordingly the index in the equation

$$R = k' \ I^n_{abs.}$$

will not be equal to unity and the reaction is probably not a simple one.

## D. Variation of Film Size.

Most of the films used contained approximately
0.12g. of substrate, as this quantity was found to give
an even film over the rear face of the reaction vessel.
To find the effect of drastically reducing this amount
of substrate, a film was made with approximately one-
tenth of the usual quantity of $TiO_2$ but was treated in
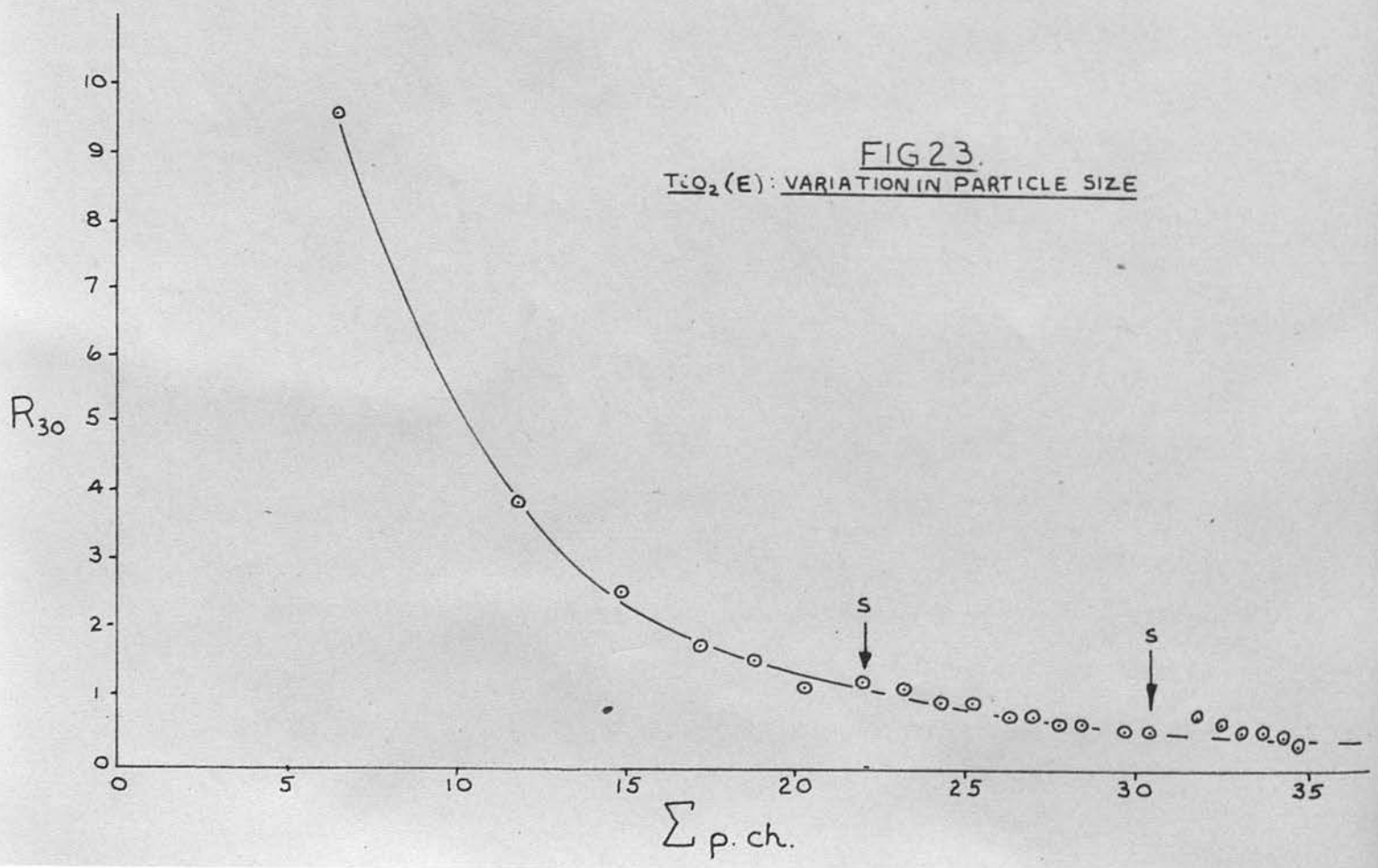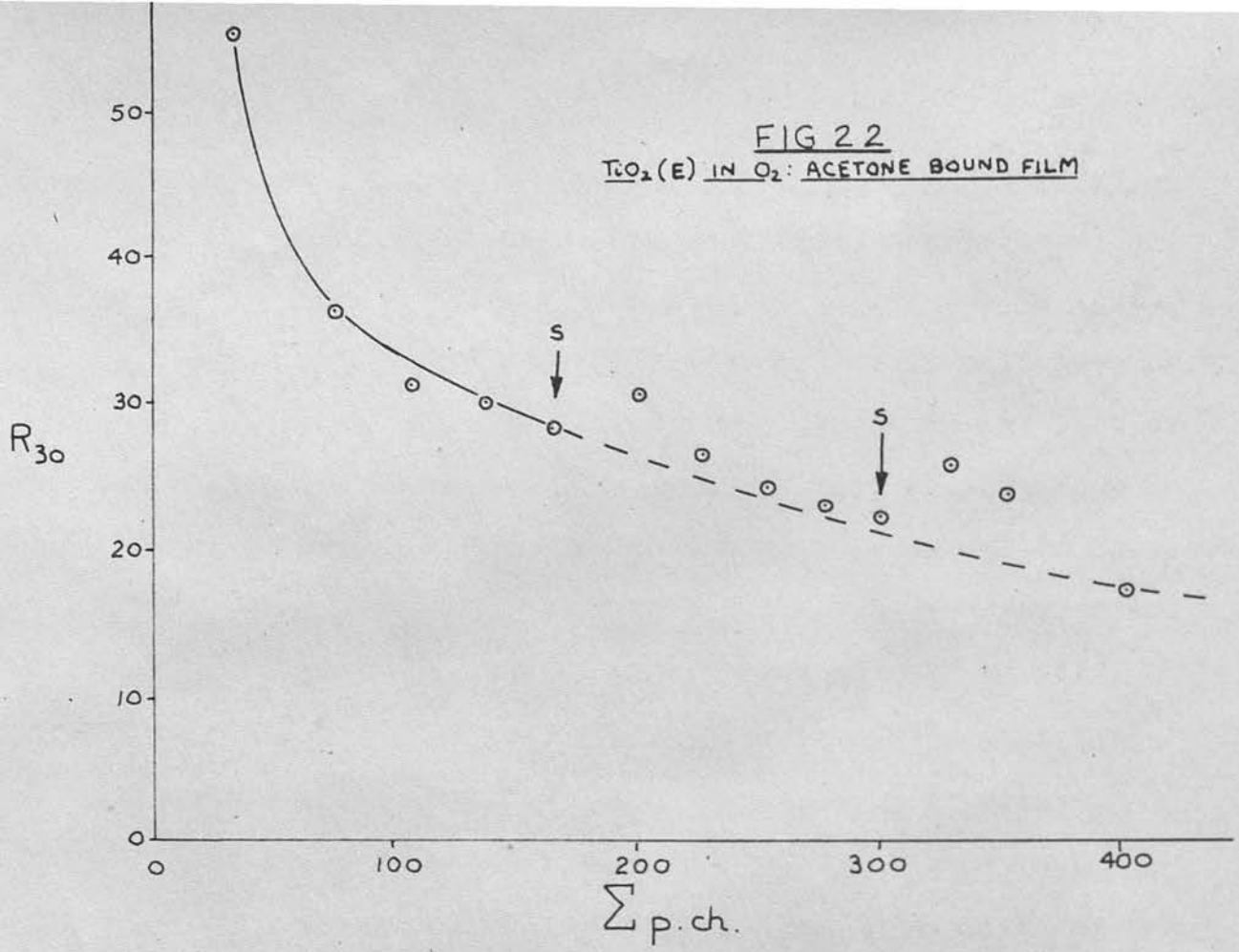the normal way in other respects.

Wt. of $TiO_2$ (sample D)  —  0.014g.

Volume of reaction vessel—  26.75 ml.

Sensitivity of gauge  —  0.042 m.m./Scale division.

The results obtained were calculated as rates $(R_{30})$
and the following figures were plotted in Fig. 21.

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|---|---|---|---|---|---|
| 21.7 | 12.3 | 1.3 | 66.5 | 1.5 | 100.6 |
| 12.7 | 28.6 | 1.25 | 68.7 | 1.0 | 103.1 |
| 9.0 | 39.0 | S | S | S | S |
| 6.6 | 46.8 | 1.05 | 73.6 | 1.0 | 109.5 |
| 4.6 | 52.5 | 1.05 | 78.5 | 0.7 | 112.1 |
| 3.4 | 56.4 | S | S | 0.7 | 116.3 |
| 2.5 | 59.4 | 1.0 | 83.7 | 0.3 | 135.7 |
| 2.2 | 61.8 | 0.9 | 93.5 | 0.25 | 146.4 |
| 1.9 | 63.8 | E | E | 0.15 | 151.6 |
| 1.4 | 65.3 | 1.8 | 99.0 | | |

With this smaller amount of $TiO_2$, an approximately
linear relationship exists finally between the rate and
the total pressure decrease.  On evacuation, rates are

FIG 22
$TiO_2$ (E) IN $O_2$: ACETONE BOUND FILM

$R_{30}$

$\Sigma$ p.ch.



FIG 23.
$TiO_2$ (E): VARIATION IN PARTICLE SIZE

$R_{30}$

$\Sigma$ p.ch.

initially higher, but return to the expected values.
As expected from the smaller light absorption, the small
amount of $TiO_2$ is accompanied by a correspondingly
lower rate of pressure decrease.

### E. Variation in Binding Liquid

Two liquids were used during these experiments
for binding the oxides to the surface of the reaction
vessel – namely, water and acetone (A.R.).   When the
latter was used a marked increase in the rate of pressure
change was recorded.   To enable direct comparison to be
made, two films were prepared, one with each binding
liquid, and were illuminated in identical conditions.
The results obtained were (a) water bound film
(0.121g $TiO_2$, sample E):  Fig. 11.

| $R_{30}$ | $\Sigma p.ch.$ | $R_{30}$ | $\Sigma p.ch.$ | $R_{30}$ | $\Sigma p.ch.$ |
|------|------|------|------|------|------|
| 10.1 | 6.7 | 1.4 | 28.1 | E | E |
| 4.6 | 12.7 | 1.3 | 29.5 | 2.9 | 37.5 |
| 3.8 | 16.7 | 1.2 | 30.8 | 1.0 | 38.9 |
| 3.3 | 20.3 | 1.1 | 31.9 | 0.6 | 39.6 |
| 2.2 | 23.0 | 1.0 | 33.0 | 0.4 | 40.1 |
| 1.8 | 24.9 | 0.9 | 33.9 | 0.4 | 40.9 |
| 1.6 | 26.6 | 0.8 | 34.8 | 0.3 | 41.3 |

(b) Acetone bound film (0.118g $TiO_2$, Sample E): Fig.22.

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|------|------|------|------|------|------|
| 55.3 | 33.0 | 30.7 | 201.9 | 25.8 | 331.0 |
| 36.4 | 74.5 | 26.6 | 229.0 | 23.9 | 354.9 |
| 31.3 | 107.1 | 24.4 | 254.8 | 17.3 | 403.0 |
| 30.2 | 137.9 | 23.2 | 278.5 | | |
| 28.4 | 168.3 | 22.4 | 301.1 | | |
| S | S | S | S | | |

It was demonstrated that the preparation of a film with acetone rather than water resulted in a great increase in the reactivity of the sample. It was shown in the previous section (p. 60) that there was no gaseous reaction product evolved as would be expected from the oxidation of residual acetone while the magnitude of the increase was also in contradiction of this possibility. The alternative suggestion was therefore accepted i.e. that the effect is due to some physical adsorption or solubility factor whereby the surface is altered in relation to the oxygen uptake reaction.

## F Variation in Particle Size.

A quantity of the prepared sample E was further finely ground in an agate mortar until it appeared to be, visually, of a much finer texture than the bulk sample. 0.12g. of this finely ground oxide was made into a film with water and as the conditions of the experiment are identical, the results (Fig. 23) may be compared directly with these obtained for the water

bound film in section E above (Fig. 11).

| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
|------|------|------|------|------|------|
| 9.6 | 6.4 | 1.2 | 23.1 | 0.6 | 30.3 |
| 3.9 | 11.8 | 1.0 | 24.2 | S | S |
| 2.6 | 14.8 | 1.0 | 25.1 | 0.8 | 31.7 |
| 1.8 | 17.1 | 0.8 | 26.2 | 0.7 | 32.4 |
| 1.6 | 18.7 | 0.8 | 26.9 | 0.6 | 33.0 |
| 1.2 | 20.2 | 0.7 | 27.7 | 0.6 | 33.6 |
| 1.3 | 21.9 | 0.7 | 28.3 | 0.5 | 34.2 |
| S | S | 0.6 | 29.6 | 0.4 | 34.6 |

There is little difference between the two sets
of results.    This was taken as proof that the macro
surface configuration, i.e. relatively small changes
in surface area due to the use of a finer ground oxide,
did not influence the results materially.    As none
of the prepared samples were ground to a standard size,
this result allowed them to be compared directly.

## G. Temperature.

The study of the temperature effect was difficult
because of the irreproducibility of the rates with
different films.    Thus the variation of rate with
temperature was observed on one film with the temperature
change accomplished as quickly as possible.    Owing to
the experimental factor, the range in temperatures
studied was   limited to approximately $40^{\circ}C$ - the lower

FIG. 24.

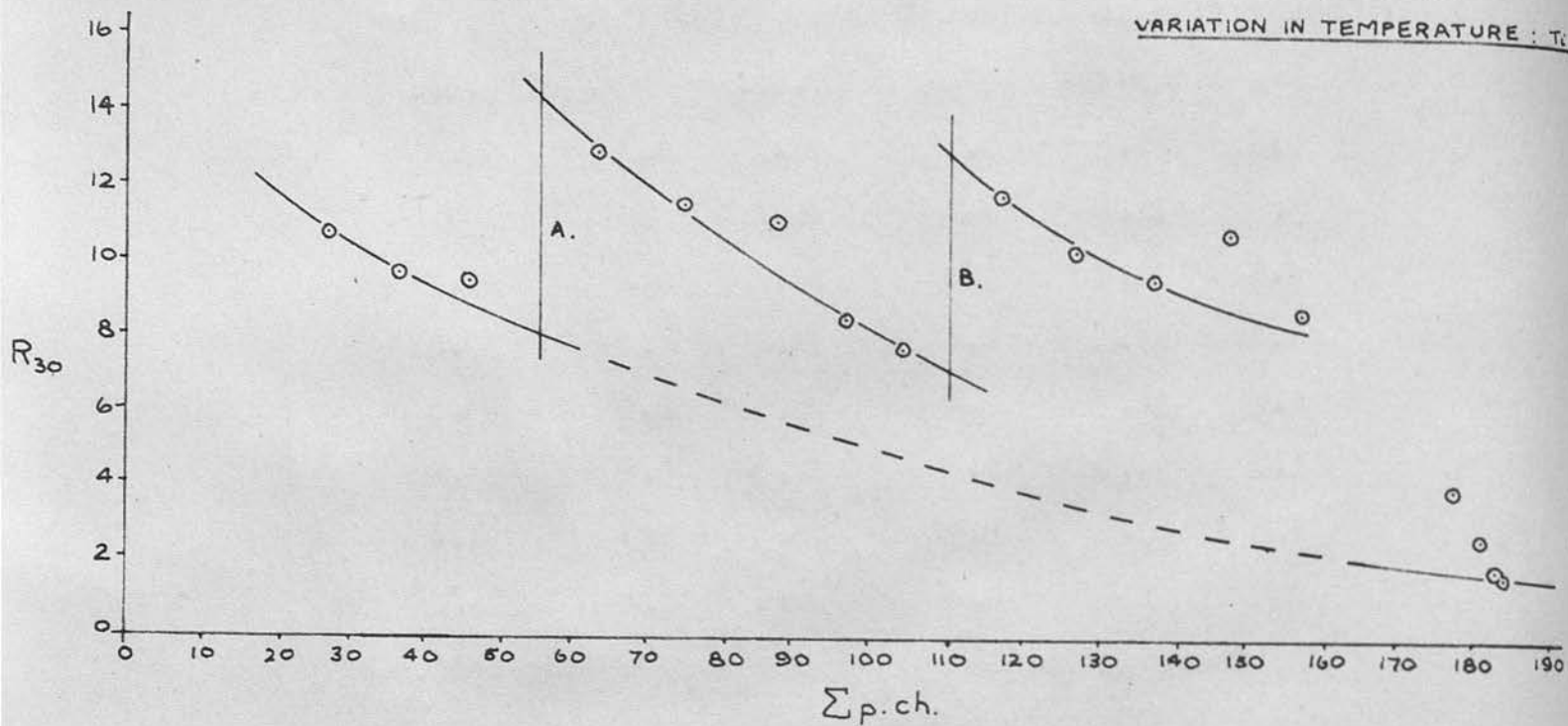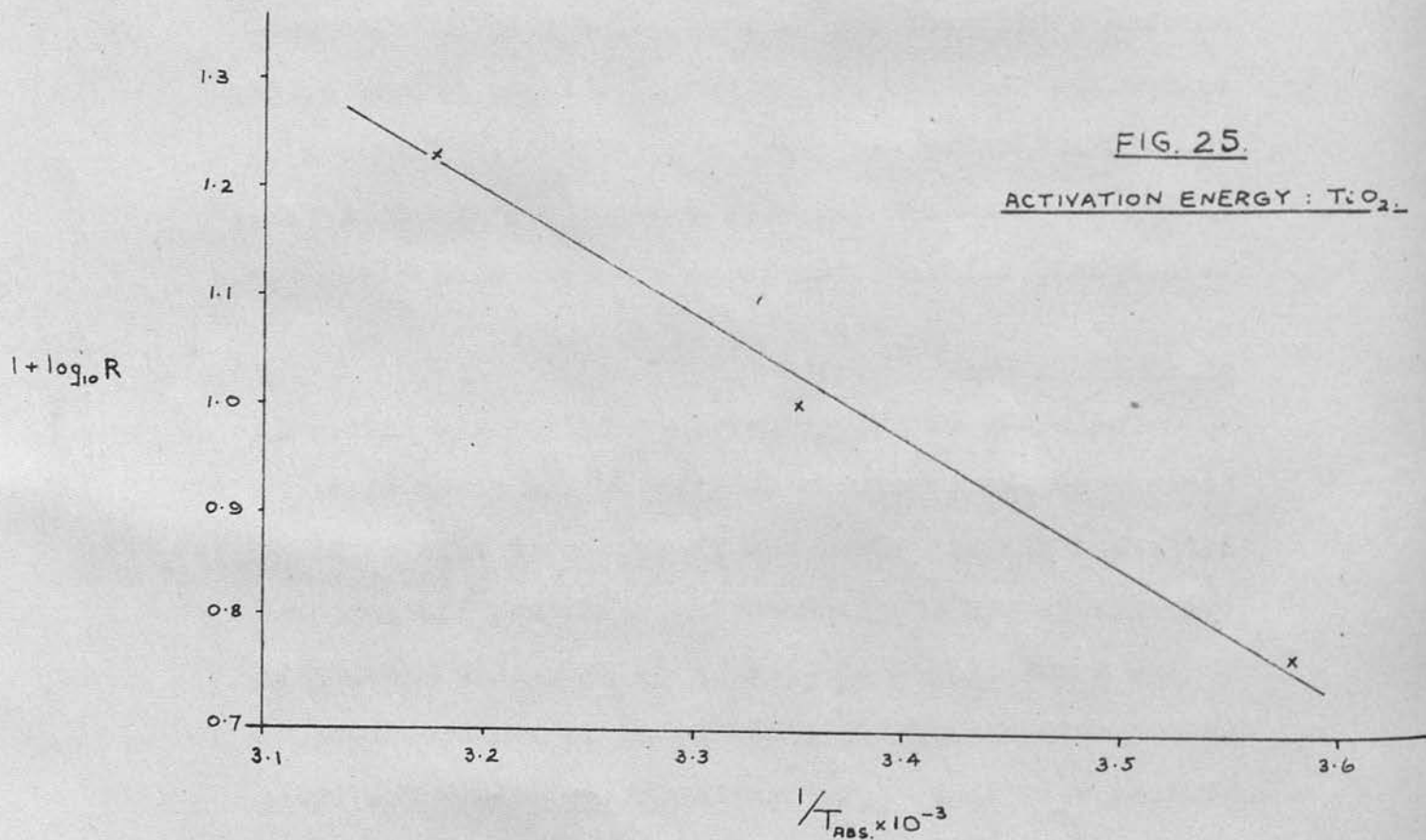VARIATION IN TEMPERATURE : $TiO_2$



FIG. 25.

ACTIVATION ENERGY : $TiO_2$

limit of 6°C being the lowest temperature easily maintained constant and the upper limit of 40°C being the highest attainable without undue softening of the Apiezon grease.

To help with the comparison of rates the initial steep part of the curve was "burned out" by illumination and the results obtained were confined to the lower more linear section. The experimental procedure was the normal manner described above except that at three points the illumination was cut off, the temperature control was reset for the new temperature and on thermostatic conditions being attained the film was re-illuminated.

The following rates were obtained and plotted in Fig. 24.

| TEMP ± 278.9°A | | TEMP = 298.5°A | | TEMP = 314.1°A | |
|---|---|---|---|---|---|
| $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. | $R_{30}$ | $\Sigma$p.ch. |
| 10.7 | 27.1 | 12.8 | 63.2 | 11.7 | 117.2 |
| 9.6 | 36.5 | 11.4 | 74.7 | 10.2 | 127.7 |
| 9.4 | 45.9 | S | S | 9.5 | 137.3 |
| | | 11.0 | 87.1 | S | S |
| 4.0 | 177.4 | 8.4 | 96.4 | 10.7 | 147.4 |
| 2.7 | 180.9 | 7.6 | 104.2 | 8.6 | 156.7 |
| 1.9 | 183.1 | | | | |
| 1.7 | 184.9 | | | | |

The increase in rate on standing in the dark for 14+ hours in 50 m.m. oxygen is shown to be small

compared with the increase due to a change in temperature. Therefore the increase in rates during the short period (1 - 2 hours) of darkness due to period required to reach thermostatic conditions was neglected in drawing the graph.

From these results it is possible to calculate the apparent energy of activation of the reaction. This energy (E) at any temperature ($T^{o}A$) is given by the equation -

$$\text{Rate} = k.e^{-E/R^T}$$

where k is a constant and R is the gas constant.

$\therefore \log_e (\text{Rate}) = \log_e K - E/R^T.$

Thus by plotting $\log_{10}$ (Rate) vs. $1/T$, the resultant straight line has a slope equal to $E/2.303R$

$\therefore E = \text{slope} \times 2.303 \times 1.99 \text{ cals.}$

From Fig. 24 by taking the rate at $298.5^{o}A$ as unity the relative rates at the other temperatures were calculated - at point A for $278.9^{o}A$ and at point B for $314.1^{o}A$. As the rates were measured as changes in pressure at different temperatures it was necessary to bring these values to the corresponding values at $273^{o}A$ by multiplying by the corresponding factors.

|  | TEMP. ($T^{o}A$) | RATE at $T^{o}A$ | EQUIV. RATE at $273^{o}A$ | RELATIVE RATE (R) |
|---|---|---|---|---|
| POINT A | 278.9 | 7.8 | 7.73 | |
|  | 298.5 | 14.3 | 13.08 | 0.59 |
| POINT B | 298.5 | 7.1 | 6.49 | |
|  | 314.1 | 12.7 | 11.03 | 1.70 |

From these results it can be seen that the rate increased with increase in temperature.

The corrected calculated values were therefore —

| RELATIVE RATE AR | TEMP. (T°A) | $4 + \log_{10}$ | $\frac{1}{T}$ |
|---|---|---|---|
| 0.30 | 478.9 | 6.77 | 2.09 x 10⁻³ |

FIG 26.

This is very small, in general, of the same type as Titanium Dioxide. The typical pressure change vs. time curve has already been given (p.38) and when replotted as a rate curve these results appear to allow of extrapolation of the total pressure change, as shown in Fig. 26. The value for this run was scale divisions with a reaction vessel of volume = 56.70 ml. and a gauge sensitivity of 0.033 m.m./scale division.

FIG 26.
ZnO IN $O_2$.
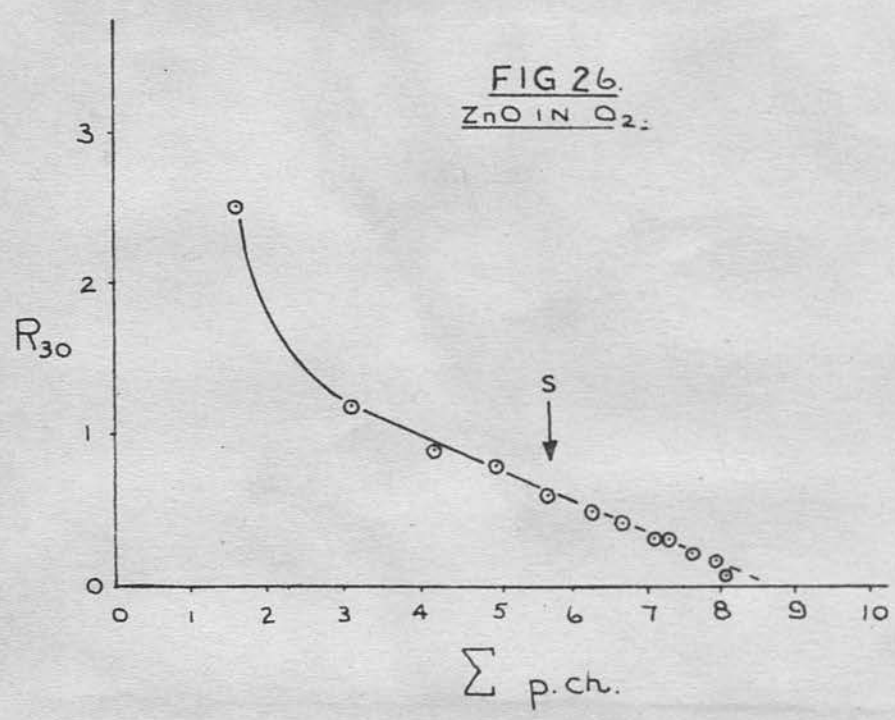
From these results it can be seen that the rate increased with increase in temperature.

The corrected calculated values were therefore –

| RELATIVE RATE (R) | TEMP. ($T^{o}A$) | $1 + \log_{10}R$ | $1/T$ |
|---|---|---|---|
| 0.59 | 278.9 | 0.77 | $3.58 \times 10^{-3}$ |
| 1.00 | 298.5 | 1.00 | $3.35 \times 10^{-3}$ |
| 1.70 | 314.1 | 1.23 | $3.18 \times 10^{-3}$ |

When plotted, as in Fig. 25, the straight line has a slope of $1.17 \times 10^{3}$. The activation energy is therefore equal to $1.17 \times 10^{3} \times 2.303 \times 1.99$ cals. i.e. 5.36 k.cals. A purely photochemical reaction would have a zero temperature coefficient; the small value of the apparent energy of activation indicates that the reaction is predominantly photochemical but is attended by a thermal reaction or reactions.

## V ZINC OXIDE.

A few runs were made with zinc oxide films to ascertain if they were, in general, of the same type as Titanium Dioxide. The typical pressure change vs. time curve has already been given (p.35) and when replotted as a rate curve these results appear to allow of extrapolation of the total pressure change, as shown in Fig. 26. The value for this run was 8.6 scale divisions with a reaction vessel of volume = 26.90 ml. and a gauge sensitivity of 0.033 m.m./scale division.

If the Hyvac pump was applied at this point of apparent cessation of the reaction and evacuation was carried on over a period of hours, then on re-illumination in a fresh 50 m.m. oxygen the pressure change vs. time curve was repeated in form.    The actual extent of this secondary uptake depended on the effectiveness of the evacuation (i.e. on time of evacuation) as the following extrapolated results show.

Evacuation for 6 hrs. stand overnight, evacuation $\frac{1}{2}$ hour.

$$\sum p. ch. = 11.4 \text{ scale divs.}$$

Evacuation for 1 hr. stand overnight, evacuation $\frac{1}{2}$ hour.

$$\sum p. ch. = 3.4 \text{ divisions.}$$

Unlike the reaction with $TiO_2$, there was no increase in rate on standing overnight in 50 m.m. oxygen.

The main features of the reaction demonstrated with $TiO_2$ were reproduced with ZnO but the increase in the rates on standing in vacuum was proportional to the extent of the evacuation.    This suggested a degradation of the photo-product at low pressures.

## Variation in Oxygen Pressure

A partially completed run was stopped by cutting off the illumination and another 50 m.m. dry oxygen was added to a similar quantity already present in the reaction vessel.    The illumination was recommenced after the additional gas had reached thermostatic conditions.

When the pressure change vs. time curve was plotted,
the two sections merged into one smooth curve showing
the independence of rate on oxygen pressure for the
pressure range 50 - 100 m.m.

## Reaction of Zinc Dust.

A film of zinc dust was illuminated in the presence
of 50 m.m. oxygen by the Osira lamp for dis-continuous periods
of 13 hours total, without any pressure decrease.    In
general at the end of any continuous run the pressure was
found to have increased in the reaction vessel by a small
amount only,  0.1 - 0.2 m.m.   This was attributed to a
heat effect and therefore the oxygen uptake by ZnO was
not due to the oxidation of metallic zinc as such.

## VI FADING OF DYESTUFFS.

## A. Chlorazol Sky Blue.

In experiments reported above results were obtained
which were taken as correlative proof that the fading of
this dye was an oxidation process.   It should therefore
be possible to study the reaction by the pressure changes
resultant from the oxygen uptake.   It was found however,
that the dye adsorbed on various oxides was sensitive to
light both in a vacuum and in the presence of oxygen.
This fact suggested that there was either a different
reaction occurring in vacuum or that there was a transfer
of oxygen from the lattice or from firmly bound adsorbed

FIG 27.

FIG 27
FADING OF CHLORAZOL SKY BLUE
[ x - IN 50 m.m. $O_2$. ]
[ O - IN VACUUM. ]
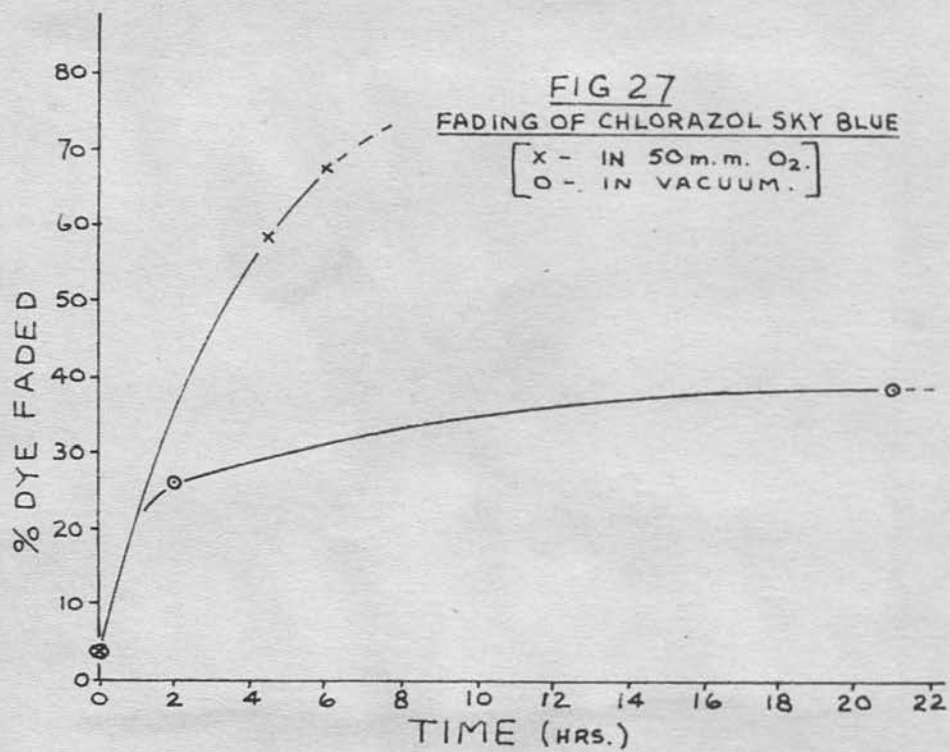
molecules. It was confirmed that the dye was stable
to light when illuminated even for very long periods
on an inert substrate like glass.

A series of runs was made with this dye on 0.12g.
films of $TiO_2$ (sample D) both in vacuum and in 50 m.m.
oxygen and the residual dye, after illumination,
extracted and measured as described above (p. 47).
The results obtained were -

| TIME OF ILLUM. (HRS.) | % DYE FADED | |
|---|---|---|
| | In 50 m.m. $O_2$ | In VACUUM |
| NIL | 4.2 | - |
| 2.0 | - | 26.7 |
| 4.5 | 58.6 | - |
| 6.0 | 67.3 | - |
| 21.0 | - | 38.6 |

In other experiments, it was found that over the
initial periods the rates of fading in oxygen and in
vacuum were similar. On this basis Fig. 27 has been
constructed.

It is probable that the 'in vacuo' fading is an
oxidation since no appreciable degradation occurs on an
inert substrate; on this basis the oxidation in
vacuum tends to a limiting value, while in the presence
of oxygen there is regeneration of the oxidising agent.

The order of sensitising activity of various

preparations of $TiO_2$, as judged by the fading of
Chlorazol Sky Blue in 50 m.m. oxygen, has already
been reported (p.47). The experiments were repeated
exactly except that the samples were evacuated to
$\sim 10^{-3}$ m.m. and illuminated at this pressure. The
order of activity of the samples was found to be

$$D > F \gg D(ignited) \gg A .$$

which is the same order as in oxygen.

In addition to this difficulty of apparent oxygen
transfer from the solid direct measurement of the
oxygen uptake of the dye was impossible owing to the
very much higher uptake by the sensitising substrate.
With those oxides whose uptake was small the rate of
fading was correspondingly low, so that in both cases
the expected uptake by the dye was within the experi-
mental reproducibility of the total uptake. Increasing
the dye would have resulted in introducing such factors
as large spacial separation between the outer layers of
the dye and the sensitising substrate.

Examination of the rate curves of dye films of
ZnO and $TiO_2$ for various conditions showed no features
which could be attributed as due to any oxygen uptake
by the dye itself. Apart from decreased rates in the
initial stages of the reaction these curves were similar
to those obtained with the oxides themselves. Such
difficulties made it impossible with the present
experimental procedure to measure, directly, the

postulated oxygen uptake of the dye.

It was, however, still possible that gaseous products were given off during degradation and it was hoped to be able to follow the reaction from this aspect.    Any evolved gas could be detected either by adding a small quantity of oxygen and measuring the residual pressure when the reaction ceases or by illuminating dyed films in vacuum.    To test the first method a film was prepared with 0.12g. $TiO_2$ (sample D) and dyed with $3 \times 10^{-3}$g. Chlorazol Sky Blue.    To the reaction vessel 14.4 scale divisions of oxygen were added and the system illuminated by the Osira.    Within 43 minutes the maximum pressure change which could be attributed to the evolution of some gas was 0.7 scale divisions and the pressure change: oxygen pressure ratio was 0.954.

Assuming that each dye molecule split off one gas molecule during oxidation, then the number of gas g.mols. evolved would be $3 \times 10^{-3}/992$.    As the reaction was carried out in a vessel of volume = 26.90 ml. and with a gauge sensitivity of 0.042 m.m./scale division this amount of gas should register a pressure change

$$= \frac{3 \times 10^{-3}}{992} \times \frac{760}{0.042} \times \frac{22400}{26.90} \times \frac{298}{273} \text{ scale divisions}$$

$$= 49.3 \text{ scale divisions.}$$

Allowing for 10% fading due to oxidation during the 43 minutes of illumination (see Fig. 27 p.78), the

pressure increase expected was of the order of 5 scale
divisions i.e. very much greater than the recorded
value of 0.7.

The same film, on the addition of more oxygen showed
a pressure change - oxygen pressure ratio of 0.945.
This value is in reasonable agreement with the previous
one (0.954) to indicate that the reduction in available
dye in position for oxidation did not affect this value.

Illumination in vacuum of samples of $TiO_2$ dyed with
Chlorazol Sky Blue did not give rise to any pressure
change as recorded by the Bourdon gauge. It was
therefore impossible to follow the degradation of the
dyestuff by this method.

The oxidation of various dyes on cellulose in
contact with pigments such as $TiO_2$ has been suggested
to be a photo-induced oxidation by a photo-chemically
produced oxidising agent. With solutions of Chlorazol
Sky Blue in diluted 20 vol. hydrogen peroxide the reac-
tion was shown to be accelerated by light. The rate of
decomposition of $H_2O_2$ under the same conditions was
also faster in the presence of light. The experimental
procedure was to illuminate by the Osira lamp at short
range a pair of test-tubes containing the test solutions;
one of the tubes being enclosed in a several-ply jacket
of photographic black paper.

FIG. 28.
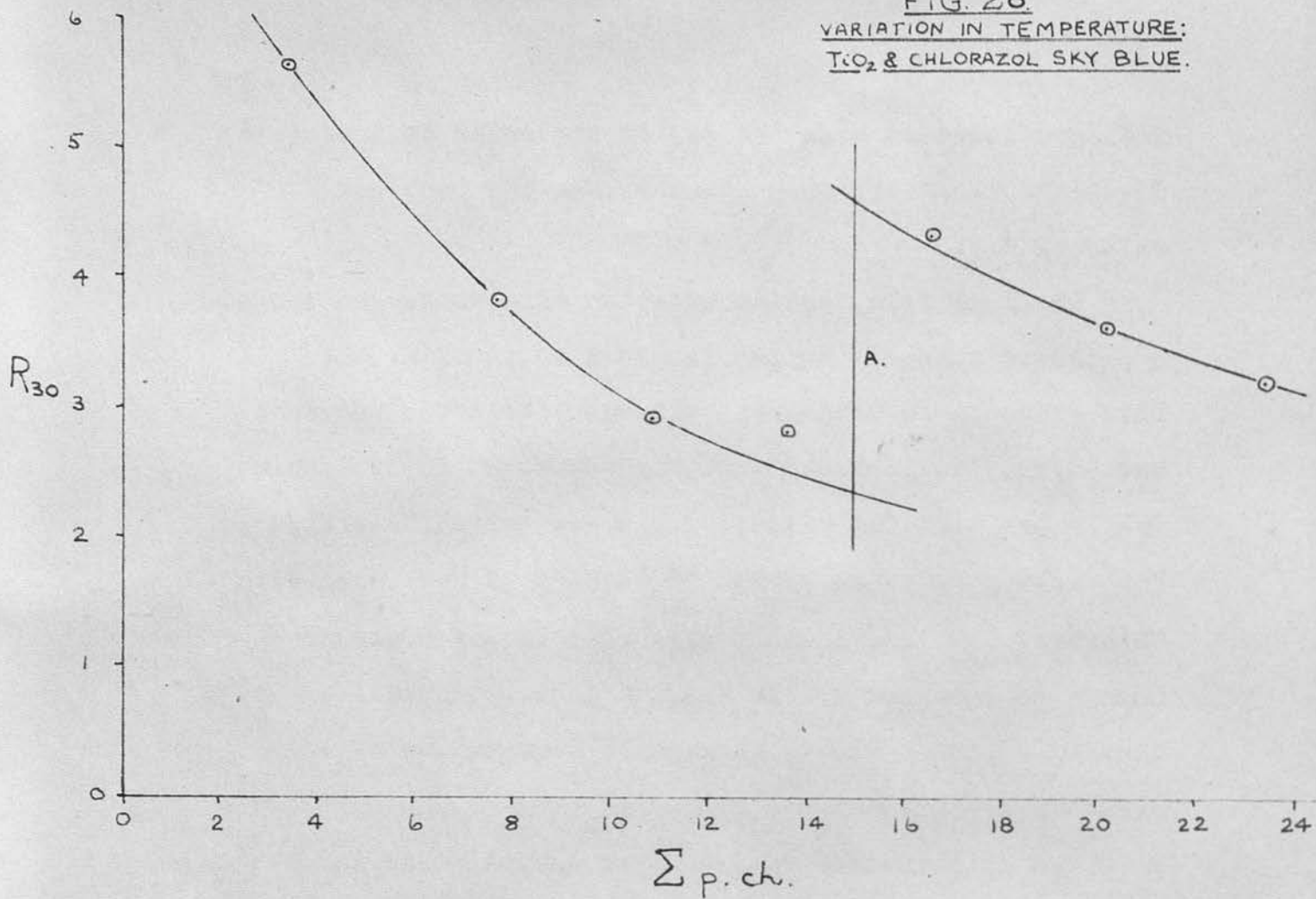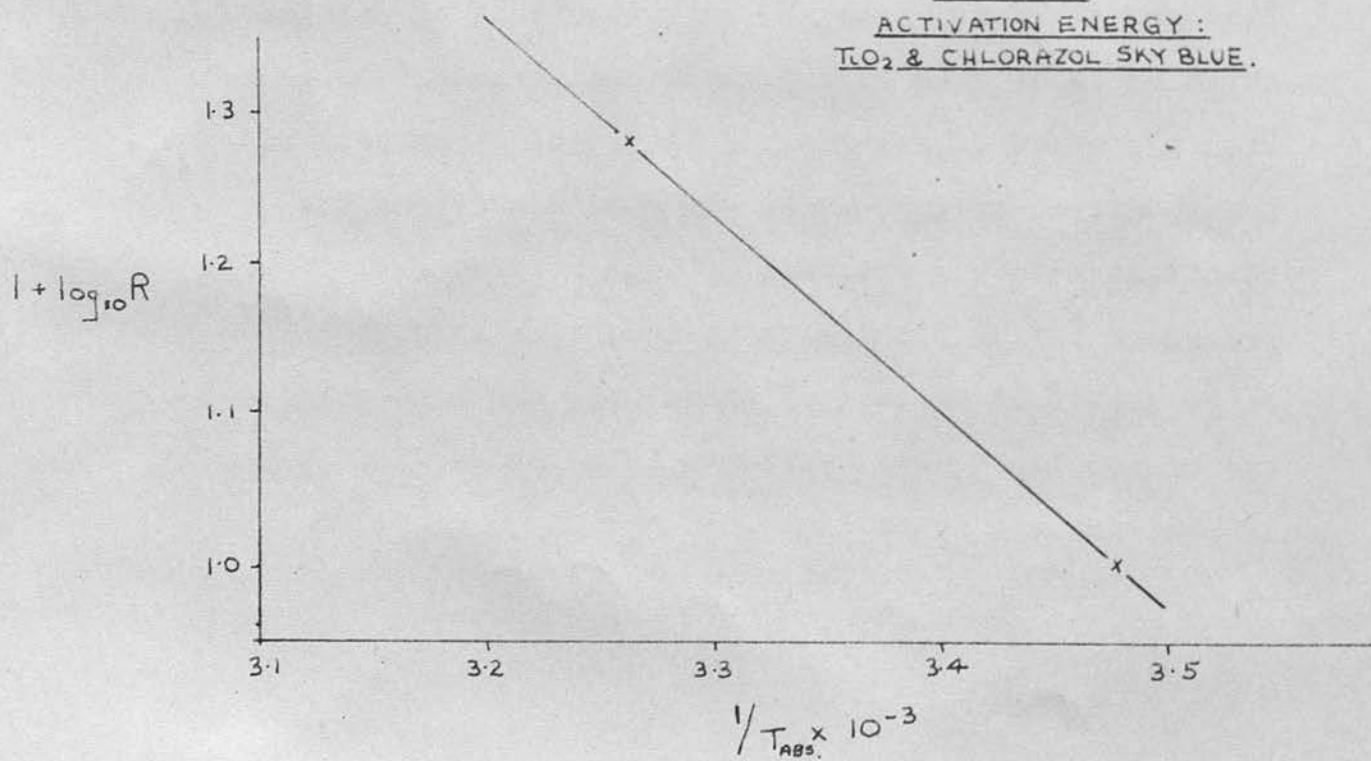VARIATION IN TEMPERATURE:
$TiO_2$ & CHLORAZOL SKY BLUE.



FIG. 29.
ACTIVATION ENERGY:
$TiO_2$ & CHLORAZOL SKY BLUE.

The effect of the presence of dye on the surface of a $TiO_2$ film during the measurement of the activation energy of the oxygen uptake was investigated. The results were obtained in a similar manner to that already described for the undyed film except that only two points were taken due to the rapid fading of the dyestuff and these points during the initial rapidly falling section of the curve.

The rates plotted in Fig. 28 were –

| TEMP = 287.1°A | | TEMP = 307.2°A | |
|---|---|---|---|
| $R_{15}$ | $\sum$p.ch. | $R_{15}$ | $\sum$p.ch. |
| 5.6 | 3.4 | 4.3 | 16.5 |
| 3.8 | 7.7 | 3.6 | 20.1 |
| 2.9 | 10.9 | 3.2 | 23.4 |
| 2.8 | 13.7 | | |

The rates taken at point A on Fig. 28 were respectively 2.4 and 4.6, which when corrected to 273°A gave the following results plotted in Fig. 29.

| RELATIVE RATE (R) | TEMP °A (T) | $1 + \log_{10} R$ | $1/T$ |
|---|---|---|---|
| 1.0 | 287.1 | 1.0 | $3.48 \times 10^{-3}$ |
| 1.92 | 307.4 | 1.28 | $3.26 \times 10^{-3}$ |

The slope of the line drawn through these points is $1.28 \times 10^3$ which gives an activation energy equal to $1.28 \times 10^3 \times 2.303 \times 1.99$ cals. i.e. 5.88 k. cals. This value is sufficiently close to the value obtained for

the undyed $TiO_2$ to indicate that the oxidation of the
dye does not introduce any new primary reaction scheme
which is predominantly temperature sensitive.

B. Malachite Green Oxalate.

The sensitising action of various substrates on the
fading of Malachite Green Oxalate was similar to that
exhibited for Chlorazol Sky Blue.    In the experiments,
the results of which are given below, o.12g. of the sub-
strate were dye with $1 \times 10^{-3}$g. Malachite Green Oxalate
and illuminated as follows :-

| SUBSTRATE | OXYGEN PRESSURE | RESULT |
|---|---|---|
| | (m.m. Hg.) | (visual examination) |
| Powdered glass | 50 | no fading |
| $TiO_2$(sample D) | 50 | marked fading |
| $TiO_2$( " " ) | $10^{-3}$ | " " |
| $TiO_2$( " " ignited) | 50 | slight fading |
| $TiO_2$( " F). | 50 | marked fading |

The faded areas showed patches of blue and purple.
The addition of small quantities of ammonia vapour
resulted in the complete fading of all green, blue and
purple areas.

There was again no difference between the dyed and
undyed rate curves apart from the initial decrease in
rates and therefore the oxygen uptake could not be
calculated.    The evolution of gases on oxidation, as
shown by Reid[19] for Malachite Green Oxalate on TlBr, was

expected to be detected by the methods described above.
However, during the illumination of a dyed film of
sample D in vacuum, no pressure change was observed
over $3\frac{1}{2}$ hours.    Illumination of similar films in
oxygen gave the following results when phosphorus
pentoxide and soda lime were and were not present in the
reaction vessel.

| ABSORBENTS | RATIO p.ch/p.O$_2$. | |
|------------|---------|---------|
| Present | 0.998 | 0.994 |
| Absent | 0.992. | |

No reaction products were therefore liberated into
the gaseous phase and the mechanism of oxidation of
Malachite Green Oxalate is therefore entirely different
on TiO$_2$ as compared with TlBr.

**DISCUSSION.**

## DISCUSSION

The main feature of the experimental results is the
discovery of the apparent oxygen uptake, on illumination,
by the sensitising oxides.   This, unfortunately, made the
second part of the original scheme of work - i.e. the kinetics
of the dye oxidation - impossible to measure directly
with the experimental set up used.

The extent and scope of this pressure decrease was
surprising as it was expected that the changes to be
measured would be due to the oxygen uptake of the dye,
the possible evolution of gas on the degradation of the
dye and perhaps small pressure changes - reversible - on
the illumination of the solid.   In the light of the
results obtained, the experimental technique used proved
effective for comparative results.

The gases used were not especially prepared or
purified - apart from the removal of water vapour - but
the reaction studied with $TiO_2$ was confined to oxygen and
it was shown that the results were appreciably unaffected
by as great an adulteration of the oxygen as to contain
50% nitrogen.   It was assumed therefore that no error
was introduced in this respect.

On occasion, the voltage applied to the Osira lamp
was unavoidably subject to fluctuation.   The stabiliser
inserted into the circuit cut any fluctuation in such
voltage to 10% of its original value.   The rate of pres-
sure change was not proportional to the light intensity
which was itself approximately proportional to the
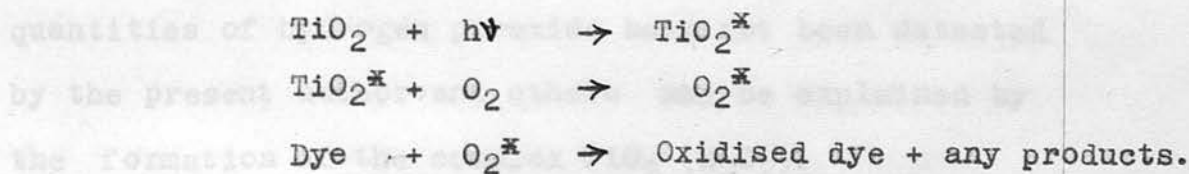voltage, but any serious drop or other

fluctuation in intensity was apparent as a break in the pressure-time curve. If these were serious the run was discarded but if the rate returned to the values expected from the original curve the inconsistent parts were neglected. From the numerous runs made, it was possible to outline a 'normal' curve and from this judge the cause of any irregularity in individual cases. During the experimental work the geometry of the apparatus was, unavoidably, altered but at any stage in the experimental results or discussion where direct comparison of quantitative results is made the geometry throughout the period of their evaluation remained constant.

The possibility of contaminants in the form of mercury vapour from the manometers, hydrocarbon oils from the Hyvac pump and Apiezon grease from the taps and quick-fit joints was fully considered. Steps were taken to limit any such action as far as was possible although no abnormalities could ever be ascribed to their presence. A small pressure (ca. 5 m.m.) of gas was maintained above the manometer at all times and the interposition of liquid oxygen traps between the pump and the rest of the apparatus served to freeze out any volatile contaminant from the former source.

To summarise very briefly a postulated theory of sensitised dye degradations as reported in the literature

involves the oxidation of the dyestuff either directly or indirectly (i.e. by $H_2O_2$) by oxygen. For the dyestuff Chlorazol Sky Blue, it was confirmed that the oxide type of sensitiser, especially $TiO_2$ was the most efficient. It was also shown that in contrast to the non sensitisers, when these oxides were illuminated in oxygen by near ultra-violet light there was an appreciable pressure decrease. If it could be shown, therefore, that the degradation of this particular dyestuff was an oxidation reaction, there was reason to investigate this oxygen uptake further to discover if the two were connected or sequential. According to the literature all known sensitised degradations are largely dependent on the presence of oxygen, as proved by the absence of any but a trace reaction in the presence of other gases. However, in the present case, there was to be considered the discovery that the dye was bleached in a vacuum, which rendered the proposed approach impracticable. The method adopted therefore, in preference to the much longer term project of the identification of the reaction products, was the comparison of the results of known oxidation with those obtained in the unknown reaction. From the results, detailed above, it was taken as proved that the degradation of Chlorazol Sky Blue by illumination when adsorbed on a sensitising oxide was due to oxidation.
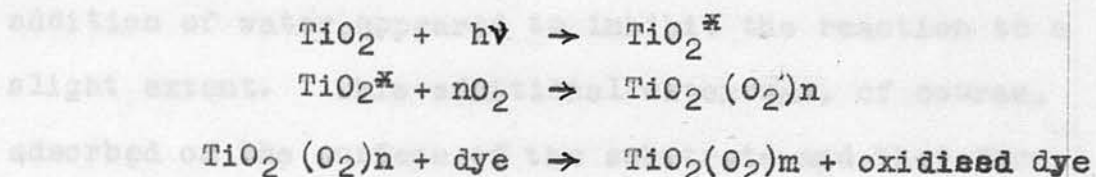
The pressure changes exhibited in the presence of these oxides have been shown in the case of $TiO_2$ to be limited to oxygen-gaseous systems alone.   The small pressure changes exhibited in the presence of nitrogen and water vapor can be attributed to the presence of impurity traces of oxygen.   A study of the pressure-time curve for nitrogen, for example, and the comparison with the similar curve obtained with low pressures of oxygen showed a great similarity between the two.   The observed maximum pressure change of 0.21 m.m. in 50 m.m. nitrogen corresponded to an oxygen content of 0.5% which lies within the limits quoted by the manufacturers. This fact - that only oxygen is reactive in this specified manner - when considered with the knowledge that the oxides were effective sensitisers for an oxidation reaction suggested that the role of the oxide may not merely have lain in the adsorption of light energy and the subsequent transference of it as chemical energy to the oxygen.   This led to the consideration that the reaction schemes proposed on previous results i.e.

$$TiO_2 + h\nu \rightarrow TiO_2^x$$
$$TiO_2^x + O_2 \rightarrow O_2^x$$
$$Dye + O_2^x \rightarrow \text{Oxidised dye + any products.}$$

or the less favoured

$$TiO_2^x + D \rightarrow Dye^x$$
$$Dye^x + O_2 \rightarrow \text{Oxidised dye + any products.}$$

only presented part of a more complicated reaction which
can be outlined by the following reaction scheme.

$$TiO_2 + h\nu \rightarrow TiO_2^{x}$$
$$TiO_2^{x} + nO_2 \rightarrow TiO_2 (O_2')n$$
$$TiO_2 (O_2)n + dye \rightarrow TiO_2(O_2)m + oxidised \ dye$$

where n and m are, respectively, $> 0$ and $> 0$.

Before the above reaction scheme, or some modifica-
tion of it, can be accepted it was necessary to prove
the absence of impurities in sufficient concentration
to account for the reaction.   Of the four suggested
possibilities, iron, chlorine and nitrogen (the latter
two present as the oxychloride and nitride respectively)
have been shown to be  absent on reactive samples but
the consideration of water built into the molecule, as
it is most certainly in various samples, presents a
more difficult problem.   The reaction proposed, with
water as the reactive agent, could be interpreted by
assuming the intermediate formation of activated water
or  oxygen as a stage in producing the final product of
hydrogen peroxide.   The fact that the requisite
quantities of hydrogen peroxide have not been detected
by the present author and others  may be explained by
the  formation of the complex $TiO_2 (H_2O_2)$.

On both reaction schemes proposed for the production
of the peroxide it can be shown kinetically that the
rate of oxygen uptake will increase with the concentration

of water available to the surface of the substrate.    In
fact, this was not found to be the case and indeed the
addition of water appeared to inhibit the reaction to a
slight extent.    This additional water was, of course,
adsorbed on the surface of the substrate and therefore
may not be within sufficiently close contact for either
the passage of chemical energy from the oxide or for
reaction with the activated oxygen.    Howefer, the rate
of the reaction is so greatly affected by the character
of the surface of the substrate, as modified by variation
in the binding liquid, that one, at least, of the rate
controlling reactions must occur at the surface.    The
presence of adsorbed water should therefore materially
increase the rate of oxygen uptake, which is contrary
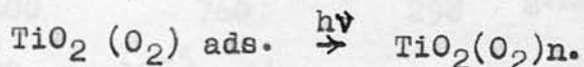to experimental results.

The oxidation of water as the main reaction did not
necessarily discount the possibility  of the production
of $H_2O_2$ in small quantities as a secondary reaction but
the various experiments described above on the production
and detection of the peroxide did not produce any confirma-
tion of this hypothesis.

It is now possible to return to the consideration
of a reaction between the substrate and the oxygen.
It has been shown that althogh the reaction occurs only
with oxygen it is independent of pressure in the higher
ranges.    Examination of the pressure-time curves for
illumination in low pressures of oxygen indicates however

that the rate becomes dependant on the oxygen concentration below a critical value - ca. $10^{-1}$ m.m. These facts indicated that the reaction occurred between the substrate and a loosely bound film of oxygen adsorbed upon it. The concentration of this oxygen film was very much higher than the instantaneous concentration of reactive centres produced by illumination of the substrate and it could therefore be regarded as constant. The first stage of the reaction may be written as a Van der Waal's adsorption -

$$TiO_2 + O_2 \rightarrow TiO_2(O_2) \text{ adsorbed.}$$
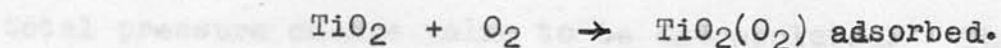
On illumination, there was a rapid uptake of oxygen which was not reversible in toto, by evacuation in the dark. It was necessary to postulate, therefore, the formation of a more strongly bound adsorption complex or of a definite chemical compound with the simultaneous replenishment of the adsorbed oxygen film from the gaseous oxygen phase. This fixation of oxygen could be represented as follows -

$$TiO_2 (O_2) \text{ ads.} \xrightarrow{h\nu} TiO_2(O_2)n.$$

The subscript n could not be calculated directly from the results given above. If the film was so constructed that it was of unimolecular thickness, this value would be easily interpretable but with the experimental arrangement of a film of considerable depth, the factors of light and gas diffusion to the

sub-surface reactive centres, introduced too many variables for the accurate determination of this value. The variation of the amount of pressure change with the quantity of substrate has been examined but again the difficulty of interpolation of the total pressure change does not give any completely sound basis for a definite conclusion to be drawn.

However, with the small amount of oxide used in one run, it was found that the latter part of the curve approximated to a straight line, which allowed a tentative total pressure change value to be extrapolated. This value was found to be 166 scale divisions which was equivalent to a pressure change of 6.97 m.m. and assuming that this was due entirely to oxygen uptake by the solid during the reaction, the g.mol of oxygen reacting was calculated thus:

In a vessel of volume of 26.75 ml. at $298^{\circ}A$ this pressure change was equivalent to -

$$1 \times \frac{26.75}{22400} \times \frac{6.97}{760} \times \frac{273}{298} \text{ g.mol}$$

$$= \quad 1.00 \times 10^{-5} \text{ g.mol.}$$

The weight of $TiO_2$ used in this experiment was 0.014g which is equivalent to -

$$\frac{0.014}{79.9} \text{ g.mol.}$$

$$= \quad 1.75 \times 10^{-4} \text{ g.mol.}$$

In these results the apparent formula for the

photo-product was $TiO_{2.12}$ which is far short of next known oxide of titanium, which is the trioxide. However, this value only represented the 'average' formula and it is possible that there was partial formation of the trioxide on certain active sites only of the preparation.

The above result was calculated on the assumption that the reaction involved $TiO_2$ being oxidised to a higher oxide. Such a scheme was proposed by Ruben[28] who suggested the formation of the yellow pertitanic acid as a reaction product. Jacobsen[22] however suggested that the reaction was a cyclic process with the formation of $Ti_2O_3$ and atomic oxygen on illumination in contact with an oxidisable medium. The cycle was completed by the thermal reoxidation of the $Ti_2O_3$ to the dioxide with atmospheric oxygen. It was difficult with this latter theory to account for the present large oxygen uptake and the lack of evidence of evolved oxygen on illumination in vacuum. The dark yellow color which these authors have reported was attributed to the reaction suggested by Williamson[30] - i.e. the oxidation of impurity traces of iron from the ferrous to the ferric state.

During the present work, the darkening of the surface has been observed in atmospheres other than oxygen and also with samples of the oxide shown to be free from iron. This appeared to discount these two

theories as possible explanations of this phenomenon
although minute traces of impurity can exert a darkening
effect out of all proportion to their concentration
and certainly several of the oxide samples only showed
a very faint yellowish tinge. The phenomenon must be
included in any general explanation of the reaction.

From the well defined facts so far established, it
was attempted to propose a theory for the sensitised
oxidation of the substances in contact or proximity to
$TiO_2$ without assuming as proved the nature of the end
product of the titanium dioxide oxidation. If such
a theory can be formulated it would resemble in nature
the theory of oxide catalysis and some such resemblance
in the experimental results has been found as the
following summary emphasises.

Taylor[65] in the Spiers Memorial Lecture (1950)
has given a very comprehensive survey of the phenomenon
of catalysis as understood at the present day. He has
recommended that Volkenstein's[66] analysis of the
reaction explained to the best advantage most of the
problematic points met. This analysis assumed the
presence of defects in the regular crystal face and in
the lattice and that the activation energy associated
with the adsorption of gases was the energy required
for the mobility of these defects, and thus the number
of sites within the activation range increases with
temperature. Taylor suggested that data previously

obtained could now profitably be examined in the light
of this theory.   With Pace[67] for instance he had
already shown that the energy required for activation
of the system had to be given to the solid catalyst
while other workers had shown that the reaction velocity
was independent of the gas pressure.

With the oxide catalysts it was found that on the
addition of oxygen to the evacuated sample, the
resultant reaction could be followed by measurement of
the conductivity of the sample.   The reaction on Zinc
oxide was explained by Bevan and Anderson[68], on the
basis of such measurements, as follows.   The oxygen
in the gas phase was adsorbed by the catalyst, when
it picked up a double negative charge to become $O^{--}$.
In a similar series of experiments with copper oxide
films, Garner, Gray and Stone[69], have proposed that
in this case the oxygen is chemisorbed from the gas
phase and then is dissociated into atoms before picking
up electrons.   They have shown that the adsorbed atoms
were appreciably mobile and can move away from the
surface adsorbed states.   An analysis of their
results has led Garner[71] to propose that the rate
determining step was either the production of atomic
oxygen or the formation of a chemical compound.   The
slow addition of oxygen to the crystal lattice has also
been proposed by Garner as a possible reaction.

Based on this theory of oxide catalysis, the following considerations may be briefly presented. On the surface of the oxide there is an adsorbed film of oxygen, of approximately constant concentration. This oxygen may be taken as fixed at a suitably activated centre at or near the surface. The rate of production of such activated centres by light absorption is normally complex and will involve the light intensity as well as the lattice geometry and general configuration; irrespective of the actual mechanism it may be represented by the equation -

$$(Ac) \xrightarrow{h\nu} (Ac)^{\text{x}} \quad \cdots \cdots (1)$$
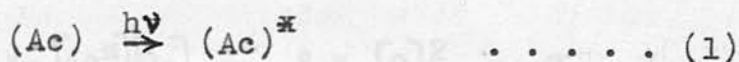
at a rate denoted by $f(I_{abs})$.

The oxygen 'fixation' may then be denoted by

$$(Ac)^{\text{x}} + O_2 \rightarrow (Ac)O + O \quad \cdots \cdots (2)$$
$$(\text{or} \rightarrow (Ac) + O + O)$$
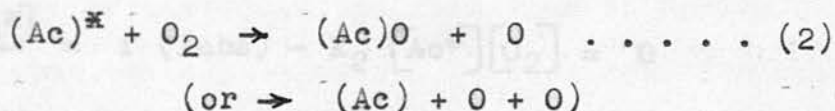
The energy required to break the $O - O$ bond is assumed to be largely balanced by the energy of formation of the bond AcO or by bonding with other suitable adjacent lattice positions. The thermal reversible formation of oxygen must also be, in general, included

$$O + O \rightarrow O_2$$

where the rate of formation of oxygen on this account is $k_3[O]^2$ and the rate of disappearance of oxygen atoms is $2 k_3[O]^2$. Further the oxygen atoms thus produced may

react with other suitable acceptors, either in the
lattice itself by some process of diffusion to or from
the interior, or by virtue of some oxidisable material
on the surface e.g. oxidisable Chlorazol Sky Blue.
Such may be represented by -

$$O + A \rightarrow OA \quad . \quad . \quad . \quad . \quad (4)$$

Two cases may then be considered

(a) Reaction (4) negligible in comparison with
    reaction (3).

If we neglect reaction (4), then for stationary
state conditions

$$\frac{d[O]}{dt} = k_2 [Ac^*][O_2] - 2 k_3 [O]^2 = 0$$

Hence $[O] = \sqrt{\dfrac{k_2 [Ac^*] O_2}{2k_3}}$

But $\dfrac{d[Ac^*]}{dt} = f(Iabs) - k_2 [Ac^*][O_2] = 0$

whence $[Ac^*] = f(Iabs)/k_2[O_2]$

therefore

$$[O] = \frac{f(Iabs)}{2k_3}$$

Now the rate of oxygen removal, as measured ultimately
by the pressure decrease, will be

$$- \frac{d[O_2]}{dt} = k_2 [Ac^*][O_2] - k_3 [O]^2$$
$$= f(Iabs) - \frac{1}{2} f(I_{abs})$$
$$= \frac{1}{2} f(I_{abs})$$

(b) Reaction (3) negligible in comparison with

reaction (4).

Neglecting reaction (3), we have

$$\frac{d[Ac^*]}{dt} = f(I_{abs}) - k_2[Ac^*][O_2] = 0$$

$$\therefore [Ac^*] = \frac{f(I_{abs})}{k_2[O_2]}$$

But $\frac{-d[O_2]}{dt} = k_2[Ac^*][O_2] = f(I_{abs})$.

Both mechanisms thus depend ultimately on the
relationship between the rate of production of activated
centres and the absorbed light intensity.

For the present conditions under which the
variation in I was examined, the rate was approximately
proportional to $\sqrt{I_{inc}}$. Thomas and Tompkins[70] have in
their study of the photo decomposition of Barium azide
investigated the relationship, between reaction rate and
light intensity, inherent in varios possible reaction
mechanisms. Their calculations regarding a closely
defined system were simplified by their justifiable assump-
tion of the constant concentration of active centres.
Such a simplification cannot be used in the present
case and a detailed analysis of the possible mechanism
awaits further experimental evidence.

As Garner[71] has pointed out, the surface oxygen
attached to the lattice is mobile if sufficiently
activated and Winther[72] has supplied furhher evidence of
this for $TiO_2$ and other oxides. In a vacuum, therefore,

illumination was assumed to energise the movement of
this oxygen to the sub-surface layers or to other avail-
able surface sites. Even if such a movement would
necessitate the liberation of oxygen gas for a short
period before its recombination, the excess of
excited active centres over the free oxygen available in
such circumstances would explain the observed fact of
constant pressure (within 0.004 m.m. ).

The final increase in rate on long standing would
be due to the continuation of the diffusion of the
oxygen into the bulk of the oxide for a short period
after illumination. This fact was supported by the
evidence obtained for $TiO_2$ in that the extent of the
increase did not vary with variation in the time of
standing. The greater increase on evacuation and
standing in a vacuum would suggest that there was also
an additional degradation of the photo-produced Ac.O at
low pressures with the diffusion of the oxygen into the
gas phase. Some evidence of this was obtained in the
increase in pressure on standing at very low pressures
i.e. with films illuminated at low oxygen pressures.

On the basis of these deductions, the shape of the
reaction curve was explained as follows. The rapidly
falling initial section was due to the reaction between
excited surface active centres with oxygen and as
these centres decreased in numbers, through degradation
by reaction, the rate fell away. The final almost

constant part of the curve was controlled by diffusion
of the 'fixed' oxygen into the interior of the film
thus freeing more surface sites.    This may be regarded
also as the production of excited active centres in the
crystal bulk and their diffusion to the surface.

The variation in reaction velocity and magnitude
with the various samples of the dioxide investigated
was attributed to the varying ease which these samples
could produce excited active centres.    This would depend
on the presence of catalytic promoters and inhibitors and
also on the variation in crystal structure on treatment
e.g. on ignition.

The oxidation reactions sensitised by $TiO_2$ were
therefore attributed to a side-reaction of this oxygen
uptake.  The results of the oxidation of Malachite Green
Oxalate have been shown to differ from these obtained by
Reid[19], who investigated the degradation of this dye
sensitised by Thallous Bromide and who proposed that the
oxalic acid molecules were attacked with the evolution
of $CO_2$ and $H_2O$.    The pressure increase which she
obtained during these reactions was not observed in the
present case but on $TiO_2$ there was strong evidence of a
color change during oxidation.    This suggested that the
dye molecules themselves were being attacked as it has
been shown that the various members of this series of
dyes owe their different colors to small changes in

constitution. Attack on the oxalic acid molecules
would have produced only the colorless carbinol as
could be shown by the addition of a small quantity of
ammonia vapor.

The mechanism of oxidation was therefore proposed
to be due not to the oxygen molecule as suggested by Reid
for her experimental conditions but to the attack by
atomic oxygen. The production of atomic oxygen has
already been shown for oxygen atmospheres; in vacuum,
etc., it is proposed that the mobile surface oxygen
is the effective agent, the dye competing with the
lattice. If such a theory were true the reaction in
Oxygen should be limited by the amount of dye present
while in vacuum the concentration of fixed oxygen would
also be a controlling factor. With the experimental
set up investigated, the amount of dye fading under
vacuum would be finite, while in a constant source
of oxygen the dye should show 100% fading. The results
obtained indicated that these results were approached.
The oxidation of the dye on a $TiO_2$ film was shown to
have no effect on the activation energy of the oxygen
uptake and this was taken as proof that the oxidation
of the dye was an integral part of the reaction
exhibited by the oxide.

Although there was strong evidence of the highly
reactive oxidising agent produced with a dry system, no

support was obtained for the theory of the production of $H_2O_2$ in the presence of $TiO_2$ and water. It was probable therefore that the long-life volatile oxidising agent observed by Egerton[14] was produced by the degradation of cellulose in the presence of water and atomic oxygen.

With the other sensitising oxides, the reaction was too slow to follow in detail but they all showed an oxygen uptake to a certain extent. Zinc oxide showed complete reversibility on standing in a vacuum but the reaction velocity was independant of the oxygen pressure over the range 50 - 100 m.m. Antimony oxide exhibited an induction period of the order of $2 \times 10^2$ minutes.

No detailed reaction scheme for the oxidation of the two dyes could be proposed on the basis of the results obtained as the experimental technique employed was unsuitable from this aspect. The oxidation of Chlorazol Sky Blue has been shown to be a thermal reaction, initiated by the action of light, as opposed to the purely photo-reaction exhibited by Eosin[35].

## SUMMARY.

1. The photo-sensitising oxides have been shown to exhibit a 'fixation' of gaseous oxygen on illumination with near U-V light. This reaction was found to be specific for oxygen among the gases investigated.

2. The method developed for the study of the photo-oxidation of plant pigments on thallous bromide has been found to be unsuitable to the study of the photo-oxidation of Chlorazol Sky Blue and Malachite Green adsorbed on various sensitising oxides.

3. The correlation between the sensitising activity of the various oxides and the various samples of $TiO_2$ and their power of oxygen 'fixation' has been demonstrated over a wide range.

4. The reaction with $TiO_2$ has been shown independent of the presence of various impurities. No bulk stoichiometric oxide was formed as a final product.

5. The production of a short-life highly-active oxidising agent has been demonstrated but no evidence of hydrogen peroxide was found when considering $TiO_2$.

6. Various physical parameters of the reaction between oxygen and titanium dioxide were investigated. They indicated that it was not a pure photo-chemical reaction.

# SUMMARY.

1. The photo-sensitising oxides have been shown to exhibit a 'fixation' of gaseous oxygen on illumination with near U-V light. This reaction was found to be specific for oxygen among the gases investigated.

2. The method developed for the study of the photo-oxidation of plant pigments on thallous bromide has been found to be unsuitable to the study of the photo-oxidation of Chlorazol Sky Blue and Malachite Green adsorbed on various sensitising oxides.

3. The correlation between the sensitising activity of the various oxides and the various samples of $TiO_2$ and their power of oxygen 'fixation' has been demonstrated over a wide range.

4. The reaction with $TiO_2$ has been shown independent of the presence of various impurities. No bulk stoichiometric oxide was formed as a final product.

5. The production of a short-life highly-active oxidising agent has been demonstrated but no evidence of hydrogen peroxide was found when considering $TiO_2$.

6. Various physical parameters of the reaction between oxygen and titanium dioxide were investigated. They indicated that it was not a pure photo-chemical reaction.

7. Zinc oxide was shown to behave in a manner similar
to that exhibited by $TiO_2$ with the exception of the
production of $H_2O_2$ in the presence of water.

8. The fading of Chlorazol Sky Blue, adsorbed on the
oxides, was demonstrated to be an oxidation reaction
occurring in vacuo and in oxygen.  In the former
case, however, the reaction ceased long before
completion of total fading.  The type of reaction
exhibited by Malachite Green  oxalate, adsorbed on
$TiO_2$, appeared to differ from that reported for the
same dye sensitised by TlBr.

9. General reaction schemes have been proposed to
account for the main features of the photo-fixation
of the gaseous oxygen and subsequently the photo-
sensitising effects of the various oxides.

10. The rapid oxygen uptake by various samples of
$TiO_2$ on illumination is proposed as an analytical
method of determining small quantities of that gas
contained in inert atmospheres.

1.  Bowen — J. Soc. Dy. Col. 1949, 65, 613

2.  Livingston — ibid. 1949, 65, 781

3.  Lewis & Lipkin — J. A. C. S. 1942, 64, 2801

    Lewis & Bigeleisen — J.A.C.S. 1943, 65, 520, 2419, 2424.

4.  Bloch — Z. phys. 1928, 52, 55.

5.  Gurney & Mott — Proc. Roy. Soc. 1938, 164A, 151.

6.  Symposium on "Semi-Conductors" held under auspices of
        the Institute of Physics, Edinburgh, 1938.

7.  Eibner — Chem. Zeit. 1911, 35, 753.

8.  Dhar — "Chemical Action of Light", (1931), p260.
        London: Blackie.

9.  Goodeve & Kitchener — Trans. Far. Soc. 1938, 34, 902.

REFERENCES.

10. Goodeve — ibid. 1937, 33, 340.

11. Wagner and Zipfel — Farben Zeit. 1932, 37, 1880.
    Zaidel — ibid. 1929, 34, 1342.

12. Vogel — Ber. 1873, 6, 1305.

13. Jodlbauer & Tappeiner — Deutsch. Arch. Klin. Med. 1905,
        82, 532.

14. Egerton — J. Soc. Dy. Col. 1949, 65, 764.

15. Landolt — ibid. 1949, 65, 659.

16. Atherton & Seltzer — ibid. 1949, 65, 629.

17. Lenie & Ritchie — ibid. 1949, 65, 714.

18. Lenie — Ph.D. Thesis., Edinburgh, 1950.

19. Reid — ibid. Edinburgh, 1950.

20. Goodeve — Trans. Far. Soc. 1940, 36, 432.

21. Goodeve — ibid. 1938, 34, 570.

1.  Bowen – J. Soc. Dy. Col. 1949, 65, 613

2.  Livingston – ibid. 1949, 65, 781

3.  Lewis & Lipkin – J. A. C. S. 1942, 64, 2801

    Lewis & Bigeleisen – J.A.C.S. 1943, 65, 520, 2419, 2424.

4.  Bloch – Z. phys. 1928, 52, 55.

5.  Gurney & Mott – Proc. Roy. Soc. 1938, 164A, 151.

6.  Symposium on "Semi-Conductors" held under auspices of
        the Institute of Physics, Edinburgh, 1952.

7.  Eibner – Chem. Zeit. 1911, 35, 753.

8.  Dhar – "Chemical Action of Light", (1931), p262.
        London: Blackie.

9.  Goodeve & Kitchener – Trans. Far. Soc. 1938. 34, 902.

10. Goodeve – ibid 1937, 33, 340

11. Wagner and Zipfel – Farben Zeit. 1932, 37, 1480.
    Keidel – ibid. 1929, 34, 1242.

12. Vogel – Ber. 1873, 6, 1305.

13. Jodlbauer & Tappeiner – Deutsch. Arch. Klim. Med. 1905,
        82, 532.

14. Egerton – J. Soc. Dy. Col. 1949, 65, 764.

15. Landolt – ibid. 1949, 65, 659.

16. Atherton & Seltzer – ibid. 1949, 65, 629.

17. Lonie & Ritchie – ibid. 1949, 65, 714.

18. Lonie – Ph.D. Thesis., Edinburgh, 1950.

19. Reid – ibid. Edinburgh, 1951.

20. Goodeve – Trans. Far. Soc. 1940, 36, 432.

21. Goodeve – ibid. 1938, 34, 570.

22. Jacobsen - Ind. Eng. Chem. 1949, 41, 523.

23. Renz - Helv. Chim. Acta 1921, 4, 961.

24. Weyl & Forland - Ind. Eng. Chem. 1950, 42, 257.

25. Winther - Z. wiss. Phot. 1921, 21, 168.

26. McMorris & Dickinson - J.A.C.S. 1932, 54, 4248.

27. Jung & Kanau - Z. physik. Chem. 1931, 15B, 45.

28. Ruben - Org. Chem. Ind. (U.S.S.R.), 1940, 7, 223.

29. Yamafuji, Nishioeda & Imagawa - Biochem. Z. 1939; 301, 404.

30. Williamson - Nature, 1937, 140, 238.

              ibid. 1939, 143, 279

              J. Mineralog. Soc. London, 1940, 25, 513.

31. Baur & Neuweiler - Helv. Chim. Acta 1927, 10, 901.

32. Chari & Qureshi - J. Indian. Chem. Soc. 1944, 21, 97.

33. Hamilton - PhD. Thesis, Edinburgh, 1951.

34. O & A. Deny - Henault - Bull. Soc. Chim. Belg. 1908, 22, 224.

35. Blum & Spealman - J. Phys. Chem. 1933, 37, 1123.

36. Kautsky, de Bruijn, Neuwirth & Baumeister - Ber. 1933, 66B, 1588.

37. Kautsky - Trans. Far. Soc. 1939, 35, 216.

38. Gaffron - Biochem. Z. 1926, 179, 157.

39. Blum - Biol. Bull. 1930, 58, 224.

40. Landolt - Melliand Textilber. 1929, 10, 533; 1930, 11, 937.

41. Egerton - J. Soc. Dy. Col. 1948, 64, 336.

42. Ashton, Clibbens & Probert - ibid. 1949, 65, 650.

43. Gaffron - Ber. 1935, 68B, 1409.

   Biochem Z. 1936, 287, 130.

44. Weiss - Naturwiss. 1935, 35, 610.

45. Franck & Livingston - J. Chem. Phys. 1941, 9, 184.

46. Weiss - Trans. Far. Soc. 1946, 42, 133.

47. Weiss - Ann. Reports. Progress Chem. 1947, 44, 60.

48. Bradbury - Phys. Rev. 1933, 44, 720.

   J. Chem. Phys. 1934, 2, 827, 835.

49. Loeb - Phys. Rev. 1935, 48, 684.

50. Vartanian & Terenin - J. Phys. U.S.S.R. 1941, 4, 173.

   Vartanian - Acta Physicochim. U.R.S.S. 1947, 22, 201.

51. Terenin - ibid 1943, 18, 210.

52. Harrison - J. Soc. Dy. Col. 1912, 28, 228.

53. Blaisdell - ibid. 1949, 65, 618.

54. Hannay - ibid 1949, 65, 637.

55. Laurie - Ph.D. Thesis, Edinburgh, 1952.

56. Hibbert - J. Soc. Dy. Col. 1927, 43, 292.

57. Haller & Ziersch - Melliand Textilber. 1929, 10, 951.

58. Lazarev - Bull. acad. sci. Petrograd. 1916, 583; Chem.

   Abs. 1916, 10, 2433.

59. Scharwin & Pakschwer - Z. angew. Chem. 1927, 40, 1008.

60. Konig - J. Soc. Dy. Col. 1913, 29, 370.

61. Mellor - 'Inorganic and Theoretical Chemistry,' (1928),

   Vol. VIII, p. 9, London: Longmans, Green.

62.  Vogel – 'Qualitative Chemical Analysis,' (1945), 3rd. ed.
                    p.321. London:  Longmans, Green.

63.  Beningis – Compt. Rend. 1940, 211, 196.

64.  Technical Data Sheet – Chance 'Coloured Optical Glass.'

65.  Taylor – Far. Soc. Disc. No. 8. 'Heterogeneous
                    Catalysis,' (1950), 9.

66.  Volkenstein – Zhurr. Fiz. Khim. 1949, 23, 917;  cited
                    by Taylor, loc. cit.

67.  Pace & Taylor – J. Chem. Phys. 1934, 2, 578.

68.  Bevan & Anderson – Far. Soc. Disc. No. 8 'Heterogeneous
                    Catalysis,' (1950), 238.

69.  Garner, Gray & Stone –  ibid. 246.

70.  Thomas & Tompkins – Proc. Roy. Soc. 1951, 209A, 550.

71.  Garner – Chem. and Ind. 1951, 70, 1010.

72.  Winther – J.C.S. 1950, 1170.

          – Far. Soc. Disc. No. 8 'Heterogeneous
                    Catalysis,' (1950), 231.