

PHOTOCHEMICAL REACTIONS OF TITANIUM DIOXIDE

by

DAVID RANKINE KENNEDY, B.Sc.

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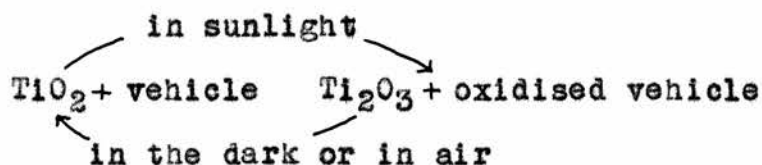
PART I

INTRODUCTION

Study of the photochemistry of titanium dioxide has largely been a result of its use in the paint and textile industries, and it is now recognised that the flaking of paints and the tendering of fabrics incorporating titanium dioxide are extensively caused by photochemical reactions involving the pigment as a "light catalyst".^{1 2 3 4 5} The aim has been to determine the mechanism of such reactions, and to inhibit the action of the TiO_2 in some way, while retaining all of its desirable pigmenting properties.

Almost all of the investigations carried out have been on paints and fabrics themselves, or on model systems which have retained most of the complexity of the paint and fabric systems. As a result, the exact role of titanium dioxide in flaking and tendering reactions has been improperly understood, and there exists a real need for information regarding the processes occurring at the titanium dioxide surface during illumination. Some consideration of the existing data on the photochemistry of TiO_2 will make this point clear.

A. E. Jacobsen¹ has studied the reactivity of TiO_2 paint pigments in a model system (TiO_2 and mandelic acid solution in air), and has correlated this reactivity with ability of the pigments to cause flaking. He attributes chalking to a cyclic reduction-oxidation reaction involving TiO_2 and the paint vehicle.



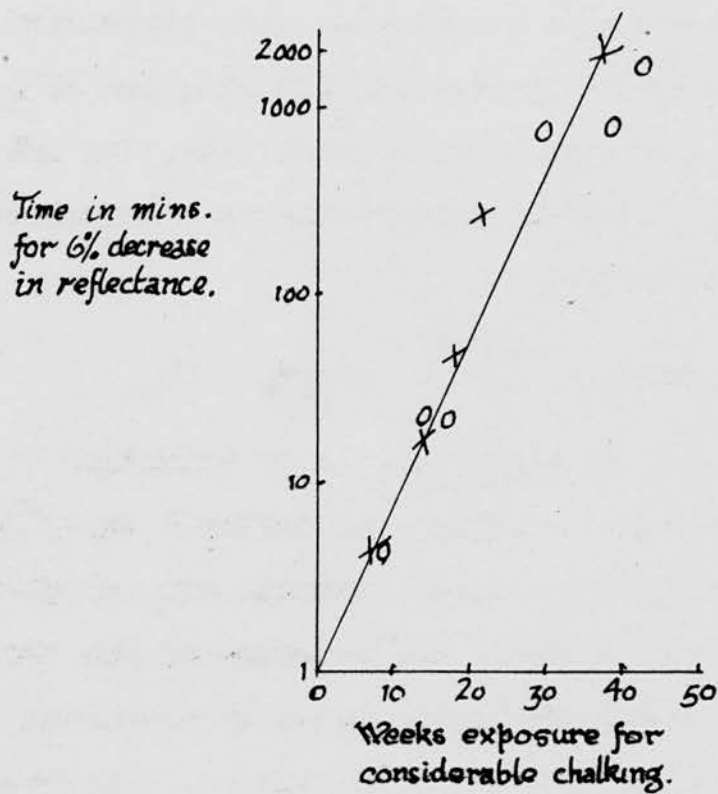
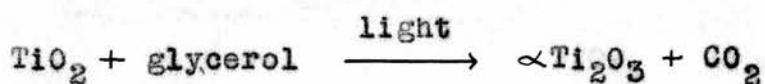


Fig 1 Relation between photo-reduction
and chalking.

This work follows closely that of Renz⁶ who claims to have detected CO₂ on illumination of titanium dioxide and glycerol, and who attributes the observed darkening of the mixture to the formation of a lower oxide, whereas Ruben⁷ favours formation of a higher oxide. Jacobsen supports his mechanism by claiming to have identified α -Ti₂O₃ by electron diffraction as an end product of illumination of a paste of TiO₂ paint pigment and glycerol. This constitutes the only direct piece of evidence reported in the literature for the production of a lower oxide on illumination of TiO₂.



Jacobsen quotes a number of media capable of oxidation in this manner, namely glycerol, aqueous solutions of tartaric acid, mandelic acid and stannous chloride, dye solutions, linseed oil, paraffin oil, and higher alcohols. He has followed the progress of the photo-reaction in a TiO₂-mandelic acid solution system by measuring the rate of darkening (decrease in reflectivity), and has correlated the reactivity of various pigments in this system with their ability to cause chalking (Fig. 1).

The darkening of titanium dioxide moistened with a silver nitrate solution on irradiation with U.V. light has been studied by Forland⁸. Where Goetz and Inn⁹ interpret the colour change as reduction of Ag⁺ to Ag, Forland proposes oxidation to Ag²⁺ on the basis of the following observations.

the oxygen liberated have been unsuccessful. Instead, Mackenzie¹² has made the important observation that titanium dioxide films can take up oxygen on illumination. It is possible that the oxide is photo-oxidised during tendering and flaking reactions, not photo-reduced, and Ruben's suggestion of higher oxide formation is worth recalling.

The work undertaken here is an extension of that begun by Mackenzie, and it is intimately connected with the two possibilities of reduction and oxidation of the surface of titanium dioxide. The model systems mentioned above have been reduced to simple TiO_2 -gas and TiO_2 -solid systems, and the effect of pre-treatment of the TiO_2 has been studied.

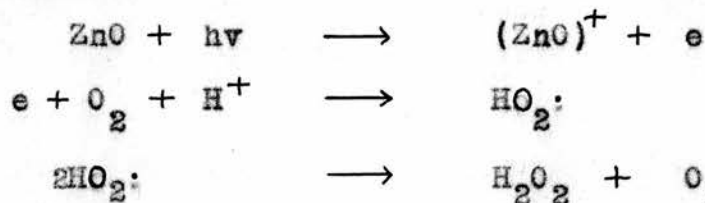
PHOTOCHEMISTRY OF RELATED SOLIDS

Reactions such as the sensitised fading of chlorazol sky blue are not specific to titanium dioxide. Mackenzie has shown that other solids, e.g. ZnO, Sb₂O₃ and Bi₂O₃, can take up oxygen on illumination and photo-sensitise the bleaching of chlorazol sky blue.

The sensitised formation and decomposition of H₂O₂ in the presence of various solids is of interest. Illumination of a suspension of ZnO either in distilled water or in a solution of hydrogen peroxide results in the same small equilibrium concentration of H₂O₂, and it has been found that the rate of formation and maximum yield of H₂O₂ are greatly enhanced by the addition of small quantities of various oxidisable organic substances (phenols, alcohols, acids).

The mechanism which has been proposed^{13 14 15 16 17 18} is as follows:-

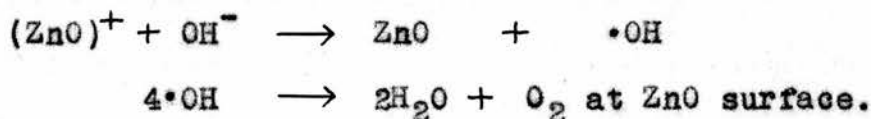
Formation



and in the presence of organic material, e.g. oxalic acid



whereas in the absence of organic material¹⁸



Decomposition

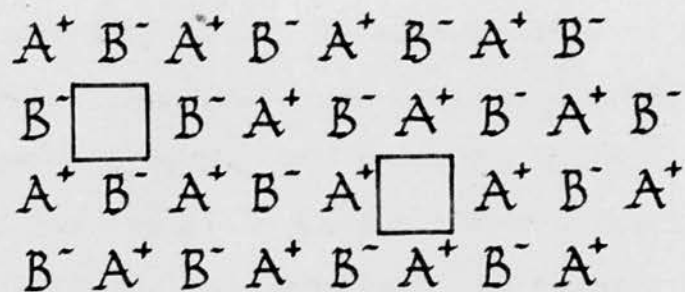
Chains initiated by $\cdot\text{OH}$.

Several attempts, made to detect H_2O_2 in illuminated suspensions of TiO_2 in water^{12 19 20} have been unsuccessful, but in general, TiO_2 photo-catalyses the oxidation of organic materials in solution, and it has been suggested¹⁹ that H_2O_2 is formed in aqueous suspensions but cannot be detected since it is strongly adsorbed on the TiO_2 surface. The surface of moist TiO_2 certainly has a strong oxidising action when illuminated, and the mechanism proposed for ZnO will bear consideration in explanation of this fact.

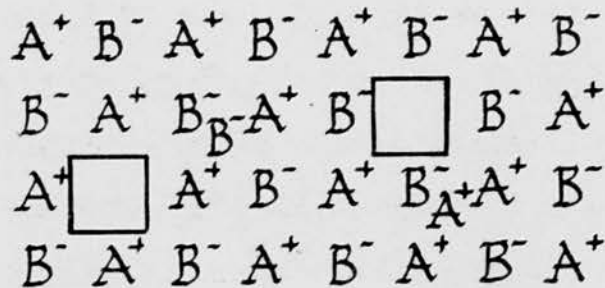
Goodeve²¹ and Markham¹³ both correlate the sensitising activity of various white pigments with their diffuse reflection spectra, and observe that, in general, the oxides which absorb the longest wavelengths are the most efficient sensitisers. The production of H_2O_2 in solid - H_2O - phenol additive systems does not depend on illumination with U.V. light, and the only restriction as to the light employed is that it should lie within the long wavelength absorption limit of the solid. A wide range of solids are effective in the reaction, e.g. CdS , CdSe , HgS , Ga_2O_3 , ZnS ²², suggesting that electronic structure is a more important criterion than actual composition.



(a) Two dimensional ideal lattice.



(b) Lattice with Schottky defects.
(A & B ion vacancies.)



(c) Lattice with Frenkel defects.
(vacancies plus interstitial ions.)

Fig. 2.

STRUCTURE OF SOLIDS²³

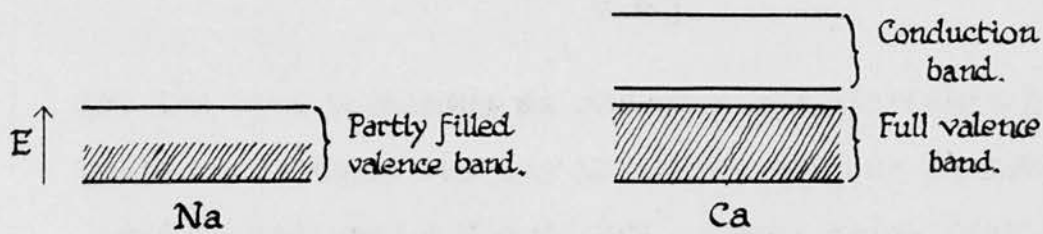
Explanation of solid state chemical reactions today rests on some generally accepted concepts regarding the structure of solids. It will be of advantage to give some preliminary discussion on these concepts, before applying them to the structure of titanium dioxide.

Crystal Structure

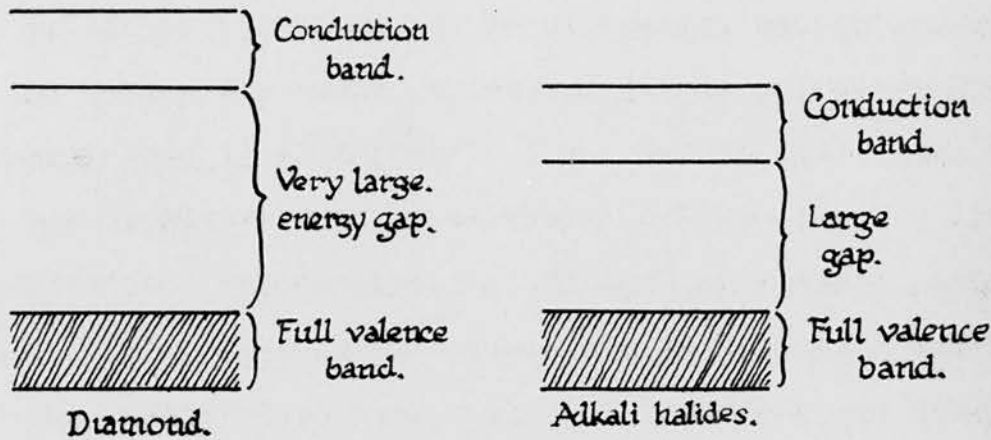
As a result of work carried out since 1912, the lattice theory of crystals has been in general substantiated, and on certain specific points expanded. Large crystals are looked upon as mosaics of tiny perfect crystallites; perfect that is in the sense that they have no macro defects such as dislocations, yet containing other defects called lattice defects, which are unlike dislocations in that they are localised at or near individual lattice positions. In a pure stoichiometric ionic crystal two possible lattice defects, namely Schottky and Frenkel defects (Fig. 2), may be illustrated. In addition to these, crystals may contain impurities where the impurity atoms or ions occupy interstitial or substitutional positions, and Schottky or interstitial defects may arise where we have deviations from stoichiometry (excess of either the electro-positive or the electronegative constituent). These lattice defects are of particular importance in the consideration of solid state reactions.

Electronic Structure

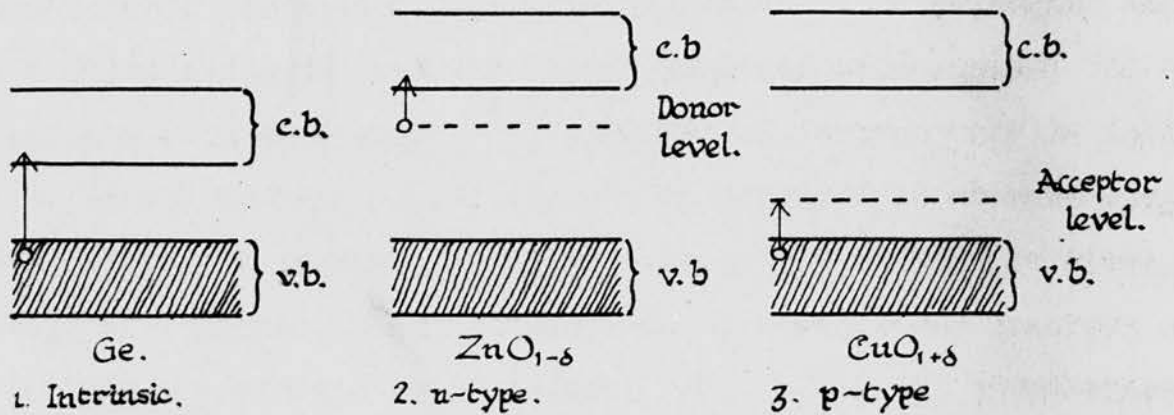
A modified Bloch model is generally used to describe the electronic levels in solids, because of the ease of explanation which it affords of conductivity phenomena. In the perfect crystal



(a) Metallic Conductors.



(b) Insulators.



(c) Semi-conductors.

Fig. 3.

the electronic orbitals are regarded as extending over all the lattice positions, and the electrons are not regarded as being localised at particular ions. The possible energies of the electrons in the crystal lie in a series of bands, which are illustrated (Fig. 3) for various types of conductor.

In semi-conductors excitation of the electrons resulting in electrical conductivity occurs thermally, since the energy gap involved is small (one or two e.v.). In intrinsic semi-conductors conduction is a result of the migration of both electrons and positive holes, whereas in impurity semi-conductors, conduction is a result of the migration of one species only, electrons in n-type semi-conductors and positive holes in p-type semi-conductors (Fig. 3c). Where the energy gap is large (several e.v.) excitation can only occur at high temperatures and the solid is a good insulator at ordinary temperatures (Fig. 3b). Excitation at low temperatures may take place, however, when the solid absorbs light of the appropriate wavelength. Absorption of a quantum gives rise to an electron in the conduction band of the solid and a positive hole in the valence band. Electrons and positive holes so produced can migrate in an electric field resulting in photoconductivity (Fig. 4). The wavelength of the light giving rise to photoconductivity is obviously related to the magnitude of the gap between the full valence band and the empty conduction band, but in some solids, e.g. NaCl, absorption of light of a wavelength longer than that which gives rise to photoconductivity can occur, i.e. NaCl has excited electron levels lying below the conduction band. When in these levels, the electrons remain localised near

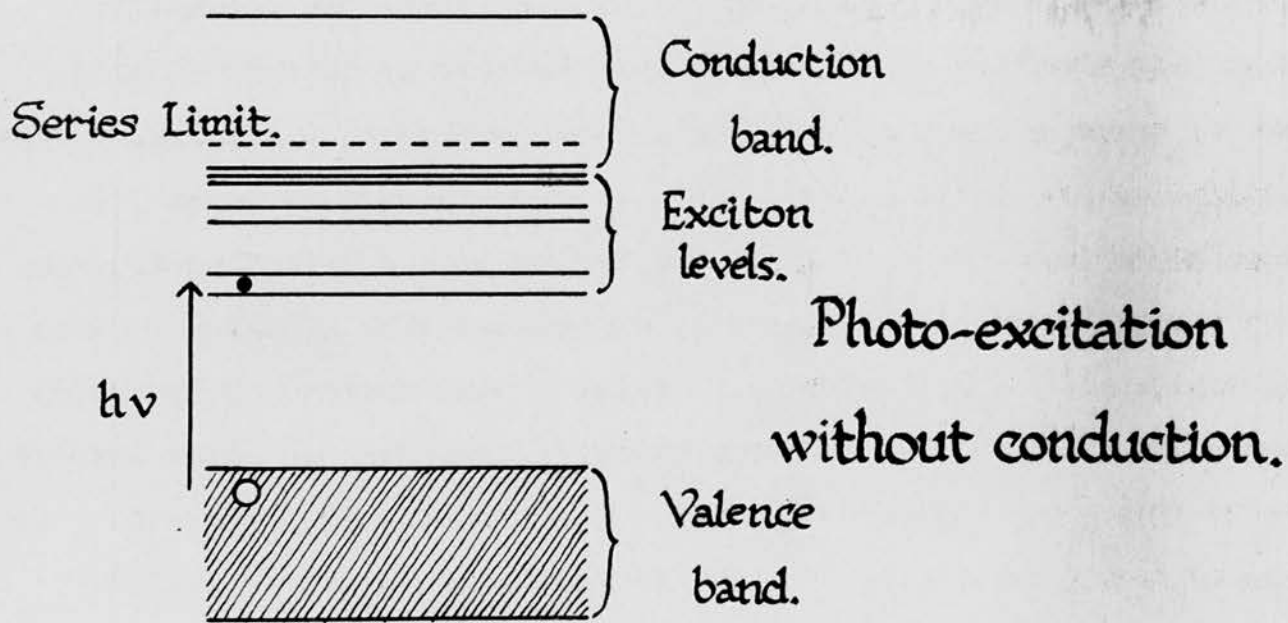
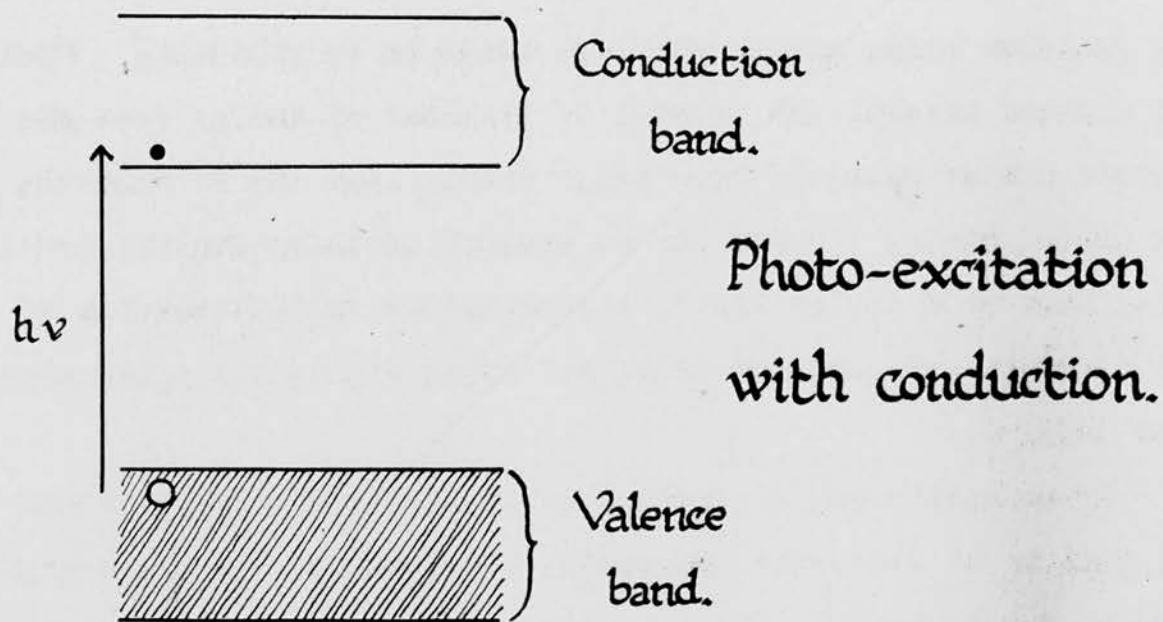


Fig. 4.

the positive holes giving what are known as an excitons. Excitons can migrate through the crystal by transfer of energy from the excited ion or molecule to a neighbouring like ion or molecule in the ground state. There may be several of these exciton levels which lead to a series limit, corresponding to dissociation of the electron and positive hole, and lying within the conduction band (Fig. 4).

As we have seen, absorption of light can give rise either to excitons or to electrons and positive holes, and these can migrate through the crystal. The excited electron can (a) undergo a radiationless transition to the ground state; (b) return to the ground state with the emission of light of a shorter wavelength than that absorbed giving either fluorescence or phosphorescence; or (c) cause a chemical reaction at the surface of the solid. Pure stoichiometric ionic solids have not been observed to fluoresce when irradiated in their first absorption band - both fluorescence and phosphorescence are generally associated with impurity centres in the lattice - but chemical reaction at the surface of the solid can occur as a result of energy transfer or actual electron transfer to or from some adsorbed molecule. If the overall process is purely one of energy transfer, then the terms photocatalyst or photosensitizer may be correctly used in describing the solid, but where the process is one of electron transfer occurring in one direction only, either to or from the solid, then the correctness of these terms is a matter for debate; it is, however, convenient to use them

to include both energy and electron transfer processes when referring to TiO_2 , ZnO etc. in reactions such as those quoted above, since it is by no means certain which process is actually taking place.

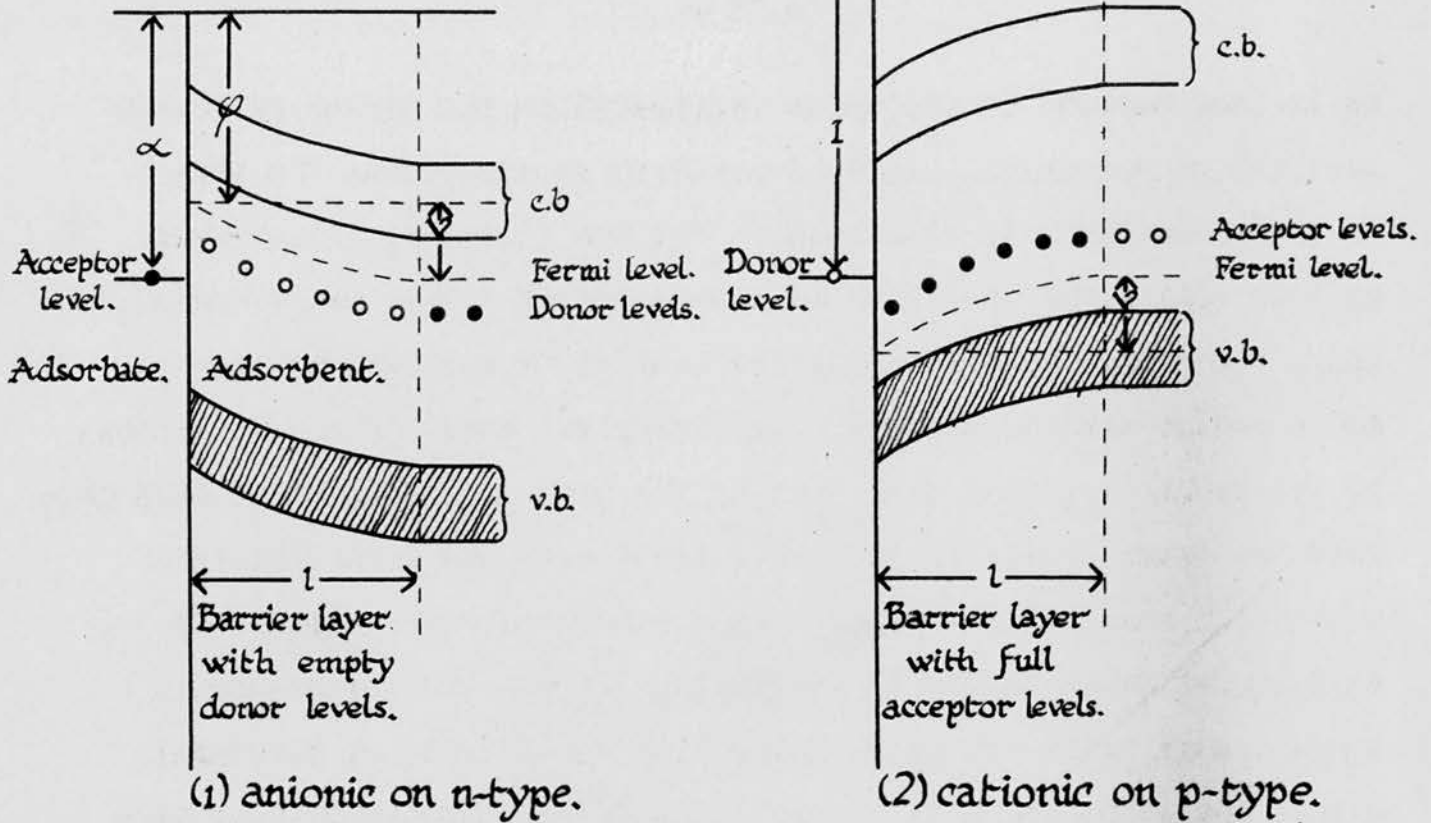
Chemisorption and Catalysis of Semi-conductors

Absorption of oxygen by TiO_2 on illumination immediately suggests some connection with chemisorption on semi-conducting oxides, and the problem must be considered from this view-point.

In recent years, the idea of electron transfer or localisation at chemisorption sites has received much consideration, and theories have been advanced to explain the fall in differential heats of adsorption with surface coverage. The factors considered to be operative include intrinsic heterogeneity, induced heterogeneity and repulsive interaction, which are important at low, medium and high surface coverages respectively. Frenkel steps, dislocations and crystal edges will be sites of high adsorption energy, and will be part of the intrinsic heterogeneity of the solid. The boundary layer theory considers the fall in heats of adsorption to be caused by the setting up of a space charge on chemisorption, giving rise to induced heterogeneity, and repulsion of charged chemisorbed molecules will be operative in the region of high surface coverage.

The boundary layer theory is of interest in discussing chemisorption on semi-conductors, since it takes into consideration the type of semi-conduction shown by the adsorbent. This is important in view of recent experimental attempts to correlate type of semi-conduction with chemisorption and catalysis. In the theory, two types of chemisorption are recognised, viz. depletive and cumulative,

(a) Depletive Chemisorption.



(b) Cumulative Chemisorption.

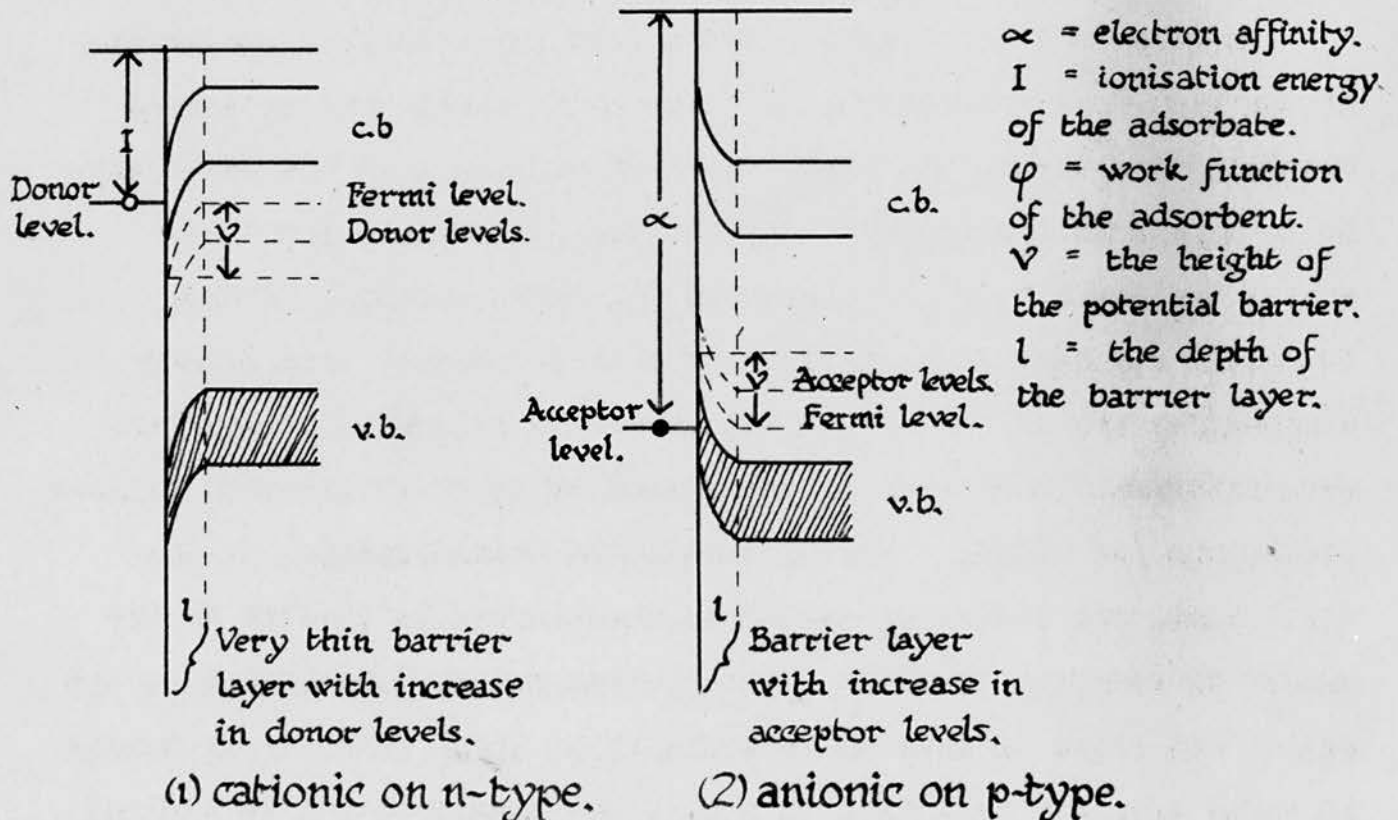


Fig. 5.

so defined because in depletive chemisorption the number of charge carriers is decreased, and in cumulative chemisorption the number of charge carriers is increased. The two types are illustrated as they will occur in theory on n-type and on p-type semi-conductors (Fig. 5). Take, for example, the case of depletive chemisorption on an n-type semi-conductor. Initially the Fermi level of electrons in the solid is higher than that in the gas, and transfer of electrons from the donor levels in the solid occurs with the formation of a negatively charged adsorbate. As a result of the transfer and the emptying of donor levels in the surface of the semi-conductor, a space charge is set up which lowers the Fermi level of electrons within the solid until it equals the potential energy of electrons in the adsorbate.

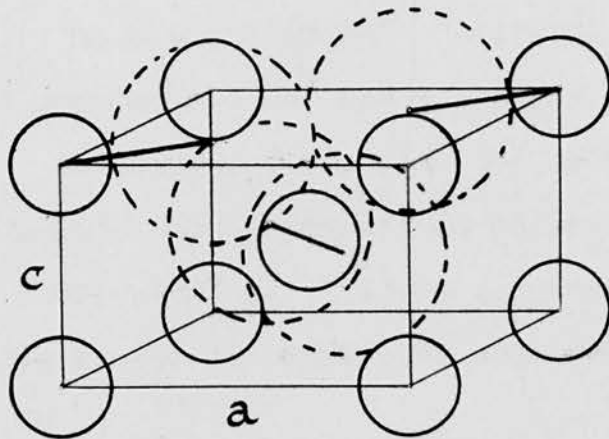
An important point which arises from the theory is prediction of the extent of chemisorption. The space charge set up during chemisorption causes the Fermi level of electrons in the adsorbent to be raised or lowered until equilibrium is reached where it equals the Fermi level of electrons in the adsorbate. During depletive chemisorption equilibrium will be reached long before a monolayer can be formed, as the number of molecules chemisorbed at equilibrium is limited by the number of donor or acceptor centres present in the solid. During cumulative chemisorption, on the other hand, the number of molecules chemisorbed is limited by the number of acceptor or donor centres which can be established in the solid, and since in general this number is large (density of levels in empty c.b. and full v.b. is high), the chemisorption is limited

firstly by the geometry of the surface, and a monolayer is formed.

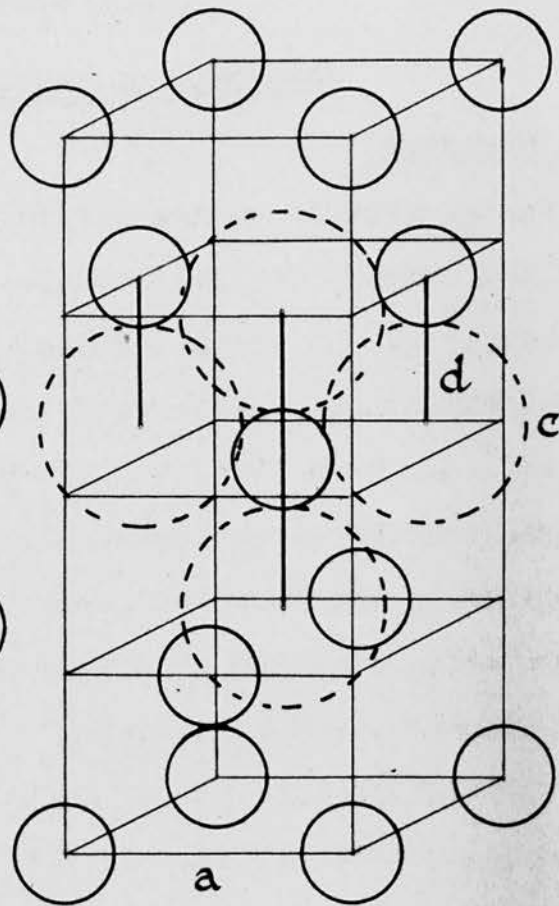
Theoretical work on the kinetics of chemisorption has centred round explaining equations of the Roginsky Zeldovich type, i.e.

$\frac{dq}{dt} = a e^{-b \cdot q}$ where q is the amount of gas chemisorbed and a and b are constants. Generally, the data are consistent with activated chemisorption occurring with a gradually increasing energy of activation, and again heterogeneity of the adsorbent surface and boundary layer formation have been invoked to explain the increase in activation energy with coverage. In some cases surface migration of the adsorbed species is considered to be rate determining, and the kinetics of the photo-absorption of oxygen by TiO_2 will be discussed in this light at a later stage.

Fig. 6.



Rutile.



Anatase.

	Anatase. ^{2.}	Brookite. ^{37.}	Rutile. ^{2.}
a	3.779	9.20	4.574
b		5.44	
c	9.493	5.14	2.950
d	1.95		1.99

Ionic radii ~ Ti^{4+} 0.64 A.
 O^{2-} 1.32 A.

STRUCTURE OF TITANIUM DIOXIDE

Crystal Structure

Titanium dioxide occurs naturally in three forms isomorphous with silica, namely Rutile, Anatase and Brookite. Pigment particles are generally of the rutile or anatase type. The unit cells of these two structures are illustrated in Fig. 6 and the parameters are given. In both forms the titanium ions are surrounded by six oxygen ions forming slightly distorted octahedra. The bonding is not entirely electrovalent, and there is evidence in X-ray and infra-red data, that two of the oxygens are more strongly bonded to the titanium than the other four.

Rutile and anatase can be prepared artificially and are used as pigments in both forms. In the solid state, transformation from anatase to the stable form rutile normally occurs around eight hundred degrees centigrade.

Samples obtained by hydrolysis of, or precipitation from aqueous solutions of $Ti(SO_4)_2$, $Ti(NO_3)_4$ and $TiCl_4$, followed by drying at $100^\circ C$, have been shown^{24 25} to give X-ray diffraction patterns which are characteristic of anatase or rutile depending on the conditions of preparation. Weiser and Milligan²⁴ propose that anatase is first formed, but since it is more soluble than rutile, it dissolves slowly with the simultaneous formation of rutile. The rate of transformation is a function of temperature, acidity and the presence of various ions, e.g. $(SO_4)^{2-}$, which may be more or less strongly adsorbed on the anatase crystallites, thus hindering the transformation.

Electronic Structure

Cronmeyer^{26 27} has studied the optical absorption of normal and reduced rutile in the form of single crystals. Normal rutile transmits well from 6,000 Å - 4,500 Å, the fundamental absorption band starting at 4,100 Å. Impurity levels have been observed giving absorption at 7,300 Å, 17,000 Å and 3,000 Å. The fundamental absorption band beginning at 4,100 Å has been correlated with the activation energy for high temperature conductivity and the peak in photo-conductivity of normal rutile. Semi-conducting TiO_2 (n-type) prepared by reduction at 800°C is deep blue arising from an absorption band with a maximum at 17,000 Å (0.73 e.v.). Conductivity-temperature plots for low temperature conductivity give an optical activation energy of 0.68 e.v., which is in good agreement with a theoretical calculation for the energy required to free the first of two electrons trapped at an oxygen vacancy - 0.74 e.v.

Diffuse reflection spectra obtained for various TiO_2 powders have shown the position of the fundamental absorption band as above for both anatase and rutile types^{13 21 28}.

Semi-conductivity

Reduced TiO_2 is an n-type semi-conductor^{27 29 30} and, as has been mentioned above, the conductivity can be attributed to the presence of oxygen ion vacancies with electrons trapped in their vicinity as Ti^{3+} . The insulating properties of reduced TiO_2 can be restored by heating to a sufficiently high temperature in oxygen.

Semi-conducting TiO_2 which cannot be oxidised in this way

can be produced by the incorporation of small amounts of impurities^{31 32}. For example, addition of small amounts of oxides of higher valency metals, WO_3 , Nb_2O_5 , Ta_2O_5 etc., gives rise to an increase in conductivity, since Ti^{4+} is replaced by W^{6+} , Nb^{5+} , Ta^{5+} in the lattice, and a corresponding number of electrons are made available for conduction. Addition of oxides of lower valency metals, Ga_2O_3 , Al_2O_3 , NiO etc. to semi-conducting TiO_2 causes a lowering in conductivity since Ti^{4+} is replaced by Ga^{3+} , Al^{3+} , Ni^{2+} with a corresponding decrease in the number of electrons available for conduction. An increase in conductivity can also be induced by incorporation of small cations such as Be^{2+} interstitially in the lattice³². These general rules are not always obeyed. For example, addition of Cr_2O_3 can increase as well as decrease the conductivity, depending on the temperature at which the conductivity is measured³¹.

Chemisorption and Catalysis

In recent years connection between catalysis and semi-conductivity of oxides has been sought and the catalytic properties of titanium dioxide and its chemisorption are undoubtedly related to its electronic structure and its exhibition of n-type semi-conduction in the reduced form.

Little direct evidence is available for the chemisorption of gases on titanium dioxide presumably because anionic chemisorption proceeds to only a fraction of a monolayer, as predicted by the boundary layer theory, and because cationic chemisorption seems to occur only at elevated temperatures. However, the studies of Winter^{33 34 35} on oxygen exchange and equilibration reactions of

oxides imply that TiO_2 must chemisorb oxygen, although only to a small extent, at temperatures under $400^\circ C$ and Hauffe³¹ has explained conductivity abnormalities of TiO_2 containing 0.7% WO_3 on the basis of chemisorption of oxygen at pressures above one millimetre. Chemisorption of CO and H_2 must occur at high temperatures as a first stage in the reduction of the oxide.

Ryerson and Hönig³⁶ have studied the sorption of NO_2 on rutile prepared from $TiCl_4$, and conclude that at temperatures near normal some chemisorption takes place on oxygen deficient sites, resulting in the detection of amounts of NO and smaller amounts of N_2O_3 and $NOCl$ in the gas phase. They suggest that such samples of titanium dioxide are deficient in oxygen, and that in NO_2 these deficiencies are made good with the partial reduction of the adsorbate to NO and N_2O_3 . The oxygen deficiency is enhanced by prolonged degassing at $400^\circ C$.

Further discussion of the general picture of the TiO_2 surface will be postponed until Part IV, where consideration will be given to results on the photo-uptake of gases by TiO_2 .

PART II

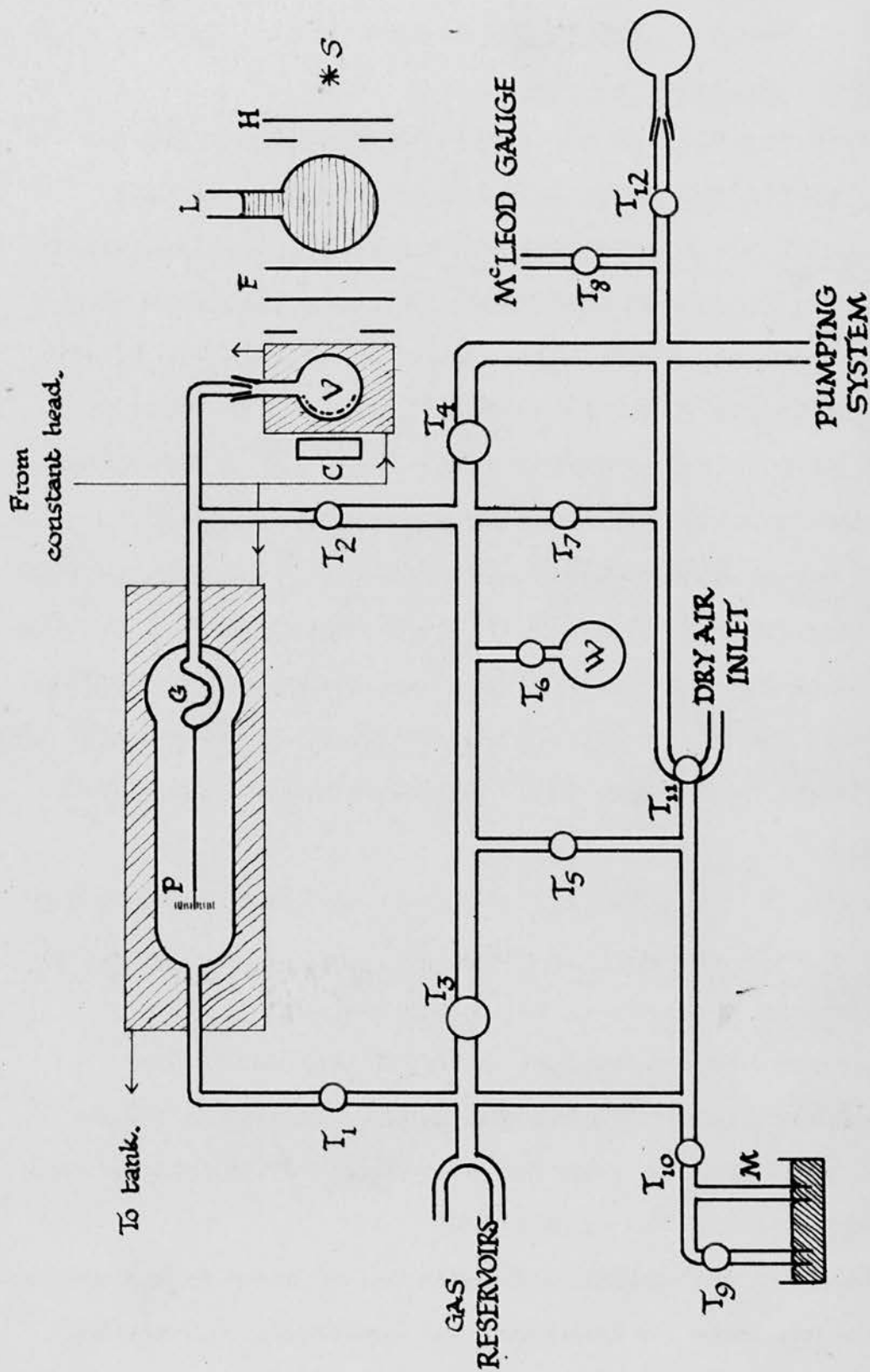


Fig. 7. Apparatus for sorption measurements.

APPARATUS

Apparatus for Sorption Measurements

The essential function of the apparatus which is shown in diagram form (Fig. 7), was to measure changes in gas pressure occurring over an illuminated film of titanium dioxide, contained in a reaction space of constant volume. Illumination of a film deposited on the rear of vessel V was effected by a source S, and the small changes in gas pressure were followed by observing the movement of the pointer of a Bourdon gauge G through a telescope, fitted with a graduated scale. Steady gas pressures could be measured by the use of either the Bourdon gauge or the manometer M; a McLeod gauge was used to determine the vacuum attained on pumping. Most of the apparatus, including the Bourdon gauge, was blown from soft glass tubing, and where necessary, ground glass joints and taps were fitted; these joints and taps were kept vacuum tight with Apiezon L grease.

Pressures ca. 10^{-5} mm. Hg. were attained by using a two stage mercury diffusion pump backed by a Hyvac oil pump; pressures ca. 10^{-3} mm. Hg. could be attained by using the oil pump alone. Diffusion of mercury and oil vapours into the apparatus was prevented by pumping the system out via a trap at liquid oxygen temperature. Provision was made for admitting various gases from storage bulbs attached to the apparatus.

The smallness of the pressure changes to be measured at overall pressures ca. 50 mm. made it necessary to thermostat the system accurately; it was particularly important that the reaction vessel

and gauge should be kept at the same temperature within close limits. This was achieved by circulating water from a large thermostat tank around the gauge jacket and the reaction vessel. The water was pumped from the tank to a constant head device, from which it was allowed to flow in a divided stream around the gauge jacket on the one hand, and the reaction vessel on the other, and then back to the main tank. The temperature of the water in the main tank was maintained at about 25°C to $\pm 0.01^{\circ}\text{C}$ by a Sunvic control in circuit with a large chloroform-mercury switch. Any change in gas pressure caused by small variation in the temperature of the water in the main tank was not registered by the gauge system, since both sides were affected, and the change on one side compensated for the change on the other.

An Osira mercury vapour lamp was used as a light source, and to prevent fluctuations in light intensity, the lamp circuit was connected to the mains via a voltage stabilising transformer. The flask L was filled with a copper sulphate solution ($\bar{=}$ 1 cm. of a solution containing 100 grms. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ /l.) and functioned both as an infra-red filter and a condensing lens. No light was passed below $3,200\text{\AA}$, the lower limit set by the glass of the apparatus. Various filter combinations were used to pass whatever lines of the mercury spectrum were required.

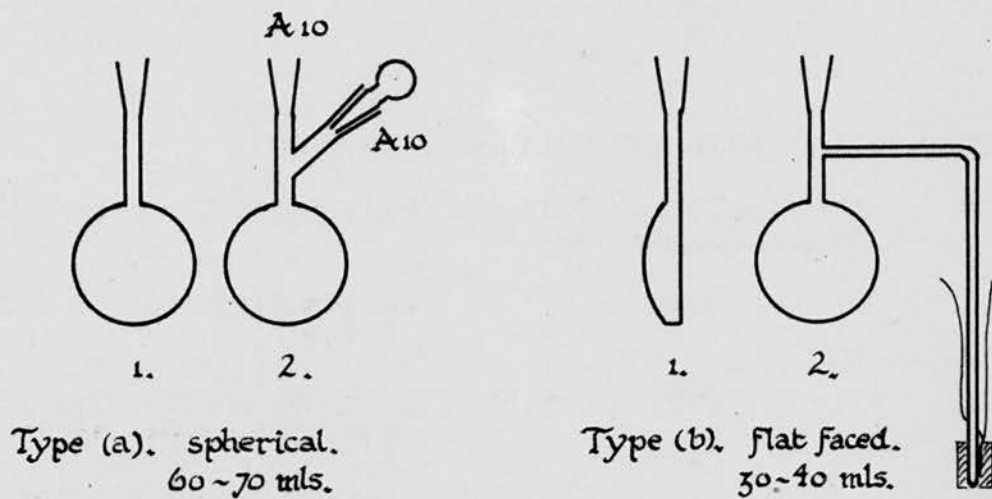


Fig. 8. Reaction vessels.

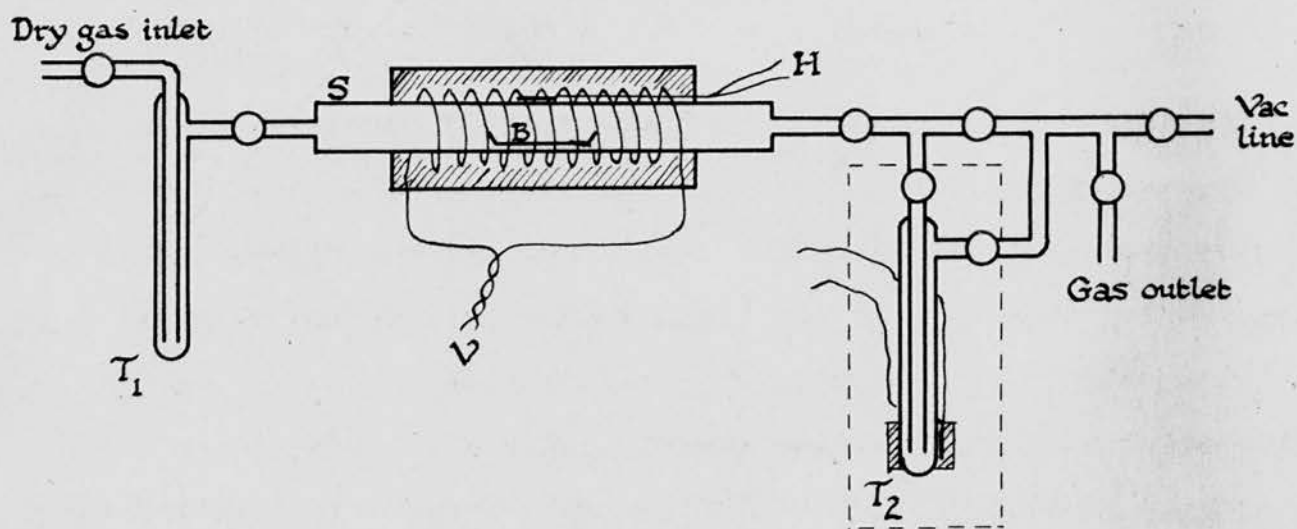


Fig. 9. Apparatus for pretreatment
of samples.

The following table gives the combinations used:-

Filter	Wavelength in A of light transmitted	Filter Combination used
1.	3,650	Wood's glass plate 2 mm. thick.
2.	4,050	1 cm. saturated aqueous copper nitrate solution and 1 cm. iodine in carbon tetrachloride: 7.5 grms./l.
3.	4,360	1 cm. cuppramonium sulphate: 50 grms. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 600 mls. 0.88 ammonia in 1 l. aqueous solution, and 1 cm. saturated aqueous sodium nitrite solution.
4.	> 4,000	1 cm. saturated aqueous sodium nitrite solution.

(Solutions were contained in 1 cm. glass filter cells.)

For the purpose of calibrating the filters to be used for reducing the intensity of 3,650A light, and for the purpose of measuring the intensity of the light transmitted by the film at various wavelengths, a barrier type photocell C was placed in the light path behind the reaction vessel. The photo-current was measured by a sensitive low resistance galvanometer in series with the photocell. Over the range of intensities used, the photo-current was assumed proportional to intensity of light impinging on the cell.

Various reaction vessels were used (Fig. 8). For the majority of experiments, spherical flasks of pyrex or soft glass with A 10 Quickfit sockets gave reaction volumes ca. 60 mls. (Type(a) Fig. 8);

side arms were fitted when carrying out experiments in the presence of some chemical absorbent (Type (a)2 Fig. 8). In experiments which necessitated the maximum sensitivity of the system, small flat-faced vessels were used (Type (b) Fig. 8), and for freezing out products of reaction, a side arm of small bore (2 mm.) was fitted (Type (b)2 Fig. 8). To estimate the temperature of the condensed products in this side arm, a thermocouple could be taped to the lower end of the side arm.

Apparatus for Pre-treatment of Titanium Dioxide Samples

Fig. 9 shows the main features of the apparatus. The silica tube S was wound with resistance wire which was connected to the mains via a Variac transformer V. The temperature of the sample contained in boat B was maintained by applying the necessary voltage across the heating element, and was estimated by means of a calibrated thermocouple H. A stream of gas could be passed slowly through the system; trap T_1 at liquid oxygen temperature removed any condensable vapours from the entering gas, and trap T_2 collected any condensable vapours evolved from the sample during treatment. T_2 was removable, and could be connected to the Bourdon gauge for the determination of the vapour pressure curves of the products; a thermocouple, which could be used to determine the temperature of the condensed products, was taped to the outside of the trap. The apparatus could be evacuated to 10^{-5} mm. Hg. by the pumping unit described above.

SOURCE, PREPARATION, AND PURIFICATION OF CHEMICALS

Titanium Dioxide Samples

Various oxide samples were used, and short notes with relevant information about them are given below. All samples were stored in a desiccator over P_2O_5 before use.

Technical samples:-

- A. Hopkins and Williams (purified grade); ground before use.
- B. British Titan Products Ltd.: Rutiox WD.
- C. British Titan Products Ltd.: Anatase HR.
- D. British Titan Products Ltd.: Rutiox HD Cr treated.
- E. British Titan Products Ltd.: Anatase HR Cr treated.
- F. British Titan Products Ltd.: prepared by the vapour phase oxidation of $TiCl_4$ to give a very pure product containing only a trace of chlorine.

Samples B, C, D and E were supplied as suspensions in water; these were centrifuged, and the oxide was washed several times with distilled water, dried over P_2O_5 in a pistol drier (16 - 30 hrs.), and finally lightly ground in an agate mortar.

Laboratory prepared samples:-

- a. 6 mls. $TiCl_4$ (B.D.H.) were added slowly to 150 mls. distilled water and refluxed for 6 hrs. The free acid was neutralised by adding a slight excess of 2N NaOH (A.R.), and the mixture was further refluxed for 6 hrs. The hydrated oxide was filtered off through a Whatman 542 paper and washed with distilled water until free of Cl^- . The oxide was then dried in a pistol drier over P_2O_5 (24 hrs.) and after grinding to a fine powder, was stored in a desiccator.

- bl. 6 mls. $TiCl_4$ (B.D.H.) were added slowly to 150 mls. distilled water and refluxed for 5 mins. A slight excess of 2N NaOH (A.R.) was added, and the mixture was refluxed for another 5 mins. Filtration, washing etc. was carried out as for a.
- b2. Repeat preparation of bl.
- c. Prepared by J. Mackenzie. A small quantity of $TiCl_4$ (B.D.H.), which had been distilled once under reduced pressure, was added to many times its bulk of water and boiled for 30 mins. The free acid was neutralised with NaOH (A.R.) and the oxide was filtered off, washed with hot water, and dried for 44 hrs. as above.
- d. Prepared by J. Mackenzie. An undistilled sample of $TiCl_4$ (Chemistry Department Museum, Edinburgh) was added to water and boiled for 30 mins; the free acid was neutralised with dilute ammonia.

Samples B and D were of the rutile form, and samples C and E were of the anatase form. The preparations a and b were designed, on the basis of ideas forwarded by Weiser and Milligan²⁴, to give rutile and anatase respectively. Samples D and E were surface treated with chromium, being supplied as suspensions in water containing a small concentration of CrO_3 (0.1%).

Gas Samples

Hydrogen, nitrogen and oxygen were obtained from cylinders (B.O.C.) and no purification was carried out other than drying over P_2O_5 and passing through a trap at liquid oxygen temperature. The oxygen was stored in a glass bulb of about 2 litres capacity attached to the apparatus. Analysis data for these gases are given below.

Oxygen	Hydrogen	Nitrogen
Oxygen 99.5% (dry)	Hydrogen 99.9% (dry)	Nitrogen 99.9%
Argon 0.5%	Oxygen 0.05%	Oxygen 0.05%
	Nitrogen 0.05%	Rare gases 0.05%

Nitric oxide was prepared by two methods:-

1. A mixture of concentrated nitric acid and concentrated sulphuric acid (4 vols./3 vols.) was shaken with mercury in a flask. The nitric oxide evolved was purified first by passing over solid potassium hydroxide, and then by repeated collection in and distillation from a cold trap into an evacuated storage bulb.
2. The nitric oxide evolved by the action of diluted nitric oxide (1:1) on copper turnings was passed into a cold saturated solution of ferrous sulphate. On warming, the resulting liquid gave off NO, which was collected and distilled from a cold trap as described above to give the pure gas.

Nitrous oxide was obtained from a cylinder (Elliott & Co., Edinburgh) and was distilled as required from a cold trap.

Carbon monoxide was prepared by the action of concentrated sulphuric acid on dry sodium formate. The gas evolved on heating gently was bubbled through a caustic soda solution, dried over P_2O_5 , and passed through a trap at liquid oxygen temperature before storing in a glass bulb connected to the apparatus.

Other Chemicals

All of the solids examined for possible photo-reaction on titanium dioxide were obtained commercially and where possible were of A.R. grade. The acetone used as a binding liquid was A.R. grade obtained from Hopkins and Williams Ltd.

EXPERIMENTAL TECHNIQUES

Calibration of the Bourdon Gauge

The platinum tip of the Bourdon gauge pointer was observed through a telescope fitted with a graduated scale; the optical axis of this telescope was perpendicular to the plane of movement of the pointer. The sensitivity of such a gauge system has been found to be constant over the pressure range 0 - 200 mms. and it was determined here at 50 mms., at which pressure the majority of experiments were carried out.

About 50 mms. dry air were admitted into the apparatus. After tap T_5 was closed the pressure was recorded accurately by reading manometer M to the nearest 0.1 mm. Some air was pumped from the gauge jacket through T_{11} and the number of divisions moved by the pointer were recorded to the nearest 0.1 division. The pointer was restored to the other end of the scale by pumping air from the gauge through tap T_7 (the pointer was allowed an excursion of about 50 divisions about the centre of the scale). This pumping procedure was repeated many times until an appreciable pressure change was registered by the manometer, and the number of divisions which the pointer travelled as the gauge jacket was evacuated, was noted each time. From this pressure change and the total number of divisions travelled by the pointer, the sensitivity was calculated as follows:-

Total pressure change	=	14.8 mms.
Number of scale divs. travelled	=	490
490 divs.	=	14.8 mms. Hg.
1 div.	=	0.0302 mm.

On repetition

$$1 \text{ div.} = 0.0308 \text{ mm.}$$

$$\text{and } 1 \text{ div.} = 0.0298 \text{ mm.}$$

$$\text{Sensitivity of gauge} = 0.0305 \text{ mms. Hg./div.}$$

Determination of reaction space volume

The volume in which pressure changes were recorded had to be known in order that they could be converted into molar quantities. For the purpose of determining this volume, a bulb W of known volume was attached to the apparatus.

About 300 mms. of dry air were admitted to the evacuated apparatus and after closing T_2 and T_{11} , vessel W, and the leads between W and the reaction vessel were evacuated. The reading on manometer M was recorded to the nearest 0.1 mm. and the air in the reaction vessel was allowed to expand into the leads after closing T_6 ; the pressures on either side of the gauge system were kept the same during this expansion by pumping out the gauge jacket through T_{11} and maintaining the gauge pointer at its equilibrium position. The pressure reached was recorded by manometer M. A second and final expansion was carried out in the same way, this time into the vessel of known volume W. From the results, the volume of the reaction space was calculated; a typical result is shown below:-

Volume of reaction space V	=	V_1
Volume leads	=	V_2
Volume of vessel W	=	$V_3 = 149.1 \text{ mls.}$
Pressure of gas in V_1	=	$P_1 = 307.2 \text{ mms.}$
Pressure of gas in $V_1 + V_2$	=	$P_2 = 192.9 \text{ mms.}$
Pressure of gas in $V_1 + V_2 + V_3$	=	$P_3 = 74.4 \text{ mms.}$

$$V \text{ is given by } V_1 = \frac{P_2}{P_1} \times \frac{P_3 V_3}{P_2 - P_3}$$

$$\begin{aligned} \text{By substitution } V_1 &= \frac{192.9}{307.2} \frac{74.4 \times 149.1}{(192.9 - 74.4)} \text{ mls.} \\ &= 58.78 \text{ mls.} \end{aligned}$$

$$\text{On repetition } V_1 = 58.93 \text{ mls.}$$

Volume of the reaction space = 58.9 mls.

Preparation of titanium dioxide films

A weighed quantity of the oxide (0.12 gm.) was introduced into the reaction vessel via a filter funnel, and a known volume of binding liquid (0.2 ml. acetone) was added to wet the oxide thoroughly. The liquid was drawn off on a filter pump, while the flask was rotated to obtain an even coating of oxide over the rear of the reaction vessel. As a result of preliminary experiments (p.32) it was clear that both the time and the extent of evacuation given to films prepared in this way were important for removal of the binding fluid; the following general procedure was, therefore, adopted for the evacuation of acetone bound films.

The flask with the film deposited as described above was evacuated to ca. 10^{-5} mm. via tap T_{12} and was allowed to stand at that pressure with intermittent periods of pumping for approximately four days; dry air was then admitted, and the flask was removed and connected to the gauge to be in position for conducting the experiment; in this new position the film was pumped and allowed to stand at 10^{-5} mm. for a further two days. A final period of evacuation to 10^{-5} mm. Hg. pressure for about an hour was always given before commencing the experiment.

Determination of oxygen uptake isotherms

The thermostat system and mercury lamp were switched on some time before commencing the experiment to allow steady working conditions to be attained. Oxygen was admitted to the system via tap T_3 to a pressure of about 50 mms., which pressure could be assumed constant during the reaction, since the changes recorded were generally less than approximately 3 mms. and since it was later shown that the rate of uptake in this pressure range is independent of pressure; if the pressure changes exceeded approximately 3 mms. more oxygen was added to restore the pressure to its original value. Taps T_1 and T_2 were closed and gauge readings were recorded for some time in the dark; no dark uptake of oxygen occurred, but the readings served as a check for temperature fluctuations. When the reading was steady, illumination of the film was begun by removing the shutter H from the lamp house. The fall in pressure which occurred was recorded by reading the gauge to the nearest 0.1 of a division at intervals of several minutes; the greater the rate of fall in pressure, the more frequently were the readings taken. Excursion of 50 divisions about the equilibrium reading was allowed, and if during a run the gauge pointer reached the end of the allowed scale, it was restored to the other end by rapid removal of some oxygen from the gauge jacket. A curve could be drawn plotting Δp (the fall in oxygen pressure in divisions) against t (the time of illumination in minutes); in a constant volume system, this is equivalent to plotting oxygen uptake in moles against time of illumination.

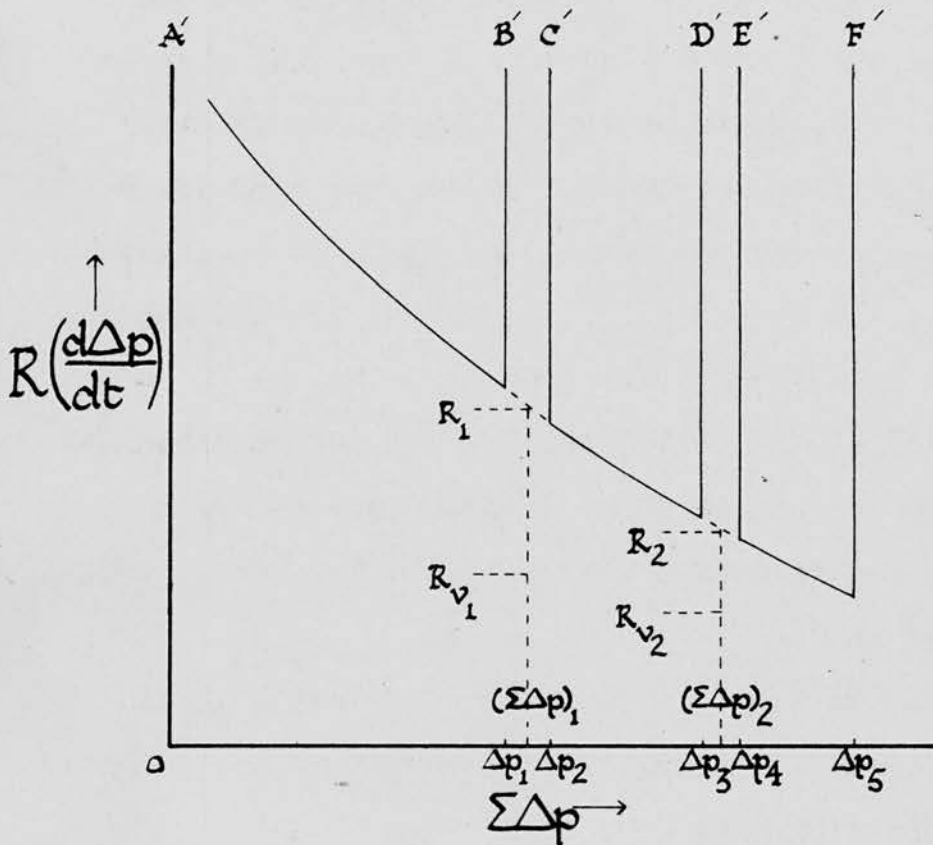
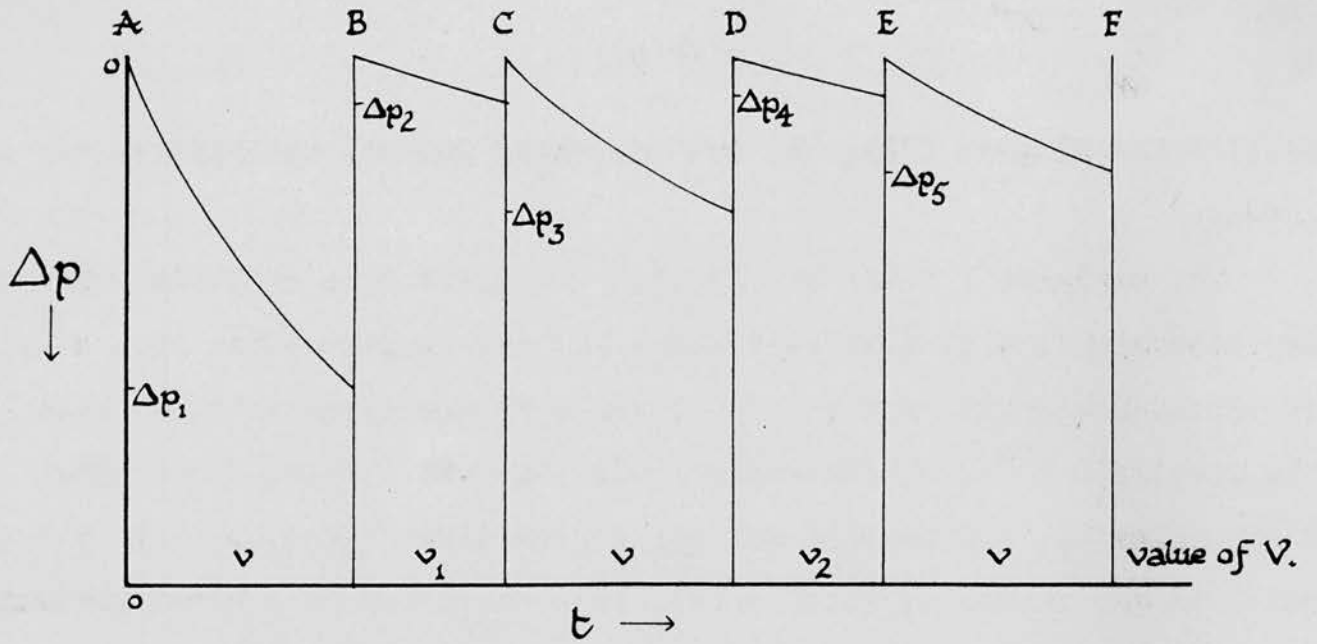
In some cases it was found necessary to carry out the runs in stages, interrupting illumination of the film to stand in the dark overnight. The effect of standing in the dark in oxygen and in vacuo was studied in some preliminary experiments (p. 32); only small increases in rate of uptake occurred, and these were only appreciable after standing in vacuo. It was, therefore, found possible to draw smooth $\Delta p - t$ curves for runs including periods of standing in the dark in oxygen.

Rate Curves

The $\Delta p - t$ curve obtained in the manner described above was divided into time intervals in which approximately the same changes in pressure had occurred. The total pressure change ($\Sigma \Delta p$ in divisions) half way through each time interval was recorded, and the rate of uptake ($\frac{d\Delta p}{dt}$ in divisions per minute) at that $\Sigma \Delta p$ was taken as the change in pressure occurring during an interval divided by the length of the interval. A plot of the values of $\frac{d\Delta p}{dt}$ against the values of $\Sigma \Delta p$ gave a 'rate curve' for the reaction.

The relative rate method

The relative rate method was devised to study the rate of reaction as a function of various conditions such as light intensity. The absolute rate of oxygen uptake is a function of many variables, viz. those which can be varied or kept constant at will e.g. light intensity and those which are independent of such control e.g. the state of the titanium dioxide film. The relative rate method takes into account the effect of the latter variables on the reaction, and the effect of a variable such as light intensity can then be followed. With the



$\Sigma \Delta p$	v	observed R.	interpolated R.	Relative Rate.
$\Sigma \Delta p_1$	v_1	R_{v_1}	R_1	R_{v_1}/R_1
$\Sigma \Delta p_2$	v_2	R_{v_2}	R_2	R_{v_2}/R_2

Fig. 10.

help of the diagram (Fig. 10) the following general description may be given.

The variable V under examination was given some suitable value v for determining a general rate curve for the oxygen uptake of a film of titanium dioxide, and a $\Delta p - t$ curve AB was obtained from which the portion $A'B'$ of the rate curve was derived. At B , V was given a new value v_1 , and keeping all other conditions the same, the $\Delta p - t$ curve BC was obtained, which gave a rate value Rv_1 at a total pressure change $(\Sigma\Delta p)_1$. V was then given its original value v , and the portion $C'D'$ of the rate curve was obtained. In this way a series of values $Rv_1, Rv_2 \dots\dots\dots$ and a series of rate curve portions $A'B', B'C', C'D' \dots\dots\dots$ were obtained; a complete rate curve was drawn $A'B'C'D' \dots\dots\dots$ and the values $R_1, R_2 \dots\dots\dots$ were interpolated at $(\Sigma\Delta p)_1, (\Sigma\Delta p)_2 \dots\dots\dots$. Change of variable V from v to v_1 caused a lowering in rate from R_1 to Rv_1 at $(\Sigma\Delta p)_1$; the fraction $\frac{Rv_1}{R_1}$ was called the 'relative rate' of the reaction for the value v_1 of variable V . To show the rate of reaction as a function of variable V , the relative rate values $(RR)_1, (RR)_2 \dots\dots\dots$ were plotted against the values $v_1, v_2 \dots\dots\dots$

The method was modified when carrying out experiments in NO , where a dark reaction occurs simultaneously with that under illumination. Either of two modifications were made, viz. -

(a) the film was allowed to stand for a long time in the dark until the dark rate was low enough to be neglected, and

(b) the dark rate was plotted as a function of time, and corrections for the rate values determined under illumination were derived from the $\frac{d\Delta p}{dt}_{\text{dark}} - t$ curve.

Pre-treatment of samples

A weighed quantity of the sample (0.3 gm.) contained in a small porcelain boat B was placed in the heating tube, where it was degassed for some hours at 100 - 200°C. The required dry gas for the treatment was then admitted slowly to the system, and when atmospheric pressure was reached, a slow stream of gas was allowed to pass through the system; when it was desired to collect any condensable products, the gas was passed through traps T_1 and T_2 at liquid oxygen temperature. The temperature was raised to the desired value and was maintained for the required length of time before isolating trap T_2 , switching off the heater and allowing the sample to cool in the stream of gas. The apparatus was evacuated at room temperature before admitting air and removing the sample. Trap T_2 was connected to the gauge for examination of the products.

Determination of vapour pressure curves

The condensed products in trap T_2 or the side arm of vessel (b)2 were kept at liquid oxygen temperature by surrounding with liquid oxygen contained in a vacuum flask, and the gauge was evacuated in readiness for measuring their vapour pressures. The temperature was estimated by means of the thermocouple taped to the bottom of the trap. After closing the gauge tap, the flask containing the liquid oxygen was removed and quickly replaced by another empty flask, which had been chilled to liquid oxygen temperature. The temperature rose slowly, and as the products distilled into the gauge, a plot of pressure against temperature was obtained. This curve was compared with data from the International Critical Tables

to identify the products. Confirmation of the identities of the products was obtained by comparing the vapour pressure curve for the products with curves obtained in the same way for known substances having the suspected identities.

PART III

RESULTS AND CONCLUSIONS

THE PHOTO-UPTAKE OF OXYGEN

The first aim in the present work was to examine in some detail the photo-uptake of oxygen exhibited by titanium dioxide, which phenomenon was first reported by Mackenzie in 1952^{1,2}. In the course of his investigations on the photo-sensitized bleaching of the dye chlorazol sky blue adsorbed on titanium dioxide powders, Mackenzie found that films of various oxides, including titanium dioxide, took up oxygen on illumination; in the case of titanium dioxide he showed that this uptake was directly related to the photo-sensitized bleaching reaction, just as Jacobsen¹ had shown that the photo-darkening of pastes composed of TiO_2 pigments and mandelic acid solutions was related to the flaking of paints containing these pigments. The experiments carried out by Mackenzie on the photo-uptake itself were only of a preliminary nature, and by extending his observations it was hoped that some knowledge of the nature and possible mechanism of this reaction would be gained, together with its relation to the electronic structure of the solid. In the first experiments, therefore, the characteristics of the oxygen reaction shown by samples of titanium dioxide prepared in various ways, and by a sample of titanium dioxide pretreated in various ways were studied.

Experiments concerned with degassing of the films

(Reversibility of the photo-uptake).

Mackenzie made the observation, that films which were left to stand for some time in the dark both in vacuo and in oxygen, showed an increased rate of uptake on subsequent illumination in oxygen.

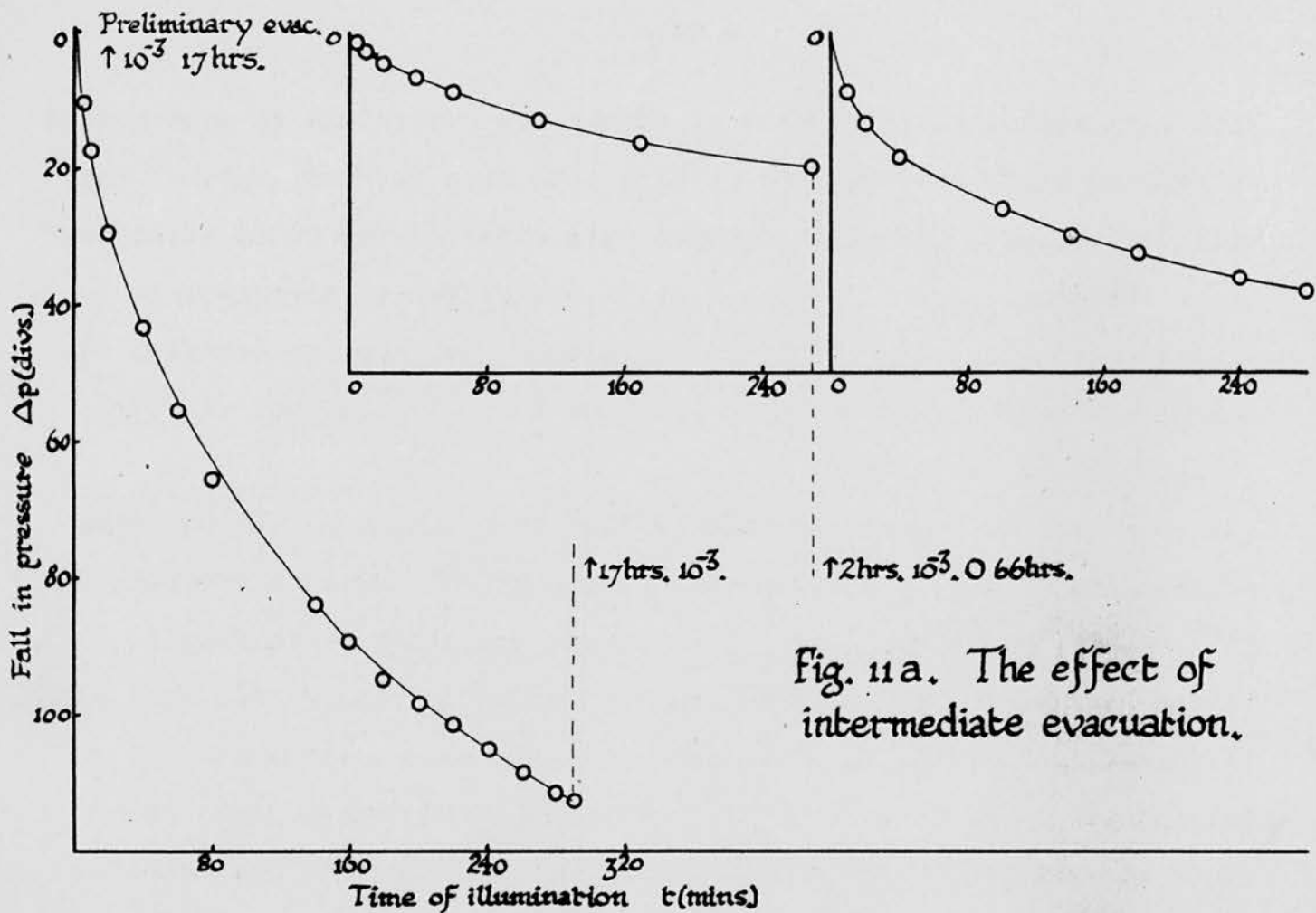
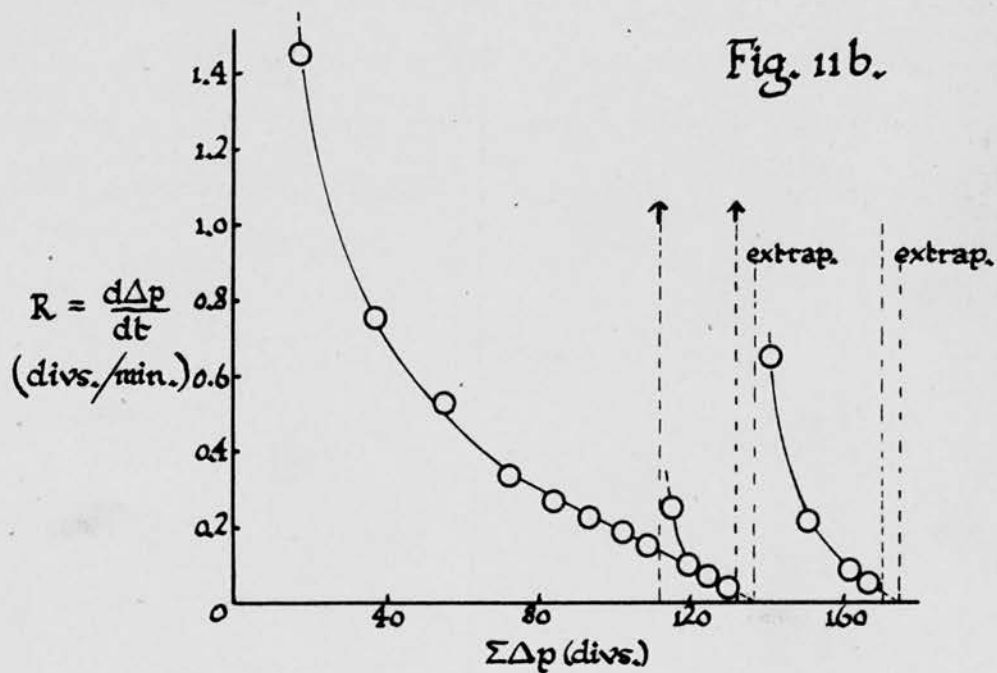


Fig. 11 a. The effect of intermediate evacuation.



This suggested that the uptake of oxygen was reversible to some extent on ceasing illumination. To enquire into this further, several runs were carried out, and uptake curves were obtained for films which were given different preliminary evacuation and different intermediate evacuation; for these experiments, pumping was carried out with the vessel attached to the gauge in position for illumination. A typical result will be described.

A film was prepared by binding 0.12 gm. sample c with 0.2 mls. acetone, and a preliminary pumping period of 17 hrs. to a pressure of 10^{-3} mm. Hg. was given. A $\Delta p - t$ curve was obtained at 24.9°C . in 52 mms. oxygen contained in a reaction vessel of volume 58.9 mls. by illuminating the film with the mercury arc, then an intermediate pumping period of 17 hrs. to 10^{-3} mms. was given and another $\Delta p - t$ curve was obtained under the same conditions. Further intermediate evacuation was given, the film being allowed to stand at 10^{-3} mms. for 66 hrs. with pumping for 1 hr. before and 1 hr. after standing, before a final $\Delta p - t$ curve was obtained. Table 1 gives the observed pressure change and time of illumination values, and the derived rate and total pressure change values; the associated curves are shown in Fig. 11.

Table 1

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
0	0	240	105.0	170	16.5
5	10.5	260	108.5	270	20.0
10	17.5	280	111.5	$\uparrow 10^{-3}$ 2 hrs. ○ 66 hrs.	
20	29.5	290	112.5	0	0
40	43.5	$\uparrow 10^{-3}$ ○ 17 hrs.		10	9.0
60	55.5	0	0	20	13.5
80	65.5	5	2.0	40	18.5
140	84.0	10	3.0	100	26.0
160	89.5	20	5.0	140	30.0
180	95.0	40	7.0	180	32.5
200	98.5	60	9.0	240	36.0
220	101.5	110	13.0	280	38.0
$\Sigma \Delta p$ divs.	$\frac{d \Delta p}{dt}$ divs./min.	$\Sigma \Delta p$ divs.	$\frac{d \Delta p}{dt}$ divs./min.	$\Sigma \Delta p$ divs.	$\frac{d \Delta p}{dt}$ divs./min.
18.0	1.425	108.5	0.153	132.5	
36.5	0.750	112.5		$\uparrow 10^{-3}$ 2 hrs. ○ 66 hrs.	
55.2	0.525	$\uparrow 10^{-3}$ ○ 17 hrs.		141.0	0.650
72.0	0.338	115.5	0.250	151.0	0.213
84.0	0.275	119.6	0.100	162.0	0.081
93.3	0.215	125.0	0.070	167.0	0.054
101.5	0.185	130.0	0.040	170.5	

Symbols:-

- ↑ Film evacuated.
- Film left standing in vacuo.
- × Film left standing in oxygen.

With sample c used during these experiments, it was found possible to extrapolate the rate curves to $R = 0$ and so obtain an estimate of the possible uptake in divisions which would have been attained on illumination for a very long time; this value was found to have increased after an intermediate period of evacuation. Referring to Fig. 11 it may be noted that, on carrying out intermediate

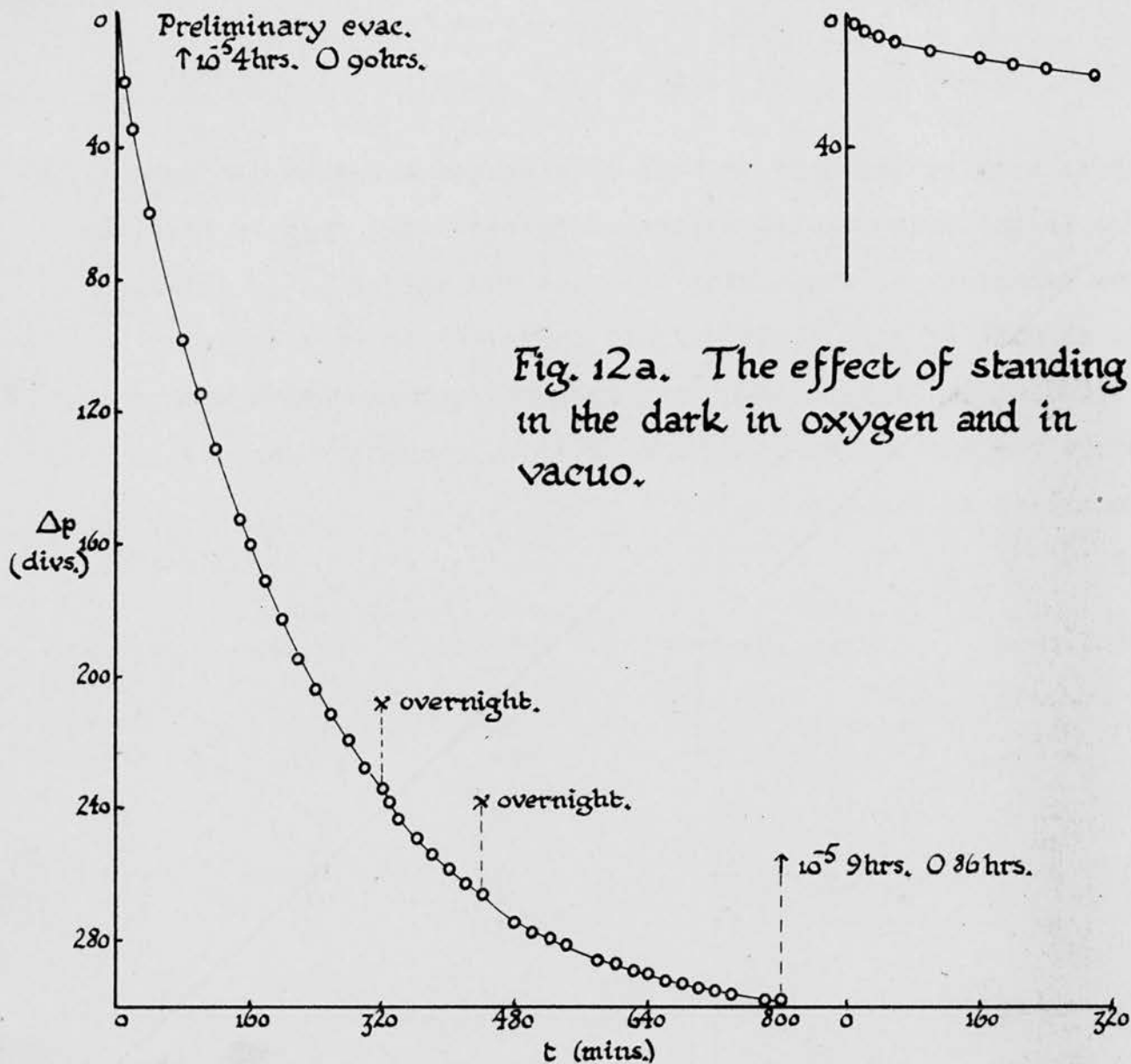
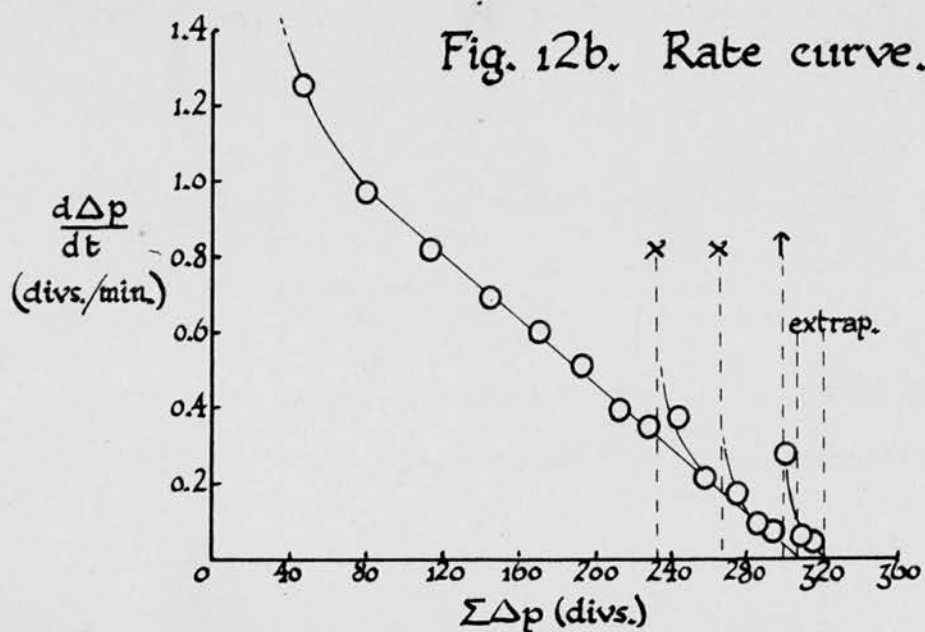


Fig. 12a. The effect of standing in the dark in oxygen and in vacuo.



evacuation both an increase in rate of subsequent uptake and an increase in the extrapolated uptake occurred; the rate of reaction was more sensitive to evacuation than was the extrapolated value, indeed, as will be noted later, small increases in rate occurred after standing in oxygen. The extrapolated uptake values were determined for the number of runs carried out, and the results are summarised in Table 2.

Table 2

	Initial evac.		Intermed. evac.		Initial $\Sigma\Delta p$ R=0 divs.	Inter. $\Sigma\Delta p$ R=0 divs.	Differ- ence divs.
	mm. Hg.	Standing time in hrs.	mm. Hg.	Standing time in hrs.			
1	10 ⁻³	17	10 ⁻³	85	137	175	38
2	10 ⁻³	23	10 ⁻³	116	167	215	48
3	10 ⁻⁴	62	10 ⁻⁴	22	188	210	22
4	10 ⁻⁵	94	10 ⁻⁵	95	306	321	15
5	10 ⁻³	23	10 ⁻⁵	70	36	46	10

The results for run number 4 are reported in detail in Table 3 below, and the $\Delta p - t$ and $\frac{d\Delta p}{dt} - \Sigma\Delta p$ curves are given in Fig. 12. The effect of standing overnight in oxygen may be observed at the points marked X.

Table 3

Weight of sample c	=	0.12 gm.
Volume of binder (acetone)	=	0.2 ml.
Temperature	=	24.9°C.
Oxygen pressure (initial)	=	52 mms.
Volume of reaction vessel	=	62.6 mls.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
$\uparrow 10^{-5}$ 4 hrs. ○ 90 hrs.		280	219.7	660	291.6
0	0	300	228.0	680	293.0
2	5.7	320	234.2	700	294.2
5	12.1	----- X overnight		720	295.2
10	20.7	330	238.7	740	296.3
15	27.9	340	243.7	780	299.5
20	34.5	360	249.7	800	299.5
30	47.7	380	253.9	$\uparrow 10^{-5}$ 9hrs. ○ 86hrs.	
40	60.2	400	258.5	0	0
60	79.8	420	261.9	10	3.5
80	98.5	440	266.2	20	5.0
100	115.0	----- X overnight		40	7.0
120	132.2	480	274.5	60	8.5
150	152.2	500	277.2	100	11.1
160	160.4	520	279.0	160	13.3
180	171.2	540	281.2	200	15.7
200	183.4	580	286.0	240	16.9
220	195.2	600	287.0	300	19.1
240	204.2	620	288.7		
260	212.0	640	290.0		
$\Sigma \Delta p$ divs.	$R = \frac{d\Delta p}{dt}$ divs/min.	$\Sigma \Delta p$ divs.	R divs/min.	$\Sigma \Delta p$ divs.	R divs/min.
$\uparrow 10^{-5}$ 4 hrs. ○ 90 hrs.		212.0	0.383	274.0	0.169
20.5	1.950	227.5	0.355	284.0	0.091
47.5	1.250	234.2		293.0	0.068
80.0	0.963	----- X overnight		299.5	
115.0	0.818	243.0	0.375	$\uparrow 10^{-5}$ 9hrs. ○ 86hrs.	
146.0	0.695	258.0	0.213	304.0	0.278
171.0	0.600	266.2		309.0	0.058
194.0	0.501	----- X overnight		315.0	0.041

It is evident from these results that two factors in the degassing procedure controlled the uptake of oxygen on a film, namely, (a) the pressure attained on evacuation, and (b) the length of time for which the film was allowed to stand at that pressure. The more efficient the pumping with respect to these two factors, then the greater was the uptake, and the smaller the additional uptake after an intermediate period of evacuation.

* * * Compilation error:- Read page 39 before page 37.

where k is a constant determined by the slope of the curve, and P is the extrapolated value $\frac{\sum \Delta p}{R=0}$.

Integration of the above gives an exponential equation, which describes the $\Delta p - t$ curve

$$P - \Delta p = P \cdot e^{-k \cdot t}$$

Not all of the samples investigated gave curves whose latter portions conformed to the above equations, for example, the following results were obtained for a run with sample bl, using the mercury arc for illumination.

Table 4

Weight of sample	=	0.12 gm.
Volume of binder (acetone)	=	0.3 ml.
Oxygen pressure	=	50 ± 1 mm.
Temperature	=	25.0°C.
Volume of reaction vessel	=	68.8 mls.
Gauge sensitivity	=	0.0295 mms./divs.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
0	0	600	108.9	1560	186.8
20	10.4	640	112.9	1600	188.8
40	18.1	680	116.9	1640	191.0
60	24.1	720	120.7	1700	194.0
80	30.0	760	124.7	1760	197.2
100	34.1	800	129.0	1770	200.1
120	38.4	840	132.6	1830	201.7
140	43.2	880	135.9	1890	205.3
160	47.1	920	139.5	1930	207.3

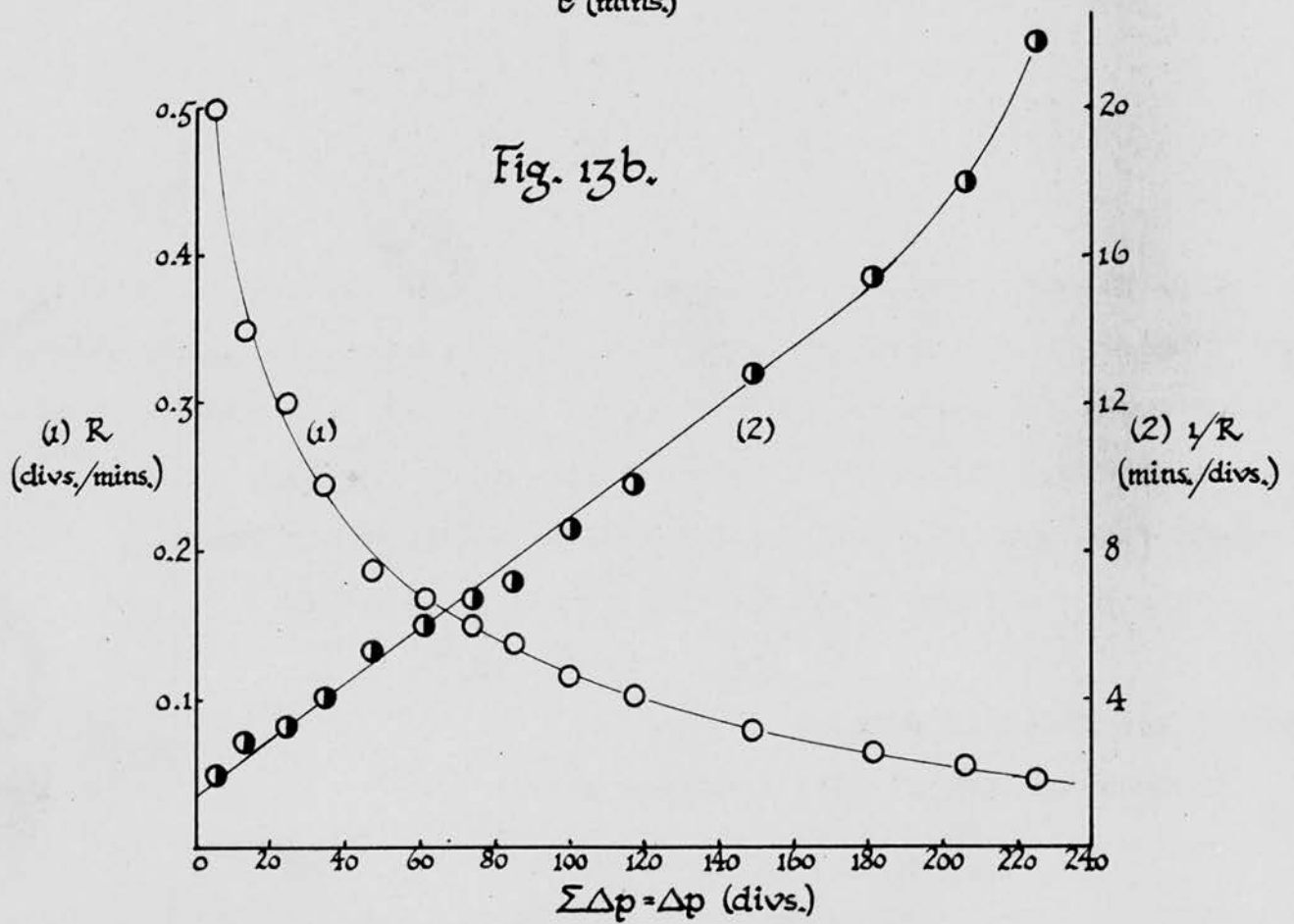
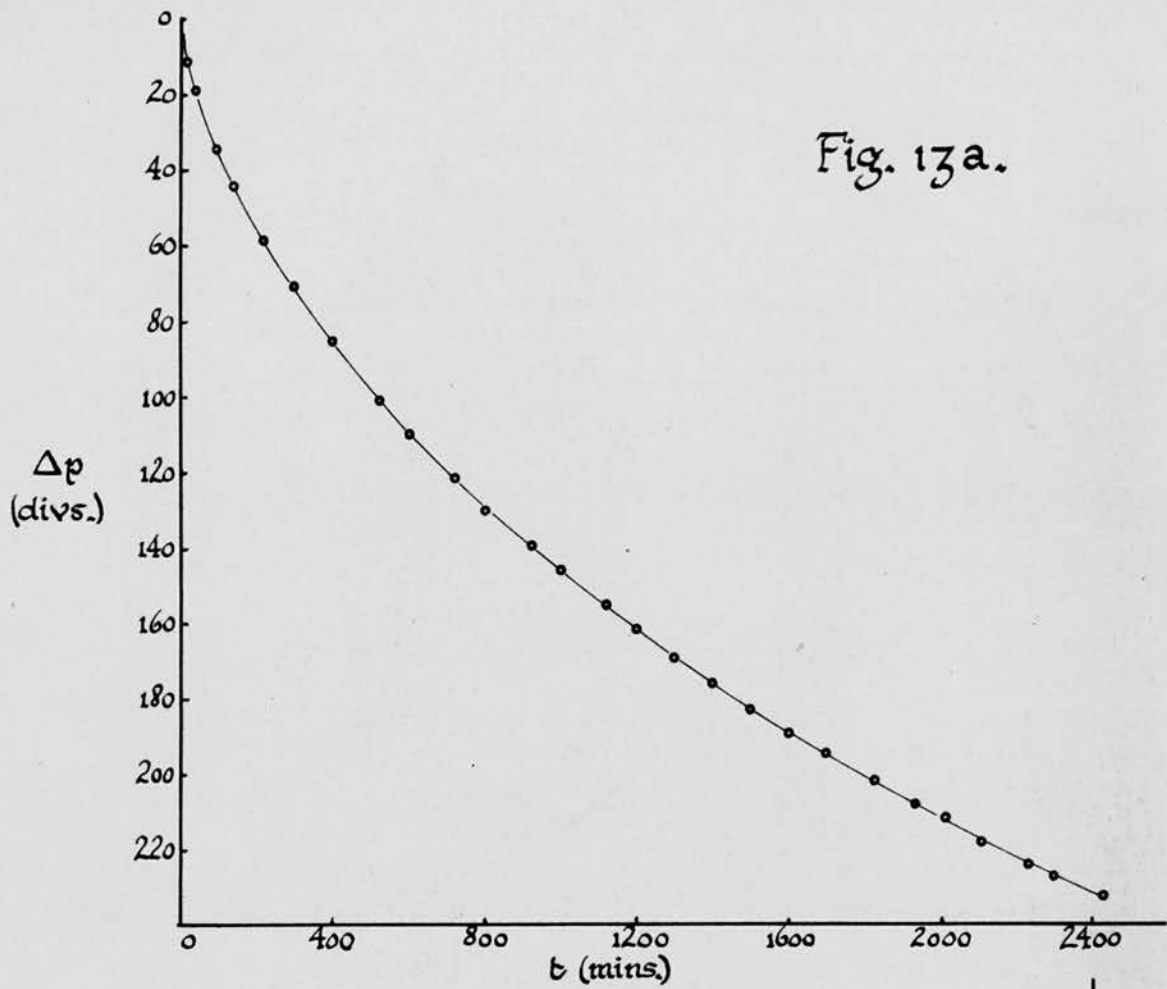


Table 4 contd.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
180	51.0	960	142.5	1970	209.5
220	58.2	1000	145.6	2010	211.3
240	61.1	1040	148.7	2030	212.9
260	64.2	1090	152.5	2070	215.7
280	67.2	1120	154.6	2090	217.1
300	70.2	1160	158.2	2110	217.8
320	73.2	1200	161.4	2170	220.8
340	76.5	1240	164.3	2230	223.7
360	79.5	1300	168.4	2300	226.7
380	82.5	1320	169.5	2360	229.5
400	85.5	1340	171.2	2390	230.7
440	90.5	1360	173.2	2430	232.0
480	95.4	1400	176.0		
520	100.3	1500	182.2		
560	104.5	1520	183.9		
$\Sigma \Delta p$ divs.	$R = \frac{d\Delta p}{dt}$ divs/min.	$1/R$ mins/div.	$\Sigma \Delta p$ divs.	R divs/min.	$1/R$ mins./div.
5.0	0.500	2.0	85.0	0.138	7.2
13.5	0.350	2.9	100.0	0.116	8.6
24.0	0.300	3.3	117.0	0.102	9.8
34.5	0.245	4.1	149.0	0.078	12.8
47.0	0.188	5.3	181.0	0.065	15.4
61.0	0.168	6.0	206.0	0.056	18.0
74.0	0.150	6.7	225.0	0.046	21.8

Fig. 13b demonstrates that the rate curve for sample b1 does not have an appreciable straight line portion in contrast to a similarly derived curve for sample c (Fig. 12b); a plot of the reciprocal of the rate against the total pressure change does, however, give a straight line over 80 % of the measured pressure change values.

The $\Delta p - t$ curve given in Fig. 13a is of the form:

$$(\Delta p + p')^2 = k'.t + (p')^2$$

where p' and k' are constants.

Differentiation of this equation gives

$$2(\Delta p + p') \frac{d\Delta p}{dt} = k'$$

✱ Compilation error :- Insert this page between pages 36 and 37.

- 39 -

It can be considered that on evacuation of the film, a slow desorption of the binding liquid occurred, and the more efficient the pumping, the smaller was the amount left adsorbed on the titanium dioxide covering active sites in the oxygen uptake; intermediate evacuation continued the removal of any of the binding liquid still adhering to the surface, and caused an increase in the rate and amount of the subsequent oxygen uptake. In run 5 (Table 2) the film was bound using a little carbon tetrachloride, and the results indicate that it is more difficult to remove than acetone on pumping; in this connection Mackenzie reported that water bound films were less active in the oxygen reaction than acetone bound films.

As a result of these experiments the pumping procedure, described in an earlier section (p.26), was adopted in all further runs.

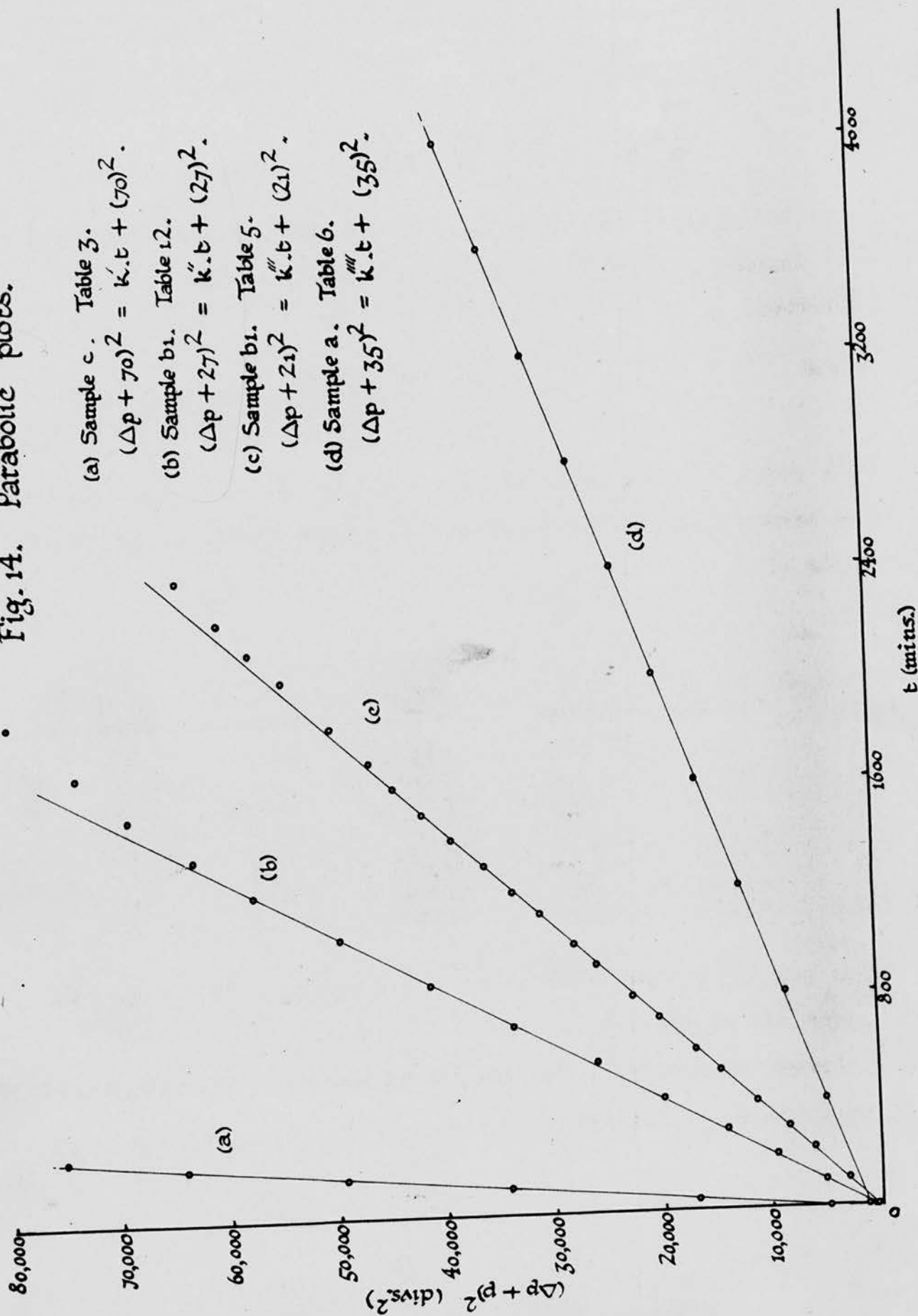
The important conclusion to be drawn from this section is, that no appreciable reversal of the photo-uptake occurs in the dark at room temperature, even on evacuation to 10^{-5} mm.

Experiments concerned with the uptake of various titanium dioxide samples, and the shape of uptake curves.

Runs described above with sample c gave rate curves, the latter portions of which were linear and allowed extrapolation to find the total uptake at zero rate of uptake; this linear portion was most marked when the preliminary evacuation was good, as in run 4. The linear part of the rate curve may be described by the equation

$$\frac{d\Delta p}{dt} = k (P - \Delta p),$$

Fig. 14. Parabolic plots.



(a) Sample c. Table 3.

$$(\Delta p + 70)^2 = k \cdot t + (70)^2.$$

(b) Sample b1. Table 12.

$$(\Delta p + 27)^2 = k' \cdot t + (27)^2.$$

(c) Sample b1. Table 5.

$$(\Delta p + 21)^2 = k'' \cdot t + (21)^2.$$

(d) Sample a. Table 6.

$$(\Delta p + 35)^2 = k''' \cdot t + (35)^2.$$

or

$$\frac{1}{\frac{d\Delta p}{dt}} = \frac{2}{K'}\Delta p + \frac{2}{K'}p'$$

From the plot of the reciprocal of the rate against the total pressure change, a value for the constant p' was derived.

Intercept ($\Delta p = 0$) : $\frac{2}{K'}p' = 1.5.$

Slope : $\frac{2}{K'} = 0.073.$

$\therefore p' = 21.$

This value of p' was used to obtain a plot of $(\Delta p + p')^2$ against t , which demonstrates well the parabolic nature of the uptake curve for sample bl.

Table 5

t mins.	$(\Delta p + 21)^2$ divs. ²	t mins.	$(\Delta p + 21)^2$ divs. ²	t mins.	$(\Delta p + 21)^2$ divs. ²
0	400	800	22500	1600	44000
100	3000	920	25800	1700	46200
220	6200	1000	27800	1830	49600
300	8400	1120	30800	2010	54000
400	11300	1200	33300	2110	57000
520	14700	1300	35900	2230	59900
600	16900	1400	38800	2390	63400
720	20100	1500	41300		

Fig. 14c illustrates such a plot, and corresponds to the data given above for sample bl.

A similar result was obtained for sample a ; the data are given in Table 6 and are illustrated by Fig. 14d.

Table 6

t mins.	($\Delta p + 35$) ² divs. ²	t mins.	($\Delta p + 35$) ² divs. ²	t mins.	($\Delta p + 35$) ² divs. ²
0	1200	1600	16300	3200	30800
400	4800	2000	19800	3600	34500
800	8400	2400	23400	4000	38200
1200	12400	2800	27000		

A parabolic plot of the data for sample c, (Table 3), which shows linearity of the rate curve, was made in the manner described above, and it was found that the parabolic equation applied for the initial part of the run (Fig. 14a).

The runs which have been considered so far, have all been carried out with laboratory prepared samples of titanium dioxide; it remains to describe the results obtained with technical samples. Uptakes were found to be much smaller, but as the following two examples show, the uptake curves were of the same character as those for laboratory prepared samples.

Table 7

Weight of sample c	=	0.12 gm.
Volume of binder (acetone)	=	0.3 ml.
Oxygen pressure	=	52 mm.
Temperature	=	24.9°C.
Volume of vessel	=	62.6 mls.
Gauge sensitivity	=	0.0295 mms./div.

Fig. 15a. $\Delta p-t$ curves.

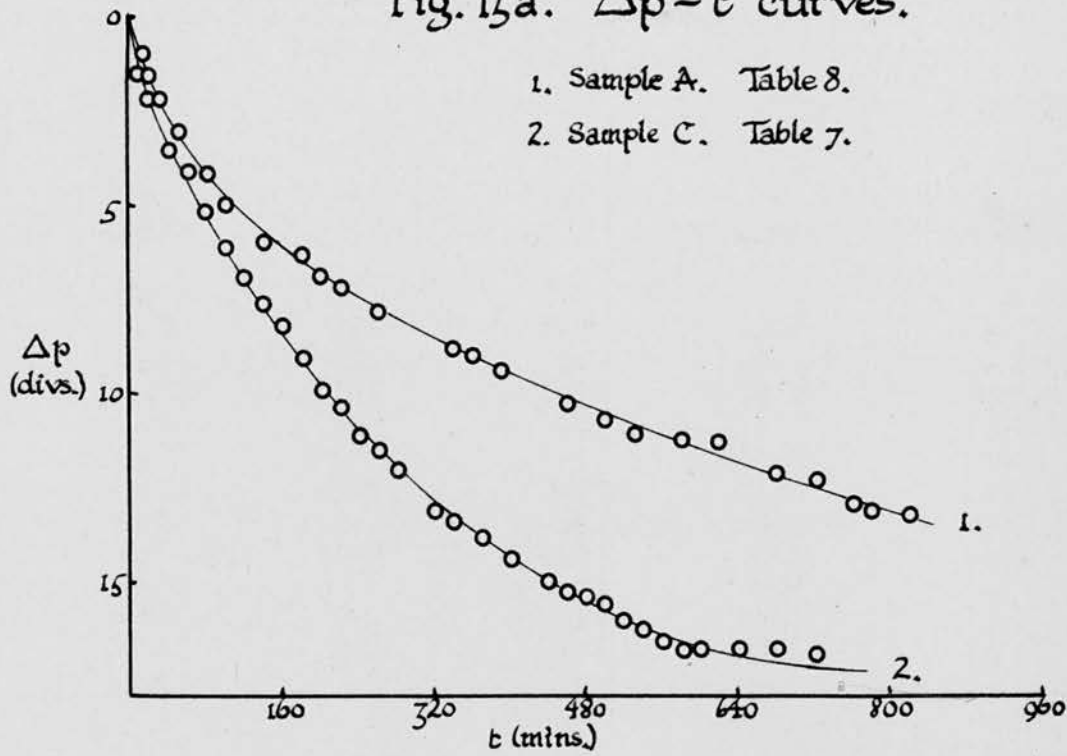


Fig. 15b. Rate and reciprocal rate curves.

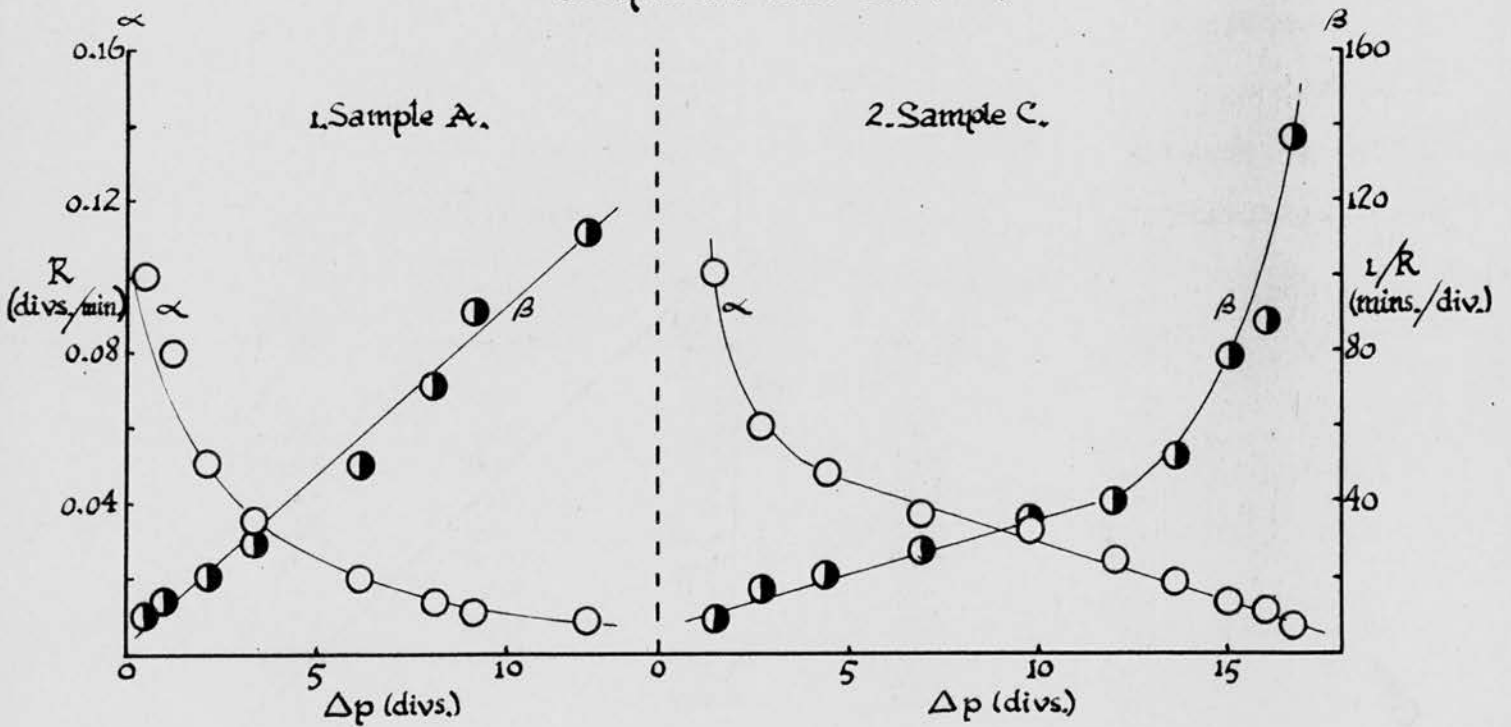


Table 7 contd.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
0	0	180	9.0	460	15.3
10	1.5	200	9.9	480	15.4
20	2.2	220	10.4	500	15.6
30	3.0	230	10.7	520	16.0
40	3.5	240	11.1	540	16.3
60	4.1	260	11.5	560	16.6
80	5.1	280	12.0	580	16.8
90	5.6	320	13.1	600	16.8
100	6.2	340	13.4	640	16.8
120	6.9	370	13.8	660	16.8
140	7.6	400	14.4	680	16.8
160	8.2	440	15.0	720	16.9

Table 8

Weight of sample A	=	0.12 gm.
Volume of binder (acetone)	=	0.2 mls.
Oxygen pressure	=	52 mm.
Temperature	=	24.9°C.
Volume of vessel	=	62.6 mls.
Gauge sensitivity	=	0.0295 mm./div.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
0	0	220	7.1	530	11.1
10	1.0	230	7.3	580	11.2
20	1.5	260	7.8	620	11.3
30	2.2	340	8.8	680	12.1
50	3.0	360	9.0	720	12.3
80	4.2	390	9.4	760	12.9
100	5.0	430	9.8	780	13.1
140	6.0	460	10.3	820	13.2
180	6.3	500	10.7		
200	6.9	510	11.1		

Sample A shows an uptake curve of a parabolic nature (Fig. 15.1) and sample C shows an uptake curve of an exponential nature over the

Fig. 16a. Δp -t curve.

Sample F, Table 9.

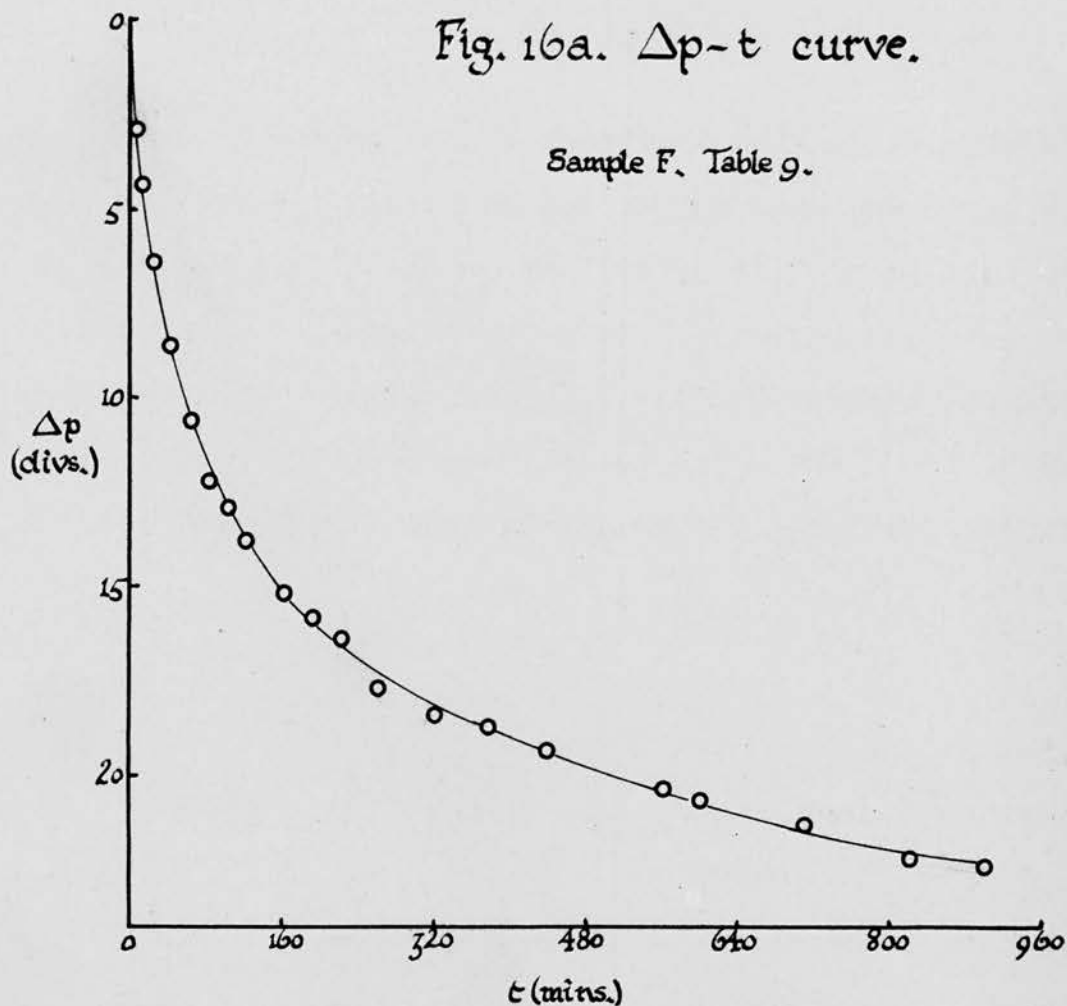
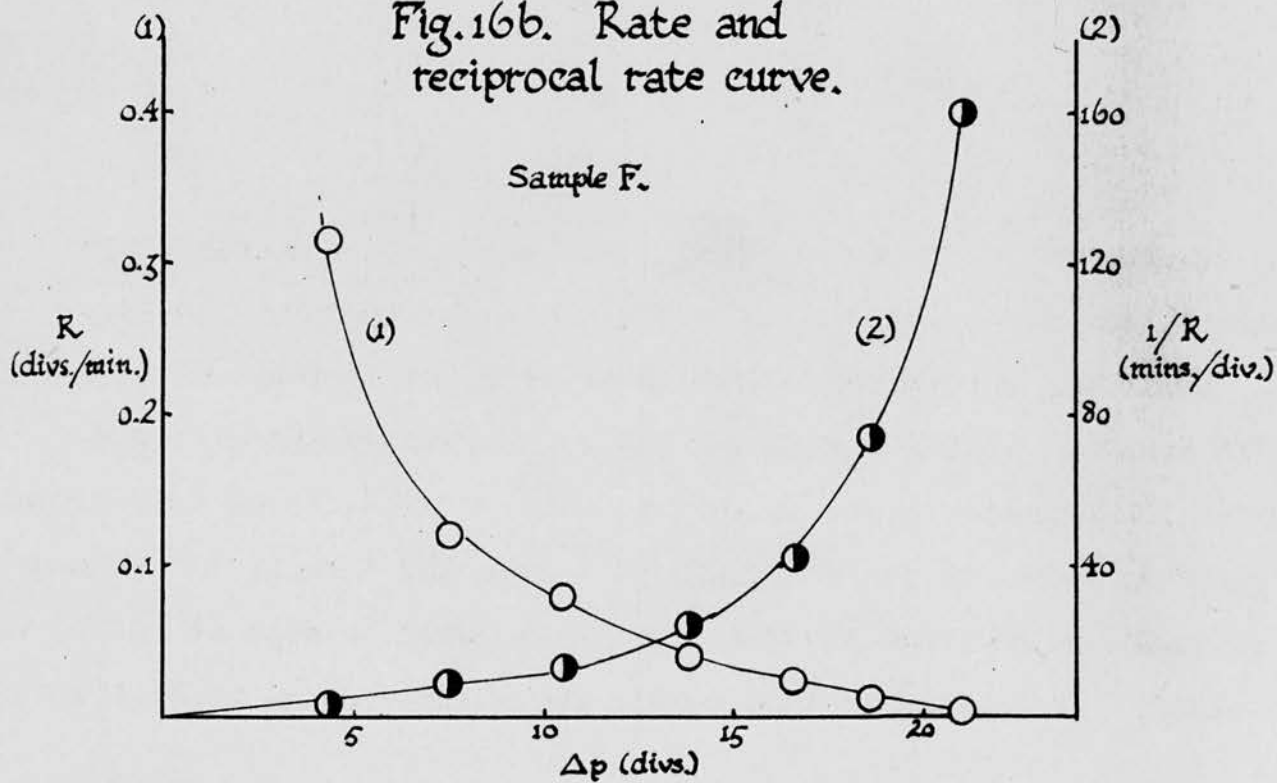


Fig. 16b. Rate and reciprocal rate curve.

Sample F.



latter portion with an initial obedience of the parabolic law (Fig. 15.2).

Mackenzie has shown that oxygen uptake is not a result of the presence of any one of various impurities in the titanium dioxide. This general conclusion was corroborated by examining the uptake of the purest titanium dioxide (sample F). Details of the experiment are given in Table 9. The uptake curve was found to be in fair agreement with the parabolic law initially, and the exponential law finally. (Fig. 16).

Table 9

Weight of sample F = 0.24 gm.

Volume of binder (acetone) = 0.9 mls.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
0	0	100	12.9	380	18.7
5	2.9	120	13.7	440	19.3
10	4.3	160	15.2	560	20.3
20	6.4	190	15.8	620	20.6
40	8.6	220	16.4	710	21.3
60	10.6	260	17.7	820	22.2
80	12.2	320	18.4	900	22.4

Results for different samples, both technical and laboratory prepared, are summarised in Table 10; unless otherwise stated, each result was obtained for acetone bound films composed of 0.12 gm. of the sample. The order of the uptake which occurred during 300 minutes illumination with the mercury lamp at 25°C. in 50 mms. oxygen is given in terms of scale divisions of pressure change. The vessels in which these pressure changes took place, were between 60 and 70 mls. in volume; in volumes of this order, and using a gauge of sensitivity

equal to 0.0295 mm./div., a change in oxygen pressure of one division corresponds approximately to an uptake of 10^{-6} moles O_2 per gm. TiO_2 . The $\Delta p - t$ curves for samples obeying the parabolic law over the complete range of pressure changes measured, are described as parabolic, whereas the $\Delta p - t$ curves for samples which give linear rate curves in the latter part of the uptake, are described as exponential.

Table 10

Sample	Notes	Uptake in 300 mins.		Shape of $\Delta p - t$ curve (later stages)
		Δp (divs.)	moles O_2 / gm. TiO_2	
c		230	2×10^{-4}	Exponential
b1		71	10^{-4}	Parabolic
		98		
b2		95		
a		28		Parabolic
F	0.24 gm.	18	10^{-5}	Exponential
A	0.3 gm.	11		Parabolic
		8		
		20		
C	Anatase	12		Exponential
B	Rutile	5		Parabolic
E	Anatase (Cr. treated)	8		Exponential
D	Rutile (Cr. treated)	3	3×10^{-6}	Parabolic

It can be seen from this table that technical samples are only one tenth as active as laboratory prepared samples, rutile is generally less active than anatase, and chromium treated samples are less

active than the corresponding untreated samples. It may be added that there is some suggestion by the results, that crystal structure is an operative factor in determining the shape of the reaction curve.

Results concerned with the pretreatment of samples

We have just seen that titanium dioxide samples may differ in the activity they show in the photo-uptake of oxygen. In the following experiments, an attempt was made to change the activity of a sample, in the hope that the origin of activity in the photo-uptake would be revealed. The effect of heating in oxidising and reducing atmospheres was given particular attention.

Sample b1 was chosen for the experiments, and the first of these, summarised below, were carried out at or below 400°C. After treatment in various gaseous atmospheres, the uptake of the sample was measured in the usual way. Treatment at 400°C or 150° - 200°C resulted in a small decrease in weight of the sample (1%) irrespective of the gas in which treatment was carried out; the weight of the sample after treatment was found to increase steadily, no doubt because of the adsorption of water vapour from the atmosphere, and it was, therefore, not possible to use the change in weight of the sample during treatment at 400°C as an indication of the development of slight non-stoichiometry.

Table 11

Treatment	Colour	O ₂ uptake after 300 mins. (divs.)
None	Cream white	98 70
400°C in O ₂ for 5 hrs.	Yellow	131
400°C in H ₂ for 5 hrs.	Grey	92
400°C in CO for 3 hrs.	Brownish grey	68
150-200°C at 10 ⁻⁵ mm. for 8 hrs.	Cream white slight darkening	138
150-200°C at 10 ⁻⁵ mm. for 12 hrs.	Cream white slight darkening	124

In the above table two interesting points are evident. Thorough drying of the powders has resulted in a slight increase in activity. Treatment in either an oxidising or a reducing atmosphere at 400°C has had little effect on the subsequent oxygen uptake in spite of the fact that some change in the oxide surface has occurred as indicated by the change in colour on treatment, and in spite of the fact that this surface change is likely to have been chemisorption of the gas, if not reduction of the surface in the case of H₂ and CO treatment.

Table 12 below gives details of the oxygen uptake of sample b1 after 5 hours heating in hydrogen at 400°C, and it will be seen from Fig. 14b that the shape of the uptake curve was unchanged by this

treatment; the run was carried out under the usual conditions.

Table 12

t mins.	($\Delta p + 27$) ² divs. ²	t mins.	($\Delta p + 27$) ² divs. ²	t mins.	($\Delta p + 27$) ² divs. ²
0	700	560	25900	1350	62500
100	5000	700	33500	1510	68600
200	9600	860	41200	1670	73400
300	14200	1040	49300		
420	19900	1210	57100		

The second set of experiments was carried out at 400°C, and to give an estimate of the reduction caused by treatment in hydrogen at this temperature, the water evolved was trapped out in T₂, and was estimated by the vapour pressure method. It was found that, on heating at 800°C, sample b1 gave off carbon dioxide and water; these were identified and estimated by their vapour pressure curves (the estimate in the case of water only gave a lower limit for the quantity evolved, since this was sufficient to give the saturation vapour pressure of water.) As has already been noted above, the change in weight on treatment could not be determined accurately since the dried sample adsorbed water vapour during the weighing procedure, but in conjunction with estimation of the water produced by hydrogen treatment, an estimate of the change in weight gave some idea of the extent to which the sample had been reduced, since this reduction was quite appreciable at 800°C.

Table 13 gives the results of the experiments including oxygen uptake, loss in weight, CO₂ and H₂O estimates, and colour change for each treatment.

Table 13

Treatment of Sample bl	O ₂ Uptake in 300 mins. (divs.)	Weight treated (gms.)	Loss in weight (gms.)	CO ₂ evolved (moles)	H ₂ O evolved (moles)	Colour after treatment
Dried 10 ⁻⁵ 150-200°C for 12 hrs.	124					Cream white
Evac. 10 ⁻⁵ at 800°C for 4 hrs.	1.1	0.27		52 × 10 ⁻⁶	>116 × 10 ⁻⁶	Blue
In N ₂ at 800°C for 4 hrs.	0.9	0.28	0.015	55 × 10 ⁻⁶ and 12.5 × 10 ⁻⁶	>39 × 10 ⁻⁶ moles NO ₂	White
In O ₂ at 800°C for 4 hrs.	1.2	0.37	0.018			White
In H ₂ at 800°C for 3 hrs. (after preliminary 10 ⁻⁵ at 800°C for 2 hrs.)	1.8	0.30	0.025	1 × 10 ⁻⁶	>116 × 10 ⁻⁶	Dark blue
In N ₂ at 800°C for 3 hrs. (after preliminary 10 ⁻⁵ at 800°C for 2 hrs.)		0.30		1 × 10 ⁻⁶	8 × 10 ⁻⁶	
In CO ₂ at 800°C for 4 hrs.						Grey
Evac. 10 ⁻⁵ at 800°C for 4 hrs. (Apparatus without sample)		Nil		1 × 10 ⁻⁶	22 × 10 ⁻⁶	

From these results the information given in Table 14 was derived.

Table 14

CO ₂ content of sample bl	190 × 10 ⁻⁶ moles/grm.	≅ 0.8 %
H ₂ O content of sample bl	> 330 × 10 ⁻⁶ moles/grm.	≅ > 0.6 %
Loss in weight in H ₂ attributable to reduction		3.0 %
Corresponding oxygen deficiency	TiO ₂ - 0.15	
H ₂ O produced by hydrogen treatment	360 × 10 ⁻⁶ moles/grm.	≅ 0.6 %
Corresponding oxygen deficiency	TiO ₂ - 0.03	

It is clear that treatment in vacuo and in hydrogen at 800°C resulted in the production of a deficiency of oxygen in the titanium dioxide, and that the results do not indicate an increase in oxygen uptake as a result of the production of such a deficiency, rather do they indicate a large decrease in activity, which may be associated entirely with the temperature of treatment.

The effect of change in pressure on the rate of oxygen uptake

The relative rate method was used for studying the effect of change in oxygen pressure. For the determination of the rate curve, a value of 52.0 mms. was chosen, and the light intensity (mercury arc without a filter) and temperature (25°C) were kept constant throughout. At high pressures the change in gas pressure caused by uptake of the TiO₂ film was a negligible fraction of the total pressure, but at lower pressures this was not so, and rate values had to be quoted

Fig. 17a. The Relative Rate Method.
Variation of oxygen pressure- Table 15.

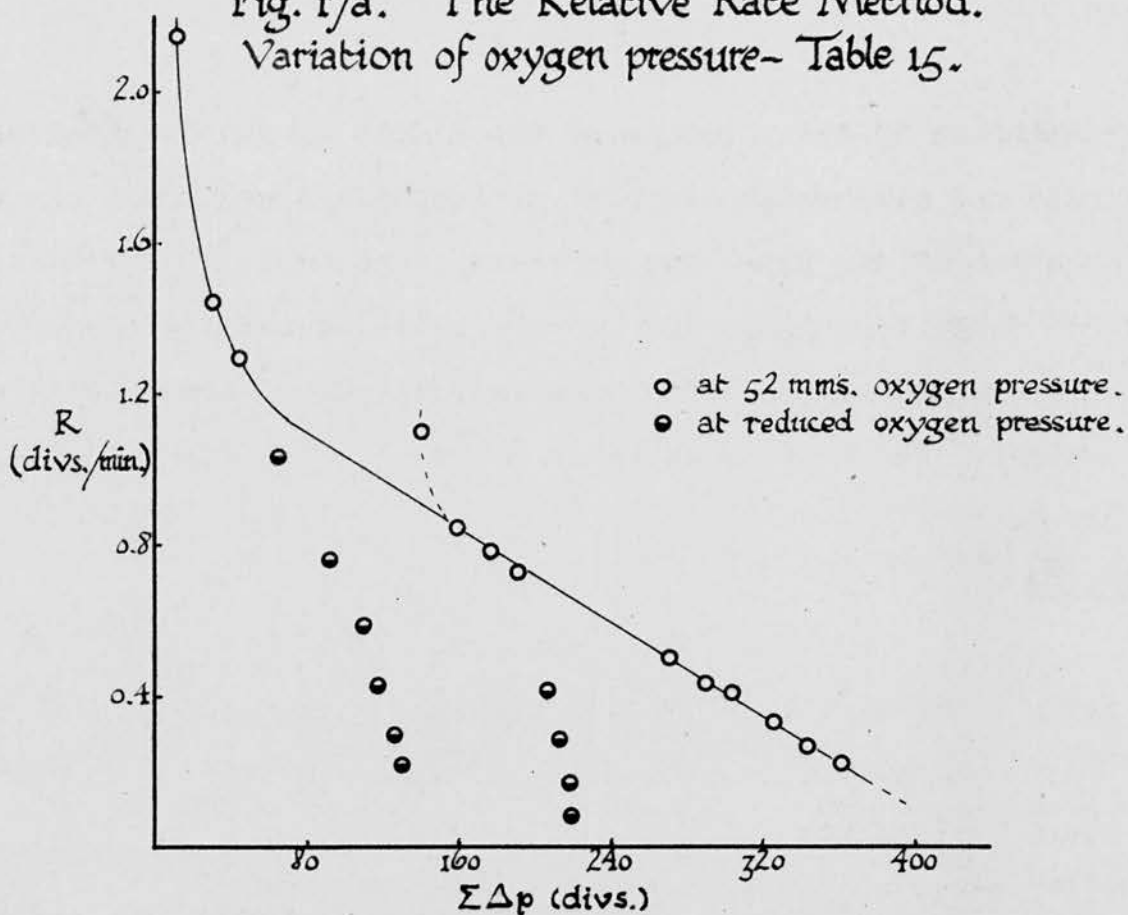
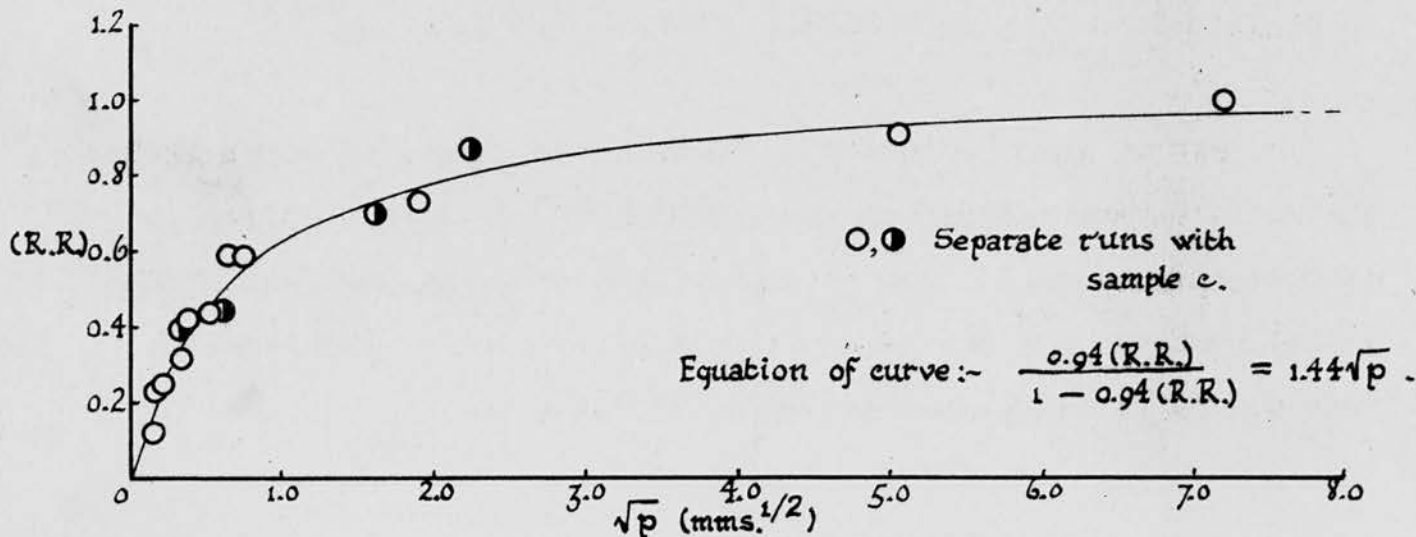


Fig. 17b. Dependence of rate of O_2 uptake on O_2 pressure- Tables 16. & 17.



corresponding to the pressure at the middle of the interval over which the rate was measured. At high pressures the manometer was used for measurement of the total gas pressure, whereas at low pressure the Bourdon gauge was used; at intermediate pressures a correction was applied to the manometer reading using the changes recorded by the gauge. The results given in Table 15 below were obtained using sample c.

Table 15

$\Sigma\Delta p$ divs.	R divs./min.	p mms.	$\Sigma\Delta p$ divs.	R divs./min.	p mms.
12.5	2.150	52.0	176.0	0.790	52.0
29.2	1.450		191.0	0.730	
43.0	1.300		198.7		
49.0			205.9	0.417	0.40
65.0	1.040	25.5	214.5	0.285	0.15
80.2			217.8	0.170	0.05
92.1	0.766	3.65	219.0	0.080	0.02
103.4			219.4		
109.8	0.585	0.56	270.5	0.500	52.0
117.8	0.425	0.27	289.0	0.438	
125.2	0.300	0.11	306.0	0.413	
127.8	0.220	0.03	325.0	0.333	
128.8			343.0	0.275	
141.0	1.110	52.0	360.5	0.221	
159.6	0.850				

As may be seen in Fig. 17 a smooth curve could be drawn through the rates determined at 52.0 mms., and for each of the rate values at reduced pressure, a corresponding rate value at 52.0 mms. could be interpolated and the relative rate calculated. The relative rate values so calculated are given in Table 16.

Table 16

p mms.	\sqrt{p} mms. $^{\frac{1}{2}}$	(RR)	p mms.	\sqrt{p} mms. $^{\frac{1}{2}}$	(RR)
52.0	7.21	1.00	0.15	0.39	0.42
25.5	5.05	0.91	0.11	0.33	0.315
3.65	1.91	0.73	0.05	0.22	0.255
0.56	0.75	0.59	0.03	0.17	0.24
0.40	0.63	0.595	0.02	0.14	0.12
0.27	0.52	0.44			

These results were found to be in agreement with an equation of the Langmuir type for dissociative adsorption:

$$\frac{\theta}{1 - \theta} = A\sqrt{p} \text{ where } \theta = k(R.R), k$$

and A are constants, and p and (R.R) are the pressure and relative rate values. The equation may be re-written:

$$1 + A\sqrt{p} = \frac{A}{k} \times \frac{\sqrt{p}}{R}$$

A plot of $\frac{\sqrt{p}}{R}$ against \sqrt{p} gave a straight line and enabled the values of k and A to be determined giving for sample c:

$$\frac{0.94(R.R)}{1 - 0.94(R.R)} = 1.44 \sqrt{p}$$

Fig. 17b shows the experimental values in good agreement with this equation.

Additional values were determined using another film of sample c, (Table 17) which gives an exponential type uptake curve, and a film of sample A, (Table 18) which gives a parabolic type uptake curve; the values for sample A were less accurate, since the rates of uptake with this sample were much lower than those with sample C.



Fig. 18. Dependence of rate of O_2 uptake on O_2 pressure - Table 18.

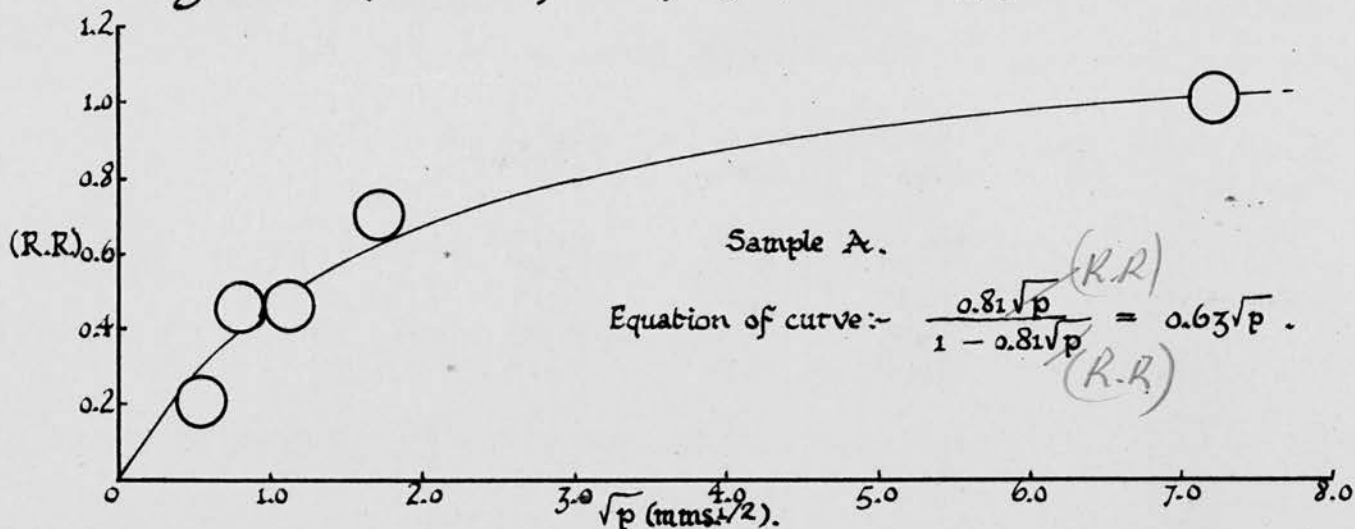


Fig. 19.

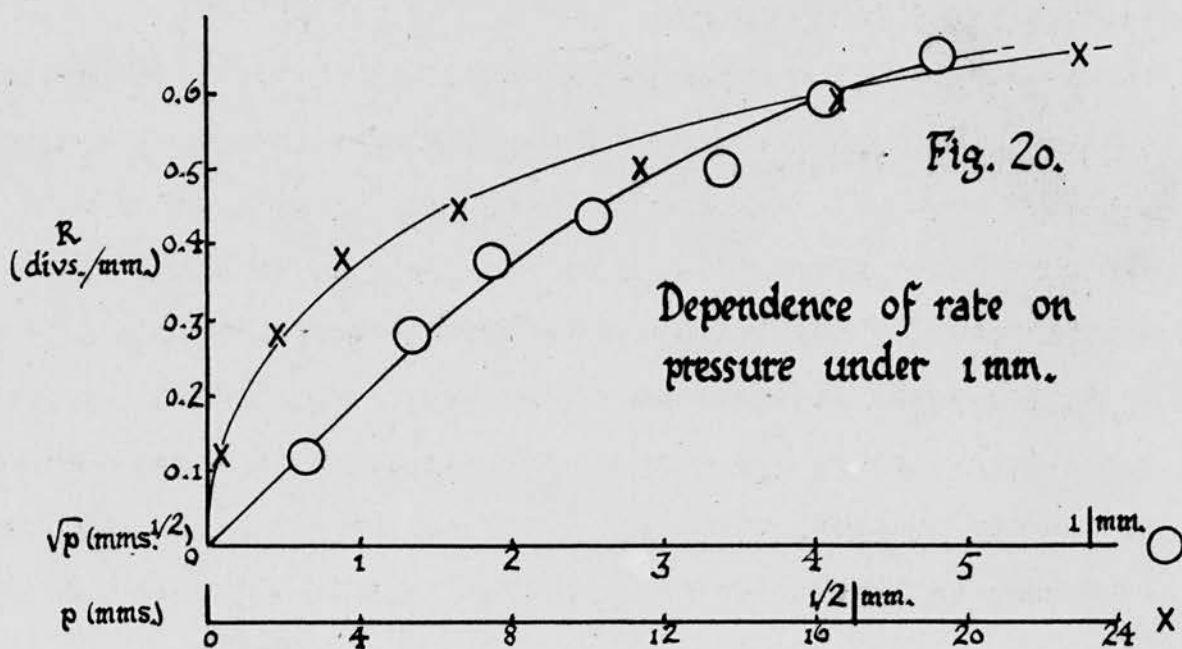
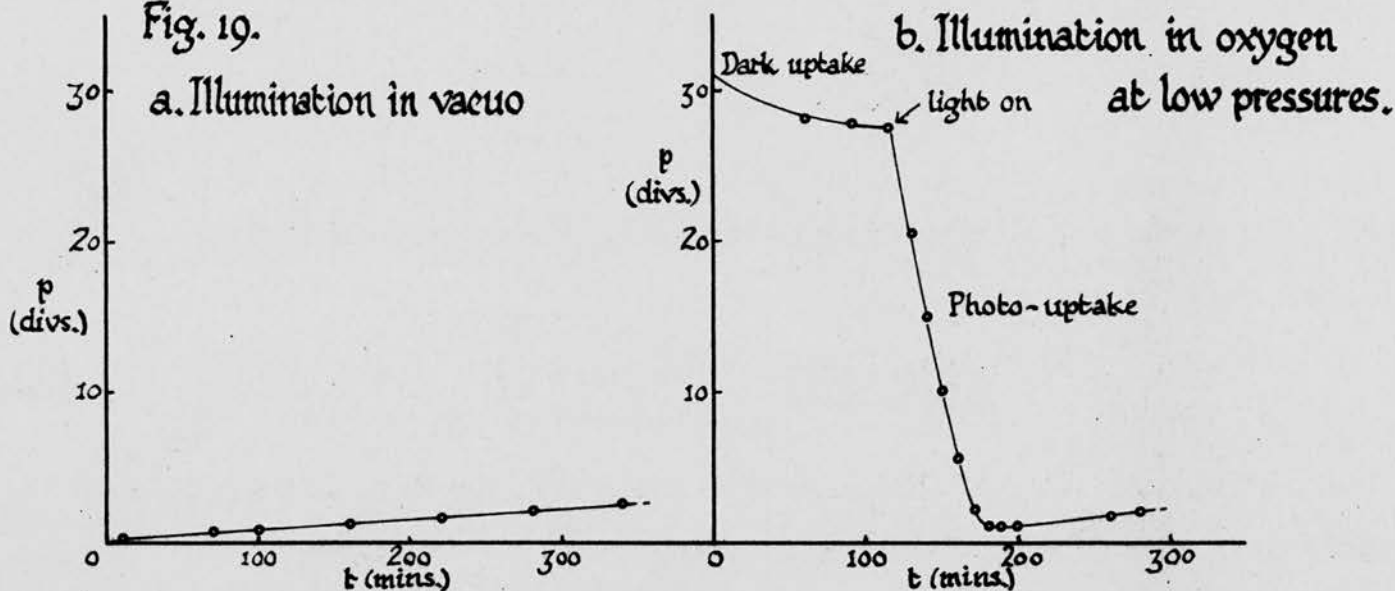


Table 17

p mms.	\sqrt{p} mms. ^{1/2}	(R.R.)
52.0	7.21	1.00
5.00	2.24	0.87
2.60	1.61	0.70
0.38	0.62	0.44
0.12	0.35	0.40

Table 18

p mms.	\sqrt{p} mms. ^{1/2}	(R.R.)
52.0	7.21	1.00
2.97	1.72	0.70
1.23	1.11	0.46
0.59	0.77	0.46
0.28	0.53	0.20

Fig. 18 shows the results for sample A in fair agreement with the equation:

$$\frac{0.81(\text{R.R.})}{1-0.81(\text{R.R.})} = 0.63 \sqrt{p}$$

The additional results for sample c are shown in Fig. 17b in agreement with the equation obtained using the other film.

Results at low oxygen pressures

In carrying out the experiments described in the last section, it was noted that on illuminating TiO_2 in oxygen pressures around 50 divs., a 98% pressure decrease occurred, and in accordance with an observation of Mackenzie's¹² this was followed by an extremely slow pressure increase. The following experiment was carried out using sample b2 in a small reaction vessel of type (b)2, and it was shown that on illumination by the mercury lamp in vacuo, a small amount of some gas was evolved, which did not condense when the side arm was surrounded in liquid oxygen; following this illumination in

vacuo, a slow dark uptake which was not to be observed except after illumination in vacuo, occurred on admitting oxygen; on illumination in this low pressure of oxygen, a rapid decrease in pressure occurred followed by a small increase. Table 19 gives the pressures recorded by the gauge at intervals under the various conditions described and is illustrated by Fig. 19.

Table 19

t mins.	p divs.	t mins.	p divs.	t mins.	p divs.
Illum. in vacuo		In O ₂ in the dark		40	5.5
0	0	0	31.2	50	2.2
10	0.3	60	28.2	60	1.0
70	0.8	90	27.8	70	1.0
100	0.9	120	27.5	80	1.0
160	1.3	Illum. in O ₂		140	1.8
220	1.7	0	27.5	160	2.0
280	2.3	10	20.5		
340	2.6	20	14.9		
Evac. O ₂ admitted		30	9.9		

Rates were calculated for illumination in these low pressures. A plot of R against \sqrt{p} shows that below 1 mm. the rate became proportional to the square root of the pressure in accordance with the Langmuir adsorption equation for dissociative adsorption, whereas a plot of R against p does not give a straight line at low pressures as would be expected if the results were in accordance with a Langmuir adsorption equation for non-dissociative adsorption (Fig. 20).

Table 20

p divs.	\sqrt{p} divs. ^{1/2}	R div./min.
23.0	4.80	0.65
16.6	4.07	0.59
11.4	3.38	0.50
6.6	2.51	0.44
3.5	1.87	0.38
1.8	1.34	0.28
0.4	0.63	0.12

An experiment was also carried out in which a film of sample bl, which had previously been illuminated in oxygen for 2,000 mins. resulting in an oxygen uptake ca. 3×10^{-4} moles O_2 /gram. TiO_2 , was illuminated by the mercury lamp in vacuo. No change in pressure was recorded after 160 mins. illumination.

The results in this section show that at low pressures, all of the oxygen admitted was absorbed by the oxide, and that on illumination of films in vacuo, no oxygen was given off to pressures greater than 0.01 mm. A small amount of an unidentified gas was evolved from freshly prepared films when illuminated, and this was probably H_2 or CO to be associated with the solvent used for preparing the films.

The effect of change in light intensity on the rate of oxygen uptake

In order to study the effect of change in light intensity using monochromatic light, it was first of all necessary to determine which line of the mercury spectrum was active in the oxygen uptake reaction. Goodeve²¹ has shown that TiO_2 powders have an adsorption threshold at 4,000A; this observation and others concerned with the fundamental absorption band of titanium dioxide (p. 14) have been supported by experiments reported below.

By using a photocell placed in the light path behind the reaction vessel, the intensities of light passed by filters 1, 2 and 3 were estimated as percentages of the intensity of light passed in the absence of a filter. Estimates so obtained were approximate, being dependent on the assumption (valid over the

Fig. 21.

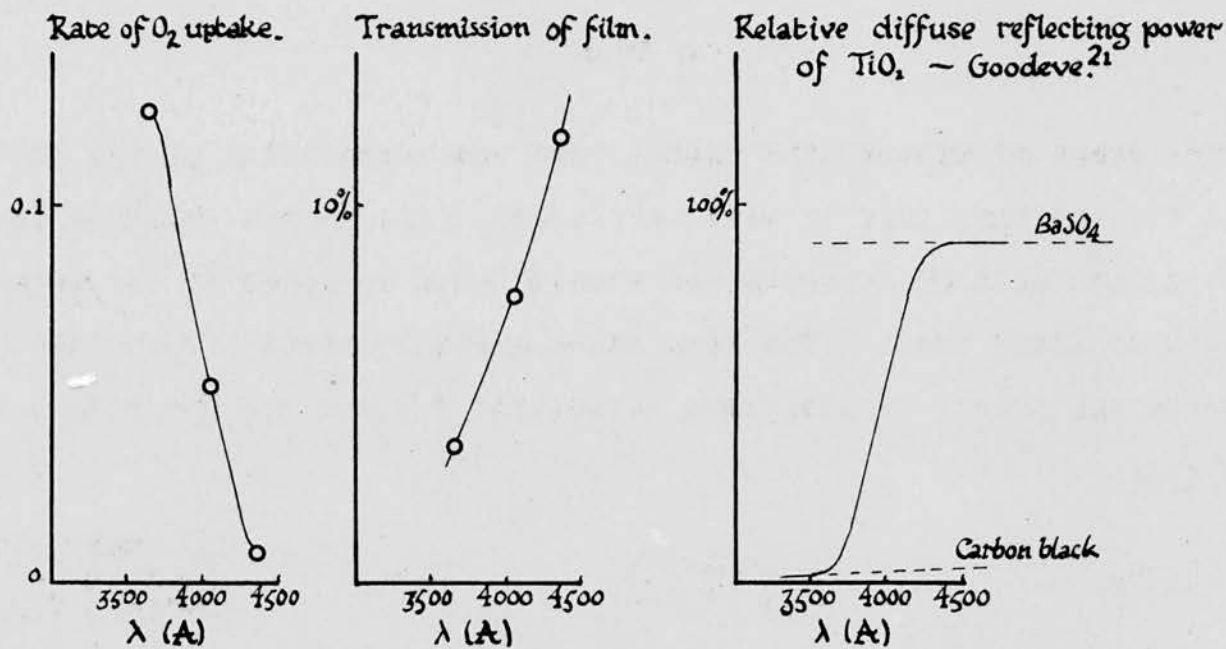
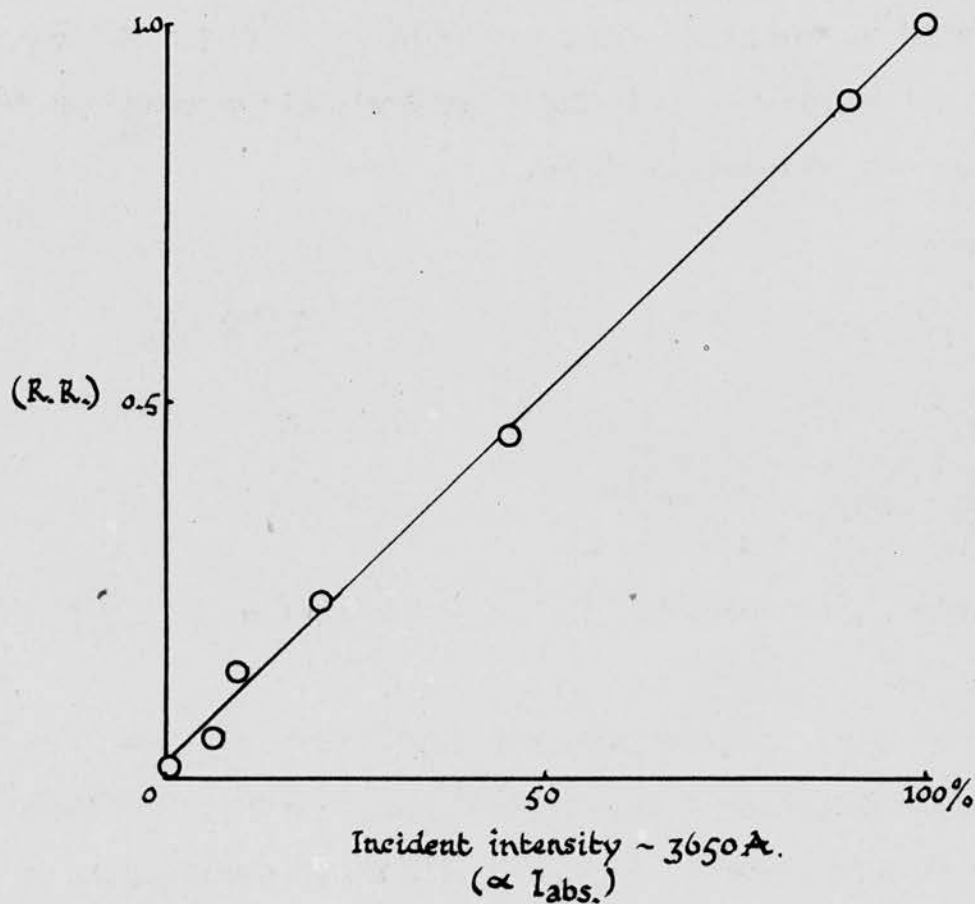


Fig. 22. Dependence of rate of O_2 uptake on the intensity of 3650 \AA light.



narrow range of wavelengths used), that the sensitivity of the photo-cell did not vary greatly with wavelength. Using the relative rate method, the rate of reaction was studied as a function of the wavelength of light used. The rate curve was determined without the filters and relative rates were calculated for each of the filters.

Table 21

Filter	λ (A)	Intensity % of total	(R.R.)	R.R. per unit intensity of incident light
1	3650	4.32	0.530	0.123
2	4050	2.56	0.132	0.052
3	4360	10.9	0.086	0.008

The figures in Table 21 show that the 3650A line is the one which is primarily responsible for the reaction, and the following data show that the percentage of light transmitted by the film was lowest with light of wavelength 3650A.

Table 22

Filter	Wavelength	% transmitted by the film
1	3650 A	3.7
2	4050 A	7.6
3	4360 A	11.8
None	3200 A	15.2

Fig. 21 shows that these results may be correlated with those of Goodeve²¹.

Filter 1 was used to give monochromatic light and the rate of reaction was now studied as a function of the intensity of 3650A light incident on the film. The light intensity was reduced by placing calibrated filters in the light path between the reaction

vessel and the lamp; the filters were calibrated using the photocell, and the results were checked in a Unicam spectrophotometer. The value of the transmissions obtained using the photocell were unaltered by having a film of titanium dioxide in the light path in front of the photocell, thus demonstrating, that the percentage of light absorbed by the film was independent of the intensity of the incident light, or that the intensity of 3650A light absorbed by the film was directly proportional to the intensity of 3650A light incident on the film. Relative rates were calculated for the reduced intensities, and the following data, obtained with sample d in a vessel of the type (b)1, show that the rate of uptake was directly proportional to the intensity of 3650A light absorbed by the film (Fig. 22).

Table 23

Intensity of 3650A light incident on film (\propto intensity absorbed) %	Relative Rates
100	1.00
90	0.90
45.5	0.455
20.3	0.235
9.4	0.140
6.1	0.050
0.25	0.018

These results were checked by using a film of sample b1 and reducing the light intensity to 45.5% at different stages of the uptake. It is evident from the following table that no change in the light intensity dependence occurred as the uptake proceeded.

Table 24

Intensity of 3650A %	Relative Rates	$\Sigma\Delta p$ (divs.)
45.5	0.425	53
45.5	0.485	168
45.5	0.480	259

Simultaneous illumination with 3650A light and light >4000A

A film of sample b2 in a vessel of type (b)1 was illuminated with the mercury lamp with filter 1 in position, and a rate value was obtained over 40 minutes. After this time, the light from a 250 watt projection lamp which was passed through filter 4, was also allowed to fall on the film, and another rate value was determined. This was followed by determining a rate value with the 3650A light alone, and with the light >4000A alone. The results in Table 25 show that light >4000A had no effect on the reaction which could be ascribed to the reversal of a trapping process during the uptake.

Table 25

	Illumination	Rate over 40 mins. divs./min.
1	3650A	0.310
2	3650 + >4000A	0.320
3	3650A	0.250
4	>4000A	0.025

Liberation of iodine from a KI solution by photo-adsorbed oxygen

Voltz and Weller³⁸ have used the liberation of iodine from a potassium iodide solution to estimate the oxygen adsorbed on chromic

oxide. This method was adapted here in an attempt to estimate the photo-absorbed oxygen.

A film of titanium dioxide, which had been exposed for some time in oxygen was suspended in 10 mls. distilled water to which 2 mls. concentrated hydrochloric acid and 1 ml. of a fresh 20% solution of potassium iodide were added. The suspension contained in the stoppered reaction vessel was allowed to stand for some time in the dark before titrating with a 0.1 solution of potassium thiosulphate using a starch indicator. Two other experiments were carried out simultaneously with that described above, using firstly, a similar quantity of the oxide which had not been exposed to light in oxygen, and secondly, the reagents alone. On the assumption that one adsorbed oxygen molecule reacted with KI to give one free iodine molecule, an estimate of the adsorbed oxygen was made for the exposed and unexposed sample, leading to an estimate of the photo-absorbed oxygen, which could be compared with that obtained from the decrease in pressure observed on illumination in oxygen. The results are summarised in Table 26.

Table 26

Sample and time of standing in KI solution	Estimate of adsorbed O ₂ by I ₂ liberation (moles O ₂ /gram. TiO ₂)		Estimate of photo-absorbed O ₂ (moles O ₂ /gram. TiO ₂)	
	Exposed	Unexposed	By I ₂	By Δp
b1 1/2 hr.	15 × 10 ⁻⁶	5 × 10 ⁻⁶	10 × 10 ⁻⁶	135 × 10 ⁻⁶
b1 1/2 hr.	25 × 10 ⁻⁶	7 × 10 ⁻⁶	18 × 10 ⁻⁶	190 × 10 ⁻⁶
b2 3 hrs.	44 × 10 ⁻⁶	13 × 10 ⁻⁶	31 × 10 ⁻⁶	170 × 10 ⁻⁶

The estimates of adsorbed oxygen based on I₂ liberation,

increased with the time allowed for reaction both in the case of exposed samples and unexposed samples; it is likely that the adsorbed oxygen only reacted slowly with the potassium iodide, if indeed reaction of adsorbed oxygen was responsible for the production of free iodine. For the longest time allowed (3 hrs.) the estimate of the photo-absorbed oxygen was only 20% of the known photo-uptake.

The photo-uptake of oxygen - Summary

An irreversible uptake occurred when titanium dioxide films were illuminated in oxygen with light of wavelength ca. 3650A, and in low pressures this uptake was complete to within the lower limit of measurement (0.01 mm.). The amount of oxygen taken up in a given time of illumination was dependent on the sample and its pretreatment; there is evidence that the photo-uptake was not a result of the presence of impurities in the oxide, or of deficiency of oxygen, although these may have had an effect on the uptake, and there is evidence that the temperature of pretreatment was an important factor in determining the subsequent uptake.

The kinetics of the uptake may be described as follows. In the initial stage of uptake a parabolic law was obeyed:-

$$(\Delta p + p')^2 = k'.t + (p')^2$$

and in the later stages of uptake an exponential law was obeyed:-

$$(P - \Delta p) = P.e^{-k.t}$$

At any stage of the uptake, the rate was controlled by the oxygen

pressure:-

$$\frac{d \Delta p}{dt} = \text{const. } \theta, \text{ where } \frac{\theta}{1 - \theta} = A \sqrt{p}$$

and by the intensity of 3650A light absorbed by the film:-

$$\frac{d \Delta p}{dt} = \text{const. } I_{\text{abs.}}$$

It was not possible to correlate the amount of oxygen taken up on illumination with the liberation of I_2 from a KI solution.

ILLUMINATION OF TITANIUM DIOXIDE IN THE PRESENCE OF VARIOUS GASES

The following experiments were carried out to find some simple photo-oxidation occurring at the titanium dioxide surface, which could be studied easily, using the Bourdon gauge system. The possible photo-oxidation of H_2 , CO and NO in accordance with Jacobsen's scheme was investigated together with the possible reaction of H_2 , CO and NO with photo-absorbed oxygen. The photo-decomposition of N_2O on the oxide surface was also considered.

Hydrogen

Samples which had taken up oxygen were illuminated in about 50 mms. hydrogen at $25^{\circ}C$, and the rates of uptake in 50 mms. oxygen were noted before and after hydrogen treatment. No pressure decrease was observed in hydrogen either in the dark or under illumination with the mercury lamp. In view of the possible production of water, two of the experiments were carried out in vessels of type (a)2 with P_2O_5 contained in the side arm. The rate of uptake of oxygen after treatment was determined in these two experiments with a small amount of hydrogen present, and no change in rate from that before treatment was noted; the region of oxygen uptake used for the experiments was that where almost a constant rate of uptake occurred with increasing amount taken up. The results obtained are shown in Table 27.

Table 27

Sample	$\Sigma \Delta p_{O_2}$ divs.	Illumin. t mins.	in H_2 Δp divs.	RO_2 before divs./min.	RO_2 after divs./min.
B	6.7	200	0.0	0.007	0.010
a (in presence of P_2O_5)	163	140	0.0	0.024	0.024 (+ 1mm. H_2)
b1 (in presence of P_2O_5)	232	120	0.2	0.070	0.068 (+ 5mm. H_2)

Carbon Monoxide

A film of titanium dioxide (sample b2) was illuminated in 50 mms. CO both in the absence and presence of soda lime, which was contained in a side arm of the vessel. The results are given below.

Table 28

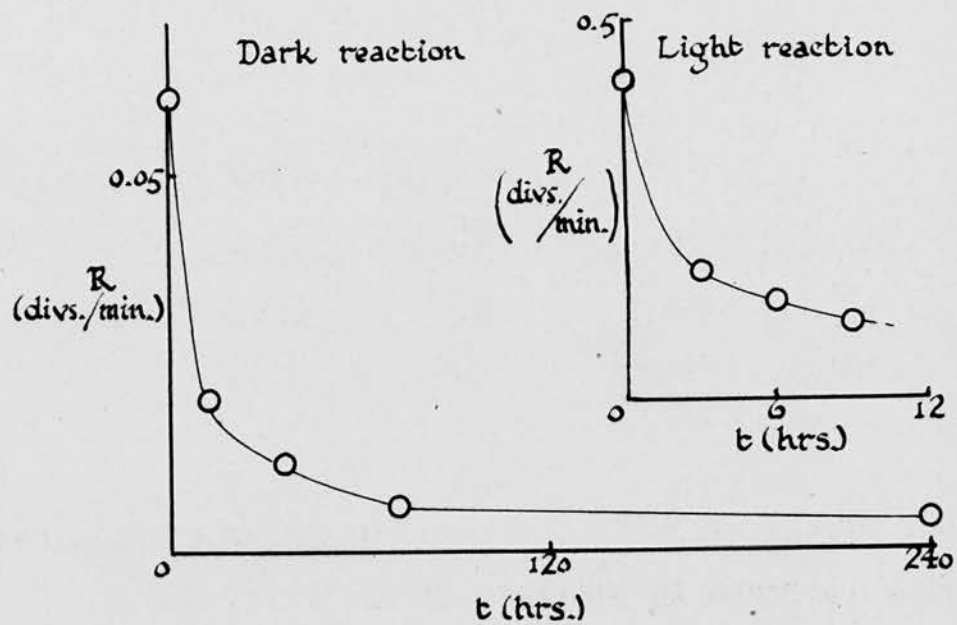
	Rate of pressure decrease divs./min.	
	In dark	Under illum.
1. In absence of soda lime	0.000	0.004
2. In presence of soda lime	0.028	0.034
After uptake of 22 divs. O_2 at 0.284 divs./min.	0.030	0.031

No evidence of photo-uptake or of reaction with photo-absorbed oxygen was obtained.

Nitrous Oxide

A film of sample b2 was illuminated in 26.8 divs. of N_2O in a vessel of type (b)2. The increase in pressure measured was shown

Fig. 23. Reactions with NO.



to be similar to that which occurred on illuminating a film of sample b2 in vacuo. The nitrous oxide could be frozen out by lowering the temperature of the side arm of the vessel in liquid oxygen. The pressure of nitrous oxide remained unchanged on illumination.

Table 29

t	p	p N ₂ O frozen out	p N ₂ O
mins.	divs.	divs.	divs.
0	26.8	0	26.8
225	28.5	1.7	26.8

Nitric Oxide

Admission of nitric oxide to a film of titanium dioxide was followed by a slow decrease in pressure in the dark, and on illumination with the mercury lamp, a rapid pressure decrease occurred which was comparable in rate with that in oxygen. Using films of sample b2 in vessels of type (a)1, the rates of pressure decrease were determined at intervals both in the dark and under illumination. Rate values relating to the light reaction alone were obtained by subtracting rates in the dark from rates under illumination. In Table 30 below, values, which are the average for several experiments in 30 mms. NO (prep. 1 or prep. 2) at 25°C, are given. The dark and light reactions are compared in Fig. 23.

Table 30

Time of reaction hrs.	Rate of dark reaction divs./min.	Rate of light reaction divs./min.
0	0.060	0.42
6		0.17
12	0.020	0.13
18		0.10
36	0.012	
72	0.006	
240	0.004	

Summary

The experiments described above demonstrated that there was no photo-reaction of hydrogen and carbon monoxide with titanium dioxide, and there was no indication that these gases reacted with oxygen taken up by the solid under illumination. It was also shown that there was no photo-decomposition of nitrous oxide in films of titanium dioxide, but a slow dark reaction and a rapid photo-reaction of nitric oxide with the TiO_2 was demonstrated, and the following section is concerned with further examination of this photo-reaction.

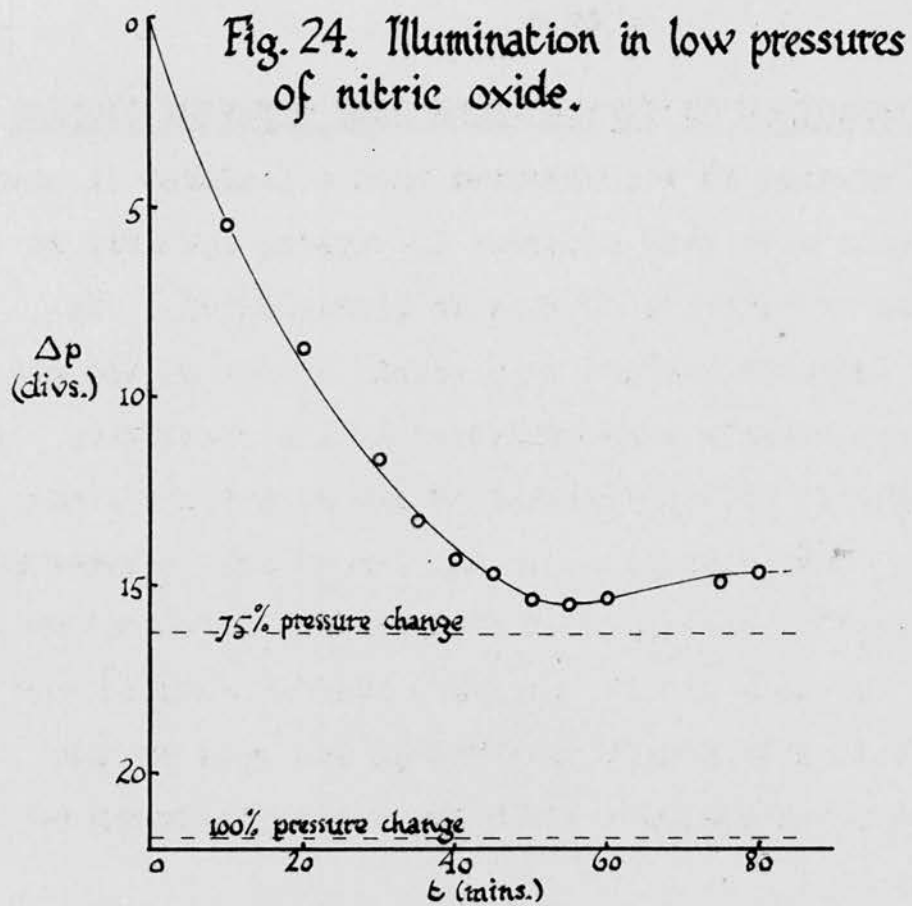
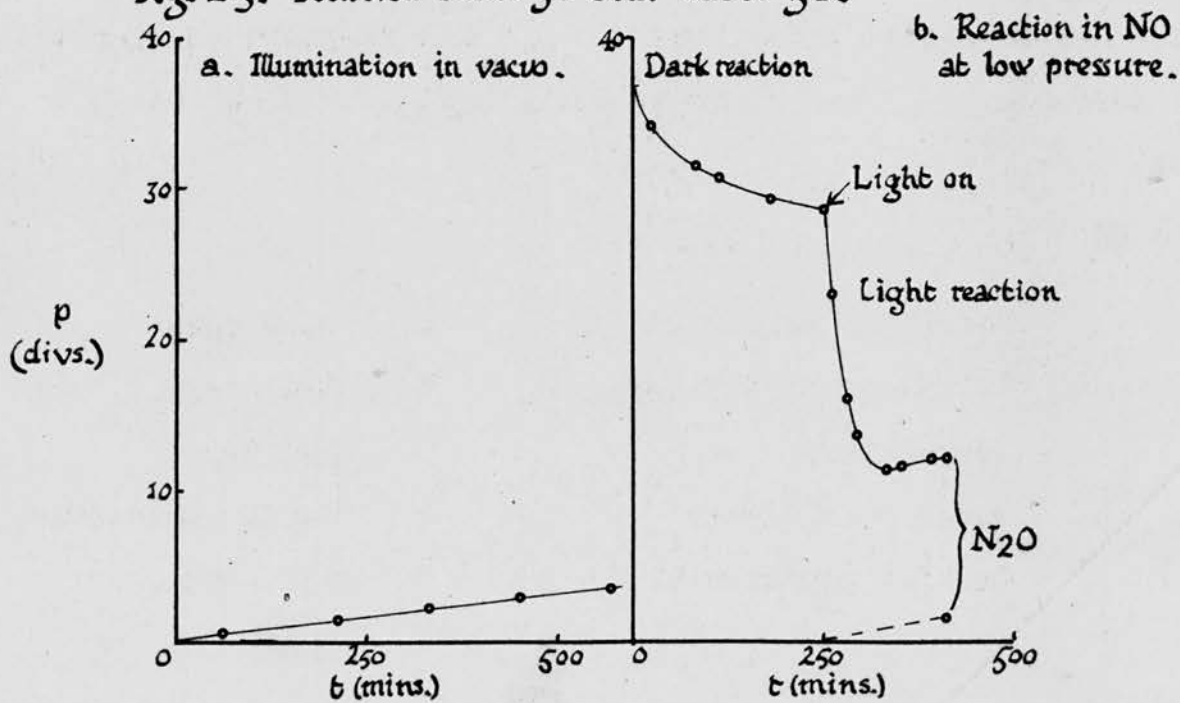


Fig. 25. Run 2a Table 32 and Table 34.



THE PHOTO-REACTION OF NITRIC OXIDE WITH TITANIUM DIOXIDE

In the last section it was observed that a decrease in pressure, which was comparable with that observed in oxygen, occurred on illuminating films of titanium dioxide in nitric oxide. To discover if this decrease was due to a simple uptake of the gas or not, several experiments were conducted at low pressures. A detailed investigation of the kinetics of the reaction was not carried out as had been done with oxygen, indeed such a study may not have been possible, because of the additional complication of a dark reaction, but some results were obtained concerning the effect of light intensity and NO pressure on the rate of the reaction, and the relationship between the two photo-reactions was investigated.

Illumination in low pressures of NO

A film of oxide in a vessel of type (b)1 was illuminated in less than 1 mm. of nitric oxide (prep. 1). The pressure changes which were recorded are given in Table 31, and Fig. 24 shows the $\Delta p - t$ curve.

Table 31

Weight of sample b2	=	0.12 gm.
Volume of binder (acetone)	=	0.3 mls.
Temperature	=	25.0°C.
Gauge sensitivity	=	0.0305 mins./div.
Initial pressure of NO	=	21.7 divs.

Table 31 contd.

t mins.	Δp divs.	t mins.	Δp divs.	t mins.	Δp divs.
0	0	35	13.3	55	15.5
10	5.5	40	14.3	60	15.4
20	8.7	45	14.7	75	14.7
30	11.7	50	15.4	80	14.7

These results do not correspond to the complete uptake of NO, but rather to only 75% of the complete uptake. As has been reported (p 52), a film of sample b2 similarly illuminated in vacuo gave an increase of 0.8 div. in 80 mins. In the absence of such an increase in pressure, the final observed pressure given in Table 31 would have been 15.5 divs. not 14.7 divs. The percentage decrease in pressure attributable to reaction of NO with the film is, therefore, $\frac{15.5}{21.7} \times 100$ or 71.5.

The experiment was repeated using the same film but with preparation 2 of NO, and the general shape of the reaction curve was confirmed; it was noted that a dip in the reaction curve occurred, corresponding to a maximum decrease in pressure, before a more or less steady value of Δp was attained. A second estimate of the percentage decrease in pressure was obtained from the results: $\frac{13.8}{18.7} \times 100$ or 73.5.

The gas, which remained after illumination at low nitric oxide pressures, was examined by carrying out some experiments in a reaction vessel of type (b)2, where any condensable fraction of the residual gas could be frozen out for examination by the vapour pressure curve method. The results given in Table 32 show that all of the products of the photo-reaction of NO were condensed at

liquid oxygen temperature, and that they correspond in pressure to 25% of the original gas. The small amount of residual gas, which did not condense at -183°C , can be identified with that evolved on illumination of the film in vacuo.

Table 32

Film	PNO divs.	t mins.	Δp divs. & Temp. of side arm		Condensable products		Uncondensable residue divs.
			+17°C	-183°C	divs.	%	
1(a)	41.7 prep.2	150	31.7	39.5	7.8	18.7	2.2
(b)	44.4 prep.2	250	28.2	41.4	13.2	29.7	1.0
					Average	24.2	
2(a)	36.8 prep.2	160	24.8	35.3	10.5	28.6	1.5
(b)	43.5 prep.1	160	31.4	41.5	10.1	23.2	2.0
					Average	25.9	

Vapour pressure curves were obtained for the condensed gas, which was identified as nitrous oxide; the figures in the following table were obtained in experiment 1(b) of Table 32, and are compared with similarly obtained figures for a sample of pure N_2O . The vapour pressure curves were similar up to thermocouple reading 87 where the pressure attained represented the total amount of gas produced in experiment 1(b).

Table 33

Temp. °C	Thermocouple reading	Pressures by gauge (divs.)	
		Unknown gas from 1(b)	Known sample of N ₂ O
-183	106	0	0
	105		
	100	0.2	
	96		0
	95	0.8	
	94		0.5
	93		1.1
	92		2.5
	90	4.0	
	89	8.0	
	87	13.0	13.5
	85	13.0	27.0
	83		29.5
+17	0	13.2	30.0

In experiment 2(a) the film was illuminated in vacuo before admitting Nitric oxide; details of the experiment are given below and show that after illumination in vacuo, a dark uptake occurred similar to that in oxygen (Fig. 25); the normal dark rate at such low pressures was only about one tenth of that observed after illumination in vacuo.

Table 34

t mins.	p divs.	t mins.	p divs.	t mins.	p divs.
Illum. in vacuo		0	36.8	30	16.0
0	0	20	34.1	40	13.5
60	0.7	80	31.5	60	12.2
210	1.4	110	30.8	80	11.2
330	2.2	180	29.2	100	11.7
450	2.9	250	28.7	140	12.0
570	3.4	Illum. in NO		160	12.0
10 ⁻⁵ 16 hrs.		0	28.7	In liquid O ₂	
In dark in NO		10	22.8		1.5

The results, then, show that illumination of titanium dioxide films in low pressures of nitric oxide resulted in a 25% (pressure) production of nitrous oxide, which was present as free gas at the completion of the reaction.

The effect of change in nitric oxide pressure on the rate of reaction

The relative rate method was used to study the effect of change in nitric oxide pressure, but a modification was made because of the dark reaction; the film was first allowed to stand in the dark in nitric oxide for some time, when the rate of the dark reaction reached a low constant value, which was then neglected in studying the photo-reaction. This variation in technique was adopted rather than the other described on page 29, since the possible dependence of the rate of the dark reaction on pressure made it impossible to estimate a correction to be subtracted from rates of the photo-reaction determined at reduced pressures. For three main reasons the results obtained were less accurate than those for the oxygen uptake; there was a dark reaction with nitric oxide; the photo-reaction was not simply an uptake of the gas; and it was not as justifiable as it was with oxygen to neglect the change in gas pressure resulting from reaction, since the rate of reaction was substantially dependent on nitric oxide pressure at high pressures. The relative rates given below in Table 35 were determined at 25°C for prep. 1 of nitric oxide over a film of sample b2, illumination was made by the mercury lamp, and the rate curve was obtained at 30 mms.

Fig. 26a. Dependence of rate of NO reaction on pressure of NO.

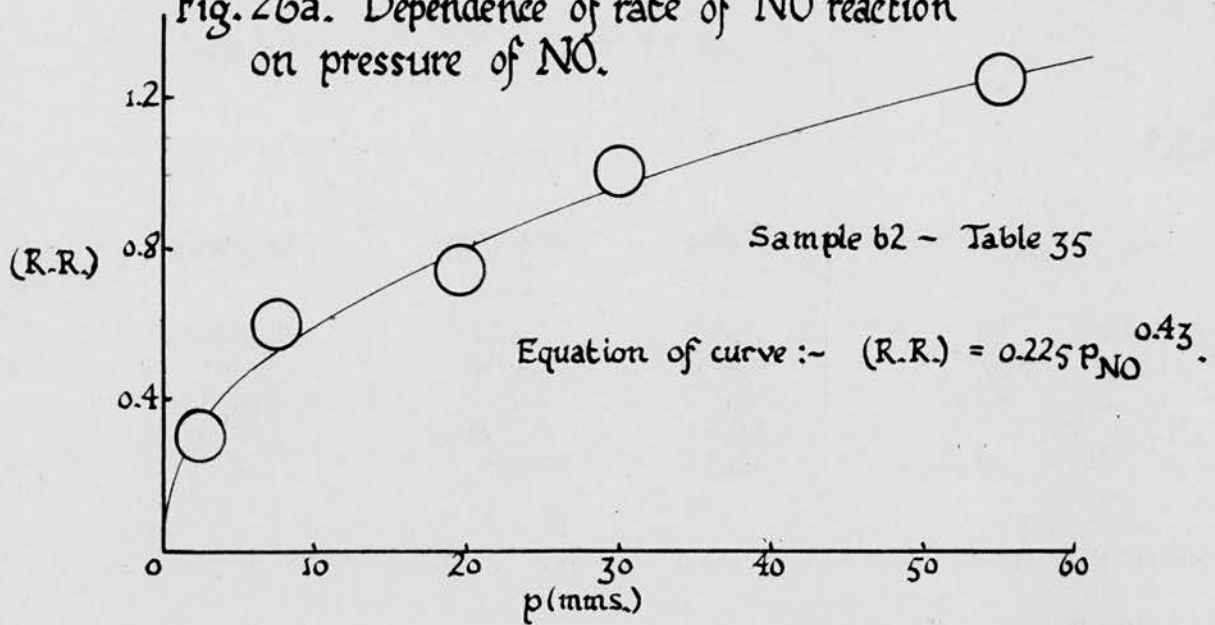


Fig. 26b.

Freundlich plot.

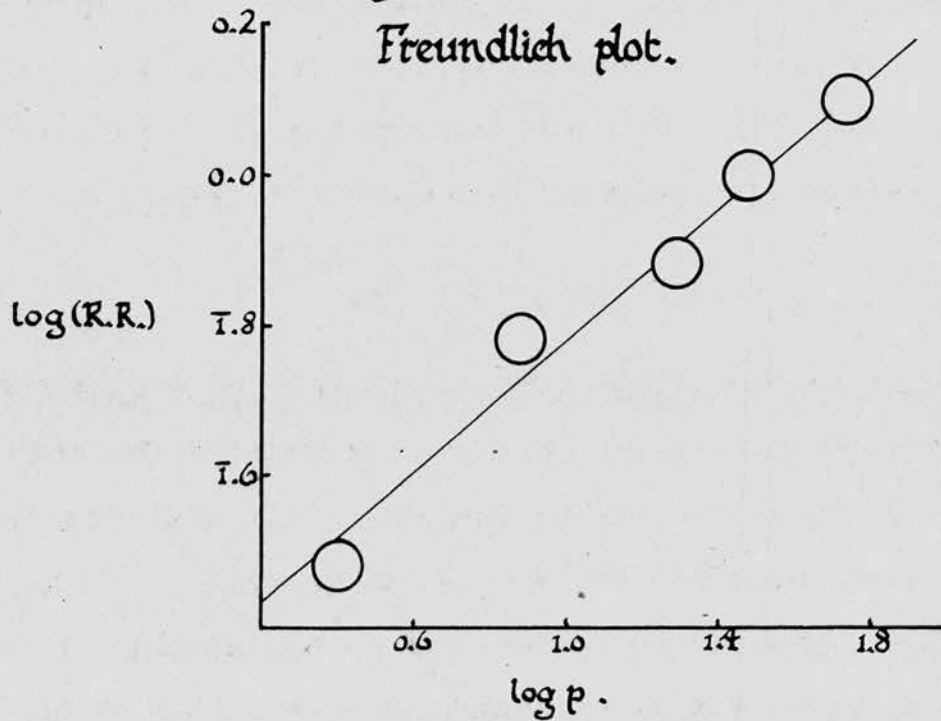


Table 35

p_{NO} (mms.)	(R.R.)	Log p_{NO}	Log (R.R.)
55	1.25	1.74	0.10
30	1.00	1.48	0.00
19.5	0.75	1.29	$\bar{1}.88$
7.5	0.60	0.88	$\bar{1}.78$
2.5	0.30	0.40	$\bar{1}.48$

Fig. 26b shows that the results are in agreement with a Freundlich type equation:-

$$(R.R.) = C p_{NO}^n$$

$$\text{or } \log (R.R.) = n \log p_{NO} + \log C$$

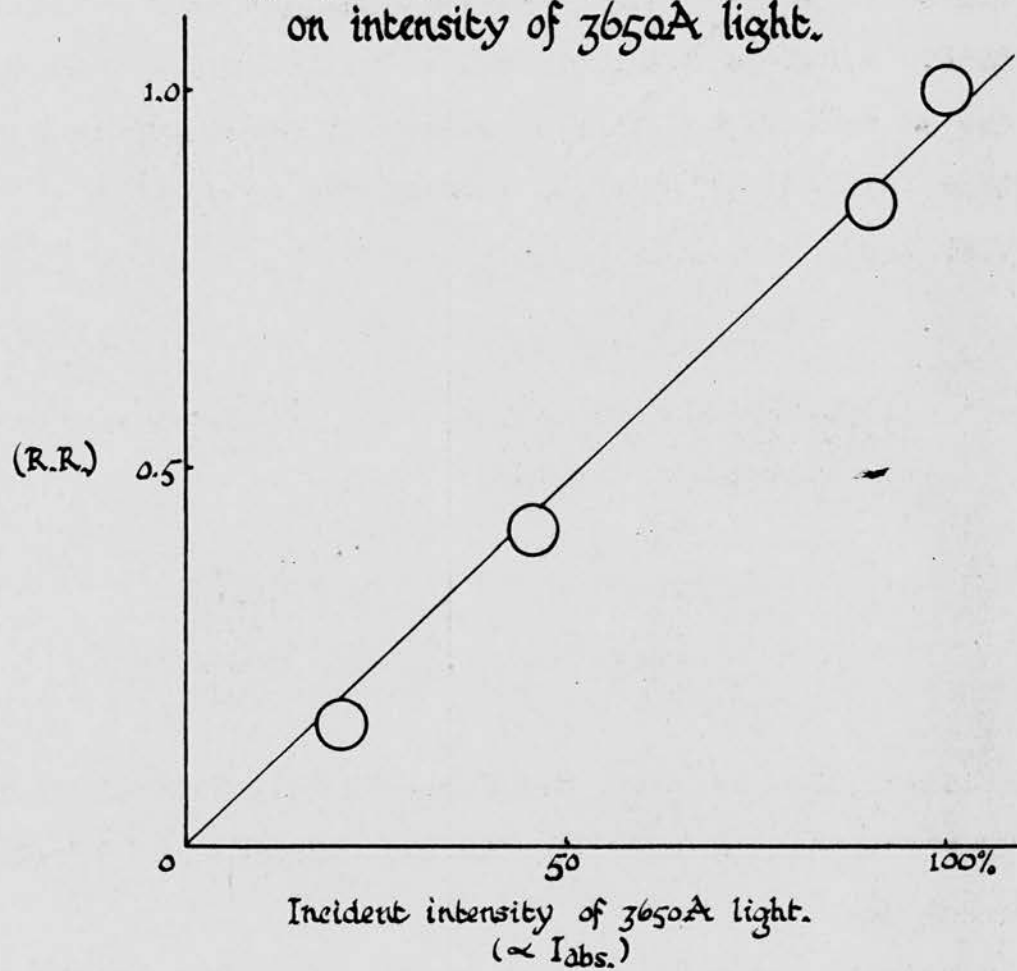
(C and n are constants; (R.R.) and p_{NO} are values of the relative rate and nitric oxide pressure respectively.) From the $\log (R.R.) - \log p_{NO}$ plot, values of C and n were derived and Fig. 26a shows the experimental values in agreement with a curve of equation:-

$$(R.R.) = 0.225 p_{NO}^{0.43}$$

The effect of change in light intensity on the rate of the reaction

The 3650A line of the mercury spectrum was shown to be active in the reaction, and in the following experiment its intensity was reduced in the manner described for the oxygen reaction. The second modification of the relative rate method was applied where the dark rates were plotted against time, and corrections to be subtracted from the rates under illumination were derived from the curve. A rate curve was drawn for the maximum light intensity,

Fig. 27. Dependence of rate of NO reaction on intensity of 3650Å light.



plotting corrected rate values (values of the rate of the photo-reaction alone) against total pressure change values (the sum of the changes caused by the dark and light reactions). As before values for the rate at maximum intensity were interpolated corresponding to the rates at reduced intensity (also corrected for the dark reaction), and the relative rates were calculated. The following results were obtained at 25°C with a film of sample b2 contained in a vessel of type (b)1 and using prep. 2 of nitric oxide at a pressure of 50 mms.

Table 36

Intensity of 3650A light incident on the film (\propto intensity absorbed) %	Relative Rates
100	1.0
90	0.85
45.5	0.42
20.3	0.16

Fig. 27 shows that the rate was directly proportional to intensity of 3650A light incident on the film, or the intensity of 3650A light absorbed by the film.

Relationship between the nitric oxide reaction and the oxygen uptake

(1) The effect of intermediate illumination in nitric oxide on the photo-uptake of oxygen.

Illumination was carried out in the usual way, using a film of sample b2 in 52 mms. oxygen, and part of a rate curve was obtained for the oxygen uptake. The oxygen was then pumped off and was

Fig. 28 Intermediate photo-treatment in NO. ~ Table 37.

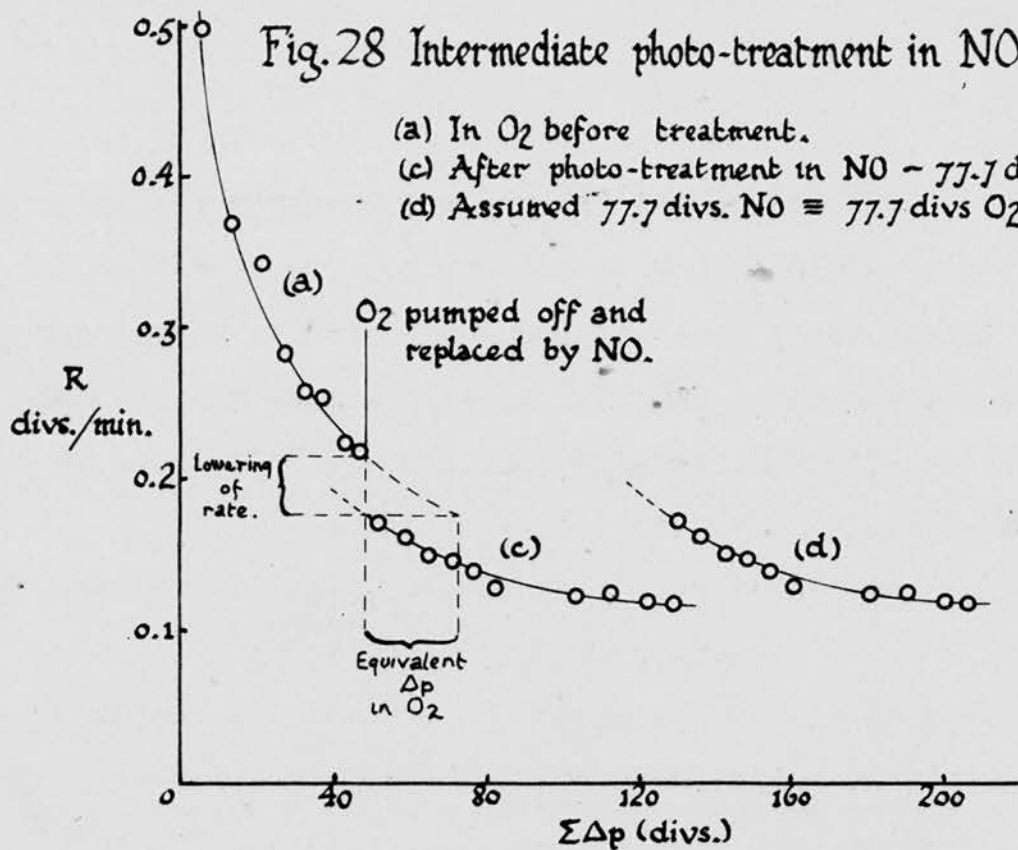
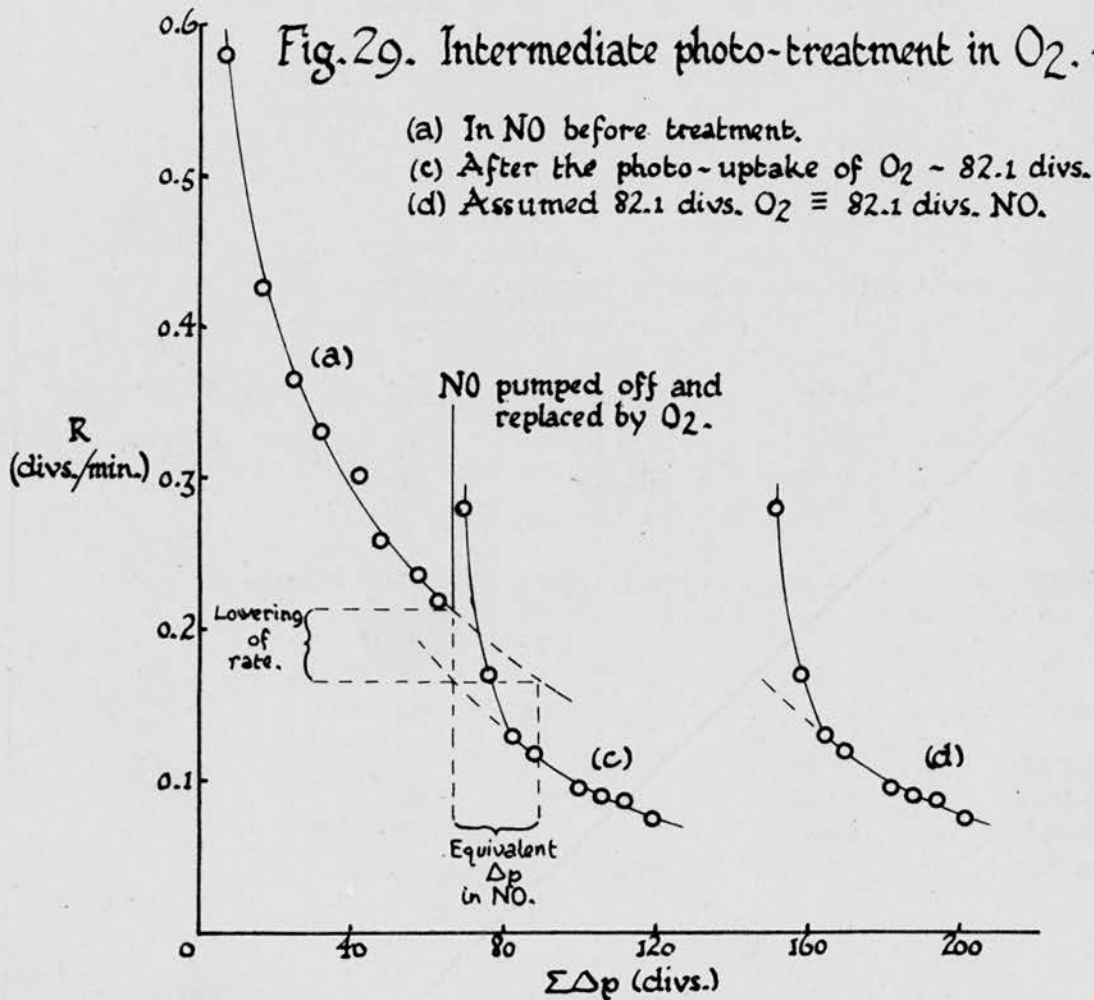


Fig. 29. Intermediate photo-treatment in O_2 . ~ Table 38.



replaced by 30 mms. nitric oxide, and part of a rate curve was obtained for the nitric oxide reaction (the rate values were corrected for the dark reaction). The NO was pumped off and the uptake of oxygen was continued at 52 mms. pressure. Table 37 gives the rate values, and Fig. 28 shows that the illumination in NO resulted in a decrease in the rate of uptake of oxygen (section (a) to (c)), but that the decrease was not as great as would have occurred after intermediate treatment in oxygen with an equivalent number of divs. change in oxygen pressure during treatment (section (a) to (d)). A completely smooth rate curve would have been obtained by adding approximately 24 divs. to the $\Sigma\Delta p$ values for section (c), i.e. 78 divs. Δp in NO = 24 divs. Δp in oxygen, both changes in pressure under illumination causing the same lowering in the rate of uptake of oxygen.

Table 37

(a) Illumination in 52 mms. oxygen for 160 mins.					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
5.5	0.510	27.1	0.285	42.5	0.225
13.4	0.370	32.5	0.260	47.0	0.220
20.8	0.345	37.7	0.255	49.1	
(b) Illumination in 30 mms. nitric oxide for 360 mins. (dark rate = 0.01 divs./min.)					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
4.5	0.420	37.5	0.220	70.0	0.165
12.2	0.335	46.0	0.190	81.3	
18.5	0.290	53.6	0.178	Corrected	$\Sigma\Delta p$
27.3	0.268	61.0	0.178	77.7	

Table 37 contd.

(c) Continuation in 52 mms. oxygen for 630 mins.					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
52.5	0.173	77.2	0.140	122.6	0.120
59.4	0.163	82.6	0.130	129.7	0.120
65.5	0.150	103.9	0.125		
71.5	0.148	112.8	0.126		

(d) Figures for (c) assuming that (b) was carried out in oxygen giving an uptake of 77.7 divs.					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
130.2	0.173	154.9	0.140	200.3	0.120
137.1	0.163	160.3	0.130	207.4	0.120
143.2	0.150	181.5	0.125		
149.2	0.148	190.5	0.126		

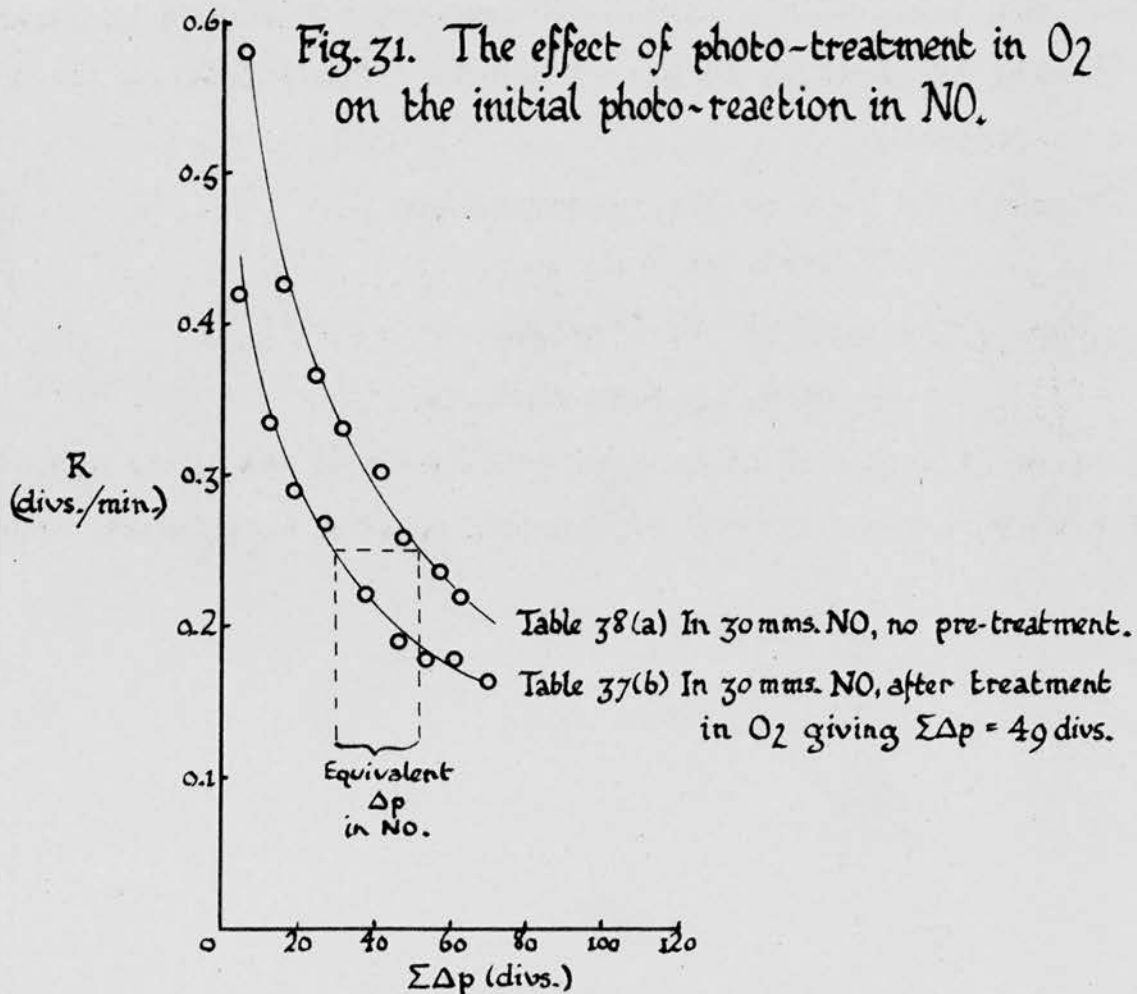
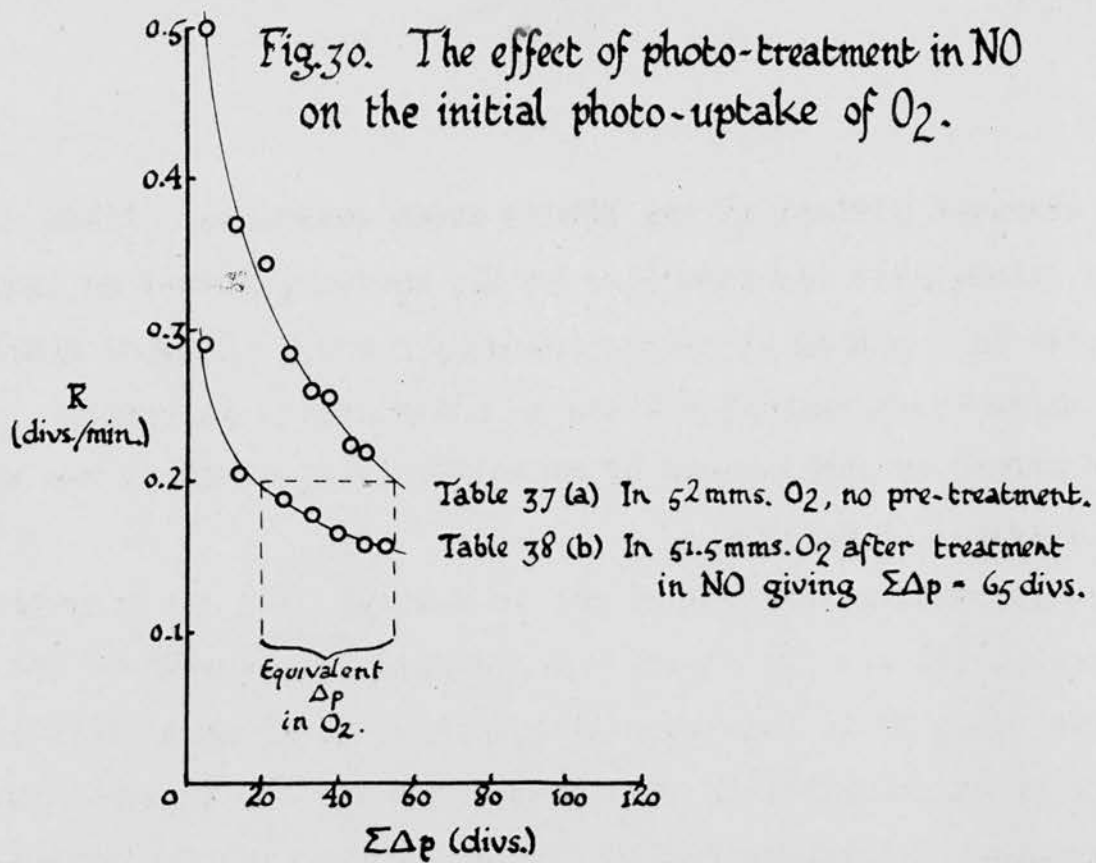
(2) The effect of intermediate illumination in oxygen on the photo-reaction with nitric oxide.

An experiment was carried out as in (1) above, illuminating a film of sample b2 firstly in nitric oxide, then in oxygen, and finally in nitric oxide again. Since the rate of the nitric oxide reaction is appreciably dependent on pressure, the initial pressure on admitting the gas for the second time was lowered to approximate closely to the NO pressure at the end of the first illumination. It may be seen from Fig. 29 that the intermediate treatment in oxygen lowered the rate of the nitric oxide reaction, and the following relationship was derived: $82 \text{ divs. } \Delta p \text{ in } O_2 = 22 \text{ divs. } \Delta p \text{ in NO}$, both changes in pressure under illumination causing the same lowering in the rate of the reaction in nitric oxide. The data are given in Table 38.

Table 38

(a) Illumination in NO for 200 mins. Initial pressure of NO = 31.0 mms. (dark rate = 0.009 divs./min.)					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
6.5	0.581	31.5	0.331	57.4	0.236
16.5	0.426	41.5	0.301	62.0	0.219
24.2	0.366	47.2	0.259	66.4	
(b) Illumination in 51.5 mms. O ₂ for 480 mins.					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
5.0	0.290	33.0	0.178	52.6	0.158
14.0	0.205	39.9	0.165	65.0	0.151
25.7	0.188	46.2	0.159	82.1	
(c) Continuation in NO for 550 mins. Initial pressure of NO = 29.0 mms. (dark rate = 0.004 divs./min.)					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
69.4	0.280	87.0	0.118	111.4	0.088
75.9	0.170	98.9	0.095	118.4	0.075
81.9	0.130	104.9	0.090		
(d) Figures for (c) assuming that (b) was carried out in NO giving a pressure change of 82.1 divs.					
$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.	$\Sigma\Delta p$ divs.	R divs./min.
151.5	0.280	169.1	0.118	193.5	0.088
158.0	0.170	181.0	0.095	200.5	0.075
164.0	0.130	187.0	0.090		

It may be noticed that section (c) of the curve in Fig. 29 shows an initial high rate which falls rapidly and this in spite of the fact that the periods of evacuation between the sections (a) and (c) were kept short (10 mins.). It was possible that this was due to desorption



of some adsorbed product of the nitric oxide reaction. Films which had been illuminated for some time in NO, however, showed no increase in pressure in standing in vacuo, and only a small increase similar to that shown by an untreated film, on illumination in vacuo.

(3) The effect of preliminary illumination in O_2 or NO on the subsequent reaction in NO or O_2 .

Some supporting information may be derived from the experimental data given in (1) and (2) above. Comparison may be made of the rate curves for Table 37(a) and Table 38(b), and Fig. 30 shows that pre-treatment by illumination in nitric oxide lowers the initial rate of oxygen uptake. Similarly Fig. 31, which illustrates the curves for Table 38(a) and Table 37(b), shows that photo-pretreatment in oxygen lowers the rate of reaction in nitric oxide. The following relationships can be derived.

In lowering the rate of the oxygen uptake

$$65 \text{ divs. NO} \approx 34 \text{ divs. } O_2$$

In lowering the rate of the nitric oxide reaction

$$49 \text{ divs. } O_2 \approx 22 \text{ divs. NO}$$

Table 39 summarises the relationships derived from the above experiments together with similarly derived relationships from another two experiments.

Table 39

No. of divs. NO \equiv 1 div. O ₂ in lowering the rate of oxygen uptake		No. of divs. O ₂ \equiv 1 div. NO in lowering ² the rate of the NO reaction	
Preliminary treatment	Intermediate treatment	Preliminary treatment	Intermediate treatment
1.90	3.25	2.25	3.75
1.95	3.05	1.80	3.85
Av. 1.9	3.2	Av. 2.0	3.8

The photo-reaction with nitric oxide - Summary

A decrease in pressure, which was comparable with that observed in oxygen, occurred on illuminating films of titanium dioxide in nitric oxide with light of wavelength 3650A. In low pressures of nitric oxide a 25% (pressure) production of nitrous oxide occurred giving a decrease in pressure of approximately 75%.

The rate of the reaction was studied as a function of the nitric oxide pressure and 3650A light intensity and it was found that

$$\frac{d \Delta p}{dt} = \text{const. } P_{\text{NO}}^n$$

and $\frac{d \Delta p}{dt} = \text{const. } I_{\text{abs.}}$

Preliminary or intermediate photo-treatment of films in oxygen caused a decrease in the subsequent rate of the nitric oxide photo-reaction, and preliminary or intermediate photo-treatment in nitric oxide caused a decrease in the subsequent rate of oxygen uptake.

ILLUMINATION OF TITANIUM DIOXIDE WITH VARIOUS ADSORBED SOLIDS

The following experiments were conducted, again with the object of finding some simple reaction at the oxide surface capable of further examination in the Bourdon gauge system. Films of titanium dioxide were prepared using as binding liquids, solutions of various solids in acetone or water, and these films were given the usual preliminary evacuation before illumination first in vacuo, and then in low pressures of oxygen. Some of the solids examined, namely mandelic acid, tartaric acid, and silver nitrate have been reported to give solutions, which are photo-oxidisable in the presence of titanium dioxide (p 2); the others, namely oxalic acid, potassium oxalate, and cinnammic acid are known to give solutions which photo-oxidise in the presence of zinc oxide (p 5). The pressure changes observed in vacuo and in oxygen are given below in Table 40a.

In neither of the experiments was there observed an increase in pressure due to the evolution of the products of any photo-reaction between the adsorbed solid and the titanium dioxide, and in low pressures of oxygen, the usual uptake of oxygen attributable to the oxide alone was observed. All of the films studied did, however, show some darkening on illumination.

Table 40a

Composition of the film	Illumin. in vacuo		Illum. in O ₂		
	t mins.	Increase in pressure divs.	t mins.	Initial pO ₂ divs.	Δp max. divs.
0.12 grm. sample b2 plus					
(1) 0.5 mls. of <u>anhydrous oxalic acid solution</u> 0.1 grm./100 mls. acetone	360	2.0	140	28.6	28.0
(2) 0.5 mls. <u>potassium oxalate solution</u> 0.1 grm./100 mls. water	40	0.2	280	16.8	15.7
(3) 1 ml. <u>cinnamic acid solution</u> 1 grm./100 mls. acetone	180	0.7	240	30.0	29.0
(4) 1 ml. <u>tartaric acid solution</u> 1 grm./100 mls. acetone	12.0	0.5	260	30.0	26.5
(5) 1 ml. <u>mandelic acid solution</u>	290	1.0	190	27.0	26.0
(6) 5 mls. <u>AgNO₃ solution</u> 0.5 grm./100 mls. water	40	0.0	120	20.0	3.0
			Slow uptake not examined to completion		

Table 40b

	Illumination in H ₂ O			Illumination in H ₂ O + O ₂		
	Initial pH ₂ O divs.	t mins.	Δ p increase divs.	Initial pO ₂ divs.	t mins.	Δ p decrease divs.
(4)	23	40	1.4	34	50	2.3
(5)				Rapid uptake of O ₂ in dark followed on illumination by		
	20	180	2.7	18	60	8.8

It was possible that the presence of water vapour would fulfil a necessary condition for photo-reaction, and, therefore, the films from experiments (4) and (5) were illuminated in water vapour, and in water vapour and oxygen together. After evacuation, water vapour was admitted and the pressure was allowed to reach a steady value. Illumination was then commenced. Only slight increases in pressure occurred, and after ceasing illumination some oxygen was admitted. When steady pressures were reached, illumination was continued and a fall in pressure, which may have been uptake by the TiO₂ alone, was observed. The results are shown in Table 40b.

Summary

In the above experiments no increase in pressure was observed under various conditions (in vacuo, in oxygen, in water vapour, and in water vapour and oxygen together), as a result of photo-reaction of various solids adsorbed on titanium dioxide.

PART IV

DISCUSSION

THE PHOTO-UPTAKE OF OXYGEN

Structure of the Films

The results described in part III refer to thin films of powder particles, and if they are to be used to gain insight into the processes occurring at a single titanium dioxide-gas interface, then it is necessary to define the role played by the structure of the film in their determination. The essential point to be considered is that each crystal of titanium dioxide in a film receives a different amount of light; for example, a crystal situated at the back of a film must receive little light in comparison with one situated at the front. In contrast, the temperature of a crystal in a film does not depend on the position of the crystal in the film, nor does the gas pressure over the crystal depend on position where gaseous diffusion effects are absent.

Consider two possible processes occurring at the surface of a single crystal of titanium dioxide on illumination. Firstly, consider a parabolic process. Where Δp_1 is the decrease in oxygen pressure occurring over the crystal in time of illumination t , and where k_1 is a function of the temperature, the oxygen pressure and the intensity of the light absorbed by the crystal, then the process is described by:-

$$\begin{aligned}(\Delta p_1)^2 &= k_1 \cdot t \\ \text{or } \Delta p_1 &= \sqrt{k_1} \cdot \sqrt{t}\end{aligned}$$

and the rate of pressure decrease is given by:-

$$R_1 = \frac{d\Delta p_1}{dt} = \frac{k_1}{2\Delta p_1}$$

$$\text{or } R_1 = \frac{\psi(T) \cdot \varphi(p) \cdot f(I_{\text{abs.1}})}{2\Delta p_1}$$

Secondly, consider an exponential process described by:-

$$P_1 - \Delta p_1 = P_1 \cdot e^{-k_1 \cdot t}$$

where P_1 is a constant representing the change in pressure over the crystal as $t \rightarrow \infty$. The rate of pressure decrease is given by:-

$$R_1 = \frac{d\Delta p_1}{dt} = k_1 \cdot P_1 \cdot e^{-k_1 \cdot t}$$

$$= k_1 (P_1 - \Delta p_1)$$

$$= \psi(T) \cdot \varphi(p) \cdot f(I_{\text{abs.1}}) \cdot (P_1 - \Delta p_1)$$

Now suppose that there are many such crystals forming a film of titanium dioxide. For the parabolic process the rate of pressure decrease over the film is given by:-

$$R = R_1 + R_2 + \dots = \frac{k_1}{2\Delta p_1} + \frac{k_2}{2\Delta p_2} + \dots$$

$$= \frac{\psi(T) \cdot \varphi(p) \cdot f(I_{\text{abs.1}})}{2\Delta p_1} + \frac{\psi(T) \cdot \varphi(p) \cdot f(I_{\text{abs.2}})}{2\Delta p_2} + \dots$$

$$= \psi(T) \cdot \varphi(p) \cdot \left\{ \frac{f(I_{\text{abs.1}})}{2\Delta p_1} + \frac{f(I_{\text{abs.2}})}{2\Delta p_2} + \dots \right\}$$

Where for each crystal in the film $f(I_{\text{abs.}}) = \text{constant} \times \text{intensity of light incident on the film, e.g. } f(I_{\text{abs.1}}) = K_1.I$, then:-

$$R = \psi(T) \cdot \varphi(p) \cdot I \cdot \left\{ \frac{K_1}{2\Delta p_1} + \frac{K_2}{2\Delta p_2} + \dots \right\}$$

Similarly for the exponential process the rate is given by:-

$$R = \psi(T) \cdot \varphi(p) \cdot I \cdot \left\{ K_1(P_1 - \Delta p_1) + K_2(P_2 - \Delta p_2) + \dots \right\}$$

It may be concluded then, that for either process, the rate of uptake over a single crystal and the rate of uptake over a film composed of many crystals depend on temperature, oxygen pressure and incident light intensity in the same way; i.e. the same laws relate the rate of uptake to the three variables, whether a single crystal or a film is under consideration.

Consider next the uptake over a film when temperature, pressure and light intensity are kept constant. The following equations hold in the parabolic and exponential cases respectively:-

$$\Delta p = (\sqrt{k_1} + \sqrt{k_2} + \dots) \cdot \sqrt{t}$$

$$\text{and } \Delta p = P_1 + P_2 + \dots + P_1 \cdot e^{-k_1 t} + P_2 \cdot e^{-k_2 t} + \dots$$

The $\Delta p - t$ curves obtained are parabolic and the sum of several exponentials respectively. The second curve, which is the sum of several exponentials, will be a simple exponential, where $k_1 = k_2 = \dots$, that is, where the intensities of light absorbed are the same for all crystals. This condition may hold for the crystals situated at the front of the film, and these are the most important in the uptake, since they receive most of the light. It is easy to see, that if

parabolic and exponential laws are observed in experiments using films of titanium dioxide powders, then these laws may almost certainly be taken to apply in experiments conducted over single crystal surfaces.

The magnitude of the uptake

One of the questions which may immediately be asked regarding the oxygen uptake, is whether it is an absorption or adsorption process, and there is, therefore, interest in comparing the amounts of oxygen taken up with the surface areas of the samples. Technical samples of titanium dioxide usually have surface areas of the order of ten square metres per gram, and laboratory prepared samples dried at temperatures below 400°C probably have areas around one hundred square metres per gram. (There is some reference in the literature to TiO_2 powders of such high area, and Voltz and Weller³⁸ have found that chromic oxide samples of similar preparation have areas up to four hundred square metres per gram.) Theoretical uptakes may be calculated on the assumption that each surface titanium ion is a site for the adsorption of one atom of oxygen. For technical and laboratory samples having specific surface areas as quoted, such a calculation gives uptakes of 5×10^{-5} moles O_2/gram . TiO_2 and 5×10^{-4} moles O_2/gram . TiO_2 respectively. These values are greater than the maximum uptakes observed for two samples showing exponential type curves, namely 2×10^{-5} moles O_2/gram . TiO_2 for sample C and 3×10^{-4} moles O_2/gram . TiO_2 for sample c; taking into consideration that observed uptakes must be lower than is possible, as a result of film structure, this represents good agreement.

Another question, which has already been partly answered by the above considerations, is concerned with the relationship between oxygen uptake and semiconductivity. The n-type semiconductivity, shown by titanium dioxide in the reduced form, is attributed to the presence of oxygen ion vacancies in the crystal lattice, corresponding to a deficiency of oxygen, and it may therefore be imagined, that the photo-uptake of oxygen is a process of filling up of oxygen vacancies. In view of the magnitude of the uptake, such a process must involve diffusion of ions in the titanium dioxide lattice, and even in the surface layers this must be regarded as an unlikely occurrence at 25°C; blue titanium dioxide, which has oxygen vacancies, does not recover whiteness on standing at room temperature either in the dark or under illumination; no transport of Ti⁽⁵¹⁾ has been observed in barium metatitanate powders³⁹; and no appreciable exchange occurs between the surface of TiO₂ powders and gaseous oxygen below 400°C^{34 35}. Even if diffusion were possible in the bulk of the crystal, explanation of the photo-uptake as the filling of oxygen vacancies requires that there be a considerable concentration of such vacancies in the samples, and where this is due to deficiency of oxygen, the samples should be blue in colour; an uptake of 10⁻⁴ moles O₂/gram. TiO₂ corresponds to a deficiency of TiO₂ - 0.02. The explanation is, then, in opposition to the fact that all of the samples, which exhibit photo-uptake of oxygen are white, and to the observation (p.49) that the production of a deficiency of oxygen in a sample does not incur an increased uptake of oxygen. The filling of oxygen vacancies on illumination is not to be ruled out completely, but can only account for a small fraction of the observed uptake.

The idea that the photo-uptake is a result of the presence of other impurities in the oxide, succumbs to a similar argument, besides which, the work carried out by Mackenzie on the presence of impurities in the oxide samples, and some additional observations made in the course of the present work, show that there is no direct connection with any impurity in the solid. Mackenzie has shown that the photo-uptake of oxygen is not a direct result of the presence of impurities such as iron, chlorine and nitrogen in laboratory prepared samples, and this conclusion is supported by the observation (p43) that a sample of titanium dioxide prepared in the vapour phase from $TiCl_4$, showed an uptake rivalling that of other commercial samples. Again, however, the possible effect of impurities on the uptake, which may be regarded as a property of perfectly pure titanium dioxide, is not over-ruled, and discussion of this effect in relation to chromium treatment will be given later.

The above arguments lead to consideration of the photo-uptake as a surface phenomenon, a problem of adsorption, and this idea will be further developed.

The Kinetics of the uptake

(a) Rate of uptake as a function of oxygen pressure.

It can be stated, that the rate of photo-uptake of oxygen at a titanium dioxide surface depends on pressure, according to the following two equations:-

$$R = \frac{d\Delta p}{dt} = \text{const. } \theta \quad \text{and} \quad \frac{\theta}{1-\theta} = A\sqrt{p}$$

This may be interpreted simply, as meaning that the photo-reaction

proceeds from a chemisorbed layer of oxygen atoms, there being two consecutive reactions with oxygen, first a rapid reversible dissociative adsorption in accordance with a Langmuir type equation, followed by a further slow rate-determining reaction of the adsorbed oxygen.

(b) Rate of uptake as a function of I_{abs} .

At a single titanium dioxide crystal surface the rate of uptake of oxygen is directly proportional to the intensity of light absorbed within the fundamental absorption band of the crystal. Absorption of one quantum results in the production of an electron in the conduction band and a positive hole in the valence band of the crystal. Excited electrons so produced may recombine in some way with the positive holes, or may cause a reaction such as the uptake of oxygen. De-excitation by reaction will be a rare occurrence compared with the normal recombination, and it may be assumed that the number of electrons in the conduction band is not affected by the oxygen uptake. Direct combination of the excited electrons with the positive holes, accompanied by the emission of light, has not been observed in pure crystals (p. 9), and it is more likely, that the recombination takes place indirectly via the trapping of the conduction electrons at empty levels lying below the conduction band, thus resulting in a radiationless transition to the ground state. Where such a trapping process applies, the number of electrons in the conduction band is directly proportional to the intensity of the light absorbed. The rate of oxygen uptake, then, is directly proportional to the number of electrons in the conduction band of the crystal.

(c) Rate of uptake as a function of the amount taken up.

Two laws are obeyed, initially the parabolic law, given by:-

$$R = \frac{d\Delta p}{dt} = \text{const.} \frac{1}{\Delta p + p'}$$

and finally the exponential law, given by:-

$$R = \frac{d\Delta p}{dt} = \text{const.} (P - \Delta p)$$

The parabolic law suggests a diffusion process similar to that found in the oxidation of metals, and the exponential law suggests, that in the later stages of the uptake, the number of adsorption sites available limits the uptake.

The theory developed by Wagner⁴⁰ explains the parabolic law observed in the oxidation of metals. A film of oxide forms over the surface of the metal, and this grows by the diffusion of ions through the film (oxygen ions in or metal ions out). The rate of oxidation is governed by the rate of diffusion of the ions through the film, and since the thickness of the film determines the concentration gradient of the diffusing ions across the film, the rate of diffusion is inversely proportional to the thickness of the film, i.e. it is inversely proportional to the extent of oxidation. The basic equation developed by the theory is:-

$$\frac{dm}{dt} = \frac{\text{const.}}{m}$$

where m is the observed increase in weight of the metal due to the formation of the oxide. If there already exists a film of oxide before the experiment is begun, then the observed rates are given by:-

$$\frac{dm}{dt} = \frac{\text{const.}}{m + m'}$$

where m' is the increased weight, corresponding to the film of oxide formed prior to the experiment.

The parabolic law observed in the initial stage of the photo-uptake of oxygen on titanium dioxide may well be explained by a diffusion of adsorbed oxygen across the surface in a two dimensional analogy of metallic oxidation. Comparison of the equation for the initial stages of the uptake with that for the oxidation of metals, gives some indication of the significance of the small constant p' . p' may signify that the process of oxygen adsorption has proceeded to some extent before the initial experimental observations are made. As the photo-uptake proceeds and the number of surface sites left available becomes smaller, then this number will become the most important factor in determining the rate of uptake, and the exponential law will apply.

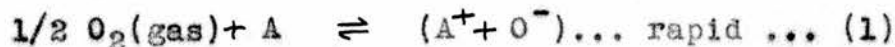
A scheme for the photo-uptake of oxygen

The following main points are proposed as a basis for explanation of the results obtained, and they form a scheme which describes the photo-uptake of oxygen at a titanium dioxide crystal surface.

(a) There exist two main types of sites on the titanium dioxide surface, where the chemisorption of oxygen can take place; on both types, chemisorption takes place with the donation of electrons from the crystal to the oxygen to form the chemisorbed species O^- .

(b) At sites A reversible chemisorption takes place at 25°C in accordance with a Langmuir type isotherm for dissociative adsorption:

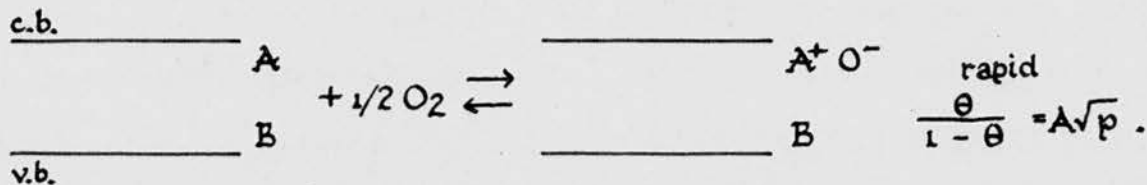
$\frac{\theta}{1-\theta} = A\sqrt{p}$; equilibrium is reached rapidly



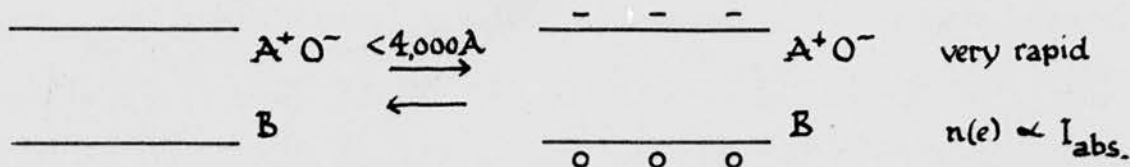
(c) Chemisorption on sites B occurs at 25°C only on illumination

Fig. 32. Photo-uptake of O₂ at a TiO₂ surface.

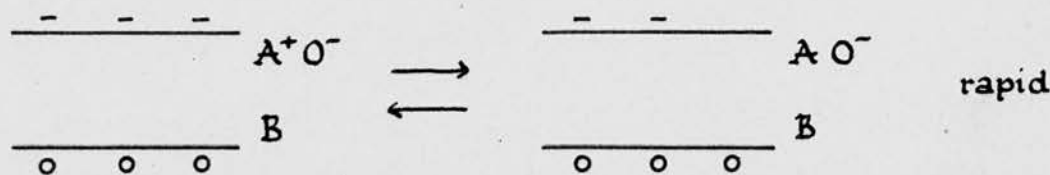
(1) a Reversible chemisorption at A sites.



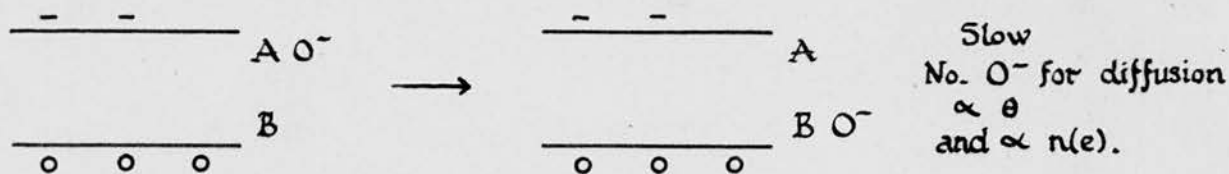
b Absorption of light.



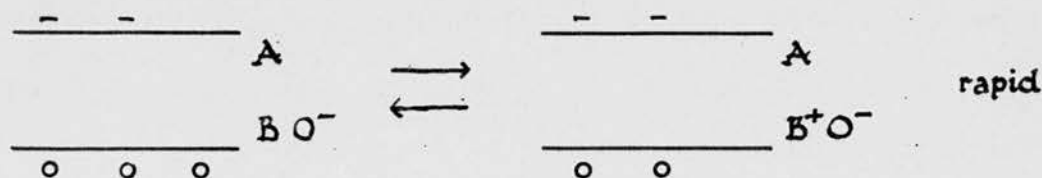
(2) Trapping of electrons at A levels.



(3) Diffusion from A sites to B sites.

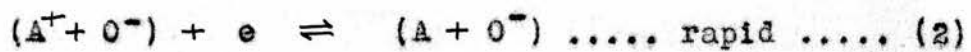


(4) Trapping of positive holes at B levels.



with light $<4000\text{\AA}$ and is virtually irreversible. The number of B sites is much greater than the number of A sites.

(d) A small fraction of the electrons in the conduction band of the titanium dioxide crystal become trapped at empty A levels, freeing the reversibly chemisorbed O^- for diffusion across the surface.



Only a very small fraction of the empty A levels became occupied by electrons from the conduction band, and the process of electron trapping and release is fast and reaches equilibrium almost instantaneously. The number of the diffusing species, i.e. the number of $(A + O^-)$ is at any instant proportional both to the number of electrons in the conduction band and to the number of A sites occupied by oxygen, i.e. the number of $(A^+ + O^-)$.

(e) The reversibly chemisorbed oxygen, freed by the trapping process, diffuses across the surface to the B sites, where rapid combination takes place with the positive holes of the valence band to form an irreversibly chemisorbed species.



Fig. 32 shows the complete process of photo-uptake in relation to the potential energy diagram for titanium dioxide, and illustrates equations (1), (2), (3) and (4) given above; the empty A levels are shown as lying below the conduction band, but these may in fact lie above the conduction band and the trapping of conduction band electrons may be, therefore, a process with a small energy of activation.

Explanation of the results

The proposed scheme meets the main requirements of the kinetics of the oxygen uptake. Initially the diffusion process gives a parabolic type uptake curve, which later changes to an exponential type uptake curve as the number of sites left available becomes small and rate determining; the stage of the uptake where the exponential law takes over from the parabolic law will depend on the relative numbers of the A and B sites, the rate of diffusion across the surface, and the actual structure and distribution of the A sites. At all stages of the uptake the rate is proportional to the intensity of the light absorbed by the oxide, and to the fraction of the A sites occupied by oxygen. In addition to meeting these requirements, a possible explanation of a preliminary experiment carried out by Mackenzie¹² is indicated by the scheme; he found that the oxygen uptake had a small positive temperature coefficient (5 k. cal./mole). It is possible that this may be primarily associated with activation necessary for the diffusion of oxygen across the surface, but since there are several possible temperature dependent stages involved, the observed figure cannot definitely be ascribed to the diffusion stage of the reaction only.

Attention may now be turned towards other features of the results. As has already been shown, the differences between the uptakes shown by technical and laboratory prepared samples may be interpreted, in accordance with the proposed scheme, as largely due to differences in their surface area, and this idea may be extended to cover the

differences in uptake induced by treatment at various temperatures. Hughes⁴¹ has shown that two processes, which result in large decreases in the specific surface areas, occur on heating precipitated samples to temperatures above 600°C, namely growth of crystallites and sintering; growth of crystallites is a limited process, whereas sintering is an unlimited process. The differences in surface area existing between technical and laboratory prepared samples are due to the crystallite growth process; the technical samples undergo calcining at high temperatures, but subsequent grinding and milling reduces the effect of sintering without affecting the size of the crystallites. The growth processes can together account for the hundredfold decrease in uptake observed on treatment of a precipitated sample at a temperature of 800°C; in addition to decreasing the surface area, treatment at 800°C may cause a drastic reduction in the number of A sites, since they are probably very active in the sintering process. The only effect on the uptake observed on treatment at temperatures up to 400°C was a slight increase in activity, and this is almost certainly a result of "opening up" of the surface by removal of strongly bound water from between the aggregated crystallites. The fact that no effect was observed (p.46), which may be attributed to treatment in reducing atmospheres, suggests that the photo-uptake is largely independent of non-stoichiometry of the samples, and that the gases, if they are left chemisorbed on the surface in any appreciable amounts after treatment, do not interfere with the photo-uptake.

Examination of the technical samples has shown that anatase is more active than rutile, and that there is a difference in the shape of their

uptake curves; anatase shows predominantly exponential curves, whereas rutile only gives the parabolic type of curve. Rutile samples do generally have smaller surface areas than anatase samples, but this difference is not great enough in itself to explain the observed differences in the photo-uptake of oxygen. Other factors may be involved; rutile may have a much smaller number of A sites than anatase; the rate of diffusion of oxygen atoms freed by electron trapping may be smaller on rutile than on anatase; and processes other than the oxygen uptake, which lead to the de-excitation of conduction band electrons, e.g. fluorescence, may be more active in rutile than in anatase. This latter factor has been discussed by Hughes⁴¹ and Winter⁴² in relation to the chalking of paint films and the fading of tinted paint films containing titanium dioxide and zinc oxide pigments. Anatase and French process zinc oxide were active photochemically but showed no fluorescence, whereas rutile and American process zinc oxide, which showed some fluorescence, were less active photochemically.

It is unlikely that the reduction of oxygen uptake by surface treatment with chromium is merely caused by covering of the surface sites for oxygen adsorption; titanium dioxide pigments surface treated with Mn^{2+} or Cr^{3+} ions show a decreased activity in the light damaging of matted rayon materials^{2,5}, but treatment with other ions, e.g. Fe^{3+} , can make the tendering worse.⁵ The reduction in activity by chromium treatment most likely includes a surface electrical effect in its causes. The adsorbed chromium probably forms electron trapping centres at the surface which can

accept the conduction band electrons; in this or some other way the probability of electrons reaching the surface sites (Empty A levels) in the oxygen uptake is decreased. Adsorbed foreign oxides are known to cause phototrophy in titanium dioxide; titanium dioxide with adsorbed oxide impurity develops colouration on exposure to u.v. light. McTaggart and Bear⁴³ have studied this phenomenon in detail, and the effect of chromium on the photochemical activity of titanium dioxide is undoubtedly related to its ability to form colour centres when the treated sample is illuminated.

The difference in sample activity and the effects of sample pre-treatment can be summarised as due to a variety of factors; surface area, surface heterogeneity (distribution of A and B sites), surface diffusion, bulk electronic structure and surface electronic structure all play a part in determining the activity in the oxygen uptake.

OTHER PHOTO-REACTIONS

Illumination in hydrogen and carbon monoxide

It was hoped that some reaction would be found giving support to either of the two ideas which obtain from the literature on the photochemistry of titanium dioxide. Jacobsen¹ suggests that photo-oxidations at the surface of titanium dioxide are a result of a cyclic reduction-oxidation of the oxide, and further that the absorption of light causes a reduction of the surface; this idea is approved by Weyl and Förland¹⁰. In this cyclic scheme, however, light may cause an oxidation of the surface as was originally suggested by Ruben⁷ and not a reduction. On the basis of the first of these ideas, illumination of TiO_2 in hydrogen and carbon monoxide would be expected to give oxidation of the gases with the production of water and carbon dioxide, whereas on the basis of the second idea, production of water and carbon dioxide would only be expected in the presence of oxygen, and photo-absorption of hydrogen and carbon monoxide would be possible in the absence of oxygen.

The results reported in part III do not support either of these mechanisms; if any of the possible reactions did in fact take place, then they must have done so extremely slowly, at rates which would have made any further examination fruitless.

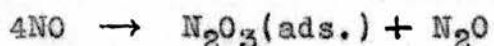
Illumination with adsorbed solids

The results obtained with adsorbed solids in dry conditions parallel with those obtained with hydrogen and carbon monoxide; no products of oxidation were evolved either in the presence of oxygen or in vacuo. It must be emphasised that the results do not

prove the absence of all reaction, indeed the observation that the films darkened on illumination indicates some reaction which may undoubtedly be classified with the bleaching in vacuo of chlorazol sky blue adsorbed on TiO_2 . The two experiments carried out in the presence of water vapour gave similar results to those in dry conditions. It remains possible that oxidation of the adsorbed substances does in fact take place, but either this is slow, or the products of the oxidation remain bound to the surface of the oxide under the conditions of the experiment. It is certain, however, that any such oxidation is not capable of elucidation by the applied methods.

The photo-reaction with nitric oxide

On illumination of films under nitric oxide it was expected that nitrogen dioxide would be formed as an oxidation product, but it is clear from the results at low pressures, that the overall reaction with reference to the nitric oxide may be represented by the following equation:-



There is no direct evidence for the presence of N_2O_3 adsorbed on the TiO_2 as such; the formula merely indicates the stoichiometric nature of the adsorbate which must be accepted in order to explain the principal experimental observation, that photo-reaction with nitric oxide gives on average a twenty five per cent production of nitrous oxide, which is the only gaseous product attributable to the nitric oxide. The words 'on average' are used advisedly, since there is some variation between experiments in the percentage nitrous oxide produced. This variation suggests that the reaction takes place

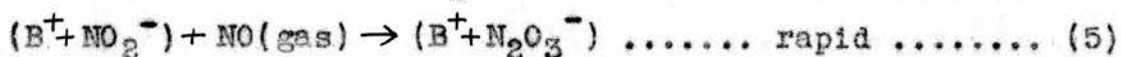
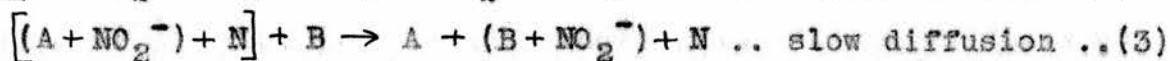
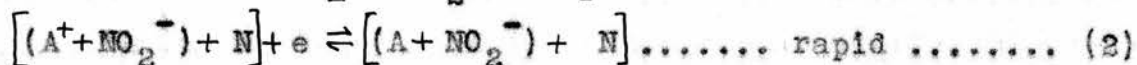
in stages which may get out of step, resulting in a production of N_2O greater or less than the average figure; certainly the variations are rather larger than would be expected from errors in measurement.

The reaction with nitric oxide is of a much more complex nature than that with oxygen, but it has several features in common with the oxygen uptake; like the oxygen uptake, the nitric oxide reaction depends on the absorption of light ca. 3650A by the titanium dioxide, and the rate of the reaction is proportional to the intensity absorbed; the results expressing the rate of the reaction as a function of nitric oxide pressure may be interpreted as being due to the progression of the reaction from an adsorbed layer of gas; the shape of the reaction curve for nitric oxide, in so far as it has been examined, seems to be of the same nature as that shown for the uptake of oxygen on the same sample; and the rates of reaction with nitric oxide are very similar to those with oxygen (this last similarity is especially noticeable at low pressures, where both reactions show a dark uptake after illumination of the film in vacuo).

The results concerned with the relationship between the nitric oxide and oxygen reactions show quite clearly that the reactions are similar, but not identical with respect to the titanium dioxide surface, and that they mutually interfere. It can be concluded that each reaction must result in the covering of some of the surface sites active in the other. It is possible, that the surface sites are the same for both reactions, for example, they may be surface titanium ions in each case, but the reactions may differ in that they express preference for

different crystal planes, in other words, there may be a geometric factor involved, which is different for each reaction.

The following tentative scheme shows how the experimental observations may arise.



A and B are sites for chemisorption as proposed in the scheme for oxygen uptake. As with the oxygen reaction, the rate is determined by the diffusion stage (3), giving proportionality to the intensity of 3650A light absorbed and to the fraction of A sites occupied. (5) and (6) are competitive reactions, and occurrence of one in preference to the other, such as may happen at very low NO pressures, will lead to variation in the percentage N₂O produced. It is assumed that the initial stage of reaction, (1), is a rapid reversible chemisorption and it follows, that no nitrogen atoms are produced by reaction (1) such that they are free to combine rapidly with themselves or with nitric oxide, since rapid production of N₂ or N₂O is not observed in the dark. The nitrogen atoms only become free in this sense during the slow rate determining step of the photo-reaction. It is interesting to note, that Freundlich type isotherms may exist in theory, both for non-dissociative and for dissociative adsorption, e.g.

$$\theta = \text{const. } p^x$$

and

$$\theta = \text{const. } p^{\frac{1}{2}} x$$

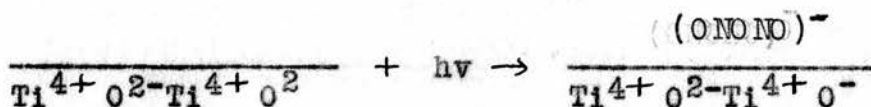
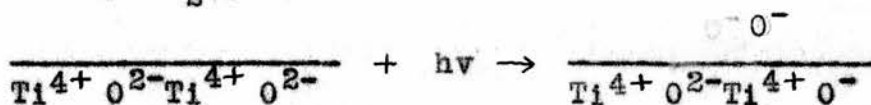
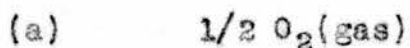
but experimental distinction of the kind drawn for Langmuir adsorption (p.53) is not possible, without previously gained knowledge of the value of constant . . . The close approximation of the observed isotherm to

$$R.R. = \text{const. } p^{\frac{1}{2}} \quad (\text{p.70})$$

does not imply dissociative adsorption of NO.

GENERAL DISCUSSION

The overall photo-reaction with oxygen and nitric oxide is chemisorption. In the case of oxygen, it has been proposed that the final chemisorbed species be represented by O^- in line with modern ideas, and to explain the similarity between the oxygen and nitric oxide reactions, the final chemisorbed species in the nitric oxide reaction is best represented as $N_2O_3^-$. The overall reactions at the B sites may be represented as follows:-



The basic reaction, which occurs at the titanium dioxide surface on illumination, is the transfer of electrons from the titanium dioxide to oxygen or N_2O_3 . No evidence of electron transfer to the titanium dioxide was found; for instance illumination in hydrogen and carbon monoxide did not result in cationic chemisorption of these gases. There is no support for the idea that the tendering of fabrics and the bleaching of chlorazol sky blue etc. are mainly a result of electron transfer from these substances to the titanium dioxide. This possible mechanism is not disproved, however, and the bleaching of chlorazol sky blue in vacuo may yet be explained on this basis.

It was shown that films of TiO_2 did not give off oxygen ($\Delta p < 0.01 \text{ mm.}$)

even after they had photo-sorbed quantities of oxygen, and no evidence was obtained suggesting reaction between the photo-adsorbed oxygen and various gases and solids. These results, in conjunction with the failure of attempts to estimate the photo-adsorbed oxygen by liberation of iodine from a KI solution, are evidence of the irreversible nature of the oxygen uptake. In general, all of the experimental work reported in part II casts doubt on the correctness of Jacobsen's cyclic scheme, whether it is the photo-liberated or the photo-adsorbed oxygen which is accepted as causing the oxidations at the surface of titanium dioxide. It would seem to be, that in these oxidations, the presence of water is important; this may be understood by considering the reactions producing H_2O_2 described in part I.

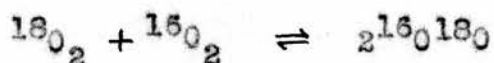
It has already been mentioned that the samples of TiO_2 which showed most activity in the oxygen uptake also showed most activity in the sensitised fading of chlorazol sky blue. It may be said that a similar relation generally exists between the oxygen uptake and other reactions at the surface of titanium dioxide. Results obtained by Krasnovskii and Gurevich⁴⁴ are relevant to this argument. They found that rutile was a less active photocatalyst than anatase for the oxidation of linseed oil and linoleic acid by atmospheric oxygen in toluene and ethanol solutions, and that adsorption of Cr^{3+} reduced the photocatalytic activity. Similar differences in activity are observed in the tendering of fabrics incorporating TiO_2 pigments. If all of these reactions are due in the first instance to the availability of electrons at the titanium dioxide surface under illumination, then their parallel relationship with the photo-uptake of oxygen is easily understood. If, on the other hand, these reactions are due to

the availability of positive holes at the surface then their parallel relationship with the photo-uptake of oxygen is not so easily understood. It is proposed, therefore, that the basic step in all of the reactions, oxygen uptake, nitric oxide reaction, oxidations in solution, fading of adsorbed dyes, phototrophy, tendering and flaking reactions, is the making available and possible transfer of electrons at the solid surface on absorption of light.

It was observed that the illumination of TiO_2 films in vacuo was accompanied by the liberation of small amounts of an unidentified gas, which did not condense at liquid oxygen temperature. This was probably either CO or H_2 , and can probably be associated with the binding liquid acetone, or with the small amounts of water and CO_2 present in the samples. The production of this gas was accompanied by the creation of active sites which could take up oxygen or react with Nitric oxide in the dark. The usually observed dark reaction with nitric oxide was very slow at low pressures, much slower than that observed after illumination in vacuo. The sites created are probably electron donor sites (B sites) from which electrons can be raised to the conduction band at room temperature without the absorption of light.

The A sites are not so easily visualised as are the B sites. However, the parabolic equation requires that diffusion proceeds from positions on the surface^{48 49} in a fashion analagous with diffusion from surfaces in the oxidation of metals, and among the possibilities concerning the identity of these lines, we may include Frenkel steps, dislocations, and crystal edges. The important point

is that reversible chemisorption of oxygen occurs at the A sites, and this chemisorption involves dissociation of the oxygen molecules. The A sites may, therefore, be identified with the sites on which the equilibration of oxygen occurs. Winter³⁴ has studied the dissociation of oxygen at magnesium oxide and zinc oxide surfaces in detail, by following the equilibration reaction:-



$$(E = 22\text{k. cal. mole}^{-1} \text{ for ZnO})$$

It is instructive to take note of the general scheme, which he gives for the equilibration reaction, and for the exchange of ^{18}O with oxide surfaces. Adsorption-desorption, accompanied by equilibration, occurs on an array of closely packed active sites at low temperatures ($\ll 400^\circ\text{C}$); as the temperature is raised, migration across the surface becomes possible and is rate determining in the equilibration ($< 400^\circ\text{C}$); at higher temperatures (ca. 400°C) exchange with the oxide surface takes place. In other words, the exchange reaction shows the same characteristics as photo-adsorption.

The photo-reactions of titanium dioxide demonstrate the heterogeneous nature of the surface - a geometric factor is apparent - and the dark reaction observed with nitric oxide, provides yet another example of this. The rate of the dark reaction falls off rapidly with time to reach a low and almost constant value, and in this respect it resembles the photo-reaction. Further information is needed before its relation to the picture of the titanium dioxide surface presented here, and its relation to the chemisorption of

$\text{NO}_2 - \text{N}_2\text{O}_4$ ³⁶ can be discussed. A slow dissociation or rearrangement at the A sites (reaction (1) (p.97)) should, however, be considered among other possibilities.

Discussion of the differences in sample activity, and the effect of chromium treatment introduces the electronic factor, which may be further considered in relation to the idea of electron transfer upon the photo-adsorption of oxygen. The general idea of electron transfer in the chemisorption of gases on oxide semi-conductors arose from the measurement of conductivity changes on chemisorption^{45 46 47}, and two types of chemisorption are recognised. These are depletive chemisorption, in which the conductivity decreases on adsorption, and cumulative chemisorption, in which the conductivity increases on chemisorption. The conductivity changes which would occur during the photo-adsorption of oxygen on titanium dioxide at room temperatures may be predicted. Generally, the resistance of the white titanium dioxide samples, such as were used in the photo-adsorption experiments, will be high; hard evacuation will increase this resistance slightly because of the removal of adsorbed water. On the admission of dry oxygen the resistance will increase slightly, corresponding to the depletive chemisorption at the A sites (Fig. 5(a)(1)). After illumination in oxygen for some time, when an amount of oxygen will be irreversibly chemisorbed at the B sites, the resistance will be lower because of conduction by the positive holes trapped at B levels; chemisorption at the B sites is cumulative (Fig. 5(b)(2)). In fact a change from slight n-type conduction to p-type conduction must take

place in the titanium dioxide surface during the photo-adsorption of oxygen. Conductivity measurements made before and after the photo-adsorption of oxygen would obviously be important, but there are many practical difficulties to be surmounted (see Note on p.106).

In part II the development of a barrier layer on electron transfer was discussed. In the depletive case, the height of the barrier is considerable and may be expected to affect the kinetics of transfer and determine the total amount of gas chemi-sorbed, whereas in the cumulative case, the barrier is not high and may not affect the kinetics of chemisorption; the amount of gas chemi-sorbed is then determined by the surface area. The photo-adsorption of oxygen is of the cumulative type, and the barrier layer which develops (Fig. 5(b)(2)) will not, therefore, be expected to influence the kinetics of the uptake. Chemisorption on n-type (blue) titanium dioxide probably takes place thermally, but being depletive, only a small surface coverage may be expected in contrast to the photo-adsorption.

As has already been said, other oxides photo-adsorb oxygen and act as photo-sensitizers in various reactions. The formation of hydrogen peroxide is photocatalysed by a wide variety of solids including ZnO, which also photo-adsorbs oxygen. Electron transfer under illumination has been suggested in the mechanism of H₂O₂ production, and the fact that a wide variety of solids of various composition are active in the production, suggests that electronic structure is more important than chemical composition. It is to be expected that electronic structure is an important factor in oxygen

uptake, more important, that is, than composition. It is possible then, that substances, other than oxides, may show photo-absorption of oxygen. Several fundamental criteria may be imagined for this phenomenon to be observed on any solid. The electronic structure of the solid must be such that it absorbs the necessary light, but the fundamental absorption band must not be near the red end of the spectrum where thermal excitation is possible. The presence will be necessary of a small number of 'active' electron donor sites which can be ionised thermally giving reversible chemisorption, or of some sites, where direct electron transfer may occur. The specific surface area must be at least of the order of ten square metres per gram, and the surface of the solid must not be substantially covered by the chemisorption of oxygen at room temperatures.

The subject matter of this thesis was introduced by drawing attention to its importance in the paint and textile industries, and as a final point, therefore, it may be argued that the industrial importance of the phenomenon of photo-adsorption of oxygen by TiO_2 is matched by its academic importance. General study of photo-adsorption of gases on solids may contribute to knowledge regarding the catalytic and other properties of solids, which depend on their geometric and electronic structure.

NOTE:-

Mr. J. Simpson of Edinburgh University Chemistry Department has attempted to measure the change in conductivity of a compressed pellet of a titanium dioxide powder (sample A) after the photo-uptake of oxygen, using an apparatus of the type described by Jacobs⁵⁰. The results were not conclusive, since the pellet could not be sufficiently intensely illuminated to cause a substantial uptake of oxygen, and since the resistance of the pellet was near the upper limit of measurement (10^{15} ohms). Two observations, which may be of importance, were, however, made. Initial evacuation of the pellet was accompanied by an increase in resistance (10^9 ohms - 10^{13} ohms) which was undoubtedly due to the removal of adsorbed water. Illumination in vacuo with an Osira mercury lamp resulted in a decrease in resistance (10^{13} ohms - 10^{12} ohms), but in 50 mms. oxygen this decrease was not observed. This effect, due to the presence of oxygen, is probably related to the decrease in the photo-conductivity of CdS crystals, which is caused by the presence of oxygen, and which has been attributed to the formation of a barrier layer on the chemisorption of the gas on n-type CdS⁵¹.

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