A

THESIS

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

ENTITLED

The Photoelectrochemistry of some
Semiconductors; in particular
Mercury(II) Sulphide

by

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STATEMENT

The work contained in these pages was performed in the laboratories of the Chemistry Department, University of Leicester, between October 1976 and September 1979. No part of this work has been, is, or will be, presented for any other degree.

C. J. Willsher
March 1980
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Parts of this work have been published:


Other parts of the work may form future publications.

A patent has been taken out on mercury(II) sulphide, entitled 'Photochemical electrode', official number 7913420, filed on 18 April, 1979. This patent combines two provisional specifications [16766/78 of 27 April, 1978 and 47745/78 of 8 December, 1978].
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CHAPTER ONE

SOME PRINCIPLES OF SEMICONDUCTOR PHOTOELECTROCHEMISTRY
CHAPTER ONE

1.1 Introduction

"One day's average sunlight if converted into mechanical energy could lift the entire earth's crust of 300m thickness up by more than 2m" [1]. It is most fortunate that Nature has not seen fit to utilise insolation in such a dramatic manner. Fossil fuels represent natural storage of sunlight over a very long time span, and plant photosynthesis is the only relatively fast means of converting and storing solar energy. Large-scale harnessing of sunlight by man seems an essential task, now that coal, oil, and natural gas are being rapidly exhausted. The sun provides a plentiful energy input, which maximises in the form of visible radiation at the earth's surface, and it would appear reasonable to use something of the earth that is also plentiful, in the harnessing process. Water is in great abundance, so, can visible light be used to produce a storable fuel from water?

The standard Gibbs free energy for liquid water formation is -237 kJ mol\(^{-1}\) [2]

\[
H_2(g) + \frac{1}{2}O_2(g) = H_2O(1); \quad \Delta G^\circ = -237 \text{ kJ mol}^{-1} \quad [1-1]
\]

This means that 2.45 eV per molecule of energy are theoretically required to obtain gaseous oxygen and hydrogen from liquid water. Hydrogen would be a useful fuel, burning cleanly in air to return water (and possibly oxides of nitrogen). 2.45 eV correspond to radiation of wavelength 505 nm - visible light. But the ocean does not decompose when the sun rises.

The dissociation energy of the H-OH bond is 498 kJ mol\(^{-1}\) at 298° K [3]. This corresponds to 5.16 eV per molecule, or radiation of wave-
length 240 nm. It is the formation of high energy intermediates, such as H* and HO*, that prevents visible photolysis of water. UV photolysis, by excitation into the triplet state which then decomposes to form H₂ and O₂, has been observed [4], but these wavelengths lie outside the terrestrial solar spectrum [5].

The standard potential for water electrolysis is 1.23V [6] - this corresponds to radiation of wavelength of about 1000 nm. Taking into account hydrogen and oxygen overpotentials, energy of around 1.7 eV could electrolyse water if the facility for the necessary multi-step process (OH⁻ oxidation, H⁺ reduction) can be provided. The semiconductor/electrolyte junction offers a possibility in such harnessing of optical energy.

### 1.2 Fundamental Properties of the Semiconductor/Electrolyte Junction

A semiconductor is a material with no free charge carriers at absolute zero, but will conduct a charge if the carriers can move. Conduction is via electrons in the conduction band or by positive holes in the valence band or by both. The Fermi energy defines the electrochemical potential of electrons in the solid, and for a pure material lies mid-way between the band edges. An n-type semiconductor has electrons as majority carriers, and conducts when these are free to move in the conduction band. Electron vacancies, or positive holes, in the valence band are majority carriers for p-type semiconductors. The Fermi energy can be varied by introducing dopant impurities into the material: an electron donor incorporated into the lattice of n-type material can inject an electron into the conduction band. This has the effect of raising the Fermi level closer to this band. An electron acceptor in p-type material can inject holes into the valence band -
the Fermi level moves closer to the valence band edge.

When majority carriers are not free to move in their respective bands, the material is an insulator. A threshold energy - the band gap energy (Eg) - is the difference between the valence band top and conduction band base. The band-gap energy for different materials varies over a large range, and semiconductors with Eg corresponding to the energy of visible radiation will become conductors upon suitable illumination. This, however, has simply converted an insulator into a conductor; no current flow ensues since no potential gradient exists to permit movement of charge carriers. It is the presence of a space-charge layer in the semiconductor when in contact with a suitable electrolyte that provides this potential gradient.

The Fermi level of an electrolyte is related to the species present by their standard redox potentials, with corrections for concentration. A solid and electrolyte in contact achieve equilibrium by equalisation of their Fermi energies. This is brought about by electron transfer, and results in a double layer, which can be a parallel-plate or space-charge double layer. Figures 1.1 and 1.2 illustrate this. Fig. 1.1 shows the parallel plate double layer as a function of energy vs distance in (a) and potential vs distance in (b). This type of double layer has two plane sheets of charge and is found for a metal-electrolyte junction. The space-charge double layer is shown in Fig. 1.2, which develops for the semiconductor-electrolyte contact, and consists of a plane charge sheet in the electrolyte and distributed charge in the semiconductor. A metal cannot accommodate a space-charge because the carriers are free to flow. The charge on the solid must be neutralised by the electrolyte. A layer of ions is therefore attracted to the surface, forming the Helmholtz double layer. For a metal-liquid con-
Metal-Electrolyte: Energy vs Distance

Semiconductor-Electrolyte: Energy vs Distance

Metal-Electrolyte: Potential vs Distance

Semiconductor-Electrolyte: Potential vs Distance

\( E_F \) = Fermi level of solid
\( E_R \) = Fermi level of liquid
\( E_C \) = Bulk Conduction Band Edge of Solid
\( E_V \) = Bulk Valence Band Edge of Solid
tact, if the electrolyte Fermi level lies above the metal Fermi level, electrons are transferred from the reducing agent to the metal until this rate equals the electron transfer rate from the Fermi level to the solution oxidising agent. All the potential difference in a metal-electrolyte junction is therefore found in the electrolyte Helmholtz double layer. No such electron transfer happens at an insulator-electrolyte junction, and ion adsorption-desorption determines the Helmholtz double layer potential. Both electron transfer and ion adsorption-desorption operate at the semiconductor-electrolyte contact: the latter controls the Helmholtz double layer voltage and the former the space-charge in the semiconductor, such that net electron transfer is zero. In the electrolyte, beyond the Helmholtz double layer, is the Gouy layer, a diffuse space-charge region. This has little influence on processes at the semiconductor/electrolyte interface.

For the space-charge double layer, it is assumed that the charge distribution in the solid beneath the surface is immobile and independent of space-charge layer depth (the Schottky model). If there are \( N_D \) completely ionised bulk donor atoms per unit volume ("bulk" means beyond the space-charge layer), with \( N_A \) acceptor atoms similarly, and \( e_B \) bulk electrons plus \( p_B \) bulk holes, then

\[
N_D + p_B = N_A + e_B \quad \text{(electroneutrality)} \quad [1-2]
\]

In the Schottky model, the space-charge region is depleted of minority carriers and surface states will capture majority carriers. In an n-type semiconductor, the number of bulk electrons is given by:

\[
e_B = N_D - N_A \quad [1-3]
\]

The charge in the space-charge region (\( \rho \)) per unit volume is
\[ \rho = q(N_D - N_A) \]  

[1-4]

where \( q \) is the electronic charge

since charge in bulk = space charge.

If the space charge region exists for a distance \( x_o \) from the interface, then

\[ \rho = 0 \text{ for } x > x_o \]  [1-5]

and \( \rho = q(N_D - N_A) \) for \( x < x_o \)  [1-6]

The Poisson equation gives potential change with distance as a function of charge density:

\[ \frac{\delta^2 \phi}{\delta x^2} = \frac{-\rho}{\varepsilon_0 x} \]  [1-7]

\( \phi \) = potential
\( x \) = distance
\( \varepsilon \) = dielectric constant
\( \rho \) = charge density
\( \varepsilon_0 \) = permittivity of free space.

Substituting for \( \rho \) from eqn [1-4] into [1-7] gives

\[ \frac{\delta^2 \phi}{\delta x^2} = \frac{-q(N_D - N_A)}{\varepsilon_0 x} \]

so

\[ \frac{\delta \phi}{\delta x} = \frac{-q(N_D - N_A)}{\varepsilon_0 x} \int \delta x \]

\[ = \frac{-q(N_D - N_A)x + C_1}{\varepsilon_0} \]  [1-8]

so \( C_1 \) is the constant of integration.

Now \( \frac{\delta \phi}{\delta x} = 0 \) when \( x = x_o \) (inner edge of the space charge layer)

so \( C_1 = \frac{-(-q(N_D - N_A))x_o}{\varepsilon_0} \)  [1-9]

so

\[ \frac{\delta \phi}{\delta x} = \frac{q(N_D - N_A)(x_o - x)}{\varepsilon_0} \]  by substituting for \( C_1 \) in [1-8]

Simplifying:

\[ \int \delta \phi = \frac{A(x_o - \lambda)}{\varepsilon_0} \delta x \]

where \( A = \frac{q(N_D - N_A)}{\varepsilon_0} \)
and 
\[ \phi = A x_0 x - \frac{A x^2}{2} + C_2 \]  
[1-10] 

\( C_2 \) is the constant of integration

At the inner edge of the space-charge layer \( \phi = \phi_b \) (the bulk potential) and \( x = x_0 \).

So 
\[ \phi_b = A x_0^2 - \frac{A x^2}{2} + C_2 \]

i.e. 
\[ C_2 = \phi_b - A x_0^2 + A x_0^2 \]  
[1-11] 

Substituting for \( C_2 \) in [1-10]:

\[ \phi = A x_0 x - \frac{A x^2}{2} + \phi_b - A x_0^2 + \frac{A x_0^2}{2} \]

or 
\[ \phi_b - \phi = \frac{A x^2}{2} + A x_0^2 - A x_0 x - \frac{A x_0^2}{2} \]

\[ = \frac{A}{2} (x - x_0)^2 \]

\[ = \frac{q(N_D - N_A)(x - x_0)^2}{2 \varepsilon_0} \]  
[1-12] 

Equation [1-12] gives the relationship between potential change from the semiconductor bulk to any distance from the surface \( x \) in the space charge layer - subject to the conditions imposed in equations [1-9] and [1-11] to evaluate the integration constants.

At the surface, \( x = 0 \) and a surface potential of \(-V_s\) is defined, so [1-12] becomes

\[ V_s = \frac{q(N_D - N_A) x_0^2}{2 \varepsilon_0} \]  
[1-13] 

Equation [1-13] is the Schottky relation, and is used to calculate the depth of the space-charge region \( (x_0) \) from bulk semiconductor properties \( (N_D, N_A, X, \varepsilon_0) \):-
100 Å might be a typical value for a space-charge depth.

Equation [1-14] indicates the depth of the space-charge region is proportional to the square root of potential and in equation [1-12] the dependence of \( \phi_b - \phi \) upon \( x^2 \) explains the parabolic nature of the "band bending" (Fig. 1.2(a)) noting that 'potential' and 'energy' are directly relatable. An important feature of the semiconductor-electrolyte interface is that all the potential change occurs entirely within the space-charge region, and any changes in the Helmholtz double layer brought about by altering potential-determining ions' concentration do not affect the voltage drop beneath the semiconductor surface.

Figure 1.3 illustrates a doped n-type semiconductor in contact with a redox electrolyte, the Fermi level or redox potential \( (E_R) \) of the latter lying at lower energy than the semiconductor Fermi level. The band bending can be referred to the potential in the solid bulk as constant (Fig. 1.3(b)), or to the vacuum level \( (E_v) \) (Fig. 1.3(d)). In the former case, the conduction and valence bands in the bulk \( (E_{C(B)} \) and \( E_{V(B)} \)) have the same energy before and after junction formation, but the surface band edges \( (E_{C(S)} \) and \( E_{V(S)} \)) are raised to \( E'_{C(S)} \) and \( E'_{V(S)} \). The electrolyte Fermi level rises from \( E_R \) to \( E'_R \). In the latter case, the solvent contains the standard and the bulk bands are lowered in energy to \( E'_{C(B)} \) and \( E'_{V(B)} \); the semiconductor Fermi level falls from \( E_F \) to \( E'_F \). This Fermi energy is defined by electron availability in the bulk, so it moves with the bulk bands but is unbent in the space-charge layer ('S', on Figs. 1.3(b) and (d)).

Throughout this thesis, the model of Figs. 1.3(c) and (d) will be used. The vacuum level is related to the \( \text{H}_2/\text{H}^+ \) level by

\[
x_0 = \sqrt{\frac{V_0 x_e_0}{q(N_D - N_A)}}
\]

[1-14]
Fig. 1.3(a)
Before equilibration. Bulk bands constant.

Fig. 1.3(b)
After equilibration. Bulk bands constant.

Fig. 1.3(c)
Before equilibration. Vacuum level (E_0) constant.

Fig. 1.3(d)
After equilibration. Vacuum level (E_0) constant.
\[ E_e = -qE_e^\Phi - 4.73 \]  \hspace{1cm} [1-15]

\( E_e \) is in electron-volts

\[ E_e^\Phi = 0.0V \) (definition)

The constant of 4.73 eV is the absolute energy of the \( \text{H}_2/\text{H}^+ \) couple [7].

Fig. 1.3(d) indicates surface band edges are unaffected by an electric field beneath the surface. At the surface, \( E_F' \) is more distant from \( E_C(S) \) than it is from \( E_C(B) \) in the bulk, and is closer to \( E_V(S) \). The surface conduction band has a lower fractional occupancy for electrons and surface valence band has a higher fractional occupancy for holes, compared to the bulk, as determined by the Fermi Distribution Function:

\[ f = (1 + \exp[(E - E_F)/kT])^{-1} \]  \hspace{1cm} [1-16]

\( f = \) fractional occupancy of non-degenerate energy level, \( E \).

At the surface, hole density exceeds electron density, and the double layer is called an inversion layer: the space charge region is a depletion zone for majority carriers. An inversion layer for a p-type semiconductor forms when a junction exists with an electrolyte of \( E_R \) higher in energy than \( E_F \). Fig. 1.4 illustrates this. Applying equation

\[ \text{Fig. 1.4} \]

\text{Inversion layer formation for p-Semiconductor/Electrolyte junction.}
to the surface energy bands reveals that electron density exceeds hole density. If, for an n-type semiconductor, $E_R > E_F$, the net band bending is downwards, causing electron density to exceed hole density at the surface. An accumulation layer is formed. For p-type material, $E_F > E_R$ to produce such a layer and upward band-bending. Only the semiconductor-electrolyte junction that results in an inversion layer is of use in harnessing optical power.

In Figures 1.3(a), 1.3(c) and 1.4(a), the value of $E_F$ is called the flat-band potential ($V_{FB}$). This is the Fermi energy of a semiconductor with unbent bands and hence no space-charge layer. $V_{FB}$ is an important parameter in semiconductor electrochemistry.

The Fermi energy of semiconductor in an electrolyte can be obtained from the potential difference ($V$) between the solid and a reference electrode of Fermi level $E_F^{\text{ref}}$

$$V = -(E_F - E_F^{\text{ref}})/q$$  \[1-17\]

If $E_F^{\text{ref}} = 0$,

$$-qV = E_F$$  \[1-18\]  

Thus the solid state electron energy scale can be related to the electrochemical scale through equation [1-15], or generally:

$$E_{\text{redox}} = -qE^\Phi$$  \[1-18\]

$E_{\text{redox}}$ is the electrolyte Fermi level in eV and $E^\Phi$ is the tabulated redox potential for electrolyte species, in volts; $q$ is the electronic charge.

As will be discussed in section 1.4, it is not easy to state exactly what value $E_{\text{redox}}$ will adopt, and the treatment of charge carriers existing conveniently in valence and conduction bands only is somewhat simplified. This model does, nevertheless, produce a basic guide to
The features of a semiconductor/electrolyte junction.

1.3 The Energy of Semiconductor Bands

The positions of bulk band edges and the Fermi level relative to the vacuum are determined by a number of factors. The valence band can be considered as the energy range of bonding orbitals with a contribution from non-bonding electrons if applicable. The conduction band represents normally unoccupied anti-bonding orbitals. Thus the nature of the elements forming the semiconductor controls the band edges and band gap. The Fermi level, as stated in section 1.2, lies within the band gap, and is fixed by electron/hole availability as determined by impurity atoms. Measured electron affinities (EA) correspond to the energy needed to promote a conduction band electron to the vacuum level, and measured work functions (W) represent the difference between Fermi and vacuum levels. The semiconductor electron affinity can be related to the electronegativities of the constituent atoms. Butler and Ginley suggest a relationship for this [8]

\[
EA = (X_A X_B)^{1/2} - \frac{1}{2} E_{g(AB)} \quad [1-19]
\]

where \(X_A\) and \(X_B\) are electronegatives for atoms A and B and \(E_{g(AB)}\) is the band gap for compound AB. EA can be related to the flat band potential \(E_{FB}\)

\[
EA = 4.73 + E_{FB} - (E_C - E_F) - V_H \quad [1-20]
\]

\(E_C - E_F\) is the difference between the conduction band base and the Fermi level, and \(V_H\) is the potential drop across the Helmholtz double layer. When equal positive and negative charges are adsorbed on the semiconductor surface (the point of zero zeta potential - PZZP), \(V_H = 0\), EA is directly relatable to \(E_{FB}\). Re-writing equation [1-20]:

\[
EA = 4.73 + E_{FB} - (E_C - E_F) - V_H \quad [1-20]
\]
\[ E_{FB} = EA + (E_C - E_F) + V_H - 4.73 \]

Now the work function \( W \) equals \( EA + (E_C - E_F) \), so
\[ E_{FB} = W + V_H - 4.73 \]  \[\text{[1-21]}\]

when \( V_H = 0 \) in eqn [1-21], \( E_{FB} \) is relatable to the work function.

These last two equations are important in linking solid state properties to the flat band potential.

1.4 The Energy of Electrolyte Levels

Matters are not quite so straightforward in the electrolyte. Ions' energy varies with solvation, occupied and unoccupied levels are at different energies (Franck-Condon shift), and the occupation of energy levels are determined by concentrations of oxidised and reduced forms, and temperature. A convenient starting point is the standard redox potential of a couple \( (E^\circ) \). \( E_R = E^\circ \) if the couple is one-equivalent and \([Ox^+] = [Red] \).

Generally \( E_R = E^\circ + kT \ln ([Red]/[Ox^+]) \)  \[\text{[1-21]}\]

where \([Ox^+] \) and \([Red] \) are respective concentrations of oxidised and reduced components in \( Ox^+ + e^- \Rightarrow Red \) [9].

Fig. 1.5 illustrates energy state distribution in the electrolyte. Two distinct states, \( E_{OX^+} \) and \( E_{red} \) exist due to different solvation for the charged species. Thermal changes in solvation account for a thermal distribution of energy states. The separation of the most probable states of \( Ox^+ \) and red is \( 2\lambda \). \( 2\lambda \) depends upon dipole-dipole interactions and is characteristic of particular solution species.

As will be discussed later, electron transfer between semiconductor and electrolyte can occur only if filled electrolyte levels overlap empty semiconductor levels, and vice versa. In Fig. 1.5, an empty
Fig. 1.5

N-type semiconductor junction with redox electrolyte containing Ox+/Red couple. The hatched pear-shaped state is an occupied level, and the open pear-shaped state unoccupied.

level in the semiconductor is the conduction band or a hole in the valence band.

1.5 The Semiconductor-Electrolyte Junction as a Schottky Barrier

In solid state physics, a Schottky barrier exists when a metal and semiconductor form a junction. The actual barrier is the space-charge region beneath the semiconductor surface. It is generally accepted that an analogous barrier exists when the metal is replaced by an electrolyte. One publication discusses the "Schottky Barrier analogue" and investigates the semiconductor's properties that determine the barrier height [10]. The heat of formation of metal (semiconductor atom) - oxygen (electrolyte/solvent atom) bond is important if the semi-
conductor is polarisable. At the flat band potential, no barrier exists, so there should be a relationship between metal-oxygen bond heat of formation and $E_{FB}$. A linear relationship is found for various oxide materials, thus confirming the model. Whatever means are employed to describe the semiconductor/electrolyte junction make no difference to the observation that it can be employed to drive electrons through suitable circuitry.

1.6 The Incorporation of Semiconductor-Electrolyte Junctions in Electrochemical Systems, and Illumination of the Semiconductor

Placing a semiconductor, inert metal counter electrode, and reference electrode (optional) in a redox electrolyte with the semiconductor and counter electrodes connected via an external circuit, forms an electrochemical cell. Three circuit diagrams are indicated in Figure 1.6, and conditions for obtaining current flow with inversion and accumulation layers at p- and n-type semiconductor/electrolyte interfaces are discussed below.

(i) **n-type semiconductor: inversion layer**

The situation for the energies of semiconductor, electrolyte and metal counter electrode in the dark is shown in Figure 1.7. When the circuit is open, the Fermi level of the three components is equal, as it is for a closed circuit and no potential applied to the semiconductor with respect to the metal. In the latter case, a current can flow in the dark only if a strong reducing agent is present in solution, with reduction potential negative of $E_{C(S)} - E'_\text{red}$ in Figure 1.7. This species injects electrons into the semiconductor's conduction band; these travel the external circuit and are captured from the metal electrode by the oxidised half of the couple, provided $E_{ox^+}$ lies below
Fig. 1.6(a)
Circuit for measuring potential.

Sc = Semiconductor electrode
R = Reference electrode
C = Counter electrode
Re = Redox electrolyte
V = Voltmeter
A = Ammeter
P = Potentiostat

Fig. 1.6(b)
Circuit for measuring current with provision for applying a potential to the semiconductor.

Fig. 1.6(c)
Circuit for measuring voltage drop across a variable load.

Fig. 1.7
n-type semiconductor, electrolyte and metal in the dark.
The semiconductor has an inversion layer.
$E_F(\text{metal})$. No such current flows in the dark if the reducing agent has $E_{\text{red}}$ below the conduction band edge, and if $E_{\text{OX}^+}$ lies above $E_F$ (metal), electrons will accumulate in the metal and raise $E_F(\text{metal})$ until it reaches $E_{\text{OX}^+}$ and discharge can occur. But this causes raising of the semiconductor's Fermi level and reduction in band bending. For $E_{\text{red}}$ lying between the band edges, a current can flow upon suitable illumination of the semiconductor - Fig. 1.8.

![Diagram](image)

**Fig. 1.8**

The situation from Fig. 1.7 at high intensity illumination. $[V_B = \text{biasing voltage needed if electrons are to discharge at } E'_{\text{OX}^+}]$

Light of energy equal to or greater than the semiconductor band gap promotes valence band electrons to the conduction band. The space-charge of the inversion layer brings holes to the surface and pushes electrons to the bulk. The hole at the surface of the valence band can accept an electron from $E_{\text{red}}$, and this electron travels the external circuit, and if $E_{\text{OX}^+}$ lies below $E_F(\text{metal})$ it can reduce $\text{OX}^+$ to red. But if the oxidised half of the couple lies at $E'_{\text{OX}^+}$, then electrons will accumulate in the metal, as above, and lower the current. But if a potential of at least $(E'_{\text{OX}^+} - E_F)$ is applied in the form of a positive
bias to the semiconductor, $E_F^{'}$ is raised to $E_{OX}^{+}$, allowing electron discharge, and the semiconductor bands are further bent by the amount $(E_{OX}^{+} - E_F)$, giving more effective electron hole pair separation.

An n-type semiconductor can therefore exhibit an anodic dark current with a strong reducing agent, or an anodic photocurrent if photogenerated holes can capture electrons from a milder reducing agent and favourable conditions exist for electron discharge at the cathode.

At open circuit, the same process occurs upon illumination, but no current flows. Electrons build up in the conduction band, and a negative photovoltage is measured. The maximum photovoltage $V_{ph}$ equals the flat-band potential minus $E_{\text{redox}}$ of the electrolyte (Fig. 1.9)

$$V_{ph} = E_F^{'} - E_R$$  [1-22]

$E_F^{'}$ is the same as the flat band potential.

---

Fig. 1.9

An n-type semiconductor with inversion layer under high intensity illumination at open circuit. The flat-band condition is theoretically attained.
(ii) **n-type semiconductor: accumulation layer**

Figure 1.10 illustrates this situation. Any electrons injected into the conduction band are immediately forced to the surface by the downward band bending, and illumination creates conduction band electrons that undergo the same fate. No majority carrier can enter the semiconductor from the electrolyte: this kind of system has no value in creating an electron flow from illumination.

![Energy Diagram](image)

**Fig. 1.10**

An n-type semiconductor with accumulation layer.

(iii) **p-type semiconductor: accumulation layer**

A p-type semiconductor with an accumulation layer is useless - see Figure 1.11. Holes in the valence band are responsible for conduction, but the upward band bending sweeps these to the surface and renders conduction impossible.

(iv) **p-type semiconductor: inversion layer**

This is analogous to (i). Figure 1.12 shows such a system. In the dark, a valence band hole can allow conduction if there is a strong oxidising agent in the electrolyte, with $E_{OX}^+$ positive of the $E_V(S)$. $OX^+$ captures electrons, and the reduced form of the couple can inject electrons into the metal, provided $E_{\text{red}}$ is negative of $E_F(\text{metal})$. A
Fig. 1.11
A p-type semiconductor with an accumulation layer.

Fig. 1.12
An inversion for a p-type semiconductor in the dark. The reaction $OX^+ + e^- \rightarrow \text{red}$ can occur in the electrolyte.
cathodic dark current results. If the oxidising agent has an energy of $E'_{ox^+}$, a current can flow only upon suitable irradiation - see Figure 1.13.

An oxidising agent of energy $E_{ox^+}$ can capture electrons that have been promoted across the forbidden gap by illumination of band-gap energy. The space-charge layer forces them to the surface, and $OX^+$ captures them. Red can inject these electrons into the metal cathode, provided $E_{red}$ lies as in Fig. 1.13. But if the reduced half of the couple is at $E'_{red}$, the metal Fermi level must be dropped - this is achieved by biasing the semiconductor negatively by an amount $(E_F - E'_{red})$. Thus $E_F$ of the semiconductor is raised, the band bending increases by an amount $(E_F - E'_{red})$, and the metal Fermi level falls to meet $E'_{red}$.

At open circuit, holes are swept to the interior of the valence band and thus the semiconductor acquires a positive photovoltage. At high illumination intensity, the bands approach the flat band condition
\[ V_{ph} = E_R - E_F' \]  

\( V_{ph} \) is the maximum photovoltage and \( E_F' \) corresponds to the flat band potential.

![Energy level diagram](image)

**Table 1.1** summarises the characteristics of n- and p-type semiconductor-electrolyte systems and conditions needed for current flow.

The foregoing discussion is simplified in that surface-states are not mentioned, and it is assumed that photogenerated carriers react only with electrolyte species or contribute to conduction. They can react with the semiconductor lattice and cause decomposition.

The systems discussed in (i) and (iv) have potential for conversion of solar energy to chemical or electrical energy [11] if the semiconductor band gap corresponds to a wavelength of sunlight. Other factors must be considered with the principles outlined above: depth of the space charge layer; absorption coefficient for light of a given wavelength; minority carrier diffusion from the bulk and electron-hole recombination. For an optimum system, every majority carrier will contribute to conduction and every minority carrier be captured by the
<table>
<thead>
<tr>
<th>Semiconductor Type</th>
<th>Space Charge Layer Type</th>
<th>Conditions for current to flow in dark</th>
<th>Conditions for photocurrent to flow</th>
<th>Sign of photopotential</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>Inversion</td>
<td>Reducing agent with $E_{\text{red}}$ negative of conduction band edge. The current is anodic.</td>
<td>Irradiation with $E_{\text{hv}} &gt; E_{\text{g}}$, and a reducing agent with $E_{\text{red}}$ negative of valence band edge. The current is anodic.</td>
<td>Negative. The maximum photopotential = $E_{\text{FB}} - E_{\text{R}}$</td>
</tr>
<tr>
<td>n</td>
<td>Accumulation</td>
<td>No current can flow.</td>
<td>No current can flow.</td>
<td>No photopotential generated.</td>
</tr>
<tr>
<td>p</td>
<td>Inversion</td>
<td>Oxidising agent with $E_{\text{ox}^+}$ positive of the valence band edge. The current is cathodic.</td>
<td>Irradiation with $E_{\text{hv}} &gt; E_{\text{g}}$, and an oxidising agent with $E_{\text{ox}^+}$ positive of the conduction band edge. The current is cathodic.</td>
<td>Positive. The maximum photopotential = $E_{\text{R}} - E_{\text{FB}}$</td>
</tr>
<tr>
<td>p</td>
<td>Accumulation</td>
<td>No current can flow.</td>
<td>No current can flow.</td>
<td>No photopotential generated.</td>
</tr>
</tbody>
</table>

**TABLE 1.1 - SUMMARY OF CHARACTERISTICS OF SYSTEMS WITH FOUR KINDS OF SEMICONDUCTOR ELECTROLYTE JUNCTIONS**

(a) The semiconductor acts as photoanode.
(b) The semiconductor acts as photocathode.
electrolyte. This could be achieved by either having all the electron-hole pairs separated entirely within the space-charge region - the light absorption coefficient is such that its penetration depth is less than the length of the space-charge layer, so all the charge carriers are generated in a field which can immediately separate them and prevent recombination - or by the rate of hole diffusion from the bulk being very fast, to prevent electron-hole pair recombination in the bulk. The latter condition is necessary if the light penetrates beyond the space-charge layer. These optimum circumstances are usually rendered less efficient by carrier re-combination at the surface.

One other useful system is depicted in Figure 1.15, which allows

![Circuit Diagram](image)

**Fig. 1.15**

measurement of the flat band potential of the semiconductor with a capacity bridge. The space-charge region can be considered as one plate of a capacitor and conventional capacitance measurements yield
$V_{FB}$ and the density of donor/acceptor atoms by application of the Mott-Schottky relationship [12]:

$$C^{-2} = \frac{2}{q\varepsilon\varepsilon_0n_0} \left( V - V_{FB} - \frac{kT}{q} \right)$$  \hspace{1cm} [1-24]

$C$ = capacitance of space-charge layer; $q$ = electronic charge; $\varepsilon$ = semiconductor dielectric constant; $\varepsilon_0$ = permittivity of free space; $V$ = applied voltage; $V_{FB}$ = flat-band potential; $k$ = Boltzmann constant; $T$ = absolute temperature; $n_0$ = carrier concentration.

A plot of $C^{-2}$ against $V$ yields a straight line when $V$ is varied in Figure 1.15: the intercept on the $C^{-2}$ axis yields $V_{FB}$ and $n_0$ can be obtained from the slope.

Titanium dioxide single crystal has been investigated in an electrochemical system with aqueous electrolyte and platinum counter electrode. The flat-band potential and conduction band were determined by reducing agents injecting electrons into TiO$_2$ in the dark [13], with the valence band edge measured by photo-induced oxidation of less powerful reducing agents [14].

The result of illuminating a semiconductor in an electrochemical cell is called a Becquerel Effect, after E. Becquerel who reported the phenomenon in 1839 [15]. The effect has attracted interest from time to time. Williams studied a number of binary semiconductors [16] and tried to rationalise their instability. Some workers have studied electron transfer reactions at illuminated semiconductors [17,18], dye sensitization (and super-sensitization) with ZnO [19,20,21,22], GaP [23], perylene [24], SnO$_2$ [25], and recently CdS has been shown to N-de-ethylate Rhodamine B [26]. A study of the reduction of K[Au(CN)$_2$] to gold at illuminated Ta$_2$O$_5$ has indicated non-homogeneous hole distri-

-25-
bution at the surface [27]. The ZnS/H₂O interface has been activated with divalent metals [28] - but references 16 to 28 illustrate a little of the "academic" study of semiconductor/electrolyte systems and the associated Becquerel Effect. The use of semiconductors in solar energy harnessing was probed by Stephens et al. in 1955 to form hydrogen peroxide from water [29], but in the early 1970's, Fujishima and Honda reported the negative shifting of the water oxidation potential at illuminated TiO₂ [30] and then confirmed photoelectrolysis of water [31].

Thus, a simple phenomenon observed in 1839 had to wait over 130 years before its full potential was begun to be realised. Research on many semiconductors has been performed since 1972 - this is briefly reviewed in Chapter 2.

1.7 Application of Semiconductor/Electrolyte Systems to Conversion/Storage of Optical Energy

The circuits of Fig. 1.6 and the systems described in sections 1.6 (i) and (iv) can be employed in optical energy conversion/storage. Whether conversion or storage, or both, occurs, depends upon the nature of the redox electrolyte. It is assumed for the moment that the semiconductor's sole function is to provide and separate electron-hole pairs upon illumination - possible decomposition is dealt with later - and these electrons and holes are exchanged with electrolyte redox species. In other words, a valence band hole can thermodynamically accept an electron from a reducing agent only if a filled solution level is placed to accept a valence band hole, and similarly for a conduction band electron and a solution oxidising agent (Figure 1.5). It is the resultant chemistry occurring from such carrier exchange that
determines the operational mode of a potential solar cell.

Three modes can be distinguished: photovoltaic; photoelectro-synthetic and photocatalytic.

(i) Photovoltaic

An electron flow is induced by light and the electrolyte undergoes no net chemical change, as shown in Figure 1.16. Red is oxidised at the semiconductor to Ox*, and this is reduced at the metal. No net chemical change ensues, and a photocurrent flows. This mode provides energy conversion. An analogous situation exists for a p-type semiconductor.

(ii) Photoelectrosynthetic

Two redox systems are involved, Red/Ox* and Red'/O'x* - see Figure 1.17. Red is oxidised to Ox* at the semiconductor and O'x* is reduced to Red' at the metal. A photocurrent flows but the electrolyte has changed in composition - Red and O'x* are consumed, Ox* and Red' are produced:
Energy has been stored in $Ox^+$ and $Red'$ with light driving the unfavourable reaction for their formation. This mode therefore involves energy conversion (photocurrent) and storage ($Red'$ and $Ox^+$).

\[ \text{Red} + O'x^+ \xrightarrow{hv \text{ spontaneous}} \text{Red}' + Ox^+ \]

(iii) **Photocatalytic**

This mode is similar to the photoelectrosynthetic one, except that direction of the reaction induced by light is spontaneous anyway, and the light acts to reduce the activation barrier. The solution redox couples' energies are shown in Fig. 1.18. The same chemical reactions as in (ii) occur:

\[ \text{Red} + O'x^+ \xrightarrow{hv \text{ spontaneous}} \text{Red}' + Ox^+ \]

but the products are not energy-rich compared to the reactants. No energy is stored, but a photocurrent can be drawn while $Red$ and $O'x^+$
Fig. 1.18

Energies and solution redox couples for n-type semiconductor-electrolyte-metal solar cell operating photocatalytically. Two redox couples participate - (Ox+/Red) and (O'x/Red').

If the electrolyte is aqueous and the redox couples are H₂O/O₂ and H⁺/H₂, then a semiconductor with suitably placed band edges can assist the "photoelectrolysis" of water upon illumination. The semiconductor anode evolves oxygen and the metal cathode hydrogen. This has been achieved with strontium titanate/aqueous electrolyte/platinum, with no energy input other than near UV light [32]. "Photoelectrolysis" is the specific term for the photoelectrosynthetic mode when oxygen and hydrogen are evolved from water. For this mode to operate, oxygen must be absent from the metal cathode, as it is more easily reducible than H⁺. If oxygen is present, the mode of operation changes to photovoltaic - oxygen is produced from water at the anode and reduced back again at the cathode. Such a system has been reported for titanium dioxide [33].

More than one mode may operate at any one time, depending on the solution redox couples. An external bias will be needed if the metal
Fermi level lies below the energy of the oxidised half of the couple (Fig. 1.8). Analogous operational modes exist for p-type material/electrolyte/metal - and the combination of n-type semiconductor as photoanode and p-type material for photocathode can obviate biasing requirements and provide better energy harnessing circumstances. Figure 1.19 demonstrates this. Two types present themselves: homotype, as in (a), where the same material forms both electrodes, and heterotype, as in (b), for different semiconductors as the electrodes.

In the homotype system, irradiation of the n-type semiconductor with light of energy greater than $E_g$ causes electron flow in the conduction band as before. The electron travels the external circuit (omitted in Fig. 1.19), but can only participate in conduction on arrival at the p-type semiconductor electrode if this is also illuminated with band-gap energy light. The photogenerated holes and their flowing into the valence band, effectively transport the electron to the surface, where it is promoted by light into the conduction band and forced to the surface by the space charge layer. Thus the energy of this electron, initially in the valence band of the n-type photoanode (or initially belonging to a solution reducing agent), is now that of the p-type semiconductor's surface conduction band edge. If it had arrived at a metal cathode, it would have the energy of the common Fermi level (Fig. 1.19(a)), but utilising a cathode of the same material as the photoanode, but p-type, has effected a slight raising of its reducing power. However, this increase is quite small, and could be improved upon by having a p-type photocathode with a higher conduction band edge. Thus the anode and cathode must be of different materials. This is the heterotype p-n cell, as shown in Fig. 1.19(b).

The same journey for an electron takes place in the heterotype as
Fig. 1.19(a)

Homotype p-n system ~ n- and p-type samples of the same material forming photoanode and photocathode. The band gap (E\(_g\)) is the same at each electrode, as are the surface band edges.

Fig. 1.19(b)

Heterotype p-n system ~ different materials form photoanode and photocathode. The n-type semiconductor's band gap [E\(_g\)(n)] is different to that of the p-type [E\(_g\)(p)], and the surface band edges are not the same.
for the homotype system, but the greater gain in energy occurs at the
p-type semiconductor/electrolyte junction, where light promotes the
electron to the higher conduction band edge (surface). Thus simultan-
eous illumination of the p- and n-type semiconductors can produce holes
in the photoanode and electrons at the photocathode with a much larger
energy difference than if a single semiconductor/electrolyte/metal
system was irradiated. One obvious requirement of the p-n system is
that the n-type material's conduction band should be higher in energy
than the p-type semiconductor's valence band. Nozik has presented
discussion of p-n systems [34] as summarised above, and noted that for
the homotype cell, the net available energy equals the material's band
gap, but for the heterotype system, the net available energy can be the
sum of the materials' band gaps, provided the difference between their
flat-band potentials is minimal and the difference between the majority
carrier band edge and Fermi level is minimal. Nozik observed that a
cell comprising n-TiO$_2$/p-GaP evolved oxygen from TiO$_2$ and hydrogen
upon suitable irradiation. Yoneyama et al., using the same materials,
noted a deterioration in the GaP [35]. Ohashi et al. fully investigated
this system, along with n-TiO$_2$/p-CdTe, n-SrTiO$_3$/p-CdTe, and n-SrTiO$_3$/p-
GaP, and observed stability for at least two hours [36,37].

Nozik has reported the novel "photochemical diode" [38]. A semicon-
ductor is bonded to a metal layer via an ohmic contact to form a
"Schottky-type diode" or n- and p-type semiconductors sandwich a metal
via ohmic contacts, giving "p-n (homo- or hetero-) type diodes". An
n-GaP/Pt Schottky-type diode in H$_2$SO$_4$ produced hydrogen from the
platinum face upon illumination with GaP decomposing. Photogenerated
holes in the GaP move to the surface and oxidise P$_3^-$ with photogenerated
electrons crossing to platinum and reducing H$^+$. Simultaneous illumina-
tion of an n-TiO₂/p-GaP heterotype diode in H₂SO₄ evolves oxygen at TiO₂, by holes oxidising H₂O, and hydrogen at GaP by electrons reducing H⁺.

Odagiri has patented [39] a cell for higher conversion efficiency photoelectrochemistry, comprising a wide band gap n-type semiconductor and smaller band gap p-type semiconductor separated by ion-conductive or ion-exchange membranes, with dyes and/or redox agents in the different compartments. The wide band gap material is illuminated first, with the longer wavelength light passing on to the smaller band gap compound.

1.8 Theoretical Requirements for Efficient Semiconductor/Electrolyte Solar Cells

The semiconductor itself should possess certain properties: - a band gap between 1.0eV and 2.5eV; an electron affinity for p-type material of 3.0eV to 4.0eV; and a flat-band potential positive of +0.42V (versus the standard hydrogen electrode, SHE) for p-type semiconductors, and negative of 0.0V (versus SHE) for n-type materials. These conditions are noted by Bockris and Uosaki [40]. Anderson and Chai, however, consider the largest band gap should be 1.8eV [41]. Kung et al. [10] have concluded that for n-type oxides, the flat band potential becomes more positive as the band gap decreases, and this would appear to restrict such semiconductors' use in solar cells. The flat-band potential parameter has been linked to the performance of several n-type titanates at zero bias and their electronegativities [42]. The electronegativity is related to the electron affinity - equation [1-19] - and the electron affinity should be as small as possible for n-type materials, so that the conduction band edge supplies
electrons at the cathode with a high reducing power. Strontium titanate can assist hydrogen evolution from water with no input electrical potential [43].

The matching of semiconductor surface bands and electrolyte redox levels is crucial. Bolts and Wrighton [44] have correlated flat-band potentials and current-voltage curves for a number of semiconductors. For water photoelectrolysis, the band gap should be less than 3.0eV, the H$^+$ reduction level slightly below the conduction band, the valence band below the OH$^-$/O$_2$ level, with the conduction band at least 1.23eV above this level. This then places a minimum band-gap requirement of 1.23eV. If the band bending exceeds 1.23V (the thermodynamic potential for water electrolysis), illumination alone can electrolyze water: valence band holes oxidise OH$^-$ or H$_2$O to O$_2$, and conduction band electrons reduce H$^+$ to H$_2$. Overvoltage is a problem. Butler defines oxygen overvoltage as the energy difference between the valence band top and the OH$^-$/O$_2$ level [45], and notes that no hydrogen overvoltage will exist for a cathode of large area.

The question of overpotential, plus other factors, is raised by Manassen et al. [46] in evaluating electrochemical energy conversion. Oxygen reduction at an illuminated n-type semiconductor must have a high overpotential, so oxygen formation has a high overpotential. The gap between $E_{\text{redox}}$, for species other than H$_2$O/OH, and the valence band top should be at least 0.6eV to prevent hole injection from this redox couple, opposing the photo-effect. Residual band bending must remain upon illumination to keep the space-charge layer operative. They estimate that all these factors, plus the energy difference between the Fermi level and conduction band, mean that the maximum band bending is less than the optical band gap by one electron-volt. So if at least
1.23V in band-bending is required to electrolyse water (Bolts and Wrighton, ref. 44), then the smallest band gap semiconductor employable would have \( E_g = 2.23 \text{eV} \). Allowing for gas evolution overpotential, this will realistically work out at 2.7eV, at least. The peak of solar irradiation has now been passed, so Manassen et al. suggest a p-type semiconductor cathode to complement a smaller band gap n-type material, and illumination of both, as a p-n cell. The authors of this paper present a somewhat pessimistic view, and are not totally correct, as in later chapters of this thesis are results of a 2.0eV band gap semiconductor that assists water photoelectrolysis, with a platinum cathode.

Reported optimum conditions for unassisted water photoelectrolysis vary, but parameters can be obtained by considering two fundamental constants - the peak of solar irradiance at 550nm, and the thermodynamic decomposition potential of 1.23V for water. Light of 550nm corresponds to 2.25eV of energy, so the semiconductor's band gap must lie between 2.3eV and 1.25eV. The \( \text{H}^+ / \text{H}_2 \) level should lie at lower energy than the conduction band, and the \( \text{OH}^- / \text{O}_2 \) level above the valence band - Figure 1.20. Suitable illumination of the semiconductor provides holes that can accept electrons from \( \text{OH}^- \) and provides electrons at the metal cathode of sufficient energy to reduce \( \text{H}^+ \). This is analogous to Fig. 1.17. The position of the conduction band \( (E_{c(S)}) \) is determined by the electron affinity, and since \( E^\Phi_{\text{H}^+ / \text{H}_2} = -4.73 \text{eV} \) on the absolute scale [7], this should be no greater than 4.73eV if protons are to be reduced at the metal. For electron affinities larger than 4.73eV, the excess amount must be provided either by an external bias, or chemically, perhaps by having a pH gradient between anode and metal cathode [47].

The basic requirements for optimum water electrolysis using sunlight with an n-type semiconductor and metal are, therefore:
**Fig. 1.20**

Energetic requirements for water photoelectrolysis with n-type semiconductor/electrolyte/metal system.

(a) In the dark

(b) Under illumination
(a) $2.3\text{eV} > E_g > 1.25\text{eV}$

(b) $E_{\text{OH/O}_2} > E_V(S)$

(c) $E_{\text{H}^+/\text{H}_2} < E_C(S)$

(d) $E_A < 4.73\text{eV}$

(e) The semiconductor should be stable.

Stability is the biggest problem - photogenerated minority carriers react with the lattice instead of electrolyte species. (If majority carriers react with the semiconductor's atoms, instability in the dark occurs).

1.9 Decomposition of Semiconductors in contact with an electrolyte

A hole in a semiconductor's valence band represents a missing bonding electron, and an electron in the conduction band is equivalent to a partly occupied antibonding orbital. Thus the bonding situation is weakened as soon as majority carriers are free to move. Decomposition can result if an electrolyte species bonds to a semiconductor atom and further weakens the lattice. Nucleophiles attack valence band holes, and conduction band electrons are susceptible to capture by electrophiles. These processes are oxidative decomposition and reductive decomposition, respectively, as rationalised by Gerischer and Mindt [48]. For a polar binary semiconductor, $A^{\delta^+}$-$B^{\delta^-}$, they propose mechanisms for the two decomposition types:

**Oxidative Decomposition:**

$$[A^{\delta^+}B^{\delta^-}] + \text{Nu}^{\delta^-} \rightarrow (ANu)^+ + B^+ + e^- \quad (\text{i})$$

or $$[A^{\delta^+}B^{\delta^-}] + \text{Nu}^{\delta^-} + p^+ \rightarrow (ANu)^+ + B^+ \quad (\text{ii})$$

$\text{Nu}^{\delta^-}$ is an electrolytic nucleophile, $e^-$ an electron, and $p^+$ a positive hole.
Reaction (i) can occur in the dark, but for (ii) illumination is necessary to generate positive holes in n-type material.

Reductive Decomposition:

\[
[A^\delta^+ - B^\delta^-] + E^{\delta^+} \rightarrow (BE)^- + A^+ + p^+ \quad (iii)
\]

or

\[
[A^\delta^+ - B^\delta^-] + E^{\delta^+} + e^- \rightarrow (BE)^- + A^- \quad (iv)
\]

\(E^{\delta^+}\) is the electrophile, often \(H^+\).

Reaction (iii) can take place in the dark, but for p-type material (iv) can only proceed upon illumination.

If the semiconductor is polarised anodically, oxidation of the more electronegative component may occur, and similarly for reduction of the more electropositive component upon cathodic polarisation. Table 1-2 gives examples of this, taken from reference 48.

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Decomposition Products with anodic polarisation</th>
<th>Decomposition Products with cathodic polarisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>(Cu^{2+}, O_2)</td>
<td>Cu, (H_2O)</td>
</tr>
<tr>
<td>GaP</td>
<td>(Ga^{3+}, P^0, P^{3+})</td>
<td>?</td>
</tr>
<tr>
<td>CdS</td>
<td>(Cd^{2+}, S)</td>
<td>Cd, (H_2S)</td>
</tr>
<tr>
<td>ZnO</td>
<td>(Zn^{2+}, O_2)</td>
<td>Zn, (H_2O)</td>
</tr>
</tbody>
</table>

Table 1-2. Decomposition Products of some Binary Semiconductors (after Gerischer and Mindt, Ref. 48)

Williams has discussed semiconductor dissolution in terms of the Gibbs Free Energy of all possible reactions [16]. That which possesses the most negative \(\Delta G^\circ\) is likely to occur. For example, cadmium sulphide:

\[
CdS + Cd^{2+} + S + 2e \quad \Delta G^\circ = +20 \text{ kcal mol}^{-1} \quad \text{ANODIC DECOMPOSITION}
\]
CdS + 2e → Cd + S^{2-} \quad \Delta G = +50.7 \text{ kcal mol}^{-1}

CATHODIC DECOMPOSITION

Thus anodic decomposition is thermodynamically preferred, and is observed.

Williams states that when decomposition occurs and the positive ion is preferentially solublised, a photovoltaic effect will be generated only if the semiconductor is n-type. A negative charge remains in the solid after the positive ion leaves, and it is neutralised by light-induced electron promotion to the conduction band with these electrons free to flow to the interior and reduce the negative charge. A p-type material would exhibit no photovoltaic effect, since this would result in a further build up of electrons at the surface and increase the residual negative charge. For negative ion solublisation, an analogous argument is employed to show that only p-type semiconductors can exhibit photovoltaic properties. Illumination generates minority carriers - electrons - to neutralise the net positive charge left by negative ion solublisation. In an n-type semiconductor, photogenerated surface holes would increase the surface positive charge.

Williams applied his predictions to a number of binary materials, with some success, but did not consider kinetic effects. Thermodynamic criteria can be easily assimilated, but when an observed phenomenon is contrary to that expected energetically, the 'kinetic control' factor is invoked. The relevant \( \Delta G^\circ \) for a specific reaction can be considered a "Decomposition Potential" - either anodic or cathodic - \( E_D(\text{Anodic}) \) or \( E_D(\text{Cathodic}) \) - and included in energy diagrams of the semiconductor-electrolyte interface. If a decomposition level is situated so that it can accept majority carriers, then the semiconductor can thermodynamically decompose in the dark. Cathodic decomposition of n-type
material can occur upon application of a large negative voltage to bring about electron degeneracy at the surface, provided an acceptor decomposition level lies below the conduction band edge [49]. Similarly, anodic decomposition of a p-type semiconductor with a large applied positive potential can occur if a donor decomposition level lies above the valence band edge. But, the solvent can preferentially decompose if, for the n-type material above, it can accept the degenerate valence band electrons. To achieve this, the solvent decomposition level should lie at lower energy than the cathodic decomposition level. For p-type material, the hole degeneracy at the valence band surface will not lead to anodic decomposition as above, if the solvent decomposition level lies above the anodic decomposition level [49].

A semiconductor-electrolyte system stable in the dark can become unstable upon photogeneration of minority carriers. The condition for complete photostability is that anodic and cathodic decomposition levels lie outside the band gap [49,50,51]. If one decomposition level lies between the bands, then that kind of dissolution is thermodynamically possible, unless a redox reaction can compete [50]. Figure 1.21 illustrates this. In (a), for n-type material, cathodic decomposition cannot occur in the dark or light, since \( E_{\text{D(CATHODIC)}} \) is above the conduction band (\( E_C \)). Photogenerated holes in the valence band (\( E_V \)) are energetically capable of accepting electrons from the anodic decomposition level and causing dissolution. The redox couple can also inject electrons into the valence band, and it is the relative position of the decomposition level and \( E_{\text{Redox}} \) that determines stability. If the decomposition level lies at \( E_{\text{D(ANODIC)}} \), positive of \( E_{\text{Redox}} \), then stability ensues, since hole transfer from the redox level is more
Fig. 1.21(a)
N-Type Semiconductor/Electrolyte Junction showing cathodic decomposition level ($E_{D(\text{cathodic})}$) and two possible positions of the anodic decomposition level ($E_{D(\text{anodic})}$).

Fig. 1.21(b)
P-Type Semiconductor/Electrolyte Junction, with $E_{D(\text{CATHODIC})}$ and $E_{\text{REDOX}}$ placed for photostability.
favourable energetically, but if it lies at $E_D(\text{ANODIC})$, decomposition will occur, and the oxidised form of the redox couple can cause anodic decomposition in the dark too, by accepting electrons from the decomposition level [50]. Thus, for a n-type semiconductor, photo-anodic oxidation can be prevented if $E_{\text{redox}}$ is negative of $E_D(\text{ANODIC})$. This model has been used to explain the stability of TiO$_2$ [52] and the suppression of CdS solublisation by alkaline sulphide/polysulphide solutions [51,53].

Figure 1.21(b) shows the stabilisation of a p-type semiconductor susceptible to cathodic reductive decomposition, by having $E_{\text{redox}}$ positive of the cathodic decomposition level. Gerischer [49,51] states that the $\Delta G$ value for the decomposition reaction should include the free energy of the hydrogen reference electrode, and then be converted to a decomposition potential according to

$$E_D = -\frac{\Delta G}{nF} \quad [1-25]$$

$n$ is the number of electrons in the decomposition and $F$ is Faraday's constant.

The semiconductor Fermi level upon illumination splits into quasi-Fermi levels for electrons and holes, since these carriers' individual Fermi energies alter on illumination. Gerischer correlates the decomposition potential, $E_D$, of equation 1-25 with the minority carrier surface quasi-Fermi energy - see figure 1.22. The electron quasi-Fermi level remains close to the conduction band for n-type material, but the hole quasi-Fermi level approaches the valence band within the space charge layer on suitable irradiation. If $E_D(\text{ANODIC})$ is positive of $E^*_F(+)$ (case (i) on Fig. 1.22), then photoanodic oxidation will not occur. If $E_D(\text{ANODIC})$ is negative of $E^*_F(+)$, then decomposition is thermodynamically possible, as in (ii) and (iii). In (ii), $E_{\text{redox}}$ can
N-type semiconductor-electrolyte junction, showing electron quasi-Fermi level \( E_{\text{F}(-)} \) and hole quasi-Fermi level \( E_{\text{F}(+)} \), and three possible relative positions of solution redox level and anodic decomposition level \( E_{\text{D(ANODIC)}} \). [Taken from p.1426 of Ref. 49.]

Fig. 1.22

Satisfy photogenerated holes in preference to \( E_{\text{D(ANODIC)}} \), so stabilisation by solutions species is possible. This cannot occur in (iii) and semiconductor dissolution results. For p-type materials, photocathodic reduction can occur if \( E_{\text{D(CATHODIC)}} \) is positive of the electronic quasi-Fermi level, but stabilisation is possible if the solution \( E_{\text{REDOX}} \), or its decomposition level, lies below \( E_{\text{D(CATHODIC)}} \).

Memming, using a semiconductor disc/platinum ring electrode system, has determined the contributions of electrode dissolution of n-type materials and hydrogen evolution at p-type materials, and oxidation-reduction currents due to the redox electrolyte [54]. He discovered that some reducing agents effectively compete with anodic dissolution, and oxidising agents with hydrogen evolution. For example, with n-GaP and Fe(CN)_6^-^4^-, the photocurrent is entirely due to ferrocyanide oxida-
tion, but thermodynamically, gallium phosphide should decompose. He suggests that charge transfer from adsorbed species to surface states is involved. This means that the thermodynamic requirements are overridden by such states, or by imperfections like 'kink sites' that have been employed to provide a model for semiconductor decomposition [49].

1.10 Surface States in Semiconductor Photoelectrochemistry

A localised energy level at a semiconductor surface capable of exchanging electrons with the solid or the electrolyte, is called a surface state. An intrinsic state results from a break in lattice periodicity, and a Shockley state is found where a surface atom has electrons in orbitals directed towards the surface and do not experience 'exchange energy' stabilisation, as if they overlapped with similar filled orbitals in the bulk. A 'dangling bond' is formed - a donor state. A Tamm state exists where a surface atom has a different electron affinity to bulk atoms [55].

A significant role of surface states is to act as a centre for electron-hole recombination. This is illustrated by Figure 1.23 for an n-type semiconductor. Light generates the electron-hole pair: surface holes are trapped by $A^n$ if no electrolyte species can compete, and $A^{n+1}$ is produced. Any electrons propelled into the bulk in the conduction band by the space charge layer contribute to a negative photovoltage or positive photocurrent - but if $A^{n+1}$ can trap electrons faster than they move into the bulk, they are returned to the valence band via the surface state, and $A^{n+1}$ is reduced back to $A^n$.

(a) $h^+ + e^- \rightarrow h^+ + e^-$ - light induced carrier separation
(b) $h^+ + A^n \rightarrow A^{n+1}$ - hole trapping by $A^n$
A surface state $A^{n+1}/A^n$ at the Semiconductor/Electrolyte interface acting as electron-hole recombination centre.

\[
\begin{align*}
\text{(c)} & \quad A^{n+1} + e^- \rightarrow A^n \quad - \text{electron trapping by } A^{n+1} \\
& \quad h^+ + e^- \rightarrow \text{recombination of carriers - sum of reactions (b) and (c)}
\end{align*}
\]

A similar situation has been elucidated by Miyake et al. [56], in the photocatalytic properties of TiO$_2$ powder. The $A^{n+1}/A^n$ system is not a surface state, but a solution redox couple. It is noted that oxidation of $A^n$ by valence band holes and reduction of $A^{n+1}$ by conduction band electrons is much less efficient than if the electrons travel an external circuit and are available for reduction at a platinum cathode. Participation of both bands of a semiconductor in simultaneous oxidation/reduction is an inefficient process - presumably due to surface states.

The action of an electron acceptor surface state is important when the valence band of an n-type semiconductor lies a long way below the level of the electrolyte reducing agent, and this level is just above the surface state. The electron from the reducing agent is transferred to the photogenerated hole via this state. For example, in the
TiO₂/H₂O junction, the O₂/OH⁻ level lies a long way above the valence band. Dutoit et al. have shown the valence band top for TiO₂ lies at -2.75eV (vs SHE) at pH 4.8 [14]. At this pH, E⁰_{O₂/H₂O} = +0.93V (vs SHE) [6] and the valence band edge on this scale lies at +2.75V. A gap of 1.8V exists between a photogenerated hole and the electron to be injected into it. Morisaki et al. observed a cathodic photocurrent with n-TiO₂ at 900nm in an oxygenated electrolyte [57]. They attributed this to a photogenerated electron leaving the semiconductor for dissolved oxygen via a surface state 1.7eV above the valence band. Frank and Bard have postulated a surface state with TiO₂'s band gap [58], and a cathodic current at n-CdS in an OH⁻/S²⁻ electrolyte at -1.6V applied potential is also attributed to a surface state [59].

The surface state 1.7eV above TiO₂'s valence band must be both a donor and acceptor state, and should be included in discussion of the TiO₂/electrolyte interface [60]. It is of limited value to present a semiconductor/liquid junction in terms of band edges, band bending, and electrolyte levels only. These provide a basis from which interpretation of experimental results is possible, but surface states and specific ion adsorption must be considered in any meaningful treatment of semiconductor-electrolyte cells.
CHAPTER TWO

A BRIEF REVIEW OF SEMICONDUCTORS EMPLOYED IN OPTICAL ENERGY CONVERSION WITH AN ELECTROLYTE JUNCTION
CHAPTER TWO

2.1 Introduction

Relatively few semiconductors have been thoroughly investigated for potential usage in solar energy harnessing, and it becomes clear that two types exist: those which are stable but respond to short wavelengths at the end of the terrestrial solar spectrum, and those whose band gap allows visible light to be employed, but are unstable. Reported research describes these two kinds and the attempts to extend the spectral response of the former group to longer wavelengths, and to effect stabilisation of the latter group. Efforts to discover semiconductors which combine the advantages of both categories have been described too. In this chapter, the literature will be selectively reviewed for each material investigated.

2.2 Titanium Dioxide, TiO₂

This was the first semiconductor whose behaviour under illumination led to the conclusion that a potential existed for solar energy harnessing, and a great deal of work has now been done on it. This will be reviewed under the general titles of: TiO₂ type; energetics; specific reaction type; factors influencing photochemical reactions; instability; and miscellaneous work.

2.2.1 Type of TiO₂ employed

(a) Single Crystal - rutile, reduced

Fujishima and Honda noted an anodic current upon illumination [30,31] with oxygen evolution at TiO₂ and hydrogen at a platinum black cathode [31] in an aqueous electrolyte, and pronounced it to be stable as no
titanium ions were detected in solution. They concluded photogenerated holes in TiO₂ were responsible for water oxidation, and electrons at platinum reduced H⁺ to H₂. Nozik investigated in greater depth this phenomenon [61], presenting an energy balance equation which accounts for an anodic biassing necessity for gas evolution - arising from an oxygen overpotential at TiO₂. Wrighton et al. presented a thorough study of such water photolysis [62], concluding (i) H₂ and O₂ are produced from water only, as determined by deuterium labelling, (ii) TiO₂ is a true photoassistance agent - H₂ : O₂ = 2 : 1 - and the photocurrents passed correspond to the volumes of collected gases, (iii) the wavelength response is controlled by the band gap, (iv) a 1% storage efficiency by H₂ production can be achieved. In a one-compartment cell, with 2M NaOH as electrolyte and a bias of +0.25V applied to TiO₂ (the minimum bias needed for gas evolution), the quantum efficiency for H₂ production was 0.01 (input light intensity = 8 × 10⁻⁶ ein. min⁻¹). Larger quantum efficiencies (0.04) were noted for a two-compartment cell with alkali at TiO₂ and acid at the platinum counter electrode.

(b) Chemical Vapour Deposited (CVD) TiO₂

Single crystals are expensive, and means of obtaining TiO₂ in polycrystalline form are desirable. Hardee and Bard describe one such means [63]. Vapourised tetra-isopropyl orthotitanate and water form TiO₂ on a titanium substrate, which is then heated under vacuum to reduce its resistance. This, and the platinum counter electrode, evolve gases in an aqueous electrolyte when the TiO₂ is illuminated with light of energy greater than that of TiO₂'s band gap, although the current is smaller than for an identical experiment with rutile single crystal. It is proposed that less carrier recombination occurs in a single crystal, along with more efficient light absorption,
and the presence of anatase (another form of TiO₂) in the CVD electrode may be detrimental. This electrode has been the subject of further reports [64]. Thinner films give higher photocurrents, and thicker films give curves similar in shape to those for single crystal rutile.

(c) Thermally oxidised titanium

Heating titanium metal plates in an oxygen atmosphere in an electric furnace, and heating such plates in a fire of town gas has produced an oxide layer showing photoelectrochemical properties [65]. The latter method, with a flame temperature of 1300°C, gave TiO₂ whose photocurrents were only slightly smaller than those of a rutile crystal electrode. A TiO₂ anode, of area 0.17m², prepared by heating Ti in gas, caused hydrogen evolution at platinum black cathodes (with 1M NaOH as anolyte and 0.5M H₂SO₄ as catholyte) at the rate of 1.1 g.day⁻¹ in Japanese sunlight, representing an energy conversion efficiency of 0.4%.

Houlihan and Madacsi oxidised titanium metal by heating it in natural gas [66], concluding the optimum temperature and heating time was ~1200°C and 7-8 minutes respectively. Some electrodes had their wavelength response red-shifted - attributed to lower band-gap mixed oxide phases produced in heating. Using a pH-gradient system, as above, and an anode of area 20cm², hydrogen was collected from a platinized wire cathode at the rate of 1.8 ml.hr⁻¹ with an overall energy conversion efficiency of 0.8%.

Yazawa et al. studied the effect of thermally oxidising titanium under reduced pressure [67] and gave optimum conditions as 900°C for 10 mins at 5×10⁻² torr. pressure. Dutoit et al. thermally oxidised
titanium plate in a furnace and subsequently heated the oxidised metal in hydrogen [68]. Optimum conditions are an oxidation temperature, $T_{Ox}$, of 800°C and a reduction temperature, $T_{red}$, of 700°C (other parameters were not considered). If $T_{Ox}$ is too high, a thick layer, liable to peel, is formed, and if $T_{Ox}$ is too low, the oxide will be too thin to absorb all the light. $T_{red}$ determines the extent of reduction of TiO$_2$; if it is too low, not all the oxide will be reduced, and if too high, a high donor density will result, giving a space-charge layer thinner than the light absorption depth. Heat treatment of TiO$_2$ formed by anodization has been shown to change initially amorphous material to rutile [69].

(d) **Anodically oxidised titanium**

Titanium metal can be oxidised to TiO$_2$ by making it the anode and passing a current with a platinum cathode. In a 5M KOH electrolyte [70], blue TiO$_2$ is obtained with an optimum forming time of 2 minutes at 8 mA.cm$^{-2}$. 1M H$_2$SO$_4$ has been employed in the oxidation [71] - indeed electrolyte alkalinity seems immaterial [65]. Titanium oxidised in ethylene glycol or acids gave very much smaller photocurrents than CVD TiO$_2$ [63], but heating such anodically formed material improved them [69].

(e) **Other kinds of TiO$_2$**

Rutile powder is compressed at 750°C under very high pressure to form a disc, which is then heated in a vacuum to induce conductivity [43]. The disc operates well as photoanode. Raw rutile has been made into an anode by arc-plasma spraying it on to an alumina substrate (insulating), with NiCr to form the ohmic contact [72]. The electrode showed photoresponse characteristics similar to other TiO$_2$ anodes,
although formation conditions were not optimised.

(f) Comparison of photoanodes formed by different processes

It is not easy to conclude which method produces the best photoanode, since the electrodes are investigated under different conditions. Reduced single crystal rutile is usually taken as 'standard'; Dutoit et al. consider thermally oxidised titanium performs as well [68]. Nobe et al. found anodically oxidised titanium less responsive than the single crystal [73] - and the activity of anodically formed TiO$_2$ is dependent on the pH of the electrolyte used in the oxidation. However, a single crystal electrode has been claimed to have a higher internal resistance than CVD TiO$_2$ [58], even though the polycrystalline material shows a smaller photo effect. Lower quantum efficiencies are noted for TiO$_2$ discs compared with single crystals [43].

It is interesting to compare the photoresponse of rutile single crystals at different orientations, or with differing types of surface irradiated. A crystal cut and illuminated parallel to the C-axis gave greater photocurrents than perpendicular to that axis [73], although no explanation was given. A grooved TiO$_2$ surface shows highest efficiency for the oxygen evolution current, with it lower for an abrasively roughened surface, and lowest for one with a mirror-like finish [74].

(g) Doped titanium dioxide

The intentional addition of impurities (other than what occurs when rutile is heated in hydrogen, giving oxygen vacancies, and the presence of Ti$^{III}$ or mixed oxides) is to improve current-voltage characteristics, alter the wavelength response, or reduce the resistance. TiO$_2$-mixed oxide phases, on titanium, are superior in performance to single crystals [75], the 'mixed oxide' being small amounts of Al$_2$O$_3$, SrO, Ga$_2$O$_3$, Eu$_2$O$_3$.
and \( \text{B}_2\text{O}_3 \). The band gap is unaltered by doping, but conductivity improved. Chromium-doping of TiO\(_2\) has extended the spectral response to 550 nm [76] - Cr-acceptor levels generate holes in light of this wavelength which oxidise water at the TiO\(_2\) surface. In the same paper, aluminium doping of TiO\(_2\) is reported to improve carrier generation quantum efficiency at higher than band-gap light energies, due to better carrier diffusion from the bulk.

Heating titanium metal in nitrogen gives TiN\(_{0.07}\)O\(_{1.93}\) [77]. This material, a nitrogen-doped mixture of rutile and anatase, behaves like rutile, but generates a photocurrent with light of wavelength 460 nm. This means N\(_2\)-doped TiO\(_2\) has a band gap of 2.7 eV, compared to pure rutile's 3.0 eV. However, tungsten doping shifted the band gap to shorter wavelengths, by about 60 nm [62]. Houlihan et al. have doped TiO\(_2\) by incorporating trace impurities of Al, V, Cu, Y, Ta, Nb, Mo, Ni and Pd in titanium metal, and thermally oxidising it [78]. No change in band gap is reported, but the flat-band potential is shifted. The greatest effect is with yttrium dopant, where the shift is -0.08 V.

(h) *External modification* of titanium dioxide

Doping is 'internal modification' and features like surface dye adsorption are meant by 'external modification'. Rhodamine B, covalently bound to TiO\(_2\) has been found to sensitize the photocurrent to longer wavelengths [79]. 3,3'-Diethyloxacyarbocyanine and Rhodamine B, with a supersensitizer 'Tiron' gave photocurrents at TiO\(_2\) for wavelengths longer than 500 nm, with hydrogen evolution at a platinum cathode, under anodic bias [80]. It is reported in this
paper that the tiron supersensitizer, not the dye, is consumed, and TiO₂ may simply act as co-adsorption centre for the organic molecules, although replacing it by other materials with surface -OH groups resulted in little photoactivity. Polypyridineruthenium(II) complexes in solution can generate a photocurrent at TiO₂ with sub-band gap light [81] - and the authors suggest solute species' adsorption on the semiconductor has little effect on photocurrents. In all cases, the red-shifted photocurrents correspond to the sensitizers' absorption wavelengths.

(i) Heterogeneous photocatalysis with TiO₂ powder

An interesting 'off-shoot' of TiO₂'s rôle as a photoelectrode is the suspended powder's photocatalytic properties. Aqueous cyanide solutions have been oxidised to cyanate, with anatase powder more efficient than rutile [82]. Irradiation causes electron-hole pair separation; CN⁻ is oxidised to CNO⁻ at the positive hole, and O₂ reduced to H₂O (via H₂O₂) by conduction band electrons. CN⁻ oxidation by undoped anatase in sunlight was effected at the rate of 3.1 × 10⁻⁶ mol. day⁻¹ cm⁻² (of TiO₂ exposed surface) [83]. The photo-assisted oxidation of SO₃²⁻ to SO₄²⁻ in solution at TiO₂ powder has been successful [83].

An extension of this is the 'photo-Kolbe' reaction at platinised anatase [84]. Aqueous acetic acid with Pt-TiO₂ suspended evolves CO₂ and CH₃, upon irradiation (Eₜ > Eₖ) with little C₂H₆, the normal Kolbe product. Anatase is platinised by irradiation in hexachloroplatinic acid [85]. A range of saturated carboxylic acids was investigated for photo-Kolbe reactions with combinations of platinised/unplatinised, doped/undoped, rutile/anatase [86]. In all cases, the major decomposition products were the alkane and carbon dioxide, with doped anatase or platinised powders the most efficient photocatalysts. The presence or
absence of oxygen is significant; it can trap radical intermediates or electrons, and prevent side reactions, such as radical dimerisation.

Schrauzer and Guth have investigated anatase powders containing chemisorbed water [87]. U.V. photolysis under argon produces H₂ and O₂ - with higher yields for heat-treated anatase. But photolysis in the presence of nitrogen forms O₂ plus NH₃ and traces of N₂H₄, with no hydrogen. Iron-doped rutile induces these reactions, with 0.2 weight % Fe₂O₃ giving maximum photocatalytic efficiency. N₂ photoreduction could be achieved in sunlight at room temperature and atmospheric pressure, but the light wavelength has to be shorter than 420 nm (≡TiO₂'s band gap). Acetylene can also be photo-reduced at TiO₂ to give methane, ethylene, and ethane, depending on the conditions. TiO₂ powder (unspecified) also photocatalytically reduces CO₂ in aqueous suspension by stepwise reactions to formic acid, formaldehyde, methanol, and methane [88].

2.2.2 Energetics of the TiO₂-electrolyte interface

The positions of the band edges have been determined [13,14,44] and are: conduction band base = -1.0V and valence band top = +2.0V (vs SCE) at pH 13 [44]. The band edges shift positively by 0.059V per decrease in pH unit, as does the flat-band potential, shown to be about -1.0V (vs SCE) at pH 13 by differential capacitance [44]. This value and its pH dependence confirms earlier work [89]. Thus it is possible to illustrate diagramatically the TiO₂-electrolyte junction in terms of band energies and solution redox couples. But relating the solid state scale (with the vacuum as reference) and an electrochemical scale (with the standard hydrogen electrode, SHE, as reference) according to equation (1-15) (p.10) can be a problem, since E°H₂/H⁺ has not been
absolutely fixed and varies from -4.73eV [7] to -4.48V [90]. However, if the semiconductor's bands have been experimentally determined relative to an SHE or SCE, this dilemma need not arise.

Controversy exists in the literature as to what energy states of TiO$_2$ and electrolyte equilibriate in the dark. Mavroides et al. indicate $E_{F(TiO_2)}$ and $E_{H^+/H_2}$ equalise [43] but Ohnishi et al. show $E_{F(TiO_2)}$ and $E_{OH^-/O_2}$ achieve equilibrium [91]. These two models are discussed by Rouse [60] who puts $E_{F(TiO_2)}$ at the same energy as some point between the two redox couples, with his model arrived at by stating $E_{OH^-/O_2}$ equilibriates with a surface state 1.7V above the valence band. This surface state has been mentioned before [57,58], - see p.46 - and shown to successfully capture photogenerated holes and allow their transfer to the OH$^-$/O$_2$ level [92]. On the contrary, Wrighton et al. propose that surface states of TiO$_2$ have little, if any, significance [93]. Oxygen evolution with high currents induced by laser light occurs via valence band holes with 1.5V oxidising power in excess of that thermodynamically required. Oxygen evolution at platinised platinum anodes has a large overvoltage - but this is provided for in a TiO$_2$ anode by the large separation between $E_{OH^-/O_2}$ and the oxidising agent - the valence band hole. Indeed, surface states would lower the oxygen evolution rate.

The relative position of band edges and solution redox couples has implications for the quantum efficiency of water photolysis at TiO$_2$. It is very low for an unbiassed anode because $E_{H^+/H_2}$ lies above the conduction band base, but positively biasing TiO$_2$ raises the Fermi energy of the platinum counter electrode above $E_{H^+/H_2}$, allowing proton reduction [91]. The quantum yield is not determined solely by energetics: donor density is important, and the space-charge layer
depth [94].

2.2.3 Specific reactions in a titanium dioxide cell

With an aqueous electrolyte, illumination causes the cell to operate photovoltaically ('photogalvanically' is an equivalent term [43]) if oxygen is available at the counter electrode. One such system has a fuel-cell electrode as cathode, CVD TiO₂ as anode, and gives a maximum power efficiency for 365 nm light of 1-2% [33]. A de-oxygenated catholyte causes photoelectrolytic operation - hydrogen is produced at the cathode when TiO₂ is suitably biased [43]. A pH-gradient between the electrodes replaces the need for biasing in photoelectrolytic operation [47]. Hydrogen evolution is assisted by including in the catholyte methyl viologen [95]. This is reduced in preference to protons - these form hydrogen by their reduction with the reduced form of methyl viologen. A complication in photo-assisted H₂O/OH⁻ oxidation at TiO₂ is hydrogen peroxide formation. It has been postulated [10], and now confirmed [96]. Oxygen (either intentionally present or produced on illumination) is reduced to H₂O₂ at TiO₂; this occurs in the dark.

Some reducing agents compete for photogenerated holes at TiO₂. Methanol, formaldehyde, formic acid, ethanol, lactic acid, maleic acid, tartaric acid, As³⁺, Sn²⁺, and Hg₂²⁺ act as 'current-doubling' agents [14]. These species are two-equivalent: one electron is injected into the valence band hole, leaving a meta-stable radical anion that injects a second electron into the conduction band. Cl⁻, Br⁻, SO₃²⁻ and Mn²⁺ reduce the current-doubling effect by successfully scavenging holes. Frank and Bard showed I⁻, Br⁻, Cl⁻, Ce³⁺, Fe²⁺, Fe(CN)₆⁴⁻, hydroquinone, p-aminophenol, N,N-dimethylaniline, CN⁻, ethanol and ethyl formate contribute to photocurrents at TiO₂, with the last three capable of current
doubling [97]. In mercury(II) chloride solution, illumination of TiO₂ causes a deposit of Hg₂Cl₂ on the semiconductor, while globules of mercury appear on TiO₂ when irradiated in Hg(NO₃)₂ [98]. These two reactions are more likely to be photochemical than photoelectrochemical. Rutile reduces MnO₄⁻, Cr₂O₇²⁻ and Fe³⁺ photocatalytically [56], and Cu is deposited from CuSO₄ on a TiO₂ electrode irradiated at open circuit [99]. An example of TiO₂'s strong oxidising power is the formation of peroxodisulphate ions from sulphate or bisulphate [100]. This occurs 2.7V negative of the standard potential.

Photocurrent doubling with alcohols has received more detailed attention. Reactivity decreased in the order CH₃OH > C₂H₅OH > (CH₃)₂CHOH > (CH₃)₃COH, with alcohol adsorption the controlling factor [101]. A photoelectrochemical cell with an alcoholic electrolyte operates with higher quantum yield (at 400 nm, monochromatic, and 8.1×10¹⁷ photons cm⁻² hr⁻¹) than for an aqueous one [102]. The current doubling is less effective in alkaline electrolytes [103], due to fewer active sites on TiO₂ being available and OH competing for holes.

In acetonitrile, acetate anions are photo-oxidised to ethane at TiO₂ [104], and a number of aromatic amines are shown to shift the flat-band potential negatively in accordance with the amine's ionisation potential [105]. Charge-transfer interaction between TiO₂ and amine in non-aqueous media causes this, with the most easily ionised amine interacting best and causing the biggest shift. No shifting occurs for aqueous amines, since hydrogen bonding overrides charge-transfer.

2.2.4 Factors affecting photochemical reactions

The conditions for photovoltaic and photoelectrolytic operation of a TiO₂ cell in an alkaline electrolyte have been discussed, with emphasis
on cathode conditions [106]. The largest photocurrents are seen for oxygen passing platinum, or an oxygen saturated electrolyte. If the platinum cathode is horizontal at the electrolyte surface, the largest short-circuit photocurrents result from the highest oxygen partial pressure ($p_{O_2}$) above the cathode. As $p_{O_2}$ drops, the photocurrent declines. The photocurrent is directly proportional to the cathode area, and decreases as the platinum is immersed. This is attributed to hydrogen evolution and a counter-voltage between Pt and TiO$_2$. The counter-voltage is related to the cathode immersion depth and $p_{H_2}$. (If $p_{H_2} = 1$ - hydrogen gas maintained above the electrolyte - a negative photocurrent is seen.)

In the absence of oxygen, the only reaction that can occur at platinum is proton reduction - but if the product, hydrogen, cannot diffuse away it generates the counter-voltage which, at saturation, equals TiO$_2$'s photovoltage. Hydrogen evolution at short-circuit is not observed because its partial pressure of generation is well below atmospheric pressure, and the counter-voltage means TiO$_2$ operates under open circuit conditions. An external bias increases $p_{H_2}$ to allow evolution and overcomes the counter-voltage. Cathode conditions, therefore, are crucial for efficient cell operation.

The anode-cathode area ratio has been discussed [74]. Large photocurrents are observed for a cathode much greater in area than the anode, with no hydrogen evolution at large cathodes. In other words, the larger the cathode, the more effective it is for $O_2$ reduction. Desplat has noted that photocurrents are subject to a diffusion limit of the species which inject electrons into TiO$_2$'s positive holes [107], - $\cdot\text{OH}$ in alkaline electrolytes, and $H_2O$ in neutral or basic media.

A higher quantum yield is obtained at lower light intensities, and
for alkaline, rather than acid, electrolytes [108]. High light intensities result in inefficient water photolysis - and Gissler et al. propose water splitting occurs only at very high light intensities, and the cell works photovoltaically at low light intensities [109]. They conclude TiO₂'s behaviour is complex.

The quantum yield can be influenced by donor concentration (Nₖ): it optimises at about 2.4 × 10¹⁹ cm⁻³ for TiO₂ (0.5 in 0.5M H₂SO₄, at 2V bias, at 400 nm) although theoretically, the optimum Nₖ for these conditions is 2.4 × 10¹⁴ cm⁻³ [94]. This discrepancy results from light penetrating beyond the space-charge layer. The potential-dependence of quantum efficiency is wavelength controlled [110]. For reduced TiO₂ single crystal in alkali, the quantum efficiency - 0.6 - at 1.25V maximises at 345 nm, but it is 0.2 at -0.35V and maximises at 330 nm. Therefore, maximum quantum efficiencies are red-shifted as the applied potential becomes more positive. This is because longer wavelength photons have a greater penetration depth and so need a large applied field to bring holes to the surface.

2.2.5 Stability of titanium dioxide

The chemical stability of TiO₂ has not been disproved, but surface changes in polarised rutile single crystals have resulted in a lowering of quantum efficiency [111]. This occurred in an acid electrolyte, and with shorter than band-gap light wavelengths, but high molarities of sulphate anion can prevent the corrosion due to surface pitting [112]. Oxygen evolution now occurs from the reaction of sulphate oxidation products with water, and not from the TiO₂ surface. A decline in photocurrent with time was seen in an alkaline electrolyte (not previously considered to induce corrosion [111]), and X-ray photo-
electron spectroscopy showed this was due to a return to Ti:0 stoichiometry at the electrode surface [113]. Reduction of TiO$_2$ in hydrogen causes surface oxygen deficiency and produces a mixed oxide gradient there, with associated variations in space-charge distribution.

Thermodynamically, titanium dioxide can be anodically oxidised on illumination, since this decomposition level (E$_D$) lies at higher energy than the valence band, but above E$_D$ lies the O$_2$/H$_2$O level which preferentially reacts with photogenerated holes [49,50,51]. Other redox couples are energetically capable of competing with electrode dissolution [52].

2.2.6 Miscellaneous

A novel means of biassing TiO$_2$ and using longer wavelength light has been reported by Morisaki et al. [114]. TiO$_2$ is deposited on to a commercial silicon p-n cell to form a photoanode. Short wavelength light is absorbed by TiO$_2$ with longer wavelengths passing to Si where the generated photovoltage biases TiO$_2$. Solar irradiation, with the anode and platinum cathode shorted together in alkali, yields O$_2$ and H$_2$ at each electrode respectively, with an energy conversion efficiency of 0.1% for H$_2$ production. The deposition of titanium dioxide on unstable smaller band gap materials to stabilise the latter was unsuccessful [115,116]. The spectral response was that of TiO$_2$, a cracked coating caused instability, and hole conduction through it was not observed.

Enhancement of the photoeffect in the iron-thionine system* was attempted with a titanium dioxide anode, but no improvement on a metal electrode ensued [117]. A 'thermophotoelectrochemical' cell has been proposed where the solar heating effect might improve the performance of a TiO$_2$ cell [118]. In a two-compartment system, a higher

* This is where a solution of thionine dye and ferrous ions absorbs light to form ferric ions and reduced thionine. Inert metal electrodes allow electric power to be drawn from this reaction.
maximum effective power output is obtained for a catholyte hotter than the anolyte.

The oxidation of materials at photogenerated holes in TiO₂ can cause surface deposition of an oxide layer. 'Photo-imaging', by means of different coloured oxide materials, may prove another important use of TiO₂ [119].

2.3 Strontium titanate, SrTiO₃

This n-type semiconductor is capable of photoassisting water electrolysis at zero applied voltage [32,120,121]. The flat-band potential is -1.0V vs SCE at pH 7, varying by -0.059V pH⁻¹ [120]. This large negative value is attributed to SrTiO₃'s smaller electronegativity compared with TiO₂, although its larger band gap (3.2eV) means less efficient usage of insolation [121]. Water labelling with O¹⁶ confirmed oxygen evolution was not from SrTiO₃ [32], although the H₂:O₂ stoichiometry is not exactly 2:1 in acid electrolytes due to hydrogen peroxide formation. The wavelength response corresponds to the titanate's band gap - the photocurrent action spectrum commences at 380 nm and peaks at 330 nm, where a quantum efficiency of one, for electron flow at +1.5V bias, obtains. Vanden Kerchove et al. have presented the surface band edges (conduction band = -0.7V, flat band potential = -0.6V, valence band = +2.5V, all vs SHE at pH 0) and data on the reaction of some reducing agents with illuminated SrTiO₃ [122]. Citric, oxalic, tartaric and formic acids, along with formaldehyde, methanol, ethanol and isopropanol show current doubling, with bromide and sulphite ions capable of competing for holes. The reactivity with holes of these reagents is similar to that for TiO₂.

With very high laser light intensity, SrTiO₃ undergoes no surface
visual change and generates a photocurrent of about 4800 mA cm$^{-2}$ under a 2.45W light input (351, 364 nm), and the quantum efficiency is 0.05 (defined as electrons flowing in the external circuit per incident photons) [93].

Gaseous water and carbon dioxide produce methane when they are adsorbed on a single crystal of strontium titanate in contact with a platinum foil, and the SrTiO$_3$ illuminated with light of energy greater than the band gap [123]. The action of the titanate as a true photocatalyst is not proven, as surface compositional changes and poisoning may occur.

Platinisation of an SrTiO$_3$ single crystal and subsequent irradiation of the unplatinised face in sodium hydroxide solution results in oxygen and hydrogen evolution [99]. This is the normal photoelectrochemical reaction and is equivalent to short-circuit operation in a photoelectrolytic cell.

2.4 Barium titanate, BaTiO$_3$

An anode formed from heating barium nitrate and titanium dioxide generated a photocurrent in a photoelectrochemical cell with light of wavelength 360 nm [124]. Differential capacitance revealed the flat band potential to be about -0.28V vs SCE at pH 7, varying by -0.06V pH$^{-1}$. A barium titanate single crystal electrode showed the same flat-band potential and pH-dependence, and generated photocurrents at wavelengths corresponding to its band gap (3.3eV) - even at no applied potential [125]. It is claimed that this zero bias photocurrent corresponds to hydrogen evolution at the platinum counter electrode. The crystal undergoes no change, and exhibits a "collection efficiency" (external circuit electron flow per incident photon rate) of 20-30% at 4.0eV (the maxi-
Iron-doping of BaTiO$_3$ reduces the band gap to 2.8eV, but diminishes photocurrents [126]

2.5 Iron titanates, FeTiO$_3$, Fe$_2$TiO$_4$, and Fe$_2$TiO$_5$

These were investigated in polycrystalline and mono-crystal forms by Butler and Ginley [127]. Their band gaps lie between 2.1 and 2.2eV, and flat-band potentials are +0.1V, +0.2 and +0.5V (vs SCE at pH 14) for FeTiO$_3$, Fe$_2$TiO$_4$, and Fe$_2$TiO$_5$ respectively. Although they act as photoanodes and assist water photoelectrolysis, their instability (loss of iron) and positive flat band potentials renders them limited.

2.6 Zinc oxide, ZnO

As noted in Chapter One (p.25), zinc oxide has been employed to investigate properties of the semiconductor-electrolyte junction, both in the dark and upon illumination. A major obstacle to use in photovoltaic cells is instability, since the anodic decomposition level lies between the oxygen-water couple and the valence band [49,51]. However, this has been avoided by using dissolved dyes in the electrolyte. Rose Bengal prevents dissolution of a ZnO sinter disc electrode, and the wavelength response of photocurrents corresponds to the dye's absorption spectrum not to ZnO's band gap of 3.2eV [128]. The mechanism of photocurrent generation is: the dye absorbs a photon to produce the excited state which injects an electron into zinc oxide's conduction band. Since there are no holes in the valence band, no anodic oxidation occurs, and stability ensues. A reducing agent, such as a halide, may inject an electron into the excited dye's ground state and boost the photocurrent: this is observed for the ZnO-rose bengal system, and is termed 'supersensitization'. The cell is unstable in the long term,
owing to adsorbed oxidised dye on the semiconductor surface. It was proposed that only adsorbed dye molecules sensitized the photocurrent, not those in solution; these would reduce the photon flux reaching the electrode. A ZnO-adsorbed rose bengal anode, with platinum cathode and electrolyte composed of 0.2M Na₂SO₄, 0.13 KI and 1 × 10⁻³Μ I₂ (no dye in the electrolyte) showed a power conversion efficiency of 1.5% with incident illumination of power 4.1 × 10⁻⁴W, monochromatised at 563 nm [129]. The suggested mechanism of adsorbed excited dye injecting electrons into the semiconductor's conduction band to cause photocurrents (as opposed to the excited dye transferring energy to the semiconductor to cause electron promotion from an impurity level within the band gap) has now been confirmed [130]. Dyes whose singlet or triplet excited states lie below ZnO's conduction band do not cause photocurrents.

Zinc oxide single crystal has been reported to generate photocurrents with rhodamine B, and reducing agents as supersensitizers [131]. The mechanism of supersensitization is here discussed in terms of alteration of the dye's adsorption on ZnO, and hence its electron injection properties, or of quenching the dye's fluorescence - a fluorescing dye does not inject electrons into the conduction band so effectively.

Powdered zinc oxide photocatalyses the oxidation of cyanide and sulphite anions in aqueous solution [84], and photoassists the reduction of CO₂ bubbled through water to methane, via formic acid, formaldehyde and methanol [88].

2.7 Tin(IV) Oxide, SnO₂

Photoassisted oxidation of water at polycrystalline n-type SnO₂ in
an electrochemical cell has been noted [132]. The electrode is stable, but the band gap of 3.7eV (≈335 nm) is too large for efficient insolation harnessing, although the addition of rhodamine B to the electrolyte red-shifted the spectral response. An antimony-doped SnO$_2$ single crystal in aqueous electrolyte and with a platinum cathode aided water electrolysis upon irradiation with light of wavelength shorter than 350 nm [133]. Hydrogen is evolved at platinum and oxygen at SnO$_2$ - and use of H$_2$O$^{18}$ reveals no oxygen is lost from the anode. The electron flow quantum efficiency with SnO$_2$ at the same potential as the SCE reference at 254 nm ($9.83 \times 10^{-10}$ ein. sec$^{-1}$, from a 200W high pressure mercury lamp) was 0.27. Sensitization of SnO$_2$ by rhodamine B chemically bonded to its surface gives a photocurrent at about 550 nm, with the magnitude depending on the nature of the chemical bond [79]. A quantum efficiency for photoelectrons flowing per absorbed photons in ester-linked rhodamine B of about 0.1 has been obtained in the 510-590 nm wavelength region [134]. Originally, the dye was linked to SnO$_2$ via an amide bond [135], but subsequent work revealed ester-linking produced larger photocurrents [79].

High intensity laser illumination of an SnO$_2$ anode caused no surface damage [93]. The conduction band lies at -0.7V, the valence band at +2.8V, and the flat band potential is -0.7V (all vs SCE at pH 13) [44]. It is only the large band gap that restricts efficient solar energy conversion.

2.8 Tungsten Trioxide, WO$_3$

Preliminary studies on this n-type material showed it to be stable and produce photocurrents with light corresponding to the 2.8eV band gap [136]. WO$_3$ was prepared from heating tungsten metal or thermal
decomposition of ammonium tungstate, and formed a photoanode. The potential for oxygen evolution was shifted 1.4V negatively by illumination. Similar results were obtained by Hardee and Bard with polycrystalline WO₃ [64], although the oxide formed by different methods showed slightly differing wavelength responses. This has been noted by Gissler and Memming, who also observed variations in the flat band potential of WO₃ obtained by various means [137]. The oxide's colour varies from yellow to dark blue, according to heat treatment, attributable to lower tungsten oxides. Stability and oxygen evolution on illumination in H₂SO₄ ensued - under anodic polarization, but cathodic polarization causes WO₃ to change colour. This is a substoichiometric oxide or hydrogen bronze which can be re-oxidised at positive potentials. Thus the preparation method and subsequent treatment have great influence on the wavelength response and current-voltage curves. The flat band potential of thermally oxidised tungsten is +0.55V (vs SHE at pH 0-1) and +0.2V for sputtered WO₃. On the same scale, the band edges are given as: Eₖ ≈ +0.5V and Eᵥ ≈ +3.1V, but are subject to a large variation.

The chemistry occurring in solution at an illuminated WO₃ electrode (made by thermally oxidising tungsten) depends upon the electrolyte [138]. In sodium sulphate, oxygen is evolved at WO₃, and the current-voltage curves vary linearly with pH by -59mV.pH⁻¹. For pH > 4, some instability of the oxide was noted. In a potassium chloride electrolyte, the same pH-dependence and instability is seen, but larger photocurrents obtain. Chlorine was detected in the electrolyte - so Cl⁻, and not H₂O, oxidation is occurring.

Single crystal WO₃ behaves similarly to the polycrystalline form [139]. Hydrogen tungsten bronze formation is responsible for large
currents under cathodic polarization in the dark (with an aqueous electrolyte and platinum counter electrode). Photocurrent vs applied potential curves were obtained at various pH's, and the potential for the onset of photocurrent varies by -59mV pH⁻¹. This, coupled with results of differential capacitance measurements, gives the flat-band potential as +0.3V vs SCE at pH 1.75. This is too positive to render WO₃ an improvement on titanium dioxide or the titanates, despite its extended wavelength response and possible stability.

Butler quotes a quantum efficiency of 0.5 for WO₃ at 327 nm biassed at 2V or greater [140]. The flat-band potential and its pH-dependence is again confirmed.

An aqueous suspension of WO₃ containing CN⁻ or SO₃²⁻ does not effect oxidation of these ions on illumination [84] and no similar reduction of CO₂ occurs [88].

2.9 Iron Oxide, Fe₂O₃

Chemical vapour deposition (CVD) of Fe₂O₃ onto platinum or titanium resulted in a photosensitive electrode [141]. In a neutral electrolyte, with platinum counter electrode, a photocurrent was observed at potentials positive of +0.2V vs SCE and oxygen evolution at Fe₂O₃. This onset voltage shifts negatively with increasing pH, and the n-type Fe₂O₃ remains stable in electrolytes alkaline of pH = 4. Photocurrents begin at 550 nm, corresponding to Fe₂O₃'s band gap of 2.2eV, and maximise at 380 nm. Other means of obtaining Fe₂O₃ - such as deposition on iron, heating iron plates - were unsuccessful in parallelling CVD Fe₂O₃ [64]. Photocurrent densities of 6mA cm⁻² have been noted for the thinnest films. Using sunlight and a fuel-cell air cathode with an Fe₂O₃ anode of area 10 cm², an optimum photocurrent of 8mA through a 1
Ω load, plus vigorous gas evolution, was observed. The output voltage and power are low, due to the positive flat band (≡ photocurrent onset potential).

Successful photoanodes from thermally oxidised iron or steel have now been fabricated [142]. Essentially the same results as above were obtained, although the spectral response extended to 800 nm. Anodes prepared from high purity Fe₂O₃ by pressing and sintering were employed to determine solid state properties [143] and water photo-oxidation [144]. The flat-band potential, obtained by differential capacitance is -0.17V vs SCE at pH 7, varying by about -0.06V pH⁻¹. The photocurrents with these electrodes are influenced by specific ions in solution.

In one paper, 'transient' effects in photocurrent-time plots were noted [64], and these have been further investigated [145]:-

![Photocurrent vs Time](image)

(a) Flame oxidised Fe₂O₃  (b) Sintered Fe₂O₃

Fig. 2.1: Oscilloscope plots of photocurrent vs time for pulsed irradiation of Fe₂O₃ electrodes in 1m NaOH at +0.5V bias (vs SCE) (from ref. 145).

Fe₂O₃ made by different means can have differing flat-band poten-
tials, different current-voltage curves, and different photocurrent-time plots (see Fig. 2.1). The flame-oxidised iron undergoes a decline in photocurrent after an initial overshoot [Fig. 2.1(a)]. This is attributed to a cathodic current component arising from immediate back reaction of photogenerated species. With the sintered Fe$_2$O$_3$ electrode [Fig. 2.1(b)], the current slowly increases after the initial rise, due to a second photoelectrochemical oxidation step. This illustrates (i) the complex behaviour of Fe$_2$O$_3$, (ii) the need to determine precisely photoelectrode formation conditions.

A single crystal of Fe$_2$O$_3$ produced similar results to the polycrystalline form [146] - although the 'transients' were not mentioned. It gave an optimum collection efficiency (electron flow per photon flux) of 35% at 3.6eV input light energy under a bias of +2V vs SCE. Doping a single crystal with yttrium (to give YFeO$_3$) widens the band gap to 2.6eV, but shifts the flat-band potential by -0.14V [147]. YFeO$_3$ is still stable, and might be an improvement on Fe$_2$O$_3$.

An aqueous suspension of Fe$_2$O$_3$ photocatalyses the oxidation of SO$_3^{2-}$, but not of CN$^-$ [84].

2.10 Potassium Tantalate, KTaO$_3$

The single crystal acts as photoassistance agent for water photolysis for light of energy greater than 3.5eV - the band gap [148]. The material is n-type, stable, capable of electrolyzing water at zero bias, and can show electron flow quantum efficiencies at 254 nm of about 0.4. Niobium-doped material, KTa$_{0.77}$Nb$_{0.23}$O$_3$ is slightly inferior. The photocurrent onset for both tantalates in alkali is -1.5V vs SCE, corresponding to the flat-band potential of -1.3V vs SCE at that pH, obtained by differential capacitance [44]. The conduction and valence
band edges lie above and below the $H^+/H_2$ and $O_2/OH$ couples respectively, indicating water photolysis is possible. Indeed, a platinised $\text{KTaO}_3$ single crystal in $3\text{M KOH}$ evolves $O_2$ from the semiconductor and $H_2$ from the metal when illuminated [99]. Intense laser irradiation of $\text{KTa}_{0.77}\text{Nb}_{0.23}\text{O}_3$ causes some surface changes [93].

2.11 Other oxide semiconductors

These materials have generated photocurrents but shown instability: n-$\text{V}_2\text{O}_5$, n/p-$\text{Bi}_2\text{O}_3$, n-$\text{PbO}$, p-$\text{CuO}$, p-$\text{Cr}_2\text{O}_3$, p-$\text{CoO}$ [64]; the following are stable and show a photoeffect: n-$\text{CdFe}_2\text{O}_4$, n-$\text{PbFe}_{12}\text{O}_{19}$, n-$\text{Pb}_2\text{Ti}_{1.5}\text{W}_{0.5}\text{O}_{6.5}$, $\text{Hg}_2\text{Nb}_2\text{O}_7$, $\text{Hg}_2\text{Ta}_2\text{O}_7$ [10], but MnO$_2$ and SrO are not photosensitive [64]. Some transition metal oxides (in the form of oxidised metal foils) also give photoeffects [71, 149]. An important observation on the range of oxide materials is that as the band gap decreases, the flat band potential becomes more positive [10]. This means that when the material responds to visible wavelengths, its band bending will be less effective in separating electron hole pairs produced by that light. As one parameter improves, so another deteriorates. This suggests that oxides are not ideal materials for efficient solar energy harnessing.

2.12 Gallium Arsenide, GaAs

This semiconductor can exhibit both n- and p-type conductivity, and so it could be employed as anode or cathode in a photo-cell. A cadmium-doped single crystal is p-type and evolves hydrogen upon irradiation in an electrochemical cell [74]. The wavelength response commences at 900 nm ($\equiv\text{GaAs's band gap of 1.35eV}$) and maximises at 665 nm. N-type gallium arsenide gives positive photocurrents, but undergoes dissolution [150].
This occurs because the anodic and cathodic decomposition levels lie between the bands so, thermodynamically, n- and p-type GaAs is susceptible to anodic and cathodic photoinstability [49]:

\[
\begin{align*}
\text{Anodic Decomposition} \\
\text{Cathodic Decomposition}
\end{align*}
\]

Gallium arsenide is stabilised in the presence of some redox couples: the Te$^{2-}$/Te$_2^{2-}$ couple competes successfully with anodic dissolution of n-type material, but the Se$^{2-}$/Se$_n^{2-}$ and OH$^-$/S$^2$-/S couples do not [151,152]. All these couples should thermodynamically quench dissolution, but only telluride-ditelluride is effective. Kinetic preference is suggested as the cause. For n-GaAs in 5M NaOH + 0.01M Te$^{2-}$ (Ar-purged) plus platinum cathode, the onset potential of anodic photocurrents varies with light intensity - the higher the intensity, the more negative the onset - and occurs around -1.5V vs SCE. The maximum quantum yield for electron flow (with irradiation at 632.8 nm from a He-Ne laser) is 0.54 at maximum conversion efficiency (found for the lowest input light intensity of 1.89 mW.cm$^{-2}$). However, an n-GaAs/S$^2$-/Sn$^{2-}$/OH$^-$//C is reported to show a power conversion efficiency of a few per cent, with no instability mentioned [ref. 153, for example].

Another attempt to stabilise gallium arsenide was by depositing titanium dioxide on it [115]. For n-GaAs, the CVD TiO$_2$ coating was not crack- and hole-free, and deterioration of the anode, with gallium dissolution, occurred. A complete TiO$_2$ coating was obtained for p-GaAs; anodic photoeffects due to TiO$_2$ were seen, but the cathodic currents were from electrons in GaAs transferred through TiO$_2$ to the solution. The TiO$_2$-GaAs junction generates a detrimental barrier-
potential. Sputtering insulators or wide band gap semiconductors (SnO₂, Nb₂O₅, Al₂O₃, TiO₂, Si₃N₄) onto n-GaAs failed to prevent photocorrosion [116], and similar attempts on p-GaAs were not discussed. A molybdenum oxide coating may afford stability to n-type gallium arsenide [154].

An oxide layer grows on the surface of n-GaAs during anodic dissolution: it was thought this might act as passivating agent to further decomposition [155], but a steady state of oxide formation rate equalling its dissolution rate exists.

The flat-band potential of n-GaAs is -1.5V vs SHE at pH 12, (determined by differential capacitance), and varies by -0.059V pH⁻¹ [156]. The band edges are placed as: conduction band = -1.55V (vs SHE), and valence band = -0.15V (vs SHE). For p-type material, impedance behaviour is complicated.

2.13 Gallium Phosphide, GaP

N-type gallium phosphide forms an unstable anode in a photoelectrochemical cell, decomposing thus [157]:-

\[
\text{GaP} + 9\text{OH} + 6\text{p}^+ \rightarrow \text{H}_2\text{GaO}_3^- + \text{HPO}_4^{2-} + 3\text{H}_2\text{O} \quad \text{Anodic Oxidation}
\]

P-type gallium phosphide, however, does not undergo appreciable cathodic reduction [158], although it is thermodynamically susceptible to this, since both decomposition levels lie within the band gap [49]. Deterioration of p-GaP as photocathode in a cell with a simultaneously illuminated n-TiO₂ anode was observed, and attributed to surface changes [35]. Anodic dissolution of p-GaP was observed here. The stability of p-type gallium phosphide is controlled by experimental conditions [159]. Preparation, doping, pre-treatment, electrolyte, and
illumination conditions are critical. A stable solar cell, with n-GaP and $10^{-2}$ M hydroquinone as anode-anolyte, separated by a membrane from p-GaP and $10^{-2}$ Eu$^{3+}$, the cathode-catholyte, has been reported [160]. Simultaneous illumination of the electrodes induces:

\[ \text{OH} + 2p^+ \rightarrow \text{O} \]

and \[ \text{Eu}^{3+} + e^{-} \rightarrow \text{Eu}^{2+} \]

at the anode and cathode, respectively.

Each compartment contains an inert metal electrode to allow the back reactions to proceed and produce an electric current in the dark. Thus a solar storage battery system exists. The hydroquinone stabilises GaP against dissolution.

N-type gallium phosphide is stabilised by the telluride/ditelluride aqueous couple, analogously to n-GaAs [151,152]. In a selenide electrolyte, both Se$^{2-}$ and GaP oxidation occur. The wavelength response indicates the photocurrent maximum corresponds to the band gap of 2.24 eV ($\approx$530 nm), and the onset potential for anodic photocurrents is about -1.6V, vs SCE, (pH 14). Under these circumstances, the conduction band lies at -2.2V and the valence band at +0.1V. The highest quantum efficiency for electron flow at maximum conversion efficiency is 0.12, occurring for the lowest light input power (1.64 mW cm$^{-2}$) at 454.5 nm. Kinetic factors must explain stabilisation, as investigations of n-GaP show the Fe(CN)$_6^{4-}/3$- and hydroquinone/quinone couples' oxidation currents are responsible for the observed photocurrent, with no decomposition seen, although thermodynamically, solubilisation should occur [54].
N- and p-type gallium phosphide have been stabilised by evaporating gold, palladium or silver onto the crystal [161]. For Au/n-GaP, water photo-oxidation occurs at a potential 0.6V more negative than for a gold electrode - and photo-induced reactions with other reducing agents occurs cathodic of the expected potential. For Ag/p-GaP, hydrogen evolution is seen 0.2V positive of that expected for bare gold. These results are explained in terms of minority carriers produced by light in the semiconductor passing through the metal film to react with redox species. Their oxidising/reducing potential is controlled by GaP, not the gold. No dissolution of the semiconductor ensues as it does not contact the electrolyte.

Further work on n-gallium phosphide coating reveals the metal evaporation speed is critical [162]. For slowly evaporated gold films (type A: 200 second evaporation), the current-voltage curve is like that of a gold electrode but negatively shifted [161]; for a quickly deposited film (type B: 5 second evaporation), the curve is similar to bare n-GaP, but no dissolution occurs. 'Warting' of the type B electrode results from photo-induced oxygen evolution, but inclusion of palladium in the gold deposit prevents degradation. A cell with this anode, sulphate electrolyte and platinum cathode, achieves water electrolysis at zero bias with visible illumination. The maximum photocurrent obtains at about 420 nm, and the quantum yield (electrons flowing per incident photons) at this wavelength is 25% for a power input of 0.1mW.cm⁻². This represents an energy conversion efficiency of 11%, or 1% for solar irradiance.

The explanation of differing behaviour of type A and B electrodes is as follows [162]: the slowly evaporated gold film is in the form of small grains that prevent any electrolyte reaching gallium phosphide.
Holes generated in n-GaP have the energy of its valence band, but are transported through the gold to the electrolyte. A quickly evaporated film has coarse gold grains, so the electrolyte can penetrate to the semiconductor. This part of the GaP can be oxidised to Ga$_2$O$_3$ or Ga(OH)$_3$. The oxide/hydroxide layer prevents further dissolution of gallium phosphide but allows redox chemistry to occur at potentials controlled by the energy levels of GaP. This explanation is not convincing, and is discussed again later.

Some transition metals have been deposited on p-type gallium phosphide [163]. The onset potential of cathodic photocurrents was shifted positively for platinum and palladium (Pt > Pd), hardly at all for nickel, and negatively for copper. The flat-band potential of p-GaP was determined to be +0.36V vs SCE at pH 9.3, and did not alter with a metal coating. However, the onset potential in current-voltage curves is more negative than the flat-band potential. It is suggested that the deposited metal injects photogenerated electrons into the H$^+$ reduction level (to give the observed cathodic photocurrents) at energies characteristic of that metal's Fermi level. Therefore, the cathodic photocurrent onset is not determined by the conduction band or by surface states, but can be controlled by a surface coating.

The earlier work of Nakato et al. on gold covering of n-GaP [161, 162] has been re-investigated [164]. The model for the type A electrode (no electrolyte reaches the gallium phosphide) is confirmed by illuminating a dry n-GaP/Au Schottky diode connected to a gold anode in solution: the same results as for having a n-GaP/Au electrode in the electrolyte obtain. Type B electrodes did not evolve oxygen, peeled, and allowed GaP to decompose. A blocking layer forms on gallium phosphide where the electrolyte contacts it, upon illumination. If this
layer's rate of formation is less than its removal rate, apparent stability ensues. But if it grows too thick, the current will be limited. These competing rates are controlled by electrolyte acidity and illumination intensity. The metal coating simply acts as diffusion barrier between surface electrolyte and the bulk, and concentrates incident light. Replacing the metal by a lacquer confirmed this.

Metal coatings on p-GaP have been employed to extend the spectral response beyond 1000 nm [165]. This appears due to impregnated hydrogen forming a surface state within the band gap, and instability is not seen. A coating of TiO₂ on n-GaP did not prevent dissolution, as the coating was not obtainable crack-free [115].

A single crystal p-GaP cathode, aluminium anode and electrolyte composed of titanium tetraisopropoxide, and aluminium trichloride in 1,2-dimethoxyethane, reduces N₂ to NH₃ on illumination of the gallium phosphide [166]. All the dissolved salts participate in nitrogen reduction, the aluminium anode is consumed, and light lowers the activation energy for the process (photocatalytic system). A cell with p-GaP photocathode and carbon anode effected carbon dioxide reduction in an aqueous electrolyte to formic acid, formaldehyde, and methanol [167]. An aqueous suspension of p-GaP afforded the same reaction [88].

2.14 Indium Phosphide, InP

The n-type material is unstable, but the telluride-ditelluride couple competes effectively with dissolution [168]. At low light intensities, an electron flow quantum efficiency of unity is obtained, but this falls at higher intensities due to tellurium deposited on the electrode. The photoresponse commences at 950 nm, corresponding to indium phosphide's band gap of 1.25 eV. P-type InP can act as photo-
The generation of a Becquerel photoeffect with n-type cadmium sulphide contacting an electrolyte is known to cause dissolution [16]:

\[ \text{CdS} \rightarrow \text{Cd}^{2+} + \text{S} + 2e \]

A cell composed of CdS single crystal photoanode, stainless steel cathode and electrolyte composed of methanol, methanol/water or N-methylacetamide (plus inorganic salts) has been investigated. In a KCl-H$_2$O electrolyte, light of wavelength 400 nm (not monochromatic) with a power of 0.378 mW.cm$^{-2}$ is converted into electrical energy with 4.6% efficiency at a voltage of -0.16V and current of 0.11 mA.cm$^{-2}$ [41]. However, the CdS deteriorates. Cadmium sulphide's band gap of 2.4 eV renders it capable of utilising visible irradiance - observed photo-effects commence at wavelengths corresponding to this energy. Rectangular current-voltage curves for CdS in ferro-ferricyanide indicate satisfactory power output characteristics for this system [170], but again decomposition of the cadmium sulphide occurred. The drop in output power (optimally a total energy conversion efficiency of 9.5% with respect to a 150W Xenon lamp is noted) is due to a sulphur deposit on the CdS electrode.

Cadmium sulphide is unstable because the anodic decomposition level lies negative of the water-oxygen couple in aqueous electrolytes [50,51], but thermodynamic stability may be attained by including redox couples with $E^\circ$ higher in energy than the decomposition level [51,52]. Ellis et al. have had success by adding polychalcogenide species [171,172,173]. Single crystal CdS in alkali plus sodium sulphide generates a photo-
current (with a platinum cathode) and $S^{2-}$ oxidation occurs at the crystal rather than its destruction. Sulphur forms in solution and hydrogen is evolved at platinum. Addition of elemental sulphur prevents gas evolution [171]. $Se^{2-}/Se_n^{2-}$ or $Te^{2-}/Te_2^{2-}$ couples can also compete successfully with dissolution [172], and there is no net chemical change to the electrolyte [173]. The wavelength response of the photocurrent indicates the effects correspond to cadmium sulphide's band gap and electrolyte absorption can be minimised by reducing the path length. For a CdS single crystal, platinum cathode, and electrolyte composed of 1M NaOH+1M Na₂S+1M S (argon purged), an optical to electrical energy conversion efficiency of 6.8% was obtained at 501.7 nm with an input power of 0.264 mW cm⁻². This represents an electron flow quantum efficiency of 0.59.

The presence of sulphide ions at CdS shifts the flat-band potential cathodically [174]. The larger $[S^{2-}]$, the greater the negative shift. The onset potential for photocurrents reflects this shift. It is proposed that a solar cell comprising CdS sintered disc anode, platinum cathode, and sulphide electrolyte could efficiently operate [175], although the absence of sulphur means irreversible sulphide consumption. The flat-band potential of CdS is -0.88V vs SCE, invariant with pH [89], although an exhaustive study has contradicted this, showing the potential varies by -0.059V pH⁻¹, and adopts the value of about -0.9V vs SCE at pH 10 [176]. The flat-band potential appears to vary with Na₂S concentration as well, by -0.06V pNa₂S⁻¹. This value was obtained by calculation, from Mott-Schottky plots, and corrected for the condition of net zero adsorbed surface charge. It is concluded that potential-determining species are $H^+$ and $HS^-$. 

Species other than chalcogenides are known to compete with, or
suppress, anodic dissolution. Aqueous iodide does not prevent decomposition, but its oxidation contributes to photocurrents [177]. NaI + LiClO₄ + CH₃CN does effect stabilisation of CdS, provided [NaI] > 0.2M [178]. Several reducing agents' ability to suppress CdS dissolution has been linked to their redox potentials [179]. \( \text{SO}_3^{2-}, \text{S}^{2-}, \text{S}_2\text{O}_3^{2-}, \text{Fe(CN)}_6^{4-}, \text{I}^{-}, \text{Fe}^{2+}, \text{Br}^{-} \) and \( \text{Cl}^{-} \) have increasingly positive \( E^\circ \) values from left to right, and only the first three effectively prevent decomposition. The effect of sulphide, sulphite, and thiosulphate has been probed further [180]. A very strong adsorbive interaction between these ions and the cadmium sulphide surface alters the energy structure of the interface and suppresses photo-corrosion. Surface states may play a key rôle, and are postulated to cause a cathodic photocurrent in the CdS-S²⁻/S⁻ system [181]. For the single crystal CdS-polysulphide cell, there is doubt as to long-term stability, since polycrystalline cadmium sulphide may deposit on the surface [182].

CdS anodes have been obtained in forms other than single crystal or sintered discs. Cadmium anodization in sodium sulphide yields a film showing photoelectrochemical properties [183]. The wavelength response reflects the band gap, although current-voltage characteristics are less favourable than for the single crystal [170], as the stabilising S/S²⁻ couple lowered the output photovoltage [184]. Peter discusses in detail the anodic formation of cadmium sulphide [185]. At low current densities (<5 A.cm⁻²), uniform yellow CdS is obtained, but for currents greater than 20 A.cm⁻², rough orange films form. Sprayed polycrystalline films from the reaction between CdCl₂ and \((\text{NH}_2)_2\text{CS}\) show photoelectrochemical properties [186]. The CdS is formed on a transparent conducting SnO₂ substrate, and behaviour in alkaline sodium sulphide compares favourably to single crystal cadmium sulphide. One advantage
of the SnO$_2$-CdS system is that irradiation can be performed through the SnO$_2$ rather than through the electrolyte, which avoids visible light absorption if the latter contains polysulphide. The CdS has a thickness of 200-400 nm, a wavelength response identical to that of a single crystal, and in a polysulphide electrolyte with platinum counter electrode, the short-circuit electron flow quantum yield is about 8% [187]. This is for 480 nm wavelength light, with a photocurrent of about 50 $\mu$A cm$^{-2}$ and represents a maximum power conversion efficiency of 0.5%. A similar cell (with a gold cathode) exhibited a total energy conversion efficiency of 0.02% [188]. The main problems with this system are (i) reflection losses from SnO$_2$, (ii) light transmission loss in CdS and (iii) slow rate of polysulphide species' oxidation.

Inclusion of lithium hydroxide in the cadmium chloride/thiourea produces lithium-doped CdS [189]. Photocurrents are greatly improved, as are the power output characteristics, and the short-circuit current quantum yield approaches 50% for an optimally doped anode. This is obtained with $[\text{LiOH}] = 0.001\text{M}$ in the $0.01\text{M CdCl}_2 + 0.01\text{M (NH}_2\text{)}_2\text{CS}$ spray.

A solid solution of CdS-ZnSe forms a photoanode behaving similar to CdS, but has its wavelength response red-shifted by 100 nm [190].

Cyanide ions can be oxidised to cyanate in suspension with CdS upon illumination [84] and carbon dioxide can be similarly reduced to formic acid, formaldehyde, and methanol.

2.16 Cadmium Selenide, CdSe

This n-type semiconductor has a band gap of 1.7 eV [16], and decomposes when irradiated in 1M NaOH with a platinum cathode, although addition of sodium sulphide quenches dissolution [171]. Indeed, the S$^{2-}$/S$_n^{2-}$, Se$^{2-}$/Se$_n^{2-}$ and Te$^{2-}$/Te$_2^{2-}$ couples compete efficiently with photoanodic
oxidation [172]. For the polysulphide couple, it is proposed that S²⁻ oxidation occurs at CdSe and no lattice rupture or selenium-sulphur exchange occurs [173]. The photocurrent onset potential corresponds closely to the flat-band potential in a polysulphide electrolyte [172], and photoeffects commence at about 750 nm, corresponding to CdSe's band gap. With a cadmium selenide single crystal, an electrolyte composed of 1M NaOH + 1M Na₂S + 1M S with platinum cathode, an optical to electrical energy conversion efficiency of 9.2% was obtained using 632.8 nm light of intensity 0.4 mW cm⁻². This represents an electron flow quantum efficiency of 0.52 at -0.35V applied potential [173].

Deterioration of the cadmium selenide single crystal occurs when current densities exceeding 10 mA.cm⁻² are passed [191]. The deterioration is reflected by a drop in photocurrent, which is restored by either stirring the electrolyte (NaOH+Na₂S+S) or adding selenium. Sulphur is detected in deteriorated anodes - CdS and Cd_(1-x)Se_x are present, and form a current-blocking layer. The wavelength response of such an electrode approximates to that of cadmium sulphide [182], and X-ray photoelectron spectroscopy confirms CdS is present and gives a layer about 20 Å thick [192]. S-Se exchange occurs both in the dark and under illumination.

An anode fabricated from cadmium selenide powder irradiated in 1M Na₂S/1M S/1M NaOH with a carbon cathode generated a short-circuit current density of 12 mA.cm⁻², an open circuit photovoltage of 0.67, which represents an "overall efficiency" of 5.1% in solar irradiance of intensity 71 mW.cm⁻² [193]. This "overall efficiency" is about 70% of that of a single crystal CdSe electrode, indicating the polycrystalline form can compete. CdSe has been obtained by anodisation of cadmium in NaOH + Se [194,195], although some films were too thin to effect a high
conversion efficiency [195].

Electrolytic co-deposition of cadmium and selenium on a conductive substrate forms a photosensitive anode [196,197]. In a polysulphide electrolyte, no instability ensues, but counter electrode polarisation may limit photocurrents [196]. A solar storage system involves such a cadmium selenide anode (on titanium), a counter electrode of carbon, cobalt acetate and teflon (cobalt sulphide is the active species), an electrolyte of 1M OH⁻/S²⁻, and an Ag₂S storage electrode separated from the other two by a cation specific membrane [197]. Irradiation of CdSe causes electrons to flow to both counter and storage electrodes, and by suitable arrangement of the external loads between the three electrodes, electrons can flow back from the Ag₂S storage electrode to the counter electrode in the dark:

\[ \text{Ag}_2\text{S} + 2e^- \rightarrow 2\text{Ag} + \text{S}^{2-} \quad \text{upon irradiation} \]
\[ 2\text{Ag} + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S} + 2e^- \quad \text{in the dark.} \]

A solid solution of 90% CdS + 10% CdSe formed into an anode is an improvement on either CdS or CdSe in that the flat-band potential is more negative than for the pure materials [198].

### 2.17 Cadmium Telluride, CdTe

Ellis et al. tried an n-type sample of cadmium telluride in a photoelectrochemical, and found decomposition like CdS and CdSe in an alkaline electrolyte [199]:

\[ \text{CdTe} \xrightarrow{2hv} \text{Cd}^{2+} + \text{Te} + 2e^- \]

Elemental tellurium forms on the photoanode and hydrogen evolution at the platinum cathode. A polysulphide electrolyte did not quench
dissolution, but \( \text{Na}_2\text{Te} \) completely prevents anodic oxidation. The \( \text{Te}^{2-} \) anion is oxidised by positive holes in place of CdTe:

\[
2\text{Te}^{2-} \xrightarrow{2hv} \text{Te}_2^{2-} + 2e^- \quad \text{At CdTe}
\]

\[
\text{Te}_2^{2-} + 2e^- \rightarrow 2\text{Te}^{2-} \quad \text{At platinum}
\]

A polyselenide electrolyte also quenches dissolution [172]. The wavelength response of CdTe commences at 860 nm, corresponding to the band gap of 1.4 eV, but the purple colour of \( \text{Te}_2^{2-} \) can result in electrolyte absorption losses. A photocell comprising n-CdTe single crystal anode, platinum cathode, and electrolyte composed of 5M \( \text{NaOH} + 0.18\text{M Na}_2\text{Te} \) with 633 nm irradiation at an intensity of 1.32 mW.cm\(^{-2}\) gave a maximum power conversion efficiency of 10\% (with an output voltage of 0.3V), representing an electron flow quantum efficiency of 0.65 [172]. N-type cadmium telluride has a flat band potential of about -1.5V. A p-type sample of CdTe acts as photocathode and evolves hydrogen [200]. In polysulphide electrolyte, gas evolution ceases, but CdTe does not solublise. This photocell is inefficient, showing a short-circuit electron flow quantum efficiency of 0.002, but an improvement is seen with a simultaneously illuminated n-CdSe anode. p-CdTe has been mentioned before as photocathode in a p-n cell [36,37] - see p.32 - and its positive flat band potential encourages this use [201]. Electrodeposition of cadmium and tellurium on to titanium forms a photosensitive CdTe electrode [201].

2.18 Molybdenum Sulphide, MoS\(_2\)

A major limitation of semiconductors is that the photogenerated valence band hole represents a missing bonding electron, which causes lattice weakening and increases the probability of decomposition.
Molybdenum sulphide has a valence band formed from sulphur 3p orbitals and this overlaps a band composed of molybdenum's 4d\textsubscript{2} non-bonding orbitals [202]. Light promotes these non-bonding electrons into the conduction band without disturbing valence band electrons. MoS\textsubscript{2} exists as both n- and p-types, and has been investigated for photoelectrochemical properties [202,203,204]. The n-type material decomposes, as evidenced by falling photocurrents with time, and sulphate, rather than sulphur is formed. Oxygen can also be produced [202].

\[
\text{n-MoS}_2 + 8\text{H}_2\text{O} + 18\text{h}^+ \xrightarrow{18\text{hv}} \text{MoVI} + 2\text{SO}_4^{2-} + 16\text{H}^+ \\
\text{oxidation}
\]

and/or

\[
\text{n-MoS}_2 + 2\text{H}_2\text{O} + 4\text{h}^+ \xrightarrow{4\text{hv}} \text{MoS}_2 + 4\text{H}^+ + \text{O}_2 \\
\text{stability and oxygen evolution.}
\]

p-MoS\textsubscript{2} remains stable, evolving hydrogen and hydrogen sulphide on irradiation. In 0.1M Fe\textsuperscript{2+}/Fe\textsuperscript{3+}, with a platinum counter electrode, a regenerative solar cell seems possible [203]. The band gap of 1.75 eV allows wavelengths down to 750 nm to be employed, although the energy conversion efficiency is below 1%. No quantum efficiencies have been reported [204].

2.19 Molybdenum Selenide, MoSe\textsubscript{2}

The band structure of molybdenum selenide resembles that of the sulphide, and behaves similarly to MoS\textsubscript{2} in a photoelectrochemical cell [205]. Decomposition of n-MoSe\textsubscript{2} occurs when water reacts with photogenerated positive holes:

\[
\text{n-MoSe}_2 + 6\text{H}_2\text{O} + 14\text{h}^+ \xrightarrow{14\text{hv}} \text{MoVI} + 2\text{SeO}_3^{2-} + 12\text{H}^+
\]
The water oxidation products react to form selenic acid, but species with redox couples negative of that of water do not cause corrosion. A photocell with I⁺/I⁻ present operates continuously at steady current with an energy conversion of 4-5% (light input = 21 mW.cm⁻², and the wavelength response commences at 900 nm, corresponding to the band gap of about 1.3eV).

Tributsch has investigated further the properties of holes in a semiconductor d-band [206]. He concludes that reducing agents' reaction with d-band holes is very different than with p-band holes. Any decomposition products from the reducing agent - hole interaction are reflected in the element whose band contained the hole, and if any components of the reducing agent appear in the decomposition products, then a chemical bond must have formed. It is postulated that a reducing agent forms a chemical bond to a d-band hole, but not to a p-band hole.

Synthetic MoSe₂ shows improved photoeffects to the natural crystals employed above [207].

2.20 Tungsten Selenide, WSe₂

Single crystals of the p-type material can be employed as a photocathode [208], although the current-voltage behaviour is described as 'peculiar'. Its stability appears similar to that of the molybdenum dichalcogenides.

2.21 Other Semiconductors

Solid state commercial solar cells are composed of an n- and p-type silicon homojunction. A semiconductor-electrolyte junction solar cell with Si-aqueous Na₂HPO₄ showed a conversion efficiency of 2.7% [209], but the system would decompose [210]:

-85-
Silicon dioxide forms a blocking insulating layer. Deposition of titanium dioxide on to the surface of n-Si affords stabilisation but limits the photoresponse to wavelengths shorter than TiO₂'s band gap [115]. Coating n-Si with gold and p-Si with silver effects stabilisation as for n/p GaP [161] - see pp.74-76. A cell comprising n-Si photoanode, platinum cathode, and tetra-n-butyl ammonium perchlorate + ethanol + ferrocene + ferricenium hexafluorophosphate \([\text{Fe(Cp)}^2+2\text{PF}_6^-]\) as electrolyte, remained stable and showed a light to electricity conversion efficiency of 2% at 632.8 nm (10 mW.cm⁻²), with a short circuit photocurrent quantum efficiency of nearly 0.4 [211]. The photo-induced oxidation-reduction of ferrocene/ferricenium ion at n-type silicon and resultant overall chemically is prompting further research into this system [212]. "Derivatised" n-Si, with ferrocene chemically bonded to the semiconductor, appears to have some stability in an aqueous electrolyte [212].

P-type zinc telluride, ZnTe, has been tried as cathode in photo-electric-chemical cell, but its instability and too negative flat-band potential renders it unsuitable [213]. CuInS₂ (n-type) appears more promising as a photoanode [214].

\[ 2\text{H}_2\text{O} + \text{Si} \xrightarrow{4\text{hv}} \text{SiO}_2 + 4e^- + 4\text{H}^+ \]
CHAPTER THREE

AN INVESTIGATION OF SOME SEMICONDUCTORS TO
DETERMINE PHOTOVOLTAGE AND PHOTOCURRENT GENERATION,
AND PHOTOSTABILITY
CHAPTER THREE

3.1 Introduction

Many materials remain unexplored in their possible ability to produce photoeffects with an electrolytic junction. Ideal semiconductors for optical energy harnessing have not yet been discovered, and to this end, a cursory investigation into some compounds was undertaken. The major features looked for are stability, magnitude and sign of photo-induced voltage, and magnitude and sign of photo-induced current. Those materials which appear promising are then singled out for a more detailed study.

3.2 Experimental

Figure 3.1 illustrates the optical bench employed. A 1.8 kW xenon lamp forms the light source, and is set in a cinema projector unit. Unwanted radiation wavelengths are filtered out by a solution in a 1.5l beaker, which is constantly circulated by means of a peristaltic pump through a copper coil immersed in ice. This cooling is essential, as the lamp generates enough heat to boil the solution. As indicated in figure 3.1, the optical pathlength through the filter is 11 cm. Saturated aqueous copper(II) sulphate or aqueous copper(II) chloride (about 0.3M) are employed as filters.

Figure 3.2 shows the wavelength band passed through each solution, for an optical pathlength of 1 cm. CuSO₄ is used when near ultra-violet and short wavelength visible light are required for illumination, while CuCl₂ cuts out ultra-violet and passes the peak wavelengths of visible light. The CuCl₂ filter has maximal transparency at 515 nm with a half-band width of 90 nm, and delivers light to the semiconductor.
**Fig. 3.1**

Optical Bench for investigation of semiconductor photo-properties.

cover (not air-tight) with brass connectors for electrodes and wiring.

platinum counter electrode
saturated calomel electrode

electrochemical cell
aqueous electrolyte

Bi-convex lens
*f* = 5 cm

plane-convex lens
*f* = 13 cm

1-8 kW xenon lamp

heat/uv filter

16 cm

circulation through copper coil in ice by peristaltic pump

10 cm  8 cm  6 cm  11 cm  50 cm
Fig. 3.2
Wavelength band passed by the filter solution in a cell of pathlength 1 cm.
(a) Saturated CuSO₄ (aqueous)
(b) 0.3M (approximately) CuCl₂ (aqueous)
An electrode with a power of about $2.5 \times 10^{-2}$ W/cm$^2$. A higher light intensity is delivered by the CuSO$_4$ filter, but its half-band width is unknown. The two lenses shown in figure 3.1 cause a divergent light beam to emanate from the bi-convex lens. The electrochemical cell is then placed such that optimum irradiation of the semiconductor electrode is possible.

The semiconductor electrode is a platinum mesh coated with the semiconducting material in powdered form. Figure 3.3 illustrates the mesh.

![Fig. 3.3(a)](image)

A platinum mesh which forms the conductive carrier for the powdered semiconductor.

![Fig. 3.3(b)](image)

Fine detail of the weaving of the platinum wires of the mesh shown in fig. 3.3(a).

It measures 1.5 cm by 3.0 cm and is composed of 44 wires, 1.5 cm long, interwoven with 22 wires, 3.0 cm long. These wires have a diameter of 0.025 cm, and the mesh is supported on a platinum wire of diameter 0.1 cm and length 7.5 cm, with the last 1.5 cm flattened to allow the mesh to be affixed. The electrode is quite robust, and the mesh can be rolled and unrolled without any damage occurring. The electrodes were obtained from Englehard Sales and weigh approximately 2.5 g. More
details of the mesh are given in appendix I.

A suspension, containing 2 g of the powdered semiconductor in 25 ml of de-ionised water, is treated with a Dawe Instruments Ultra-Sonic probe Type 7530A for one minute at power setting 5, to effect fine dispersion of the powder. The platinum mesh is swirled in this suspension, taken out, dried in a hot air stream, and the process repeated until an even coating is obtained. The weight of material adhering to the platinum varies from 5 to 25 mg, according to the nature of the semiconductor. This forms the light-sensitive electrode. The semiconductor-coated electrode is stored in an electrolyte for at least fifteen hours prior to irradiation. This is to allow for establishment of the semiconductor-electrolyte junction; electrodes which have had insufficient storage time to fully develop the space-charge layer do not exhibit optimum photoeffects [215].

Advantages in employing this procedure are (i) simplicity of preparation, (ii) ease of cleaning off the semiconductor after use, (iii) a large number of materials can be investigated in a short period of time. Disadvantages include (i) incomplete mesh coverage can result in a short-circuited electrode - uncovered platinum will act as a counter electrode, (ii) the semiconductor-metal junction may not be ohmic, and form a barrier to photogenerated majority carriers' passage to/from the external circuit, (iii) materials which do not adhere to platinum cannot be investigated.

The electrochemical cell used is a cut-down 100 ml beaker housed in a polystyrene box to maintain a constant temperature in the electrolyte. A plastic cover fits loosely on top of the beaker, with brass connectors for screwing in the semiconductor electrode, counter electrode (an uncoated platinum mesh) and the wires connecting these
to the measuring instruments. A saturated calomel electrode (SCE) (sealed, from Electronic Instruments Ltd.) containing approximately 4.6M KCl forms the reference electrode, and the electrolyte is 100 ml of 0.1M KCl or NaNO₃, adjusted to pH 7, but not buffered. Some electrolytes are analysed for specific elements by atomic absorption spectroscopy after illumination. The experimental conditions are given in appendix II. Potentials are measured with a Phillips High Impedance Voltmeter PM2434 (internal resistance = 10⁶ to 10⁷ Ω) using the circuit of figure 1.6(a) (p.16), and currents with the circuit in figure 1.6(b) (p.16) by a Heath Polarography Module EUA-19-2. Provision exists for varying the potential applied (or 'bias') to the semiconductor versus the SCE. Voltage- and current-time plots are obtained on a Servoscribe chart recorder. All chemicals are of 'Analar' or equivalent grade, unless otherwise stated, and electrolytes are made up with deionised water (from a 'Fionex' deioniser which contains ion-removing resins).

For those semiconductors which adhere poorly or not at all to the mesh, the investigation was performed by means of a suspension experiment. The electrochemical cell is a gas jar, of inner diameter 7 cm and height 21 cm. 2 g of the semiconductor are dispersed with the ultrasonic probe in 500 ml of 0.1M KCl or 0.1M NaNO₃ electrolyte. A piece of platinum foil, 12 cm x 10 cm, is placed around the inside of the gas jar, mostly beneath the electrolyte surface, at such a position to receive maximum irradiation from the light source, a 125W medium pressure mercury lamp (Hanovia), (in a water-cooled pyrex jacket), which is immersed in the electrolyte. A crocodile clip (clear of the electrolyte) connects the external circuitry to the platinum foil, and a platinum wire is the counter electrode (protected from irradiation), and is similarly connected to the external circuit. An SCE is the
The platinum foil is considered to transfer the semiconductor's photogenerated majority carriers to/from the measuring instruments (voltmeter or polarography module), and a magnetic stirrer bead agitates the suspension to ensure a supply of semiconductor particles between the lamp and foil. Occasionally, it was found preferable to cease stirring, as some material invariably lodged on crinkles in the foil and gave the photoeffects, which were diminished if the light intensity reaching the foil was lowered by particles swirling around the lamp. The major limitation of this experimental method is that it is impossible to know accurately the area of semiconductor under illumination.

3.3 Results

3.3.1 Qualification of electrode preparation method

The procedure outlined above (other than the suspension method) has been employed to investigate the photoelectrochemical properties of powdered titanium dioxide [215,216]. To further qualify the electrode preparation method, six semiconductors whose photoelectrochemical reactions are reported in the literature were probed, and the results then compared with known properties.

Table 3.1 presents some results of these semiconductors. The TiO$_2$ is 'Runa RG', from Laporte Industries, and has been reduced by heating in a silica tube at 1000°C for 4 hours in a stream of hydrogen. All except WO$_3$ formed a robust electrode. Instability of the semiconductor is presumed if it undergoes a large weight loss or the electrolyte becomes coloured. Both of these were observed for CdS, and also a coating on the counter electrode. The electrolyte and the solution
<table>
<thead>
<tr>
<th>Semiconductor &amp; Supplier</th>
<th>Band gap in eV</th>
<th>Weight of coating on platinum mesh in g</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in µA at 0.0V Bias vs SCE</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced TiO₂ (see text)</td>
<td>3.0</td>
<td>0.005308</td>
<td>-270</td>
<td>+17.5</td>
<td>Semiconductor electrode lost weight (17% loss)</td>
</tr>
<tr>
<td>ZnO (British Drug Houses)</td>
<td>3.3</td>
<td>0.007276</td>
<td>-286</td>
<td>+115.0</td>
<td>Semiconductor electrode lost weight (8% loss)</td>
</tr>
<tr>
<td>SrTiO₃ (Koch-Light)</td>
<td>3.2</td>
<td>0.005435</td>
<td>-110</td>
<td>+3.5</td>
<td>No instability noted</td>
</tr>
<tr>
<td>BaTiO₃ (Unknown Source)</td>
<td>3.4</td>
<td>0.008404</td>
<td>-135</td>
<td>0.0</td>
<td>No instability noted</td>
</tr>
<tr>
<td>WO₃ (British Drug Houses)</td>
<td>2.8</td>
<td>?</td>
<td>-136</td>
<td>-1.0</td>
<td>WO₃ did not adhere well to the platinum mesh</td>
</tr>
<tr>
<td>CdS (British Drug Houses)</td>
<td>2.4</td>
<td>0.008400</td>
<td>-167</td>
<td>+105.0</td>
<td>Semiconductor electrode lost weight (33% loss) and platinum counter electrode gained weight</td>
</tr>
</tbody>
</table>

**TABLE 3.1** Photovoltages and photocurrents for electrodes composed of a platinum mesh coated with some semiconductors whose photoelectrochemical properties are already known. The experimental procedure is given in the caption to figure 3.4, and in Section 3.2.
from dissolving the counter electrode deposit gave a positive spot test for cadmium. The instability of CdS has been discussed in Chapter Two (p.77). Figure 3.4 illustrates relative photocurrent versus applied potential for these semiconductors. Only cadmium sulphide was investigated in a deoxygenated electrolyte; large cathodic photocurrents for the other materials at small negative biasing potentials reflect photo-assisted oxygen reduction in the aerated electrolyte. The plot for cadmium sulphide shows a bias of -0.65 V is needed for no photocurrent to flow; this value is quite close to that of the flat-band potential quoted in the literature [89]. The weight loss noted for reduced TiO₂ is not typical of similar electrodes reported in the literature, and may be due to the semiconductor falling off the platinum mesh, although no such problem was encountered for non-reduced titanium dioxide [216]. The negative relative photopotentials shown in table 3.1 and the current-applied bias plots illustrated in figure 3.4 indicate the semiconductors show their known n-type properties (see Chapter Two). It is therefore reasonable to assume that the electrode preparation method, as described earlier, is suitable for investigating semiconducting materials.

Strontium titanate does not produce large photocurrents (figure 3.4). This material is known to cause hydrogen evolution at a platinum counter electrode at the same potential as an illuminated single crystal electrode [32]. Thus uncovered platinum at the SrTiO₃ mesh electrode should be capable of proton reduction and hence short-circuiting will take place. This is the cause of diminished photocurrents compared to TiO₂ and ZnO, in which such proton reduction does not occur at zero applied potential. Short-circuiting may be a contributory factor to the absence of photoeffects in materials described
Fig. 3.4
Plots of relative photocurrent vs applied potential for CdS (—), ZnO (x–x), reduced TiO₂(—), WO₃ (○○) and SrTiO₃/BaTiO₃ (+++). Electrolytes are aerated 0.1M KCl for WO₃, aerated 0.1M NaNO₃ for ZnO, TiO₂, SrTiO₃ and BaTiO₃ (both at pH 7, unbuffered) and nitrogen-purged 0.1M KCl with 10ml of 0.1M Na₂S for CdS. Saturated CuSO₄ acts as light filter. The semiconductors are in the form of mesh electrodes and the optical system is as in Figure 3.1.

Dark current greater than +200 µA positive of +0.4v bias

Applied Bias in Volts vs SCE
3.3.2 The response of coated mesh electrodes to light

Figure 3.5 shows photoresponse-time plots for semiconductor-platinum mesh electrodes in an aqueous electrolyte. In (a), the potential is seen to alter slowly from the dark voltage (Dv) upon irradiation to reach the level illumination value (Py). On ceasing irradiation, the potential declines slowly back to the dark reading. The time taken to attain level voltages varies from one minute to up to an hour, depending on the semiconductor and/or the electrolyte. The potential versus time plot, as indicated in figure 3.5(a), is common to every semiconductor investigated; the plots of specific materials are characterised by different time responses and magnitude and sign of the relative photo-potentials.

The shape of the potential-time plot is explained as follows: light separates electron-hole pairs, with majority carriers swept to the interior of the semiconductor and to the voltmeter to register the voltage change. The space-charge layer beneath the semiconductor surface becomes weaker as majority carriers accumulate in the bulk of the semiconductor. This results in less effective separation of photo-generated electron-hole pairs and an increased possibility of carrier recombination. Hence the rate of change of voltage decreases with irradiation time until the steady illumination potential, Py, is attained. At this point, the carrier generation rate equals the carrier recombination rate, and a steady-state equilibrium is achieved. This may represent the band-flattening situation, or one where residual band-bending exists.

Upon ceasing irradiation, majority and minority carriers recombine. Initially, this occurs at a fast rate because of the weak or non-
Fig. 3.5(a)
Plot of potential vs time for a semiconductor-platinum electrode against a reference (SCE) in an electrolyte. The direction of voltage change on illumination is unspecified. 
\[ D_v = \text{Dark Potential}; \quad P_v = \text{Illumination Potential}; \quad (P_v-D_v) = \text{Relative Photo-potential}. \]

Fig. 3.5(b)
Plot of current vs time for a semiconductor-platinum electrode and platinum counter electrode in an electrolyte. The direction of current change on illumination is unspecified. 
\[ D_c = \text{Dark Current}; \quad P_c = \text{Current Illumination}; \quad (P_c-D_c) = \text{Relative Photocurrent}. \]
existent space-charge layer present. The return of a majority carrier to its band of origin causes the space-charge layer to build up again. An increasing barrier will now exist for majority carriers to return to or near the semiconductor surface. This is reflected in the decrease of the decline rate with time of the illumination potential back to the dark potential. No minority carriers exist after the ending of illumination and those that were present have recombined with majority carriers. Thus the latter must find their way into the electrolyte via surface states to continue the photopotential decline. For example, the negative relative photopotential exhibited by n-type semiconductors is due to electrons in the conduction band. When illumination has ceased, these electrons must leave the conduction band, but can only return to the valence band if a positive hole exists there. Positive holes are only created by illumination, so conduction band electrons must tunnel through the space-charge layer to the semiconductor surface and leave either via a surface state or an adsorbed ion. The photovoltage decay has been shown to be dependent on specific electrolyte ions and follow a second-order process [216].

In figure 3.5(b) is shown a current versus time plot. An instantaneous shift from the dark current \( (D_C) \) is observed on irradiation. An "overshoot" is sometimes seen and the current quite rapidly attains a level value \( (P_C) \). An "overshoot" in the opposite direction is occasionally observed when irradiation is ceased and the dark current is restored. The time for the "overshoots" to decline to level currents does not usually exceed five minutes, and for some semiconductors no "overshoots" are observed and the plots are essentially rectangular. For an n-type semiconductor which generates a positive relative photocurrent, the decline of the "overshoot" on commencement of irradiation
is due to a cathodic current component caused by back-reaction of photo-generated species in the electrolyte. A steady-state is achieved for the level photocurrent \( (P_c) \) and the cathodic component is responsible for the "overshoot" on termination of irradiation. This "overshoot" declines back to the dark current as the cathodic reaction diminishes.

The same process occurs to produce currents and potentials under the action of light - generation and separation of charge carriers. The time response for photocurrents is very much quicker because the majority carriers flow around an external circuit and are not subject to the conditions imposed on them when they are restricted to the steady-state equilibrium within the semiconductor at open circuit.

3.3.3 Investigation of oxide materials

Twenty-one metal oxides were tested to determine their ability to give a photovoltage and photocurrents. Table 5.2 summarises the results. The 'photocurrent onset potential' quoted in this table is the bias that needs to be applied to give no net photocurrent. Useful materials should have this onset potential as negative as possible if they are n-type, and as positive as possible if p-type. This onset correlates with the flat-band potential and its value is important in evaluating the use of semiconductors in efficient optical energy harnessing [40].

(i) **Bismuth oxide, Bi\(_2\)O\(_3\)**

The green powder would not adhere firmly to the platinum mesh, and weighings of the electrode before and after use cannot be used to determine stability. No visible changes occurred in the cell, and the material is p-type as it gives a positive relative photovoltage.
<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Colour</th>
<th>Band gap in eV</th>
<th>Relative photopotential in mV</th>
<th>Relative photocurrent in μA at 0.0V vs SCE</th>
<th>Photocurrent onset potential in V vs SCE</th>
<th>Weight of material in g on the platinum mesh</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂O₃</td>
<td>Fisons</td>
<td>Green</td>
<td>2.6 - 2.9</td>
<td>+ 61</td>
<td>- 9.0</td>
<td>+0.25</td>
<td>0.007000</td>
<td>Possibly stable; n- or p-type (13% weight loss)</td>
</tr>
<tr>
<td>CdO</td>
<td>British Drug Houses</td>
<td>Brown</td>
<td>2.3</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0.015982</td>
<td>CdO gained weight (0.5% weight gain)</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>Unknown</td>
<td>Green</td>
<td>1.6</td>
<td>- 10</td>
<td>- 51</td>
<td>+0.4?</td>
<td>0.004210</td>
<td>Possibly stable; n-type? (7% weight loss)</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>British Drug Houses</td>
<td>Brown/Red</td>
<td>2.0</td>
<td>+ 35</td>
<td>-11.0</td>
<td>+0.2</td>
<td>0.009523</td>
<td>Unstable; p-type (16% weight loss)</td>
</tr>
<tr>
<td>CuO</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>1.95</td>
<td>+ 50</td>
<td>- 5.0</td>
<td>+0.25</td>
<td>0.006868</td>
<td>Possibly stable; p-type</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>?</td>
<td>- 25</td>
<td>0</td>
<td>-</td>
<td>0.006328</td>
<td>Unstable; n-type (15% weight loss)</td>
</tr>
<tr>
<td>HgO</td>
<td>May &amp; Baker</td>
<td>Red</td>
<td>1.0 -2.0</td>
<td>+105</td>
<td>Non-reproducible results: suspension experiment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgO</td>
<td>May &amp; Baker</td>
<td>Yellow</td>
<td>1.0 -2.0</td>
<td>+ 20</td>
<td>- 70</td>
<td>+0.15</td>
<td>0.008128</td>
<td>Very unstable; p-type (60% weight loss)</td>
</tr>
<tr>
<td>MoO₂</td>
<td>Pfaltz &amp; Bauer</td>
<td>Dark purple</td>
<td>?</td>
<td>0</td>
<td>Suspension experiment: see text</td>
<td></td>
<td></td>
<td>Suspension experiment; unstable, n-type</td>
</tr>
<tr>
<td>MoO₃</td>
<td>British Drug Houses</td>
<td>White</td>
<td>3.0</td>
<td>-120</td>
<td>Large dark current</td>
<td>+0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>Unknown</td>
<td>White</td>
<td>?</td>
<td>- 60</td>
<td>- 30</td>
<td>+0.2</td>
<td>0.007398</td>
<td>Unstable; n-type (10% weight loss)</td>
</tr>
<tr>
<td>NiO</td>
<td>Unknown</td>
<td>Green</td>
<td>1.8</td>
<td>- 90</td>
<td>Small and negative</td>
<td>+0.3 - +0.5</td>
<td>0.006950</td>
<td>Unstable; n-type (20% weight loss)</td>
</tr>
<tr>
<td>NiO₂</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>?</td>
<td>0</td>
<td>- 12?</td>
<td>+0.1</td>
<td>0.002952</td>
<td>Unstable; p-type? (50% weight loss)</td>
</tr>
</tbody>
</table>

..... Continued
<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Colour</th>
<th>Band gap in eV</th>
<th>Relative photocurrent in mA at 0.0V vs SCE</th>
<th>Photocurrent onset potential in V vs SCE</th>
<th>Weight of material in g on the platinum mesh</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO</td>
<td>Fisons</td>
<td>Green</td>
<td>2.3</td>
<td>+ 23</td>
<td>-</td>
<td>0.001893</td>
<td>Unstable; possibly p-type (10% weight loss)</td>
</tr>
<tr>
<td>PbO₂</td>
<td>British Drug Houses</td>
<td>Brown</td>
<td>1.5</td>
<td>+ 10</td>
<td>?</td>
<td>0.004322</td>
<td>Unstable; (5% weight loss)</td>
</tr>
<tr>
<td>Pb₃O₄*</td>
<td>May &amp; Baker</td>
<td>Red</td>
<td>2.1</td>
<td>+ 90</td>
<td>Negative</td>
<td>0.003354</td>
<td>Unstable; p-type (30% weight loss)</td>
</tr>
<tr>
<td>Sn₂O₃</td>
<td>Unknown</td>
<td>Off-white</td>
<td>2.3</td>
<td>-135</td>
<td>- 10</td>
<td>0.008096</td>
<td>Possibly stable; n-type (15% weight loss)</td>
</tr>
<tr>
<td>SnO</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>Suspension experiment</td>
</tr>
<tr>
<td>TeO₂</td>
<td>British Drug Houses</td>
<td>White</td>
<td>3.0</td>
<td>-140</td>
<td>- 8</td>
<td>0.003114</td>
<td>Very unstable; n-type (95% weight loss)</td>
</tr>
<tr>
<td>Ti₂O₃</td>
<td>British Drug Houses</td>
<td>Brown</td>
<td>2.2</td>
<td>-25</td>
<td>-300</td>
<td>0.007126</td>
<td>Very unstable; n-type (50% weight loss)</td>
</tr>
<tr>
<td>U₃O₈*</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>0.006172</td>
<td>(15% weight loss)</td>
</tr>
</tbody>
</table>

**TABLE 3.2** Photoeffects generated by some oxides coated on the platinum mesh. The light filter is saturated CuSO₄ except where there is an asterisk (*) in the "material" column; here dilute CuCl₂ is the light filter. For experimental conditions, see Section 3.2.
(ii) **Cadmium oxide, CdO**

CdO produces no photoeffects. It formed a robust, well-coated, electrode which acquired patches of white material during irradiation and showed a weight increase.

(iii) **Chromium(III) oxide, Cr₂O₃**

The small relative photopotential and positive onset potential preclude Cr₂O₃ as an efficient photoanode. Stability is uncertain: no visible changes occurred to electrodes or electrolyte, and the weight may be due to handling. Cr₂O₃ appears n-type.

(iv) **Copper(I) oxide, Cu₂O**

Although a relative photocurrent of -11μA is obtained at zero bias, and a small positive relative photopotential of +35 mV is produced, the instability of Cu₂O limits its use as a photocathode. No changes to electrodes or electrolyte could be seen.

(v) **Copper(II) oxide, CuO**

This oxide's properties show it to be p-type, and relative photopotentials exceeding +120 mV have been noted. Gas bubbles accumulated on the black CuO electrode when taking both currents and potentials on illumination, and instability of the oxide was neither confirmed nor disproved and no visible changes occurred in the cell.

(vi) **Iron oxide, Fe₃O₄**

The negative relative photopotential indicates this is n-type, but the lack of photocurrents and instability exclude its usage.

(vii) **Red mercury(II) oxide, HgO**

This would not form a coating on the platinum mesh. 2.5 g of red HgO were dispersed (with difficulty) in 500 ml of pH 7 0.1M NaNO₃ and
the suspension experiment performed. The only result obtained was a non-reproducible relative photopotential of +100 mV - no photocurrents were taken because of fluctuating dark currents.

(viii) Yellow mercury(II) oxide, HgO

This form of HgO adhered well to the platinum mesh and appears p-type from its photo-properties. The current flowing in the dark at zero bias often exceeded -500μA and caused gas evolution at the counter electrode. A large weight loss and colour change of the yellow HgO was observed.

(ix) Molybdenum(IV) oxide, MoO₂

A very small amount of the powder stuck to the platinum mesh: this electrode and a suspension experiment produced only slight photoeffects, with molybdenum detected in used electrolytes by atomic absorption spectroscopy.

(x) Molybdenum(VI) oxide, MoO₃

No MoO₃ would adhere to the platinum mesh, and a suspension experiment revealed a negative photo-induced voltage, but a lot of molybdenum was detected in solution by atomic absorption spectroscopy. This instability, plus the positive onset potential of +0.3 V, and the wide band gap render MoO₃ useless to harness visible light.

(xi) Neodymium oxide, Nd₂O₃

This is unsuitable, due to instability and a positive onset potential, despite its relative photopotential of -60 mV.

(xii) Nickel oxide, NiO

The band gap of 1.8 eV and photo-induced potential of -90 mV suggest this oxide might be useful as a photoanode. Its instability and
positive onset potential is a disadvantage.

(iii) **Nickel peroxide, NiO₂**

No reliable results were obtained with this material and it was found to be very unstable - most of the illuminated face of the semiconductor electrode was bare after irradiation.

(iv) **Lead oxide, PbO**

This does not adhere very well to the platinum mesh. Lead was detected in used electrolytes by atomic absorption spectroscopy and the counter electrode gained a brown coating; lead was detected in the acid solution which dissolved this coating. Thus PbO is unstable and unsuitable as a photo-electrode.

(v) **Lead dioxide, PbO₂**

This exhibits the same instability as PbO and produces very small photo-effects.

(vi) **Red lead, Pb₃O₄**

Despite instability (a smaller weight of red Pb₃O₄ is on the test electrode after irradiation and the counter electrode gains a yellow-gold coating), this semiconductor is interesting in that it is p-type - a relative photovoltage of +90 mV is produced - and has an onset potential of about +0.7 V versus SCE. This means it possesses a large positive flat-band potential and might be a useful photo-cathode, responsive to visible light, if it can be stabilised.

(vii) **Samarium oxide, Sm₂O₃**

The large negative relative photopotential is encouraging, although the photocurrent onset potential of +0.25 V is too positive for an ideal material. Some of the white powder fell off the mesh and it is...
not possible to use weighings to check stability.

(xvii) Tin(II) oxide, SnO

No coating on the mesh could be obtained and no photo-effects were generated with 2 g of SnO in 500 ml of KCl.

(xix) Tellurium oxide, TeO₂

This behaved in a similar fashion to samarium oxide, but TeO₂ is even more unstable. Most of the white powder had been removed from the platinum mesh, and what remained was metallic in appearance.

(xx) Thallium(III) oxide, Tl₂O₃

This oxide in n-type but its positive photocurrent onset potential and severe instability render it useless as a photo-anode. This instability is reflected in a 50% weight loss of the oxide, the gaining of a brown coating on the counter electrode, and in the electrolyte acquiring a brown colouration.

(xxi) Uranium oxide, U₃O₈

No reliable photoeffects were produced and the electrode was not checked for stability.

3.3.4 Investigation of some titanates, chromates, and carbonates

Table 3.3 shows the results of some titanates, chromates, and carbonates, coated on a platinum mesh and immersed in an aqueous electrolyte.

(i) Calcium titanate, CaTiO₃

The photoeffects indicate this material to be an n-type semiconductor although its positive flat-band potential and large band gap make it unsuitable to efficiently utilise visible light. The small weight
<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Colour</th>
<th>Band gap in eV</th>
<th>Relative photopotential in mV</th>
<th>Relative photocurrent in µA at 0.0V vs SCE</th>
<th>Photocurrent onset potential in V vs SCE</th>
<th>Weight of material in g on the platinum mesh</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiO₃</td>
<td>Alfa Inorganics</td>
<td>White</td>
<td>3.4</td>
<td>-115</td>
<td>- 1.0</td>
<td>+0.05</td>
<td>0.008602</td>
<td>Stable? n-type (6% weight loss)</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>Alfa Products</td>
<td>Off-White</td>
<td>~3.0</td>
<td>Variable</td>
<td>~ 6.3</td>
<td>~+0.1</td>
<td>0.01544</td>
<td>Stable: unknown conductivity type</td>
</tr>
<tr>
<td>BaCrO₄</td>
<td>British Drug Houses</td>
<td>Yellow</td>
<td>2.8</td>
<td>- 30</td>
<td>0.0</td>
<td>~+0.3</td>
<td>0.006155</td>
<td>Unstable; n-type (33% weight loss)</td>
</tr>
<tr>
<td>Cr₂(CrO₄)₃</td>
<td>British Drug Houses</td>
<td>Green</td>
<td>?</td>
<td>- 10</td>
<td>~ 1.0</td>
<td>~+0.3</td>
<td>0.002400</td>
<td>Unstable? n-type (25% weight loss)</td>
</tr>
<tr>
<td>NiCrO₄</td>
<td>British Drug Houses</td>
<td>Brown</td>
<td>?</td>
<td>+11</td>
<td>0.0</td>
<td>?</td>
<td>0.005606</td>
<td>Very unstable; p-type (50% weight loss)</td>
</tr>
<tr>
<td>PbCrO₄</td>
<td>British Drug Houses</td>
<td>Orange</td>
<td>2.3</td>
<td>-190</td>
<td>- 2.0</td>
<td>+0.15</td>
<td>0.007025</td>
<td>Possibly stable; n-type (8% weight loss)</td>
</tr>
<tr>
<td>CoO₂</td>
<td>May &amp; Baker</td>
<td>Dark Pink</td>
<td>2.2?</td>
<td>- 70</td>
<td>2.0</td>
<td>0.05</td>
<td>0.009861</td>
<td>Very unstable; n-type (33% weight loss)</td>
</tr>
<tr>
<td>Cr₂(CO₃)₃·Cr(OH)₃</td>
<td>British Drug Houses</td>
<td>Olive Green</td>
<td>?</td>
<td>- 50</td>
<td>2.0</td>
<td>+0.05</td>
<td>0.000804</td>
<td>Very unstable? n-type (50% weight loss)</td>
</tr>
<tr>
<td>CuCO₃·Cu(OH)₂</td>
<td>British Drug Houses</td>
<td>Pale Green</td>
<td>?</td>
<td>- 40</td>
<td>- 0.5</td>
<td>~0.0</td>
<td>0.008628</td>
<td>Possibly stable; n-type (4% weight loss)</td>
</tr>
<tr>
<td>MnCO₃</td>
<td>Hopkins &amp; Williams</td>
<td>Brown</td>
<td>?</td>
<td>0</td>
<td>0.0</td>
<td>-</td>
<td>0.011335</td>
<td>No photoeffects</td>
</tr>
<tr>
<td>NiCO₃</td>
<td>British Drug Houses</td>
<td>Green</td>
<td>?</td>
<td>- 40</td>
<td>-14.0</td>
<td>+0.2</td>
<td>0.004019</td>
<td>Possibly stable; n-type (10% weight loss)</td>
</tr>
</tbody>
</table>

**TABLE 3.3** Photoeffects produced by some titanates, chromates and carbonates coated on a platinum mesh. The light filter is saturated CuSO₄, except for compounds with an asterisk (*) where dilute CuCl₂ is employed. For experimental conditions, see section 3.2.
loss of the CaTiO₃ electrode is due to handling.

(II) Lead titanate, PbTiO₃

The conductivity type of PbTiO₃ could not be ascertained by photo-induced voltage measurements: values ranging from +140 mV to -50 mV were noted. The relative photocurrent onset potential is too close to zero for the material to be a useful photo-electrode - whatever polarity it would adopt. Thus lead titanate, despite stability, is of limited value, and its colour suggests it would respond largely to near UV light.

(iii) Barium chromate, BaCrO₄

Results show this is n-type, but the small photoeffects and instability make it of limited use. The yellow chromate is easily dislodged from the platinum mesh and the electrolyte acquires a yellow colour characteristic of the chromate anion.

(iv) Chromium(III) chromate, Cr₂(CrO₄)₃

The instability of this chromate and the small photoeffects it produces mean it is of little interest.

(v) Nickel chromate, NiCrO₄

The small photoeffects and instability of p-type nickel chromate indicate this compound has no use in optical energy conversion. The electrolyte which stored the NiCrO₄ electrode before irradiation had a brown colour.

(vi) Lead chromate, PbCrO₄

The large photo-induced potential and absence of lead in the used electrolyte, shown by atomic absorption spectroscopy, infer this compound has potential as a photo-anode. However, the photocurrents it
promotes are not very large, and attempts to repeat the relative photopotential gave readings of about -60 mV, as opposed to the -190 mV quoted in table 3.3.

(vii) Cobalt carbonate, CoCO₃

The disadvantage of cobalt carbonate is the large weight loss incurred; the illuminated electrode turned from pink to brown and the counter electrode gained a brown coating. Although a reasonable photopotential is generated, the magnitude of relative photocurrents and the positive onset limit the use of this compound.

(viii) Basic chromium(III) carbonate Cr₂(CO₃)₃·Cr(OH)₃

Only a very small amount of the fine green powder adhered to the mesh, and all of the 50% weight loss noted after irradiation cannot be attributed to photo-solublisation, as the powder was easily dislodged. This material might be useful as a photo-anode if its stability can be clarified.

(ix) Basic copper(II) carbonate, CuCO₃·Cu(OH)₂

A robust electrode was obtained which underwent only a slight weight loss - attributable to handling. This compound is n-type, although the photocurrent onset potential should preferably be more negative for efficient light harnessing. It is worth pursuing further investigations since the semiconductor electrode evolved a gas upon irradiation at large positive bias (>0.8 V).

(x) Manganese(II) carbonate, MnCO₃

No photoeffects were produced and the stability was not checked.

(xi) Nickel carbonate, NiCO₃

The semiconductor mesh electrode showed only a slight weight loss,
and this n-type material is worth further investigations despite its positive onset potential. The weight loss of the NiCO₃ electrode amounts to 10% and cannot be totally attributed to photochemical instability, and no changes occurred to the counter electrode or electrolyte.

3.3.5 Investigation of some sulphides

Table 3.4 illustrates the results of investigations into the photo-electrochemical properties of some sulphide materials.

(i) Copper(I) sulphide, CuS

Photocurrents, but not photopotentials, were produced by this material coated on a platinum mesh. Instability resulted from irradiation of CuS as the used electrolyte gained a brown colouration.

(ii) Iron(II) sulphide, FeS

4 g of the fine grey metallic powder were used in the suspension to coat the mesh. FeS behaves as an n-type semiconductor but is unstable as the test electrode had a faint yellow coating after illumination, and the electrolyte contained a yellow precipitate and smelt faintly of hydrogen sulphide.

(iii) Mercury(II) sulphide (black), HgS

A mesh-coated electrode exhibited relative photopotentials that were both positive and negative, (+27 mV, -88 mV). Anodic photo-induced currents up to +15μA were obtained at biasing voltages positive of +0.2 V. The electrolyte after irradiation was yellowish and smelt of hydrogen sulphide. The purity of this sample is in question, and in a later chapter are results of black HgS that is known to be authentic.
<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Colour</th>
<th>Band gap in eV</th>
<th>Relative photopotential in mV</th>
<th>Relative photocurrent in μA at 0.0V vs SCE</th>
<th>Photocurrent onset potential in V vs SCE</th>
<th>Weight of material in g on the platinum mesh</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS*</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>?</td>
<td>0</td>
<td>-20.0</td>
<td>+0.4</td>
<td>0.006584</td>
<td>Unstable; (12% weight loss)</td>
</tr>
<tr>
<td>FeS</td>
<td>Unknown</td>
<td>Grey metallic</td>
<td>?</td>
<td>-40</td>
<td>-3.0</td>
<td>+0.1</td>
<td>0.004862</td>
<td>Unstable; n-type (3% weight loss)</td>
</tr>
<tr>
<td>HgS*</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>0.9</td>
<td>Variable</td>
<td>0.0?</td>
<td>?</td>
<td>0.013218</td>
<td>Unstable; see text (14% weight loss)</td>
</tr>
<tr>
<td>HgS*</td>
<td>Fisons</td>
<td>Red</td>
<td>2.0</td>
<td>See text</td>
<td>See text</td>
<td>See text</td>
<td>0.007518</td>
<td>Stable?</td>
</tr>
<tr>
<td>MoS₂</td>
<td>Unknown</td>
<td>Metallic grey</td>
<td>1.9</td>
<td>[1-59 1-26]</td>
<td>-1.0</td>
<td>+0.1</td>
<td>0.001362</td>
<td>See text; (55% weight loss)</td>
</tr>
<tr>
<td>PbS</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>0.4</td>
<td>+87</td>
<td>0.0</td>
<td>0.0</td>
<td>0.009800</td>
<td>Unstable; p-type (30% weight loss)</td>
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<tr>
<td>Sb₂S₃*</td>
<td>British Drug Houses</td>
<td>Black</td>
<td>1.7</td>
<td>+2</td>
<td>0.0</td>
<td>-</td>
<td>0.008562</td>
<td>See text</td>
</tr>
<tr>
<td>Sb₂Se</td>
<td>British Drug Houses</td>
<td>Orange</td>
<td>~2.4</td>
<td>+150</td>
<td>-1.8</td>
<td>~+0.05</td>
<td>0.005700</td>
<td>Unstable; p-type (60% weight loss)</td>
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<tr>
<td>SnS</td>
<td>British Drug Houses</td>
<td>Grey</td>
<td>1.3</td>
<td>+85</td>
<td>~0.0</td>
<td>-</td>
<td>0.011140</td>
<td>Unstable; p-type (30% weight loss)</td>
</tr>
<tr>
<td>TiS₂</td>
<td>Laporte Industries</td>
<td>Brown</td>
<td>1.2</td>
<td>+20</td>
<td>+0.5</td>
<td>?</td>
<td>0.004934</td>
<td>TiS₂ gained weight p-type (3% weight gain)</td>
</tr>
<tr>
<td>WS₂</td>
<td>Alfa Inorganics</td>
<td>Grey metallic</td>
<td>1.1</td>
<td>~40</td>
<td>0.0</td>
<td>-</td>
<td>Suspension experiment - see text</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3.4** Photoeffects produced by some sulphide materials coated on a platinum mesh. The light filter is saturated CuSO₄, except for asterisked compounds (*), where dilute CuCl₂ is employed. For experimental conditions, see section 3.2.
Mercury(II) sulphide (red), HgS

With an aerated electrolyte, small photo-induced potentials (± 30 mV) were seen, but with nitrogen-purging, a negative relative photovoltage (>150 mV) was observed. The sign of the relative photocurrent at zero bias was dependent on the presence or absence of oxygen; in an aerated electrolyte, a relative photocurrent of -1.0 μA and onset potential of ~+0.25 V were obtained, but in a deoxygenated system, the photocurrent was +1.0 μA and the onset ~-0.25 V. No visible change occurred to the electrodes or the electrolyte, and the 4% weight loss to the HgS electrode is considered to be due to handling. Thus, this sulphide's stability, its capacity to give a large photopotential, and negative photocurrent onset potential suggest it may form a useful photoanode, responsive to visible light (band gap = 2.0 eV).

Molybdenum(IV) sulphide, MoS₂

MoS₂ takes the form of a metallic powder which tends to float off the platinum mesh while immersed in the electrolyte. The sample employed contained both n- and p-type molybdenum sulphide, as revealed by a plot of potential vs time with intermittent illumination - see figure 3.6.

On initial illumination at A, a positive overshoot is seen (the potential rapidly alters from -105 mV to -96 mV), - the response of p-type MoS₂. The potential then gradually decreases to -164 mV, the level illumination potential. Thus the relative photopotential of -59 mV {=-164 mV - (-105 mV)} is that of the n-type material. At B, the light is switched off, but the potential becomes more negative, and temporarily levels at -190 mV. Thus the relative photopotential of p-type MoS₂ is +26 mV {=-164 mV - (-190 mV)}. At point C, illumination
Potential vs SCE

-96 mV

-105 mV

light on

light off

light off

-164 mV

light on

light on

light off

-190 mV

-190 mV

45

30

mins

mins

Fig. 3.6
Plot of potential versus time for an MoS$_2$-coated platinum mesh against an SCE. Irradiation occurs as indicated, and experimental details are given in Section 3.2.

is recommenced and the potential returns to -164 mV, confirming the p-type effect. At D, irradiation is ceased; the potential drops temporarily to -190 mV (point E), and eventually returns to the initial dark voltage (F). The n-/p-type behaviour is reflected in photocurrent-time plots too (see figure 3.7). The relative photocurrent obtained at +0.2 V bias is anodic, but the plot contains a negative overshoot upon initial illumination and an immediate positive overshoot when irradiation is terminated. These overshoots indicate p-type components participate in the photocurrent. It seems that n-type predominates, since these results suggest electrons are majority carriers. The poor adhesion of the sulphide to the mesh means the weight loss of 55% does not necessarily infer instability.
(vi) Lead(II) sulphide, PbS

This material does not adhere firmly to the platinum gauze. A relative photopotential of +87 mV implies the sulphide is p-type. Small anodic photocurrents (about 5 μA) were noted under positive biasing voltages, and no visible changes occurred to either electrodes or electrolyte. However, with negative biasing, the platinum counter electrode gained a yellow colour (sulphur?), the black PbS electrode turned grey - due to lead - and atomic absorption analysis of the electrolyte revealed lead in solution. These features were observed whether irradiation had occurred or not, although illumination resulted in a larger weight loss of the PbS electrode and a greater lead concentration detected in solution. The photo-induced currents seen under negative bias ranged from -40 μA in a deoxygenated electrolyte to -400 μA for an aerated one. The instability of PbS is its major limitation.
(vii) Antimony(III) sulphide, $\text{Sb}_2\text{S}_3$

No photo-currents were promoted, and a relative photovoltage of +2 mV infers $\text{Sb}_2\text{S}_3$ may be p-type. Some of the black powder was dislodged from the mesh, so weighings cannot indicate stability, although no visible changes occurred to the system.

(viii) Antimony(V) sulphide, $\text{Sb}_2\text{S}_5$

This sulphide is p-type, as inferred from the positive photo-induced potential. With anodic biasing, relative photocurrents up to +10 $\mu$A were obtained. Decomposition of the $\text{Sb}_2\text{S}_5$ took place with illumination at negative applied potentials: the sulphide electrode turned metallic brown, the electrolyte contained an orange-brown precipitate and acquired a yellow-green colouration, although the counter electrode was unaltered. The photocurrents were large (a few hundred micro-amps). It may be of value to investigate $\text{Sb}_2\text{S}_5$ further, because of the large positive photo-induced potential, and to see if its decomposition can be prevented.

(ix) Tin(II) sulphide, $\text{SnS}$

Much solubilisation of this compound occurred, as evidenced by tin detection in used electrolytes with atomic absorption spectroscopy. $\text{SnS}$ is p-type, although the photo-induced potential of +85 mV is not always reproducible. Very small photocurrents were produced: this compound is of no value in optical energy harnessing.

(x) Titanium(IV) sulphide, $\text{TiS}_2$

This material dissolves in water to give a blue solution, and the positive relative photopotential indicates it to be p-type. The positive photo-induced current at zero bias means the flat-band potential will be too negative for $\text{TiS}_2$ to be an efficient photocathode, and its
stability is in question: the test electrode gains weight and the used electrolyte smells strongly of hydrogen sulphide.

\[ (x) \] Tungsten(IV) sulphide, WS\(_2\)

The metallic powder floated off the platinum gauze upon immersion in an electrolyte, so a suspension experiment was performed. The electrolyte was not stirred while experiments were in progress. Negative relative photovoltages were obtained, but after leaving the cell for a few days, the potential time plot indicated a positive component - see figure 3.8. In (a) the relative photopotential is \([+158 \text{ mV} - (+198 \text{ mV})] = -40 \text{ mV}\), and the only suggestion of deviation from n-type behaviour is the negative overshoot (*) seen on termination of illumination. In (b) positive and negative 'humps' are seen at the beginning and ending of irradiation, respectively. The positive 'hump' represents +9 mV \([= 158-149]\) and the negative one +11 mV \([= 115-104]\) and indicates a meta-stable photo-induced voltage of about +10 mV, due to p-WS\(_2\). The relative photopotential of n-WS\(_2\) here is -34 mV \([= +115 - (+149)]\). Thus this sample of tungsten(IV) sulphide is predominantly n-type, although p-type properties appear after a long immersion period.

Under anodic bias, positive photo-induced currents reflect the predominant n-type activity: at +0.2 V bias, a relative photocurrent of +34 \(\mu\)A obtains, but at larger applied voltages, the dark current exceeds +100 \(\mu\)A. Oxygen reduction with cathodic biasing causes large dark currents. It is not known if WS\(_2\) undergoes solubilisation.

3.4 Discussion

The oxides, titanates, chromates, carbonates, and sulphides reported
Fig. 3.8(a)
Plot of potential vs time for WS₂ in suspension, one day after cell has been set up. See Section 3.2 for experimental details. *
= negative overshoot.

Fig. 3.8(b)
Plot of potential vs time for WS₂ in suspension, ten days after setting up the cell. The experimental details are in Section 3.2.
in sections 3.3.3 to 3.3.5 have not been subjected to a thorough investigation. As stated at the beginning of this chapter, the aim was to pin-point potential semiconductors for optical energy harnessing and then to perform more detailed research on those selected. For the forty-three materials probed, no attempt was made to ensure identical conditions for each compound: the chemicals were used straight from the bottle with no pre-treatment, and although identical platinum meshes formed the support for each compound, the extent of mesh coverage and effective surface area may vary. It is not intended to compare the properties of one material with another.

Those which show no photoeffects may do so for the following reasons: (i) the platinum-semiconductor junction may be rectifying, and not ohmic, which would prevent majority carriers passing to the external circuit, see figure 3.9. This illustrates ohmic and rectifying junctions for n- and p-type semiconductors in contact with platinum. "Band-bending" occurs within the semiconductor due to initial mismatch between its Fermi level and that of platinum. $E_C$, $E_V$, and $E_F$ have their meanings as before. The band bending forms a barrier (rectifying junction) or an aid (ohmic junction) to majority carriers crossing to or from platinum. The material may adhere so weakly to platinum that this inhibits electron transfer. (ii) The semiconductor and electrolyte may form an accumulation layer (see p.19). (iii) Short circuiting within the electrode will limit carriers entering the external circuit. (iv) All the photogenerated carriers may react with the semiconductor lattice and cause decomposition. These factors may cause photoeffects to be smaller than they might be with a different experimental method.

A major fault, not realised until this work was nearly complete, is the failure to de-oxygenate the electrolyte. Oxygen is an electron
Fig. 3.9(a)
Ohmic Junction - no barrier to electrons flowing from semiconductor to platinum.

Fig. 3.9(b)
Rectifying Junction - a barrier exists for electron flow from the semiconductor to platinum.

Fig. 3.9(c)
Ohmic Junction - no barrier for holes moving from the semiconductor to platinum (equivalent to electron flow in the opposite direction).

Fig. 3.9(d)
Rectifying Junction - a barrier prevents holes leaving the semiconductor (i.e. no electrons can enter from the platinum).
acceptor and can influence photo-induced voltages and cause large dark currents under cathodic biasing. One feature common to all the materials used is large negative photo-induced currents at these biasing voltages; these currents are almost entirely due to oxygen reduction to the superoxide ion, \( \text{O}_2^- \). Bubbling nitrogen through the electrolyte for several hours reduces the dark current to near zero, and diminishes photo-induced currents. The 'oxygen effects' could be due to uncovered platinum exposed to the electrolyte, rather than the semiconductor itself.

Some of the materials tried were reported on in the literature during the course of the experiments. Bismuth oxide was noted to be n- and p-type, unstable, and possess a flat-band potential close to zero [64]; the sample used here was p-type. Cadmium oxide generated positive photocurrents [10] but another report states it shows no photoresponse [64]. The latter observation is confirmed here. Chromium(III) oxide is noted to be p-type, unstable, and exhibit a poor photoresponse [64]; this is confirmed here, although \( \text{Cr}_2\text{O}_3 \) appears n-type. \( \text{PbO} \) is mentioned as being n-type and unstable [64], but the sample employed here acts as p-type. The work on copper(II) oxide agrees, in terms of conductivity type and flat-band potential, with that reported by Hardee and Bard [64], although the question of stability needs investigation. \( \text{Pb}_2\text{O}_4 \) has been employed in a Schottky barrier photovoltaic cell [217], and the same publication notes that \( \text{PbO} \) can be both n- and p-type. The literature reports of \( \text{MoS}_2 \) have been described in Chapter Two (pp.83-84) and the properties noted with a mesh electrode confirm the n- and p-type behaviour.
3.5 Conclusions

Results of the brief investigations described in this chapter warrant more research on the materials listed below.

**CuO** - This oxide appears to function as a photo-cathode sensitive to visible light. Its stability needs qualification: decomposition of CuO has been communicated [48,64], but results presented here do not confirm this. The accumulation of gas bubbles on the oxide electrodes needs investigation.

**Pb₃O₄** - Instability is the main disadvantage with this semiconductor, and research is needed to elucidate the decomposition reactions and then to suppress them. The positive onset potential of relative photocurrents would render Pb₃O₄ a useful photo-cathode, and the band gap of 2.1 eV makes it sensible to visible light.

**PbCrO₄** - It would be interesting to confirm the stability of lead chromate and obtain photocurrent-applied potential plots to evaluate its use as a photo-anode. It is likely that the photocurrent onset potential is too positive, however.

**Cr₂(CO₃)₃·Cr(OH)₃** - A negative photo-induced voltage means this is an n-type semiconductor, and the relative photocurrent onset potential lies close to zero (vs SCE). Thus basic chromium(III) carbonate could operate as an anode under illumination and more work is needed to check the stability, as it feebly adhered to the platinum mesh.

**CuCO₃·Cu(OH)₂** - The same comments as above apply, except that this carbonate was not dislodged from the electrode and weighings inferred stability. Basic copper(II) carbonate occurs as the mineral 'malachite' and it may be possible to employ a mineral section as photo-anode.
Sm₂O₃, NiO, NiCO₃ - These compounds' stability needs to be affirmed and their photo-induced current onset potentials are too positive for the semiconductors to behave as efficient photo-anodes. However, in a deoxygenated electrolyte this onset voltage might shift negatively.

FeS - Iron(II) sulphide gives observable signs of decomposition, but further work could be directed to understand and eliminate instability. FeS may then afford a photo-anode.

Sb₂S₅ - The positive relative photovoltage signifies Sb₂S₅ has p-type conductivity, but stabilisation is needed to enable evaluation of its practicality as a photo-cathode. To this end should further research be directed.

MoS₂, WS₂ - Molybdenum(IV) sulphide is known to be unstable under certain conditions [202,203], but it would be worthwhile pursuing it to see whether (i) reported properties in the literature can be repeated with a mesh electrode, (ii) any other means of stabilisation exist. Tungsten(IV) sulphide is considered by Tributsch to have similar properties as MoS₂ [204]. It is of interest, therefore, to see if WS₂ is stable and can be used in a photoelectrochemical cell.

Red HgS - A detailed exploration of the photoelectrochemical properties of red mercury(II) sulphide forms the remaining chapters of this thesis.
CHAPTER FOUR

A DETAILED STUDY OF THE PHOTOCHEMICAL PROPERTIES
OF RED MERCURY(II) SULPHIDE
CHAPTER FOUR

4.1 Introduction

Red HgS (vermilion, cinnabar) was singled out in Chapter Three since it exhibited a reasonable photo-induced potential and showed no signs of immediate instability. In this Chapter, the production of currents and voltages by an irradiated red mercury(II) sulphide electrode is investigated in detail.

4.2 Experimental

An air-tight electrochemical cell with provision for gas bubbling was used for all the ensuing experiments. This is shown in figure 4.1 and occupies the same place on the optical bench as the non air-tight cell (see figure 3.1). The experimental techniques described in Chapter Three are employed, and most of the currents were measured with a Wenking LB 75L potentiostat. The water used in the HgS suspension was de-oxygenated by bubbling with nitrogen for 30 minutes before adding the sulphide, which tended to form globules, so the suspension was boiled before dispersion ultrasonically. It was necessary to repeat the dipping-drying procedure three or four times to obtain an even red coating (of average weight 0.025g) on the platinum mesh. The electrode was stored for 15 hours in a deoxygenated solution contained in a screw-top jar before measuring any photoelectrochemical properties in that particular electrolyte. Copper(II) chloride acted as heat/UV filter and light of power of about $2.5 \times 10^{-2}$ W.cm$^{-2}$ was incident on the HgS electrode.
Fig. 4.1
Air-tight apparatus for photoelectrochemical studies. (In some cases, the vessel was a 'Quickfit' 250ml flat-flange flask, in which 150ml of electrolyte was used.) The cell is housed in a polystyrene case as before, with a window 3.0×1.5 cm to allow irradiation of the mesh only.
4.3 Results

The nature of the electrolyte influences photoelectrochemical reactions at semiconductor electrodes, and such influence was very pronounced for red HgS. Sodium nitrate was used as an 'inert' electrolyte to probe photo-responses at the HgS/H2O junction where no effect of the salt is observed.

4.3.1 Red mercury(II) sulphide in a sodium nitrate electrolyte

4.3.1.1 Properties under 'standard conditions'

'Standard conditions' means the optical bench of figure 3.1 is employed (with CuCl2 filter), the electrolyte is deoxygenated 0.1M NaNO3 (pH 7 - unbuffered) with N2 bubbling very slowly through, approximately 0.025g of 'Fisons' red HgS coats the platinum mesh, and an identical uncoated mesh forms the counter electrode. Using the circuit shown in figure 1.6(a), [p.16], the HgS electrode registered a potential in the dark varying from +20mV to -110mV (vs SCE), and one upon illumination ranging from -150mV to -280mV (vs SCE). The relative or photo-induced potential lies between -100mV to -250mV. Figure 4.2 illustrates a plot of potential change with time. When a fresh electrode is used, the time taken to attain the level photovoltage is usually longer on the first illumination than for subsequent runs, and the photovoltage declines, after this first illumination, to a dark potential negative of that of the initial dark potential. However, all subsequent plots are like in figure 4.2. The adsorption/desorption of electrolyte species to/from HgS may be influenced by light, and a stable system remains once the surface has been irradiated. Potentials in the dark and upon illumination are reproducible for a given electrode, but these values are not necessarily reproducible for different electrodes. This is attributed to differences in electrolyte species' adsorption
and surface area of different electrodes. The relative photopotential is more or less reproducible.

With the circuit shown in figure 1.6(b), [p.16], no current flows in the dark when the HgS electrode is at the same potential as the reference electrode - "zero bias". Illumination produces an instantaneous positive current (an 'overshoot') which declines and levels at a value positive of the initial dark current. Ceasing irradiation returns the current to the dark value. Figure 4.3 illustrates this.

This type of photocurrent plot is seen from biasing potentials from \(-0.3V\) to \(+0.6V\). Negative of \(-0.3V\), a cathodic relative photocurrent is obtained with overshoots still present. The initial overshoot remains positive until about \(-0.6V\). At applied potentials of \(+0.7V\) or greater, a plot like that in figure 4.4 is seen.
Fig. 4.3
Photocurrent plot for red HgS held at 0.0V vs SCE under 'standard' conditions. The relative photocurrent $\text{I}_\text{ph} = (2.0 - 0.0) = 2.0 \, \mu\text{A}$.
---: negative overshoot occasionally seen on ending illumination.

Fig. 4.4
Photocurrent plot for red HgS at +0.9V (vs SCE) under 'standard' conditions.

The dark current is not zero: this is because the HgS electrode is not an insulator in the dark and bare platinum will allow a current to flow due to the applied potential. On illumination, the level photocurrent exceeds the initial overshoot. An explanation of overshoots
was presented in Chapter Three [pp.99-100]: the large applied voltage here encourages separation of more charge carriers and causes the anodic photocurrent to override the cathodic back-component.

A plot of relative photocurrent vs applied bias is shown in figure 4.5. Between ±0.7V the plot is essentially a straight line, and increasing anodic and cathodic photo-induced currents at potentials exceeding ±0.7V are due to large dark currents resulting from uncovered platinum at the semiconductor electrode. The plots of figures 4.3 to 4.5 are reproducible from electrode to electrode and the current magnitudes are invariant, more or less (see later, however, for 'darkening' of red HgS). The relative anodic photocurrent onset potential marked in figure 4.5 ranges between -0.15V and -0.35V: -0.25 is taken as average. This is the applied voltage needed to inhibit relative photocurrent production (i.e. the dark current and that on illumination are equal, although overshoots are still observed) and represents the condition of either band-flattening or of the electron-hole generation rate equalling the recombination rate with some band-bending remaining. In the former case the onset voltage equals the flat-band potential. In the latter case, it is a voltage slightly positive of the flat-band potential.

4.3.1.2 Effect of altering electrolyte pH

The standard electrolyte pH is varied from 2 to 12 by adding nitric acid or sodium hydroxide. No effect on the shape of photocurrent/photo-voltage - time plots is seen, and the relative photovoltage is unaltered. Individual voltages and the relative photocurrent onset potentials are affected - see figures 4.6 and 4.7. Voltages in the dark and on illumination fall on a line of slope -58 mV.pH⁻¹. The Nernst equation relates standard potentials to observed potentials when
Fig. 4.5
Plot of relative photocurrent vs applied potential for
red HgS under 'standard' conditions.

approx. onset potential of
relative anodic photocurrent
(= -0.25V vs SCE)
Fig. 4.6
Variation of dark potential (---O---) and potential on illumination (---X---) with 'standard' electrolyte pH for red HgS.
Fig. 4.7
Variation of onset potential of relative anodic photocurrent for red HgS with 'standard' electrolyte pH.

Applied potential in V vs SCE

slope = -0.072 V, pH$^{-1}$
Fig. 4.8
Variation of dark current (—X—) and current on illumination (—O—) for red HgS held at 0.0V vs SCE with 'standard' electrolyte pH.

Current in μA

pH
electrolyte species' concentration is altered:

\[
E = E^\circ + \frac{2.303 \ RT}{nF} \ \log_{10} \frac{[\text{Oxidised form}]}{[\text{Reduced form}]} \quad [4-1]
\]

\(E\) = observed potential; \(E^\circ\) = standard potential; \(R\) = gas constant; 
\(T\) = absolute temperature; \(F\) = Faraday constant; \(n\) = no. of electrons participating in the oxidation-reduction.

When considering pH variation, \(n=1\), [reduced form] = 1, \(T=298.15\) K and [oxidised form] = \([H^+]\).

So \(E = E^\circ + \frac{2.303 \ RT}{F} \log_{10}[H^+]\)

Now \(pH = -\log_{10}[H^+]\)

and \(2.303RT/F = 0.059V\) (if \(E^\circ\) is expressed in volts)

Hence \(E = E^\circ - 0.059\) pH \[4-2\]

Equation [4-2] predicts that a given potential will be 59 mV negative of a standard potential for each pH unit. This is found for red HgS, where potentials vs SCE become cathodic as the electrolyte alkalinity increases ~ by -58 mV.pH\(^{-1}\) (figure 4.6). The relative photopotential does not vary with pH - so band bending is unaffected, but the energies of the band edges shift negatively with increasing alkalinity. \(H^+\) and \(OH^-\) may act as 'potential determining ions' for red HgS.

In figure 4.7, the onset potential varies by -0.072V.pH\(^{-1}\). This is tolerably close to Nemstian behaviour to confirm the shifting of band edges with pH. The individual points of figure 4.7 were obtained by "sweeping" the bias at 1 mV.s\(^{-1}\), plotting the currents in the dark and light, and taking the crossover point of dark and light current plots as the onset. Figure 4.8 shows that increasing pH augments the currents at zero bias. The presence of bare platinum at the sulphide
electrode precludes an explanation of this purely in terms of HgS and its photogenerated positive holes; if the electrode were truly an insulator in the dark, no current would flow at any pH. However, the photocurrent alters more rapidly with pH than does the dark current, which means \( \cdot \text{OH} \) is oxidised at illuminated red HgS.

4.3.1.3 Wavelength response

The CuCl₂ filter was replaced by water, in which broad-band interference filters were suspended in clear polythene bags, and photocurrents and voltages obtained.* Figure 4.9 shows the action spectra. The relative photocurrent at zero bias is 0.0µA at 650 nm and rapidly rises to maximise at 550 nm. This increase corresponds to the band gap of 2.0 eV, equivalent to a wavelength of 619 nm. The photocurrent falls at shorter wavelengths, as the principal excitation energy has now been exceeded. The relative photovoltage has a similar action spectrum, but a positive value at sub band-gap wavelengths is observed. This is not seen for all samples of red HgS, and will be mentioned later (section 4.4).

4.3.1.4 Light intensity effects

Copper(II) chloride forms the heat/UV filter, and the intensity is varied by placing neutral density filters in front of the window of the polystyrene case that houses the cell. Figure 4.10 shows the variation in relative photovoltage [part (a)] and relative photocurrent at +0.3V bias [part (b)] with % transmission. 100% corresponds to the standard optical bench with no filters. The current plot is nearly linear, but the voltage shows no such relationship to % transmission. A 'light intensity' in arbitrary units was obtained for each neutral density filter with a crude selenium cell placed where the HgS electrode lies.

* Details of the broad-band interference filters are given in Appendix III.
Variation of relative photopotential (——) [left-hand axis] and relative photocurrent (—) [right-hand axis] for red HgS in 'standard' electrolyte.
Fig. 4.11(a)

Relative Photocurrent in J/A at +0.3 V bias vs SCE

Fig. 4.11(b)

Light Intensity (arbitrary units)
The 'arbitrary units' are readings on a meter coupled with a 100 Ω parallel resistance connected to the Se cell. Figure 4.11 indicates the relative photovoltage is linear with \( \sqrt{\text{intensity}} \) [part (a)], and the relative photocurrent directly proportional to intensity [part (b)]. This is expected, as the photocurrent should be proportional to the number of charge carriers available, which is proportional to the number of photons incident on the HgS. The photovoltage is not directly controlled by the carrier generation and separation rates, but is influenced by electron-hole recombination to a greater extent than are photocurrents.

Recombination results in a linear dependence of photovoltage on an intensity function less than unity - in this case, the square root. Further complications will arise from uncoated platinum in the sulphide electrode.

4.3.1.5 Stability of red HgS

The various electrodes used to obtain the results in sections 4.3.1.1 to 4.3.1.4 were not subjected to direct stability tests, but the following observations indicate gross instability is not found:

(i) used electrodes show a weight loss of 1-2% - attributable to handling; (ii) the counter electrode gains no visible or weighable coating; (iii) the used electrolyte is clear and colourless and its UV/visible spectrum contains no peaks corresponding to an Na$_2$S or Hg(NO$_3$)$_2$ solution. However, the irradiated face of the HgS electrode did occasionally become dark red/brown. This phenomenon, termed 'darkening' or 'blackening', is dealt with in great detail in Chapter Five, but is not considered a feature of 'instability' as the weight loss of a used darkened electrode is no different to that of an electrode undergoing no colour change. The electrodes mentioned above
were not irradiated for more than 3 hours at the most, and HgS solublisation might be a slow process. To check this, two separate stability experiments were performed.

2g of 'Fisons' red HgS were dispersed in 500 ml of 0.1M NaNO₃ contained in a gas jar. The suspension was vigorously stirred with a magnetic bead and irradiated for ten days with a 125W mercury lamp immersed in the suspension. The HgS and electrolyte were separated by filtration and no visible changes were observed. The electrolyte was analysed by atomic absorption spectroscopy and no solublised mercury, within the reliable detection limit, was detected (see Appendix II). A corresponding HgS/NaNO₃ suspension was stirred in the dark for ten days and identical results obtained. These features are taken as evidence for photochemical stability of red HgS in an 'inert' electrolyte.

The second stability experiment was to irradiate an HgS mesh electrode in a current-measuring circuit for a length of time and then analyse the electrolyte for mercury. The results are shown in Table 4.1. The total number of electrons passed (as relative anodic photocurrent) can be correlated to a mercury concentration if one assumes the following reaction occurs:

\[ \text{HgS} \rightarrow 2\text{hv} \rightarrow \text{Hg}^{2+} + \text{S} + 2\text{e} \] \[4-3\]

If all the photocurrent is due to electrons from the photo-anodic oxidation of HgS, equation [4-3], then one mercury atom should be solublised per two electrons flowing. Therefore:

\[ 3.35 \times 10^{17} \text{ electrons should solublise } 1.675 \times 10^{17} \text{ Hg atoms} \]

\[ 1.675 \times 10^{17} \text{ Hg atoms weigh } 1.675 \times 10^{17} \times 200 \text{ g} \]

\[ 6.022 \times 10^{23} \]
Table 4.1: Data to evaluate stability of red HgS while producing photocurrents in an NaNO₃ electrolyte

<table>
<thead>
<tr>
<th>RELATIVE PHOTOCURRENT IN μA*</th>
<th>IRRADIATION TIME IN S</th>
<th>NO. OF ELECTRONS PASSED</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.50</td>
<td>5700</td>
<td>1.77 × 10^{16}</td>
<td>Gas at both electrodes</td>
</tr>
<tr>
<td>+0.25</td>
<td>6300</td>
<td>0.98 × 10^{16}</td>
<td>Irradiated through 500-550 nm filter</td>
</tr>
<tr>
<td>+1.50</td>
<td>4500</td>
<td>4.21 × 10^{16}</td>
<td>pH 9.2 electrolyte: gas at both electrodes</td>
</tr>
<tr>
<td>+2.50</td>
<td>5700</td>
<td>8.89 × 10^{16}</td>
<td>pH 11.5 electrolyte: gas at HgS</td>
</tr>
<tr>
<td>+4.50</td>
<td>6300</td>
<td>1.77 × 10^{17}</td>
<td>pH 11.5 electrolyte: gas at HgS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.35 × 10^{17}</td>
<td>total no. of electrons passed</td>
</tr>
</tbody>
</table>

* obtained at 0.0V vs SCE
Since 250 ml of electrolyte were employed, the theoretical mercury concentration in solution should be \[
\frac{55.6 \, \mu g \cdot ml^{-1}}{250}
\]
i.e. \(0.22 \, \mu g \cdot ml^{-1}\)

Unfortunately, the lowest reliable detection limit is \([Hg] = 7.5 \, \mu g \, ml^{-1}\) (see Appendix II), and the mercury determination of the used electrolyte was below this limit. The stability, or otherwise, of red HgS while promoting photocurrents has not, therefore, been resolved.

Attempts to irradiate the electrode at positive bias for longer periods to pass a greater number of electrons usually resulted in a darkening of the HgS. So the question of stability is resolved with an investigation of the blackened form - see Chapter Five.

The assumption that each electron causing anodic photocurrents comes from the HgS lattice is somewhat dubious, as in section 4.3.1.2 it is postulated that hydroxyl ions are oxidised at photo-generated positive holes. Electrons originally associated with OH\(^-\) would contribute to photocurrents and the notion of "one solublised Hg atom per two electrons" is not completely true.

In Table 4.1 it is noted that gases are evolved from (or, rather, a gas bubble or two slowly grows at) the HgS and counter electrodes. These gases were not identified but are mentioned later. The presence of gas at the HgS electrode has a detrimental effect on photovoltages. The fresh electrode gave a typical photopotential plot (figure 4.2) but when it had been irradiated under current conditions for some time and accumulated surface bubbles, positive relative photopotentials were obtained and plots similar to those for an aerated or oxygenated electrolyte were seen - see section 4.3.1.7. The gas may be oxygen.
4.3.1.6 Effect of varying sodium nitrate concentration

NaNO₃ can only be considered as 'inert' if photo-effects are invariable with its molarity. Table 4.2 shows results of an electrode in electrolytes of various nitrate concentrations. The same electrode was employed and the first run was done in 1M NaNO₃, followed by 0.1M, .... down to water. The 10M NaNO₃ experiment was performed last in case this very high salt concentration affected the HgS. It was found that some darkening occurred for [NaNO₃] = 10M, and the 8 μg·ml⁻¹ of mercury detected by atomic absorption analysis is suspicious, as the spectrophotometer responded badly with such a concentrated solution. Table 4.2 indicates there is no marked influence on photo-effects from varying NaNO₃ since: (i) dark and illumination potentials follow no trend; (ii) the relative photopotential falls within the experimental limits seen before; (iii) the photocurrents do not vary greatly with [NaNO₃]: larger ones are found at lower concentrations where ion transport will be easier; (iv) the onset potential is nearly constant; (v) no detectable mercury is solublised, and the electrode undergoes a 0.5% weight loss after each concentration run; (vi) the response time and shape of current/voltage - time plots is the same, within experimental error. Thus sodium nitrate is confirmed as a non-participating, 'inert' electrolyte for HgS.

4.3.1.7 Effect of oxygen in the electrolyte

In an aerated electrolyte, the potential-plots are not repeatable, even for successive illuminations, and the relative photovoltage ranges from +50mV to -50mV. Current-time plots are similar to those in figures 4.3 and 4.4 although the photocurrent onset is at about +0.2V vs SCE, and very large currents are noted at negative biasing potentials (see Chapter Three). The magnitude of photocurrents is
<table>
<thead>
<tr>
<th>$[\text{NaNO}_3]$ in mol.dm$^{-3}$</th>
<th>Dark Potential in mV vs SCE</th>
<th>Illumination Potential in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in $\mu$A at 0.0V vs SCE</th>
<th>Relative Photocurrent onset potential in V vs SCE</th>
<th>$[\text{Hg}]$ in used electrolyte in $\mu$g.ml$^{-1}$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^1$</td>
<td>+ 30</td>
<td>-100</td>
<td>-130</td>
<td>+0.2</td>
<td>+1.0</td>
<td>-0.25</td>
<td>8</td>
</tr>
<tr>
<td>$10^6$</td>
<td>+155</td>
<td>-5</td>
<td>-160</td>
<td>+0.2</td>
<td>+2.0</td>
<td>-0.35</td>
<td>~3*</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>+25</td>
<td>-120</td>
<td>-145</td>
<td>+0.7</td>
<td>+2.0</td>
<td>-0.25</td>
<td>0*</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>+15</td>
<td>-130</td>
<td>-145</td>
<td>+0.4</td>
<td>+0.8</td>
<td>-0.30</td>
<td>0*</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0</td>
<td>-185</td>
<td>-185</td>
<td>+0.5</td>
<td>+3.3</td>
<td>-0.30</td>
<td>0*</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-5</td>
<td>-135</td>
<td>-120</td>
<td>+0.6</td>
<td>+3.9</td>
<td>-0.25</td>
<td>0*</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+140</td>
<td>+20</td>
<td>-120</td>
<td>+0.6</td>
<td>+3.9</td>
<td>-0.15</td>
<td>0*</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-190</td>
<td>-190</td>
<td>+3.0</td>
<td>+13.0</td>
<td>-0.25</td>
<td>0*</td>
</tr>
</tbody>
</table>

* Reading below the reliable detection limit

**Table 4.2:** Some results of a red HgS electrode illuminated in a sodium nitrate electrolyte of various molarities.
similar to a nitrogen-purged solution.

If the electrolyte is oxygen-saturated, the potential-time plot is similar to that of figure 4.2, but a very much smaller relative photovoltage of \(-50\text{mV}\) obtains. The initial plot (first illumination) is strange - see figure 4.12.

![Potential vs SCE](image)

**Fig. 4.12**
Initial and repeat plot of photopotential for red HgS in an oxygen-saturated 0.1M NaNO₃ electrolyte.

The "positive 'hump'" is seen in potential plots of an electrode that has become coated with bubbles after producing photocurrents for a long while (see section 4.3.1.5) and may be caused by adsorbed oxygen acting as an electron sink with the \(\{O_2---e^-\}\) unit subsequently de-sorbing.
and allowing a negative voltage to build up. The re-adsorption of \( \{O_2--e^-\} \) appears slow, as subsequent photovoltage plots show no "positive 'hump'". The effect of such adsorption-desorption is likely to have complex consequences on the energy of the HgS-H\(_2\)O interface and there is insufficient data to adequately explain oxygen's rôle in photovoltage and photocurrent production.

4.5.1.8 Effect of varying thickness of coating on the mesh

Table 4.3 gives some results for platinum electrodes coated with various amounts of red HgS: an alkaline electrolyte has been used to give larger photocurrents. Smaller photocurrents are observed as the mesh coating increases in weight - a thicker HgS layer has a higher internal resistance. Relative photopotentials are diminished too, as the resistance inhibits photo-generated electrons flowing to the interior of HgS to cross to platinum and register in the voltmeter. An interesting observation is the lowering of relative photocurrent with increasing bias for a given electrode. This has been observed quite generally, especially where large currents (\( > +5\mu A\)) flow. If oxygen is produced while photocurrents are generated, it may capture electrons and lower the photocurrent. This process will be more effective where bare platinum can act as a site for the formation of \( \{O_2--e^-\} \). A lighter, thinner coating of HgS will less effectively cover the platinum mesh and increase the possibility of such sites existing. A greater 'relative photocurrent fall-off' is noted for lighter coatings.

It is surprising that a platinum mesh barely covered with HgS exhibits photo-effects (see results for the electrode coated with 0.008054 g of HgS in Table 4.3). Although the thin coating affords a
<table>
<thead>
<tr>
<th>Wt. of red HgS coating in g</th>
<th>Dark Potential in mV vs SCE</th>
<th>Potential on Illumination in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in µA at given bias vs SCE</th>
<th>Onset Potential in V vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008054</td>
<td>-70</td>
<td>-280</td>
<td>-215</td>
<td>+5.0  +9.0  +7.5  +3.8</td>
<td>-0.25</td>
</tr>
<tr>
<td>0.032152</td>
<td>-95</td>
<td>-325</td>
<td>-235</td>
<td>+2.8  +5.0  +6.0  +4.0</td>
<td>-0.30</td>
</tr>
<tr>
<td>0.044308</td>
<td>-75</td>
<td>-175</td>
<td>-100</td>
<td>+1.0  +1.4  +2.3  +2.0</td>
<td>-0.20</td>
</tr>
<tr>
<td>0.069186</td>
<td>-90</td>
<td>-135</td>
<td>-45</td>
<td>+0.4  +1.1  +2.7  +2.3</td>
<td>-0.15</td>
</tr>
<tr>
<td>Bare platinum (pH 11.5 electrolyte)</td>
<td>+5</td>
<td>+5</td>
<td>0</td>
<td>0.0   0.0   0.0   0.0</td>
<td>-</td>
</tr>
<tr>
<td>Bare platinum (pH 7 electrolyte)</td>
<td>+90</td>
<td>+90</td>
<td>0</td>
<td>0.0   0.0   0.0   0.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3: Voltages and currents for a red HgS electrode in pH 11.5 0.1M NaNO₃ (N₂-purged) with different weights of sulphide on the platinum mesh.
low resistance, platinum exposed to the electrolyte might be expected to act as a counter electrode and cause short-circuiting. The observation of currents and potentials is contrary to this expectation. This implies electrons in the conduction band of HgS are of lower energy than any acceptor level of species in solution (except O$_2$) and, therefore, do not participate in short-circuiting even though they might arrive at the platinum-electrolyte interface. At non-illuminated portions of HgS, band-bending prevents conduction band electrons reaching the surface. Since relative photovoltages are lowered if oxygen is present (see section 4.3.1.7), it can be concluded that short-circuiting is important only when O$_2$ can capture electrons from the conduction band of HgS, via bare platinum. This process might be superoxide ion formation (eqn [4-4]) or the beginning of the oxygen reduction process (eqn [4-5]):

$$O_2 + e^- \rightarrow O_2^- \quad \text{superoxide ion} \quad \text{[4-4]}$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad \text{[4-5]}$$

To exaggerate the effect of bare platinum, an electrode was prepared with only one face of the mesh coated with HgS. The covered and uncovered faces were illuminated in turn, and the results shown in Table 4.4. When HgS is illuminated, small photo-effects are seen compared with the electrode bearing 0.032152 g of sulphide (see Table 4.3). The large area of uncovered platinum is seen to have a detrimental effect. When bare platinum is illuminated (along with a very small amount of HgS within the mesh weaving), larger photocurrents and voltages obtain. So if any electrons do re-enter the electrolyte from bare platinum, they are apprehended by illumination, and the earlier conclusion of oxygen reduction being the only short-circuiting process needs further qualification. A complex system of HgS/electrolyte,
Table 4.4  Some photo-effects for a platinum mesh coated on one side with red HgS (weight = 0.015038) in N₂-purged NaNO₃.

<table>
<thead>
<tr>
<th>Illuminated face</th>
<th>Relative photovoltage in mV</th>
<th>Relative photocurrent in µA at given bias vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red HgS</td>
<td>-20</td>
<td>+0.8</td>
<td>pH 11.5 electrolyte</td>
</tr>
<tr>
<td>Platinum*</td>
<td>-100</td>
<td>+1.7</td>
<td>pH 11.5 electrolyte</td>
</tr>
<tr>
<td>Platinum*</td>
<td>-150</td>
<td>+0.4</td>
<td>pH 7 electrolyte</td>
</tr>
</tbody>
</table>

* HgS in the mesh centres is irradiated too

HgS/platinum, and platinum/electrolyte junctions simultaneously in the dark and under illumination needs very detailed study to unravel the complicated processes occurring.

4.3.1.9 Electrodes made with HgS from different suppliers, pre-treated electrodes, and other means of electrode preparation.

Red mercury(II) sulphide was purchased from various other suppliers: British Drug Houses (B.D.H.), Fluka, Koch-Light, and May & Baker. Platinum meshes were coated in the normal manner. An electrode bearing black mercury(II) sulphide ('Alfa' - Lancaster Synthesis) was also prepared. Table 4.5 gives results of photovoltage and photocurrent generation by these electrodes. All the red HgS electrodes, except the sample from May & Baker, show relative photopotentials and photocurrents similar to, or larger than, those generated by 'Fisons' HgS. The Koch-Light sample blackened while taking the photovoltage, and the darkened form gives higher photocurrents. I and II are different electrodes coated with the same Koch-Light HgS; the large photocurrents and gas evolution from the platinum counter electrode in II were not
<table>
<thead>
<tr>
<th>Supplier</th>
<th>Dark Potential in mV vs SCE</th>
<th>Illumination Potential in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in μA at given bias vs SCE 0.0V + 0.2V + 0.4V + 0.6V + 0.8V</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisons</td>
<td>-30</td>
<td>-200</td>
<td>-170</td>
<td>+1.0 + 2.5 + 5.0 + 6.0 + 4.0</td>
<td>A little darkening of HgS occurred.</td>
</tr>
<tr>
<td>B.D.H.</td>
<td>+100</td>
<td>-140</td>
<td>-240</td>
<td>+2.6 + 8.5 +10.0 +10.0 + 8.0</td>
<td>No colour change.</td>
</tr>
<tr>
<td>Koch-Light I</td>
<td>0</td>
<td>-215</td>
<td>-215</td>
<td>+5.0 +11.0 +17.5 +40.0 +38.0</td>
<td>Gas bubbles at counter electrode at +0.4V,+0.6V biasing potentials. Dark crimson HgS after irradiation.</td>
</tr>
<tr>
<td>Koch-Light II</td>
<td>0</td>
<td>-205</td>
<td>-205</td>
<td>+11.0 +43.0 +44.0 +72.0 +71.0</td>
<td>Gas evolution at platinum counter electrode as above; HgS almost completely black.</td>
</tr>
<tr>
<td>Fluka</td>
<td>-200</td>
<td>-200</td>
<td>0</td>
<td>0.0 - - - - -</td>
<td>No photo-response.</td>
</tr>
<tr>
<td>May &amp; Baker</td>
<td>+145</td>
<td>+35</td>
<td>-110</td>
<td>+0.5 + 1.5 + 2.5 + 3.2 + 3.0</td>
<td>No colour change.</td>
</tr>
<tr>
<td>Alfa (Black HgS)</td>
<td>+290</td>
<td>+280</td>
<td>-10</td>
<td>0.0 + 0.2 + 1.0 + 1.8 + 4.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Results of electrodes coated with red HgS from different suppliers, in a pH 7 0.1M NaNO₃ (N₂-purged) electrolyte.
always repeatable, even with HgS from the same bottle. Fluka red HgS generates no photo-effects at all - and yet when blackening is induced - see Chapter Five - it behaves like other blackened samples. May & Baker HgS produces lower photo-effects. All the electrodes exhibit current/voltage - time plots similar to those of figures 4.2 and 4.3, although the time taken to attain level currents/voltages does vary, and the magnitude (and often the direction) of current overshoots depends on the sample. There are insufficient data on trace impurities, grain size (hence effective surface area), and nature of adhesion to platinum for the various makes of red HgS to satisfactorily explain the above results. One can merely speculate on the differing magnitudes of photo-effects and tendency to blacken: (i) differing degrees of ion adsorption on the semiconductor surface will affect electron-hole recombination and the function of surface states in photo-response; (ii) different trace impurities may increase or decrease the internal resistance by capturing or releasing charge carriers. These impurities may affect blackening and ion adsorption as in (i); (iii) the HgS grain size affects internal resistance, surface area exposed to illumination, and the barrier potential at platinum.

The results on black HgS ('metacinnabar') show it to be markedly different to the red form. It is n-type, but produces a feeble photo-response. [This is the 'authentic black HgS' referred to on p.110.]

The effects of pre-treating HgS before applying it to the platinum mesh - see Table 4.6 - are not understood. Heating at 100°C under vacuum for 72 hours has improved photocurrents, but not photopotentials, and increased the tendency to blacken. Heating at 250° for 24 hours under vacuum reduced the relative photopotential and the photocurrents, but blackening occurred only under illumination at +0.8V bias. The
<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Dark Potential in mV vs SCE</th>
<th>Illumination Potential in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in μA at given bias vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Fisons' - as received</td>
<td>- 30</td>
<td>-200</td>
<td>-170</td>
<td>+1.0  +2.5  +5.0  +6.0  + 4.0</td>
<td>Electrode blackened rapidly: no further photocurrents taken</td>
</tr>
<tr>
<td>100°C under vacuum</td>
<td>+130</td>
<td>- 55</td>
<td>-185</td>
<td>+8.2  -     -     -     -</td>
<td></td>
</tr>
<tr>
<td>for 72 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250°C under vacuum</td>
<td>+ 60</td>
<td>- 55</td>
<td>-115</td>
<td>+0.3  +2.4  +28μA @ +0.5V +43.0</td>
<td>A little blackening while irradiating at +0.8V</td>
</tr>
<tr>
<td>for 24 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>'Mixed' with black HgS</td>
<td>+80</td>
<td>-165</td>
<td>-245</td>
<td>+0.2  +0.6  +1.8  +2.0  + 2.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>'Mixed' with selenium †</td>
<td>+170</td>
<td>+140</td>
<td>- 30</td>
<td>0.0   -     +1.0μA @ +0.5V</td>
<td></td>
</tr>
</tbody>
</table>

* - The suspension to coat the mesh contained 1.8g of red HgS and 0.2g of black HgS in 25 ml of water.
† - The suspension to coat the mesh contained 1.9g of red HgS and 0.1g of Se powder in 25 ml of water.

Table 4.6: Some results of electrodes coated with red HgS (Fisons) previously heated under vacuum, and with HgS plus an impurity - in 'standard' electrolyte.
preparation method and trace impurities may have a considerable influence on darkening. The addition of black HgS as an impurity improves the photopotential but not the photocurrent, and selenium lowers photo-responses. These effects can only be speculated on, as before.

Some Koch-Light red HgS was compressed, in a device for making KBr plates, for three minutes, at a pressure of 10 psi. A disc, 0.5 mm thick and 1.3 cm in diameter, weighing about 0.2 g, was obtained. Conducting silver paint was applied to one face, then a platinum wire, 6 cm long and of diameter 0.05 cm, placed on the dry painted face and held in position by quick-setting 'araldite'. The whole of this face was covered with 'araldite', as was most of the platinum wire. After immersion in concentrated aqueous sodium sulphide to etch the surface, the HgS disc electrode was stored for 15 hours in a 'standard' nitrate electrolyte. With the normal experimental system, it registered a voltage of -100 mV vs SCE in the dark, which did not alter on illumination. No photocurrents were obtained.

A sample of natural cinnabar mineral from Almaden, Spain, was cut into a piece 1 cm x 1 cm x 1 mm and mounted and etched as for the disc above, except that no silver paint was employed. This electrode produced a relative photopotential of ~-1 mV; the dark potential was close to 0 mV vs SCE. No photocurrents were obtained. A very thin cinnabar mineral section (about 0.1 mm thick) on a glass slide mounted as above, generated no photo-effects.

The absence of a photo-response for the disc and mineral electrodes can be due to any of the following: (i) the platinum - (silver paint) - HgS contact is not made properly, (ii) the sample is too thick and affords a high resistance, (iii) the cinnabar mineral is not photo-
responsive. It is unfortunate that electrodes fabricated in this manner fail to operate, as it would be useful to gain results on an electrode where the metal carrier was definitely isolated from the electrolyte.

4.3.1.10 Variation of anode substrate and cathode material

Platinum is an expensive conductive carrier for the mercury(II) sulphide electrodes, so two other materials were tried. 'Twill weave' carbon fibre (from the Royal Aircraft Establishment) was cut to a piece measuring 2.5x2.5 cm and glued with 'araldite' to a portion of microscope slide of the same dimensions. A length of platinum wire (6 cm, diameter 0.05 cm) was inserted in the fibres and insulated from the electrolyte with polyurethane varnish. HgS was applied from aqueous suspension and adhered well to the fibre. In the 'standard' nitrate electrolyte, no photo-effects were observed. This is attributed to a non-ohmic junction between HgS and C; the C-Pt junction is assumed to be ohmic, as an uncoated carbon fibre electrode behaved normally as a cathode.

A piece of titanium mesh ('Expamet': 0.060" x 0.010" x 0.004" - 300 MPE) was platinised by making it the cathode in hexachloroplatinic acid, and passing a current (with platinum anode). A 3x1.5 cm section of the platinised Ti mesh was attached to 6 cm of platinum wire (0.05 cm diameter) to form an electrode. HgS was applied in the normal manner, but no photo-effects were observed in the nitrate electrolyte. It is proposed that the Pt-Ti junction is rectifying and prevents the observation of a photo-response at HgS.

Employing cathodes other than a platinum mesh resulted in no marked change in photocurrents - see Table 4.7. The currents are quite small, and fluctuations cannot be ascribed with certainty to either cathode.
<table>
<thead>
<tr>
<th>Cathode</th>
<th>Relative Photocurrent in μA at 0.0V vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum mesh</td>
<td>+0.9</td>
<td></td>
</tr>
<tr>
<td>Platinised platinum mesh</td>
<td>+0.8</td>
<td>Platinised as in text</td>
</tr>
<tr>
<td>Carbon</td>
<td>+1.2</td>
<td>Twill weave C-fibres, made as in text</td>
</tr>
<tr>
<td>Platinum wire 6 cm long, 0.05 cm in diameter</td>
<td>+1.0</td>
<td></td>
</tr>
<tr>
<td>Platinum wire as above, but platinised</td>
<td>+1.0</td>
<td>Platinised as in text</td>
</tr>
</tbody>
</table>

Table 4.7 Effect on zero bias photocurrent of varying the nature of the counter electrode in a 'standard' nitrate electrolyte for 'Fisons' red HgS.
material or experimental error. This topic is returned to in Chapter Five, where the larger photocurrents generated by darkened red HgS give more reliability in interpreting results.

4.3.2 Red mercury(II) sulphide in aqueous electrolytes other than sodium nitrate

It has been suggested that oxidation of the hydroxyl ion occurs at illuminated red HgS and contributes to the photocurrent. Other species may undergo such oxidation, and to probe this, sodium nitrate was replaced by electrolytes containing reducing agents.

4.3.2.1 Results from red HgS in aqueous electrolytes, most containing a reducing agent

About thirty different salts were employed, with $E_{\text{red}}$ ranging from -0.51V to +2.87V. Potentials and currents (under bias) with illumination were obtained as in section 4.3.1.1, and the results are summarised in Tables 4.8 and 4.9. The electrolyte pH is shown and must be taken into account when interpreting results, as it influences currents and voltage (see section 4.3.1.2). Plots of photo-effect against time are similar in shape to those seen in nitrate, unless specified. Stability of red mercury(II) sulphide in these various electrolytes is indicated in Table 4.10, where mercury solubilisation (detected by atomic absorption spectroscopy) is recorded for a suspension of HgS and electrolyte. The properties noted for each solution are discussed below.

$\text{Na}_2\text{S}$ - Aqueous sodium sulphide is one of the few agents that dissolves HgS, so it was employed at a concentration of $10^{-2}$ M. Potentials vs SCE are large and negative due to the high pH and a photo-induced potential close to zero obtains. Dark currents are large (±70μA @ 0.0V)
<table>
<thead>
<tr>
<th>Electrolyte (0.1M, aqueous)</th>
<th>$E^{\circ}_{\text{red}}$ in V</th>
<th>pH</th>
<th>Dark Potential in mV vs SCE</th>
<th>Illumination Potential in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S (10$^{-7}$M)</td>
<td>-0.51</td>
<td>12.2</td>
<td>-720</td>
<td>-710 to -725</td>
<td>-5, +10</td>
<td></td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>-0.49</td>
<td>9.5</td>
<td>-90</td>
<td>-205</td>
<td>-115</td>
<td></td>
</tr>
<tr>
<td>HCOONa</td>
<td>-0.12</td>
<td>7.0</td>
<td>+100</td>
<td>-5</td>
<td>-105</td>
<td></td>
</tr>
<tr>
<td>CH$_3$COONa</td>
<td>-0.20</td>
<td>7.5</td>
<td>0</td>
<td>-100</td>
<td>~-100</td>
<td></td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>+0.07</td>
<td>&lt;1.0</td>
<td>-170</td>
<td>-270</td>
<td>-100</td>
<td></td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>+0.09</td>
<td>9.0</td>
<td>-100</td>
<td>-265</td>
<td>-165</td>
<td></td>
</tr>
<tr>
<td>KCN</td>
<td>+0.37</td>
<td>11.3</td>
<td>-270</td>
<td>-460</td>
<td>-190</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>+0.40</td>
<td>13.0</td>
<td>-245</td>
<td>-285</td>
<td>-40</td>
<td></td>
</tr>
<tr>
<td>KCN(2M)</td>
<td>+0.40</td>
<td>14.0</td>
<td>-690</td>
<td>-690</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>K$_3$Fe(CN)$_6$</td>
<td>+0.5</td>
<td>10.7</td>
<td>variable</td>
<td>variable</td>
<td>+85</td>
<td>see text</td>
</tr>
<tr>
<td>KI</td>
<td>+0.53</td>
<td>7.0</td>
<td>-330 (after darkening)</td>
<td>-430</td>
<td>-100</td>
<td></td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>+0.70</td>
<td>8.0</td>
<td>-100</td>
<td>+50</td>
<td>+150</td>
<td></td>
</tr>
<tr>
<td>KSCN</td>
<td>+0.77</td>
<td>8.0</td>
<td>-100</td>
<td>+50</td>
<td>+150</td>
<td></td>
</tr>
<tr>
<td>&quot;FeSO$_4$&quot;</td>
<td>+0.77</td>
<td>3.0</td>
<td>+600</td>
<td>+470</td>
<td>+10</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$(NO$_3$)$_2$</td>
<td>+0.90</td>
<td>4.5</td>
<td>+210</td>
<td>+200</td>
<td>-10</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td>+1.08</td>
<td>7.0</td>
<td>-300</td>
<td>-300</td>
<td>-200</td>
<td></td>
</tr>
<tr>
<td>Mn(NO$_3$)$_2$</td>
<td>+1.20</td>
<td>4.3</td>
<td>-400</td>
<td>-250</td>
<td>-150</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>+1.23</td>
<td>7.0</td>
<td>0</td>
<td>-150</td>
<td>-190</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O$_3$</td>
<td>+1.23</td>
<td>7.0</td>
<td>+25</td>
<td>-120</td>
<td>-145</td>
<td></td>
</tr>
<tr>
<td>Na$_2$HPO$_4$</td>
<td>+1.23</td>
<td>9.2</td>
<td>-350</td>
<td>-325</td>
<td>+25</td>
<td></td>
</tr>
<tr>
<td>KClO$_3$</td>
<td>+1.23</td>
<td>9.2</td>
<td>-195</td>
<td>-220</td>
<td>+25</td>
<td></td>
</tr>
<tr>
<td>KBrO$_3$</td>
<td>+1.23</td>
<td>9.0</td>
<td>+15</td>
<td>-15</td>
<td>-30</td>
<td></td>
</tr>
<tr>
<td>HNO$_3$(1.5M)</td>
<td>+1.23</td>
<td>0</td>
<td>+700</td>
<td>+650</td>
<td>-50</td>
<td></td>
</tr>
<tr>
<td>TiNO$_3$</td>
<td>+1.25</td>
<td>2.0</td>
<td>+220</td>
<td>+100</td>
<td>-120</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>+1.35</td>
<td>7.0</td>
<td>-30</td>
<td>-280</td>
<td>-250</td>
<td></td>
</tr>
<tr>
<td>Ce(NO$_3$)$_3$</td>
<td>+1.44</td>
<td>2.4</td>
<td>+520</td>
<td>+550</td>
<td>-170</td>
<td></td>
</tr>
<tr>
<td>Pb(NO$_3$)$_2$</td>
<td>+1.46</td>
<td>5.0</td>
<td>+120</td>
<td>-60</td>
<td>-180</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>+2.00</td>
<td>7.0</td>
<td>variable</td>
<td>variable</td>
<td>variable</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>+2.87</td>
<td>7.0</td>
<td>-80</td>
<td>-165</td>
<td>-85</td>
<td></td>
</tr>
</tbody>
</table>

* $E^{\circ}$ for O$_2$/H$_2$O is given as no other oxidisable species is present

---

Table 4.8: Potentials adopted vs SCE, and relative photovoltages, for red HgS in some aqueous electrolytes.
<table>
<thead>
<tr>
<th>Electrolyte (0.1M, aqueous)</th>
<th>$E^{0}$ in V</th>
<th>pH</th>
<th>Relative Photocurrent in $\mu$A at given bias vs SCE</th>
<th>Onset Potential in V vs SCE of relative photocurrent</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S($10^{-3}$M)</td>
<td>-0.51</td>
<td>12.2</td>
<td>+50 +40 +80 +120</td>
<td>-0.7</td>
<td>Dark current = +280 $\mu$A @ +0.4V</td>
</tr>
<tr>
<td>KC$_2$CO$_3$</td>
<td>-0.49</td>
<td>9.5</td>
<td>+7.0 +18.0 +31.0 +60.0</td>
<td>-0.25</td>
<td></td>
</tr>
<tr>
<td>HCOONa</td>
<td>-0.20</td>
<td>7.5</td>
<td>+0.8 +2.0 +2.0 +2.5</td>
<td>+3.0</td>
<td></td>
</tr>
<tr>
<td>CH$_3$COONa</td>
<td>-0.12</td>
<td>7.0</td>
<td>+0.2 +0.7 +1.0 +1.4</td>
<td>+1.6</td>
<td></td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>+0.07</td>
<td>&lt;1.0</td>
<td>+4.5 +9.5 +11.5 +14.5</td>
<td>+15.0</td>
<td></td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>+0.09</td>
<td>9.0</td>
<td>+1.5 +2.0 +10.0</td>
<td>-0.3</td>
<td></td>
</tr>
<tr>
<td>KCN</td>
<td>+0.37</td>
<td>11.3</td>
<td>+2.4 +8.5 +14.0 +14.0</td>
<td>+17.0</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>+0.40</td>
<td>13.0</td>
<td>+3.5 +4.0 +5.0 +6.0</td>
<td>+10.0</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$(2M)</td>
<td>-0.5</td>
<td>10.7</td>
<td>~100 +1000</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>+0.53</td>
<td>7.0</td>
<td>+40 +40</td>
<td>large dark current</td>
<td></td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>+0.70</td>
<td>7.0</td>
<td>-2.7 +16.0</td>
<td>+75</td>
<td></td>
</tr>
<tr>
<td>KSCN</td>
<td>+0.77</td>
<td>8.0</td>
<td>-1.0 -0.5 +5 very large dark current</td>
<td>+17.0</td>
<td></td>
</tr>
<tr>
<td>&quot;FeSO$_4$&quot;</td>
<td>+0.77</td>
<td>4.5</td>
<td>-8.0 +2.5 large anodic dark currents</td>
<td>+0.15</td>
<td></td>
</tr>
<tr>
<td>Hg$_2$(NO$_3$)$_2$</td>
<td>+0.90</td>
<td>3.0</td>
<td>-</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td>+1.08</td>
<td>7.0</td>
<td>+17.0 +24.0 +20.0 @ +0.5V</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mn(NO$_3$)$_2$</td>
<td>+1.20</td>
<td>4.3</td>
<td>-15 -1.5 +4.0 +10.0</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>+1.23</td>
<td>7.0</td>
<td>+3.0 +7.0 +13.0 +15.0</td>
<td>+100</td>
<td></td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>+1.23*</td>
<td>7.0</td>
<td>+0.7 +1.0 +1.5 +2.0</td>
<td>+2.2</td>
<td></td>
</tr>
<tr>
<td>Na$_2$HPO$_4$</td>
<td>+1.23*</td>
<td>9.2</td>
<td>+1.0 +4.5 +8.5 +7.0 +8.0</td>
<td>-0.15</td>
<td></td>
</tr>
<tr>
<td>KCl$_2$O$_4$</td>
<td>+1.23*</td>
<td>9.2</td>
<td>+0.8 +4.2 +7.8 +11.0 +10.0</td>
<td>-0.25</td>
<td></td>
</tr>
<tr>
<td>KBrO$_3$</td>
<td>+1.23*</td>
<td>9.0</td>
<td>+0.7 +3.0 +5.0 +5.0 +3.5</td>
<td>-0.10</td>
<td></td>
</tr>
<tr>
<td>HNO$_3$(1.5M)</td>
<td>+1.23*</td>
<td>0</td>
<td>? +25 +80</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TiNO$_3$</td>
<td>+1.25</td>
<td>2.0</td>
<td>? +1.2 +4.0 +5.0 +180.0</td>
<td>±0.17</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>+1.35</td>
<td>7.0</td>
<td>+4.5 +8.0 +15.0 +15.0</td>
<td>-0.40</td>
<td></td>
</tr>
<tr>
<td>Cl(NO$_3$)$_3$</td>
<td>+1.44</td>
<td>2.4</td>
<td>-2.5 -0.8 +0.3 +8.0</td>
<td>+14.0</td>
<td></td>
</tr>
<tr>
<td>Pb(NO$_3$)$_2$</td>
<td>+1.46</td>
<td>5.0</td>
<td>+4.4 +7.5 +6.0 +6.5 +9.0</td>
<td>-0.15</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>+2.00</td>
<td>7.0</td>
<td>+0.6 +1.2 +1.1 +1.5 +2.0</td>
<td>-0.3</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>+2.87</td>
<td>7.0</td>
<td>+1.0 +2.0 +5.2 +4.5 +6.5</td>
<td>-0.33</td>
<td></td>
</tr>
</tbody>
</table>

* $E^{0}$ for $O_2$/H$_2$O is given as no other oxidisable species is present

Table 4.9: Photocurrent data for red HgS in some aqueous electrolytes
**Table 4.10** Data on mercury solublisation from red HgS in some aqueous electrolytes

<table>
<thead>
<tr>
<th>Electrolyte (0.1M, aqueous)</th>
<th>[Hg] in µg.mL⁻¹ in electrolyte in the dark *</th>
<th>[Hg] in µg.mL⁻¹ in electrolyte after illumination †</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S(10⁻⁷M)</td>
<td>5</td>
<td>20</td>
<td>Slightly darkened HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>K₃C₈O₄</td>
<td>4</td>
<td>5</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>HCOONa</td>
<td>0</td>
<td>0</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>CH₃COONa</td>
<td>0</td>
<td>0</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>200</td>
<td>65</td>
<td>Black HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>Na₃S₂O₃</td>
<td>5</td>
<td>40</td>
<td>Brown HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>KCN</td>
<td>27</td>
<td>-2,500</td>
<td>Brown HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>KOH</td>
<td>0</td>
<td>0</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>KOH(2M)</td>
<td>16</td>
<td>19</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>K₂Fe(CN)₆</td>
<td>15</td>
<td>-4,000</td>
<td>Black HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>KI</td>
<td>10</td>
<td>-1,400</td>
<td>Black HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>KIO₃</td>
<td>2</td>
<td>28</td>
<td>Brown HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>&quot;FeSO₄&quot;</td>
<td>3</td>
<td>50</td>
<td>Black HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>KBr</td>
<td>4</td>
<td>70</td>
<td>Black HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>Mn(NO₃)₂</td>
<td>18</td>
<td>19</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
<td>0</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0</td>
<td>0</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>9</td>
<td>9</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>KClO₄</td>
<td>0</td>
<td>0</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>KBrO₃</td>
<td>3</td>
<td>-600</td>
<td>Brown HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>HNO₃(1.56M)</td>
<td>10</td>
<td>10</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>TiO₃</td>
<td>2</td>
<td>2</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>KCl</td>
<td>0</td>
<td>0</td>
<td>Black HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>Ce(NO₃)₃</td>
<td>9</td>
<td>9</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>0</td>
<td>0</td>
<td>Slightly darker HgS recovered from irradiated suspension</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>6</td>
<td>6</td>
<td>No visible change to anything</td>
</tr>
<tr>
<td>KF</td>
<td>0</td>
<td>10</td>
<td>Brown HgS recovered from irradiated suspension</td>
</tr>
</tbody>
</table>

* - 1g of red HgS is stirred in the dark in 250 ml of electrolyte for ten days.
† - 2g of red HgS is stirred in 500 ml of electrolyte and irradiated with a 125W medium pressure Hg-lamp (immersed in the suspension) for ten days.
which means $S^{2-}$ is oxidised at HgS or platinum. Currents increase on illumination to a greater extent than in NaNO$_3$ at this pH, which suggest the sulphide ion is oxidised at illuminated red HgS, and gas bubbles emanate from the platinum wire counter electrode. Red HgS appears unstable in Na$_2$S on illumination.

K$_2$C$_2$O$_4$ - The magnitude of relative photocurrents implies C$_2$O$_4^{2-}$ is oxidised - and dark currents exceed +50µA positive of +0.5V bias. Voltages are unaffected, and a slight amount of mercury solubilisation ensues.

CH$_3$COONa and HCOONa - Normal photovoltages and non-increased photocurrents indicate no participation of acetate and formate occurs. No instability is noted.

SnCl$_2$ - The electrolyte was made very acidic to prevent tin hydroxides precipitating. It is most remarkable that positive relative photocurrents are seen at this pH, and the onset voltage could not be determined as a rapid dark current increase, due to Sn$^{2+}$ oxidation, took place negative of -0.45V bias. The tin(II) cation is being oxidised at illuminated red HgS, and the presence of Sn$^{2+}$ overrides the properties expected at this low pH - for example, potentials vs SCE should be about +400 mV (see section 4.3.1.2). However, considerable solubilisation and blackening of HgS takes place.

Na$_2$S$_2$O$_3$ - Normal voltage behaviour is noted, and thiosulphate oxidation does not contribute to photocurrents, although it is difficult to determine this, as S$_2$O$_3^{2-}$ oxidation is responsible for the large dark current (+155µA) at +0.4V. Darkening and mercury solubilisation is considerable.
KCN - The alkalinity of this electrolyte explains relative photocurrent magnitude, although cyanide oxidation cannot be ruled out. Normal photopotentials obtain, but red HgS is very unstable on illumination in potassium cyanide.

KOH (0.1M) - Results confirm those noted at high pH in section 4.3.1.2. A diminished relative photovoltage is seen, however, and no mercury solubilisation occurs. The diminishing of photo-induced potentials was seen in the alkaline $10^{-2}$M Na₂S electrolyte.

KOH (2M) - No photo-induced voltages are seen and dark currents are very large. HgS is unstable in this electrolyte.

K₄Fe(CN)₆ - Positive relative photopotentials were produced - see figure 4.13 - and at zero bias, a negative relative photocurrent was obtained (figure 4.14).

![Potential vs SCE](image)

**Fig. 4.13**
Relative photovoltage plot for initially-red HgS in 0.1M K₄Fe(CN)₆.
Photocurrents of between -50 and -100μA were seen from 0.0V to -0.9V bias; at +0.1V, the photo-induced current was +185μA and +1,000μA at +0.2V. The onset is estimated at +0.05V. The ferrocyanide ion has profound effects upon currents and potentials at illuminated HgS, which cannot be adequately explained with the few observations noted. It is likely that Fe(CN)₆⁻⁴ alters band bending to allow generation of a positive photo-induced voltage, and participates in photocurrent production, but a mechanism cannot be given. A local redox system of ferro-/ferricyanide will influence ion adsorption too. A great deal of mercury is solubilised on irradiation, and darkening occurs.

KL - Darkening occurs while taking the photopotential of a freshly made red electrode; all the values in Tables 4.8 and 4.9 are for blackened HgS. Oxidation of I⁻ is suggested by large photo-induced currents, and
it occurs in the dark at potentials positive of +0.25V. Much mercury solubilisation takes place. This electrolyte is dealt with in detail in section 4.3.2.2 and in Chapter Five.

$\text{KIO}_3$ - Again, blackening occurred while obtaining the photopotential, which was only +15mV. The sign and magnitude of relative photocurrents indicate iodate participates, but how it is involved is uncertain. HgS is solubilised on irradiation.

$\text{KSCN}$ - Like potassium ferrocyanide, a positive relative photopotential is generated. Rapid blackening is seen while obtaining the photovoltage, and solubilisation occurs. Photocurrents are affected too, in that the onset is quite positive. Potassium thiocyanate is discussed again in section 4.3.2.2.

$\text{Fe}^{2+}$ - This is in the form of the ammonium sulphate salt. Hardly any photo-induced potential is observed, and it is uncertain if $\text{Fe}^{2+}$ participates in photocurrents. A little mercury is solubilised, but no darkening occurs.

$\text{Hg}_2(\text{NO}_3)_2$ - A small positive relative photopotential obtains, but no photocurrents were taken as a very large dark current results from the $\text{Hg}_2^{2+}$ ion.

$\text{KBr}$ - Blackening occurs while taking the photovoltage of a fresh electrode, and the magnitude of relative photocurrents indicate Br$^-$ oxidation is happening. Solubilisation occurs upon illumination and, to a small extent, in the dark. This electrolyte is discussed in more detail in section 4.3.2.2.

$\text{Mn(NO}_3)_2$ - A 'normal' relative photopotential is seen, but it is not
possible to conclude if the manganese(II) ion is involved in photocurrent production. However, the counter electrode acquired a brown coating ($\text{MnO}_2$?) when the HgS electrode was negatively biased, and the electrolyte turned a pale green colour (due to $\text{MnO}_4^{2-}$?). A little solublisation of mercury occurred.

$\text{H}_2\text{O, NaNO}_3$ - These are included in Tables 4.8 to 4.10 to give 'reference' results for an inert electrolyte.

$\text{Na}_2\text{HPO}_4$ - Although the anion is non-oxidisable, this was tried because electrolytes in photoelectrochemical studies are often buffered at pH 9.2 with phosphate. The results indicate it interferes with photovoltages - a relative photopotential of +25mV is seen, but currents are unaffected. Solublisation of mercury occurs - whether the HgS is irradiated or not.

$\text{KClO}_4$ - Again, the anion is non-oxidisable, but perchlorate salts have been used as 'inert' electrolytes for other semiconductors. Photocurrents are as normal, but the relative photopotential has been reduced to -25mV. No solublisation occurs.

$\text{KBrO}_3$ - Much solublisation, plus darkening, happens in potassium bromate, and the relative photovoltage is only -30mV. $\text{BrO}_3^-$ has no effect on photocurrents.

$\text{HNO}_3$ (1.56M) - The high acidity of this electrolyte has lowered the relative photovoltage, and large, cathodic, unsteady dark currents make reliable photocurrent determination difficult. Physical solublisation of mercury occurs, which is unaffected by irradiation.

$\text{TINO}_3$ - The thallium(I) ion does not appear to be oxidised, as the
photocurrent magnitude and onset potential correspond to those seen at nitrate electrolyte of pH 2 (figure 4.7). A little physical solubilisation of HgS occurs.

KCl - Normal photopotentials are seen, but relative photocurrents are larger than in nitrate, which suggests Cl⁻ oxidation may occur. However, blackening takes place at anodic applied potentials, and with prolonged illumination at zero bias, which may account for enhanced photocurrents. Chloride is investigated further in section 4.3.2.2. No solubilisation of mercury obtains, but ten days of irradiation blacken the HgS.

Ce(NO₃)₃ - It is possible that the cerium(III) ion is oxidised on illumination, as shown by the +8.0μA and +14.0μA relative photocurrents at +0.6V and +0.8V applied potentials, respectively. Normal photoinduced potentials are obtained, no darkening occurs, but physical solubilisation of mercury takes place.

Pb(NO₃)₂ - The red HgS electrode darkened slightly while taking photopotentials and became almost black during photocurrent production. The used electrode was boiled in dilute nitric acid and a very small amount of lead was detected in this by atomic absorption spectroscopy. This brown deposit is likely to be PbO₂, formed from oxidation of lead(II) ions. No solubilisation of HgS is noted.

K₂SO₄ - Both positive and negative relative photopotentials were obtained, and the photocurrents quoted in Table 4.9 are for an electrode which behaved 'normally'. Sometimes, the onset of relative photocurrent was at about +0.2V vs SCE, and no reason could be discovered for the variable properties. Physical solubilisation of HgS (unaffected
by irradiation) takes place. Behaviour in sulphate is not at all straightforward.

KF - The response to light when taking potentials was slow and reduced relative photopotentials were seen. This is due to the adsorptive nature of F\(^-\) which restricts ion movement in the electrolyte and blocks surface sites at HgS. A small amount of mercury is solubilised on irradiation and very slight darkening occurs.

The above represents a brief investigation of red HgS in electrolytes, mostly containing reducing agents, and it is clear that specific ions are not only oxidised, but also can cause darkening and/or solubilisation of mercury(II) sulphide. An enhanced relative photocurrent at a given bias compared to that seen in nitrate of the same pH as the potentially reducible electrolyte, is taken as evidence for oxidation, although competition between the reducing agent and OH\(^-\) will take place. This 'hole competition' cannot be quoted as a ratio since oxidation can occur at bare platinum too. From observing enhanced photocurrents, it may be postulated that the following ions are oxidised at illuminated red HgS: S\(^2-\); C\(_2\)O\(_4\)^{2-}; Sn\(^2+\); Fe(CN)\(_6\)^{4-} (complex behaviour); I\(^-\); IO\(_3\)^- (theoretical oxidation products are H\(_3\)IO\(_6\)^{2-} or H\(_5\)IO\(_6\)); Br\(^-\); Pb\(^{2+}\). Ideally, to confirm this, the oxidation products in the reaction cell should be identified, but the trace amounts produced preclude this. The reasons for oxidation of reducing agents are dealt with in section 4.4.

Ions which cause darkening, to give brown HgS are: S\(_2\)O\(_3\)^{2-}; CN\(^-\); IO\(_3\)^-; BrO\(_3\)^- and F\(^-\). Those which induce blackening are: Fe(CN)\(_6\)^{4-}; I\(^-\); IO\(_3\)^-; SCN\(^-\); Br\(^-\) and Cl\(^-\). [In SnCl\(_2\), it is not known if Sn\(^{2+}\) contributes to darkening.] Very slight darkening is seen for S\(^2-\), and for Pb\(^{2+}\), the
brown material may be a surface coating of PbO₂. All of the ions which induce darkening cause solubilisation of mercury (except Cl⁻ and Pb²⁺). Indeed, the majority of ions investigated induce dissolution of mercury to some extent, except for CH₃COO⁻, HCOO⁻, OH⁻ (0.1M), NO₃⁻, ClO₄⁻, Cl⁻ and Pb²⁺. Those which cause great instability are CN⁻, Fe(CN)₆⁴⁻, I⁻, SCN⁻, Br⁻ and BrO₃⁻, with S₂O₃²⁻ and IO₃⁻ less effective. Halides, pseudo-halides, and their complexes or oxo-ions, with E° values lying between +0.4V and +1.1V, are responsible for the most marked degradation of red HgS. There may be a specific interaction between the semiconductor surface and ions with E° values within this range, that initiates Hg-S bond breaking and/or the darkening process (discussed in Chapter Five). Detailed work on HgS solubilised in potassium iodide is presented and evaluated in Chapter Five.

An interaction between specific ions and HgS in a redox electrolyte of given pH can cause different band bending than for nitrate electrolyte of the same pH. This difference in band bending will be reflected in the relative anodic photocurrent onset potentials. Table 4.11 indicates onset voltages obtained with redox electrolytes and those predicted for inert electrolytes of the same pH. Those ions which cause a marked deviation (0.3V or greater) in onset potential exhibit a very strong interaction with HgS, namely Sn²⁺, Fe(CN)₆⁴⁻, IO₃⁻, SCN⁻, Mn²⁺. Most of the remaining ions have an influence, but they interact specifically.

An HgS-H₂O junction with unique surface energies exists for each electrolyte, and results in specific photocurrent onset potentials, dark and illumination voltages, relative photovoltages, mercury solubilisation, and HgS darkening. Further information on specific ion interaction to rationalise the results in Tables 4.8 and 4.9 might be gleaned from varying the redox electrolyte concentration. This is
<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
<th>Observed onset of relative anodic photocurrent in V vs SCE</th>
<th>Onset potential in V vs SCE for NaNO₃ at this pH</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S</td>
<td>12.2</td>
<td>~0.7</td>
<td>-0.56</td>
<td>S²⁻ - influenced</td>
</tr>
<tr>
<td>K₂C₂O₄</td>
<td>9.5</td>
<td>-0.25</td>
<td>-0.37</td>
<td>C₂O₄²⁻ - influenced</td>
</tr>
<tr>
<td>HCOONa</td>
<td>7.5</td>
<td>-0.25</td>
<td>-0.19</td>
<td>pH - controlled</td>
</tr>
<tr>
<td>CH₃COONa</td>
<td>7.0</td>
<td>-0.20</td>
<td>-0.19</td>
<td>pH - controlled</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>&lt; 1</td>
<td>&lt;0.45</td>
<td>&gt;+0.25</td>
<td>Sn²⁺ - controlled</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>9.0</td>
<td>-0.30</td>
<td>-0.33</td>
<td>pH - controlled</td>
</tr>
<tr>
<td>KCN</td>
<td>11.3</td>
<td>-0.65</td>
<td>-0.50</td>
<td>CN⁻ + pH influence</td>
</tr>
<tr>
<td>KOH</td>
<td>13.0</td>
<td>-0.62</td>
<td>-0.62</td>
<td>pH - controlled</td>
</tr>
<tr>
<td>KOH(2M)</td>
<td>14</td>
<td>~0.6</td>
<td>&lt;-0.70</td>
<td>pH - controlled</td>
</tr>
<tr>
<td>K₄Fe(CN)₆</td>
<td>10.7</td>
<td>+0.05</td>
<td>-0.45</td>
<td>Fe(CN)₆⁴⁻ - controlled</td>
</tr>
<tr>
<td>KI</td>
<td>7.0</td>
<td>-0.35</td>
<td>-0.19</td>
<td>I⁻ - influenced</td>
</tr>
<tr>
<td>KIO₃</td>
<td>7.0</td>
<td>+0.15</td>
<td>-0.19</td>
<td>IO₃⁻ - controlled</td>
</tr>
<tr>
<td>KSCN</td>
<td>8.0</td>
<td>+0.30</td>
<td>-0.26</td>
<td>SCN⁻ - controlled</td>
</tr>
<tr>
<td>&quot;FeSO₄&quot;</td>
<td>4.5</td>
<td>+0.15</td>
<td>-0.01</td>
<td>Fe²⁺ - influenced</td>
</tr>
<tr>
<td>KBr</td>
<td>7.0</td>
<td>-0.30</td>
<td>-0.19</td>
<td>Br⁻ - influenced</td>
</tr>
<tr>
<td>Mn(NO₃)₂</td>
<td>4.3</td>
<td>+0.35</td>
<td>0.0</td>
<td>Mn²⁺ - controlled</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>9.2</td>
<td>-0.15</td>
<td>-0.35</td>
<td>HPO₄⁻ - influenced</td>
</tr>
<tr>
<td>KCIO₄</td>
<td>9.2</td>
<td>-0.25</td>
<td>-0.35</td>
<td>ClO₄⁻ - influenced</td>
</tr>
<tr>
<td>KBrO₃</td>
<td>9.0</td>
<td>-0.10</td>
<td>-0.33</td>
<td>BrO₃⁻ - influenced</td>
</tr>
<tr>
<td>TlNO₃</td>
<td>2.0</td>
<td>~0</td>
<td>+0.17</td>
<td>Tl⁺ - influenced</td>
</tr>
<tr>
<td>KCl</td>
<td>7.0</td>
<td>~0.4</td>
<td>-0.19</td>
<td>Cl⁻ - influenced</td>
</tr>
<tr>
<td>Ce(NO₃)₃</td>
<td>2.4</td>
<td>+0.30</td>
<td>+0.14</td>
<td>Ce³⁺ - influenced</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>5.0</td>
<td>-0.15</td>
<td>-0.05</td>
<td>Pb²⁺ - influenced</td>
</tr>
<tr>
<td>K₂SO</td>
<td>7.0</td>
<td>~0.3</td>
<td>-0.19</td>
<td>SO₄²⁻ - influenced</td>
</tr>
<tr>
<td>KF</td>
<td>7.0</td>
<td>-0.33</td>
<td>-0.19</td>
<td>F⁻ - influenced</td>
</tr>
</tbody>
</table>

* Values obtained from figure 4.7

Table 4.11 Relative photocurrent onset potentials in different electrolytes compared with those predicted in an inert electrolyte of the same pH.
4.3.2.2 Effect of varying the concentration of certain aqueous electrolytes which markedly affect red HgS

(i) Potassium thiocyanate, KSCN

Potentials adopted versus calomel for both red and blackened forms with different [KSCN] are found to be different, and are presented in Table 4.12, along with other results. Figures 4.15 and 4.16 illustrate graphically the potentials in columns 2 to 5. The quantity 'pSCN' is defined as:

\[ p_{SCN} = -\log_{10}[SCN^-] \]  

[4-6]

The initial dark potential is invariant with [SCN^-], (see figure 4.15), so the adsorption of thiocyanate ions is not important for fresh red HgS. The potential upon illumination is also invariant with [SCN^-] - this holds true for red or blackened forms. However, the final dark potential becomes more positive as [SCN^-] decreases, irrespective of whether the HgS has blackened or not. This infers that adsorption of the thiocyanate ion on HgS is dependent on immediate previous illumination of SCN^-, and not on either the colour of HgS or the action of light on it. Figure 4.16 indicates the relative photovoltage becomes negative at lower [SCN^-], with a linear change of -65mV.pSCN^-1. This suggests band bending is directly controlled by [SCN^-]. It must be remembered that the relative photopotential in figure 4.16 is calculated from {illumination potential - final dark potential}. If the relative photovoltage is obtained from {illumination voltage - initial dark potential}, then it would be invariant with pSCN. Hence, irradiation of SCN^- affects the nature of its adsorption on the HgS surface, and consequently, the band bending.

Figure 4.17 illustrates plots of potential vs time for irradiation
<table>
<thead>
<tr>
<th>[KSCN] in mol dm⁻³</th>
<th>Dark Potential before irradiation in mV vs SCE</th>
<th>Dark Potential after irradiation in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>+155</td>
<td>-270</td>
<td>-150</td>
<td>Hg₂S rapidly blackened</td>
</tr>
<tr>
<td>10⁻¹</td>
<td>+255</td>
<td>+200</td>
<td>+460</td>
<td>Hg₂S nearly blackened</td>
</tr>
<tr>
<td>10⁻²</td>
<td>+255</td>
<td>-140</td>
<td>-105</td>
<td>Some darkening of Hg₂S</td>
</tr>
<tr>
<td>10⁻³</td>
<td>+235</td>
<td>-60</td>
<td>-65</td>
<td>Some darkening of Hg₂S</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>+145</td>
<td>+10</td>
<td>-150</td>
<td>No colour change to Hg₂S</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>+180</td>
<td>+70</td>
<td>-175</td>
<td>No colour change to Hg₂S</td>
</tr>
</tbody>
</table>

* If blackening has occurred, the potentials in these columns are for the darkened form. If no blackening takes place, the dark potential refers to the level of voltage seen after ending illumination and the relative photopotential is calculated from this.

Table 4.12 Potentials for initially red Hg₂S in various concentrations of aqueous potassium thiocyanate electrolyte.
Fig. 4.15

Initial dark potential (X), dark potential after irradiation (●) and potential upon irradiation (○) for initially-red HgS in electrolytes of various [KSCN].

Potential in mV vs SCE

No blackening of red HgS occurs at open circuit

Blackening of red HgS occurs at open circuit

Slope = +66 mV.pSCN⁻¹

[Fig. 4.15]

Potential in mV vs SCE

No blackening of red HgS occurs at open circuit

Blackening of red HgS occurs at open circuit

Slope = +66 mV.pSCN⁻¹

[Fig. 4.15]

Potential in mV vs SCE

No blackening of red HgS occurs at open circuit

Blackening of red HgS occurs at open circuit

Slope = +66 mV.pSCN⁻¹

[Fig. 4.15]

Potential in mV vs SCE

No blackening of red HgS occurs at open circuit

Blackening of red HgS occurs at open circuit

Slope = +66 mV.pSCN⁻¹

[Fig. 4.15]

Potential in mV vs SCE

No blackening of red HgS occurs at open circuit

Blackening of red HgS occurs at open circuit

Slope = +66 mV.pSCN⁻¹

[Fig. 4.15]
Fig. 4.16

Relative photopotential for initially-red HgS in electrolytes of various [KSCN]. (10^0 M KSCN is omitted)

Relative photopotential in mV

slope = -64 mV. pSCN^{-1}

- no blackening while taking photopotentials
- blackening occurs while taking photopotentials

[KSCN] in mol.dm^{-3}
c) 0.1M KSCN

Potential-time plots for red HgS in electrolytes of various [KSCN].
of initially-red HgS in 5M KSCN [part (a)], 1.0M KSCN [part (b)] and 0.1M KSCN [part (c)]. The response to light is fast, particularly at high thiocyanate concentrations, but very small changes in voltage occur on initial illumination. Larger photovoltages obtain once HgS has darkened, and in 0.1M KSCN, subsequent irradiations make voltages vs calomel more negative [figure 4.17(c)]. Plots for [KSCN] < 10^{-2}M are similar to those normally seen for photopotentials of red HgS in NaNO₃. Table 4.13 gives selected currents and the photocurrent onset potential for red HgS in thiocyanate electrolyte of varying concentrations.

Relative photocurrents become positive as pSCN increases (excluding 5M KSCN), reflecting the change from positive to negative photo-induced potentials noted earlier - and the change in sign for both photo-effects occurs at about the same thiocyanate concentration. This also holds true for the onset potential, which takes the value of 0.0V at the same [KSCN] as produces zero photo-induced current or voltage. Current-time plots are similar in shape to those seen in nitrate. At applied potentials positive of +0.3V, very large dark currents are seen at higher concentrations, due to SCN⁻ oxidation, but it is uncertain if light-induced oxidation occurs at lower biasing voltages. Mercury solublisation was considerable for [KSCN] = 5M, 1M, and 0.1M, but did not occur for [KSCN] < 10^{-2}M. In conclusion, the thiocyanate ion adopts the rôle of blackening agent for red HgS, and controls the band bending once it has been irradiated, but it is not oxidised to thiocyanogen, \((CNS)₂\), on irradiation.

An HgS electrode which had become blackened in 0.1M KSCN and produced a positive relative photovoltage and negative relative photocurrent at zero bias, was washed, dried, and stored in 0.1M NaNO₃. A relative photopotential of -130mV and zero bias photocurrent of +5µA
<table>
<thead>
<tr>
<th>[KSCN] in mol.dm(^{-3})</th>
<th>Relative photocurrent in μA at given bias in V vs SCE</th>
<th>Photocurrent onset potential in V vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>-3.5 0.0 + 0.5 very large dark current</td>
<td>+0.18</td>
<td>Black HgS</td>
</tr>
<tr>
<td>10^0</td>
<td>-9.0 0.0 - 6.0 very large dark current</td>
<td>&gt;~+0.3</td>
<td>Black HgS</td>
</tr>
<tr>
<td>10^-1</td>
<td>-1.0 -0.8 + 7.5 +10.0 @ + 0.3V</td>
<td>+0.05</td>
<td>Black HgS</td>
</tr>
<tr>
<td>10^-2</td>
<td>-0.9 +2.4 +14.0 +15.0</td>
<td>~-0.1</td>
<td>Red black HgS</td>
</tr>
<tr>
<td>10^-3</td>
<td>0.2 +3.2 +20.0 +29.0</td>
<td>~-0.2</td>
<td>A little blackening of HgS</td>
</tr>
<tr>
<td>10^-4</td>
<td>0.5 +1.3 +10.0 +27.0G +37.0G</td>
<td>~-0.1</td>
<td>'G' means gas produced at counter electrode. Very slight darkening.</td>
</tr>
</tbody>
</table>

**Table 4.13** Relative photocurrents and their onset potential obtained for initially-red HgS in KSCN electrolyte of differing concentrations
were produced, with the photocurrent onset at -0.3V vs SCE. Thus the blackening has not greatly affected the properties of HgS hitherto obtained, and deviation from these properties is due to thiocyanate ions, not the colour change.

(ii) Potassium Chloride

Table 4.14 shows voltage data for a range of KCl concentrations, and figures 4.18 and 4.19 illustrate this graphically. Potentials in the dark are invariant with [KCl] below concentrations of 10^{-1}M, but differences are seen for higher concentrations: for red HgS ('initial dark potential' - figure 4.18) potentials vs SCE become more positive, at [KCl] >10^6M, but for blackened HgS ('final dark potential' - figure 4.18), they correspondingly become more negative. Thus, either Cl^- is adsorbed differently on red and blackened HgS with a high [KCl], or a new species is formed from Cl^- when HgS is irradiated, with different adsorption characteristics. The potentials upon illumination are somewhat erratic, but no great variation with pCl is seen. 'pCl' is defined as:

$$pCl = -\log_{10}[Cl^-]$$  \[4-7\]

In figure 4.19, a reference line has been suggested for the relative photopotential points, and a slope of -59 mV.pCl^{-1} is shown. This line holds true for [KCl] = 10^{-2} – 10^6M, but deviation might occur for other concentrations. However, the relative photopotential does vary with pCl, indicating that band bending is altered. Plots of potential vs time are not different to those normally obtained.

Table 4.15 gives current details with various concentrations of KCl. In 3.8M KCl, readings were unsteady and the relative photocurrent onset potential could not be obtained. Photocurrents are larger for
<table>
<thead>
<tr>
<th>[KCl] in mol.dm$^{-3}$</th>
<th>Dark Potential in mV vs SCE before irradiation</th>
<th>Dark Potential in mV vs SCE after irradiation$^*$</th>
<th>Potential on irradiation in mV vs SCE$^*$</th>
<th>Relative Photopotential in mV$^*$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sim 3.8$</td>
<td>+315</td>
<td>-95</td>
<td>-65</td>
<td>+30</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>$10^0$</td>
<td>+225</td>
<td>-60</td>
<td>-135</td>
<td>-75</td>
<td>HgS turned brown</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>+170</td>
<td>-30</td>
<td>-150</td>
<td>-120</td>
<td>Very slight darkening</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>+165</td>
<td>+75</td>
<td>-100</td>
<td>-175</td>
<td>No darkening</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>+140</td>
<td>+65</td>
<td>-115</td>
<td>-180</td>
<td>No darkening</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>+125</td>
<td>+35</td>
<td>-55</td>
<td>-90</td>
<td>No darkening</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+130</td>
<td>+30</td>
<td>-195</td>
<td>-225</td>
<td>No darkening</td>
</tr>
</tbody>
</table>

$^*$ The potentials in columns 3, 4 and 5 have meanings as in Table 4.12

Table 4.14  Potentials for initially red HgS in potassium chloride aqueous electrolyte of various concentration.
Initial dark potential (X), dark potential after irradiation (●) and potential on illumination (○) for initially-red HgS in electrolytes of various [KCl].

Potential in mV vs SCE

- HgS remains red on illumination at open circuit
- HgS darkens in this range at open circuit

- Initial dark potential
- Final dark potential
- Potential on illumination

[KCl] in mol dm$^{-3}$
Fig. 4.19

Variation of relative photopotential with [KCl] for red HgS.

Relative photopotential in mV

- no blackening in this [KCl] range

- blackening seen in this [KCl] range

ref. slope (-59 mV mol⁻¹)

[KCl] in mol dm⁻³
<table>
<thead>
<tr>
<th>[KCl] in mol.dm(^{-3})</th>
<th>Relative photocurrent in µA at given bias in V vs SCE</th>
<th>Onset potential of relative photocurrent in V vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3.8</td>
<td>-7.0 - 4.5 ? ? ?</td>
<td>&gt; 0</td>
<td>Unreliable currents. HgS blackened</td>
</tr>
<tr>
<td>10(^{-6})</td>
<td>-0.6 + 8.0 +10.0 +12.0 +18.0</td>
<td>-0.15</td>
<td>Black HgS obtained</td>
</tr>
<tr>
<td>10(^{-1})</td>
<td>+1.2 +12.2 +47.5G +33.5G +28.0</td>
<td>-0.28</td>
<td>G = gas evolved at counter electrode</td>
</tr>
<tr>
<td>10(^{-2})</td>
<td>-0.3 + 0.6 + 2.5 + 3.1 + 3.1</td>
<td>-0.15</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>10(^{-3})</td>
<td>+0.2 + 0.4 + 1.6 + 3.1 + 4.2</td>
<td>-0.28</td>
<td>Slight darkening of HgS</td>
</tr>
<tr>
<td>10(^{-4})</td>
<td>-0.2 + 0.6 + 1.5 + 2.8 + 4.0</td>
<td>~ -0.1</td>
<td>Very slight darkening</td>
</tr>
<tr>
<td>10(^{-5})</td>
<td>+0.1 + 0.7 + 2.0 + 5.0 + 7.0</td>
<td>-0.25</td>
<td>No change to HgS</td>
</tr>
</tbody>
</table>

Table 4.15 Some details of currents at an HgS electrode with a KCl electrolyte of different concentrations.
[KCl] = 1M and 0.1M, but at concentrations below this, they are invariant with [KCl], as is the onset potential. The larger photocurrents may be due to increased sensitivity of the blackened form, and no conclusions as to chloride oxidation can be drawn. Mercury solublisation took place for [KCl] = 3.8M and 1M, and darkening continued under current conditions down to [KCl] = 10^{-3}M. Current-time plots are similar to those in nitrate electrolyte.

(iii) Potassium bromide

The voltage details for various bromide concentrations are given in Table 4.16, and presented graphically in figures 4.20 and 4.21. The unit 'pBr' is defined as:

\[ \text{pBr} = -\log_{10}[\text{Br}^-] \quad [4-8] \]

Potentials in the dark vary linearly with pBr: more negative voltages are adopted for higher [Br^-], but only at low bromide concentrations is the illumination potential linear with [Br^-], and although this potential generally became more negative as bromide molarity increases, no trend is followed here. Figure 4.21 indicates a bromide concentration of between 10^{-1} and 10^{-2}M gives an optimum relative photovoltage. Blackening under potential conditions (open circuit) ceases at [KBr] = 10^{-3}M, although a crimson colour appeared for 10^{-4}M bromide. Potential-time plots are as normal where extensive darkening does not happen, but plots similar to that shown in figure 4.22 obtain at higher molarities.

Table 4.17 gives some current data for HgS with varying molarities of potassium bromide. The relative photocurrent falls as [KBr] decreases, and continues declining after blackening ceases (at 10^{-3}M KBr) - this is taken as evidence for Br^- oxidation. At high bromide
<table>
<thead>
<tr>
<th>[KBr] in mol.dm$^3$</th>
<th>Dark Potential in mV vs SCE before irradiation</th>
<th>Dark Potential in mV vs SCE after irradiation*</th>
<th>Potential on irradiation in mV vs SCE*</th>
<th>Relative Photopotential in mV*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>- 30</td>
<td>-275</td>
<td>-285</td>
<td>- 10</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>+190</td>
<td>-180</td>
<td>-195</td>
<td>- 15</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>+195</td>
<td>-100</td>
<td>-265</td>
<td>-165</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>+ 80</td>
<td>- 60</td>
<td>-320</td>
<td>-260</td>
<td>HgS slightly darkened</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>+165</td>
<td>+ 15</td>
<td>-100</td>
<td>-115</td>
<td>No colour change</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>+182</td>
<td>+100</td>
<td>+ 45</td>
<td>- 55</td>
<td>HgS became crimson</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+230</td>
<td>+165</td>
<td>+130</td>
<td>- 30</td>
<td>No colour change</td>
</tr>
</tbody>
</table>

* The comments in Table 4.12 apply to potentials in these columns.

Table 4.16 Potentials for initially red HgS in various concentrations of aqueous potassium bromide electrolyte.
Fig. 4.20

Initial dark potential (X), dark potential after irradiation (○), and potential upon irradiation (□), for initially-red HgS in electrolytes of various [KBr].
Fig. 4.21

Variation in relative photopotential with [KBr] for red HgS:

Relative photopotential in mV

$\text{[KBr]} \text{ in mol dm}^{-3}$
<table>
<thead>
<tr>
<th>[KBr] in mol dm$^{-3}$</th>
<th>Relative photocurrent in $\mu$A at given bias in V vs SCE</th>
<th>Onset potential of relative photocurrent in V vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>+7.0 +20 ? +20 ? +10 ?</td>
<td>large dark current</td>
<td>-0.25</td>
</tr>
<tr>
<td>$10^0$</td>
<td>-12.0 +49.0G &gt;+150G +60.0G +72.0G</td>
<td></td>
<td>-0.15</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>+11.0 +70.0G +55.0G +95.0G +40G</td>
<td></td>
<td>~-0.3</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>+3.0 +32.0 +53.0G +50.0G +55.0G</td>
<td></td>
<td>~-0.4</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>-1.0 +6.8 +32.0 +30.0 +32.0</td>
<td></td>
<td>~-0.2</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-2.0 +1.9 +7.5 +12.0 +16.0</td>
<td></td>
<td>-0.15</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>+0.1 +0.1 +2.4 +4.5 +4.7</td>
<td></td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>

Table 4.17 Some currents at an HgS electrode with different potassium bromide electrolyte concentrations.
concentrations, current-time plots are non-reproducible with very long periods for photocurrents to decay back to the dark value (several hours). In more moderate bromide molarities (1M, 0.1M) normal plots are seen, and very large initial overshoots were noted - up to +1,000 μA - and rapid gas evolution occurred at the platinum counter electrode. At lower \([\text{Br}^-]\), an anodic bias was needed to achieve gas evolution, and it was not seen for the lowest bromide concentrations. Considerable mercury solublisation took place for \([\text{KBr}] \geq 10^{-2}\)M.

(iv) Potassium iodide

Potentials are given for various iodide concentrations in Table 4.18 and illustrated on figures 4.23 and 4.24. Potentials vs calomel become more negative as \([\text{KI}]\) increases, by +82mV.pI^{-1} for the initial dark
<table>
<thead>
<tr>
<th>[KH] in mol.dm(^{-3})</th>
<th>Dark Potential in mV vs SCE before irradiation</th>
<th>Dark Potential in mV vs SCE after irradiation*</th>
<th>Potential on irradiation in mV vs SCE*</th>
<th>Relative Photopotential in mV*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>-140</td>
<td>-520</td>
<td>-540</td>
<td>- 20</td>
<td>HgS was darkened before irradiation. Complete blackening on irradiation.</td>
</tr>
<tr>
<td>(10^0)</td>
<td>-160</td>
<td>-410</td>
<td>-420</td>
<td>- 10</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>(10^{-1})</td>
<td>-105</td>
<td>-310</td>
<td>-385</td>
<td>- 75</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>-155</td>
<td>-210</td>
<td>-320</td>
<td>-110</td>
<td>HgS blackened</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>- 75</td>
<td>-105</td>
<td>-300</td>
<td>-195</td>
<td>HgS dark red</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>+ 30</td>
<td>-105</td>
<td>-310</td>
<td>-295</td>
<td>HgS slightly darkened</td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>+ 75</td>
<td>- 45</td>
<td>-255</td>
<td>-210</td>
<td>No change to HgS</td>
</tr>
<tr>
<td>(10^{-6})</td>
<td>+165</td>
<td>+ 35</td>
<td>-120</td>
<td>-155</td>
<td>No change to HgS</td>
</tr>
</tbody>
</table>

* The potentials in these columns have meanings as stated in Table 4.12.

Table 4.18 Potentials for initially-red HgS in aqueous electrolytes of various potassium iodide concentrations.
Fig. 4.23

Variation in initial dark potential (X), final dark potential (○), and potential on illumination (O), for red HgS in various [KI].

Potential in mV vs SCE

- no blackening at open circuit
- blackening occurs in this [KI] range at open circuit.

slope = +82 mV. pl⁻¹

[KI] in mol.dm⁻³
Fig. 4.24
Variation in relative photopotential of red HgS with [KI].

Relative photopotential in mV

No blackening at open circuit

Blackening occurs here at open circuit

[ KI ] in mol. dm$^{-3}$
potential when \([\text{KI}] \ll 10^{-2}\text{M}\) and for the final dark potential at all iodide concentrations, but not linearly for the illumination potential. 'pI' is defined as:

\[
pI = -\log_{10}[\Gamma^-]
\]  

[4-9]

The relative photopotential is always negative, and an optimum value is obtained for \([\text{KI}] \approx 5 \times 10^{-3}\text{M}\).

Different adsorption characteristics for red and blackened HgS of \(\Gamma^-\) at high \([\text{KI}]\) obtain, which would be quite complicated for an irradiated electrode in the process of darkening - hence the non-linear illumination plot in figure 4.23. The red electrode stored in 5M KI was dark red before illumination was performed; this suggests only a few photons are necessary for this high \([\Gamma^-]\) to induce blackening, and a true voltage vs SCE of red HgS at \([\text{KI}] > 10^{-2}\text{M}\) is difficult to obtain. Thus the non-linearity of the initial dark potential plot of figure 4.23.

Table 4.19 gives details of currents with different iodide concentrations. The relative photocurrent generally decreases as \([\Gamma^-]\) decreases, suggesting iodide is participating in current production or the blackening gives higher currents. At very high \([\Gamma^-]\), iodine will be produced in correspondingly high concentrations and may block the electrode surface for more iodide ions approaching, since it cannot easily diffuse away. This will lower the photocurrent. Darkening occurred as far as \([\text{KI}] = 10^{-5}\text{M}\) - it was induced only by photocurrent production under positive bias and not under negative bias, at these lower iodide concentrations.

Plots of photoresponse against time vary with \([\text{KI}]\) and the amount of blackening it induces. Photopotential plots of 'typical' shape are seen, with the time taken to attain the level photovoltage increasing
<table>
<thead>
<tr>
<th>[KI] in mol.dm(^{-3})</th>
<th>Relative photocurrent in (\mu A) at given bias in V vs SCE</th>
<th>Onset potential of relative photocurrent in V vs SCE</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>-0.2</td>
<td>+17.0</td>
<td>+14.0</td>
</tr>
<tr>
<td>(10^0)</td>
<td>+24.0</td>
<td>+24.0</td>
<td>Very large dark currents</td>
</tr>
<tr>
<td>(10^{-1})</td>
<td>+20.0</td>
<td>&gt;+55G</td>
<td>Very large dark currents</td>
</tr>
<tr>
<td></td>
<td>~1.3</td>
<td>~&gt;40G</td>
<td>~60G</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>+5.5</td>
<td>+29.5</td>
<td>+98.0G</td>
</tr>
<tr>
<td></td>
<td>+2.0</td>
<td>+9.0</td>
<td>+23.0</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>+2.2</td>
<td>+9.0</td>
<td>+33.0</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>+0.2</td>
<td>+0.8</td>
<td>+1.0</td>
</tr>
</tbody>
</table>

*Table 4.19* Currents at an HgS electrode with different concentrations of aqueous potassium iodide electrolyte.
as [KI] decreases - it is reckoned that a level photovoltage is not obtained until darkening is complete, and darkening occurs more slowly in lower iodide concentrations. The time taken for the decline of photovoltage on ceasing irradiation also increases as [KI] decreases. This is likely due to different adsorption characteristics of electrolyte species on the blackened/previouslly irradiated HgS, rather than a result of [I⁻], since one would expect a lower probability of surface site blocking and thus an increased photovoltage decay rate at lower [I⁻]. The photocurrent-time plot varies in shape with [KI] and the nature of the electrode. If the photopotential has been taken already (as with all the results noted here), then plots are obtained as shown in figure 4.25. At 10⁻¹M KI [part (a)], quite long periods are needed to attain level currents - and the photocurrent decline is a very extended process. For 10⁻⁵M KI [part (b)], no overshoots are noted and the response time is rapid. Figure 4.26 illustrates current vs time for a fresh red HgS electrode in 0.1M KI. An initial overshoot of about +2μA is seen, then the current very slowly builds up and levels, at a value near that seen for a previously blackened electrode. By this time, the electrode is darkened, but ceasing irradiation causes a rapid increase in current, followed by a very slow decline back to zero. The rising portion of the plot after commencing irradiation is due to blackening, and the rapid increase on ending illumination must be due to a meta-stable species injecting electrons into HgS. The nature of this species is uncertain, and may be an HgS-1 adduct.

Mercury solublisation is evident for [KI] >10⁻⁴M - the photostability of red HgS in potassium iodide is dealt with in detail in Chapter Five.
As a preliminary investigation into the photo-response of darkened red HgS in nitrate electrolyte, the used electrodes from irradiation in iodide were washed, dried, and stored in pH 7 0.1M NaNO₃ (deoxygenated). Some results are presented in Table 4.20. The HgS colour mentioned in the 'remarks' column is that of the electrode after irradiation in iodide. No colour change or mercury solubilisation occurred for these electrodes in nitrate. The results indicate: (i)
Fig. 4.26
Photocurrent plot at zero bias for a fresh red HGS electrode in 0.1 M KI.

- CURRENT
- TIME

Overshoot (exaggerated)

Light on

Light off

approx 1 hour

0 µA

+30 µA

~ + 50 µA
<table>
<thead>
<tr>
<th>([K_I]) in mol. dm(^{-3}) of electrolyte previously used with HgS</th>
<th>Dark Potential in mV vs SCE</th>
<th>Potential on illumination in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in (\mu A) at given bias vs SCE</th>
<th>Onset Potential in V vs SCE of relative photocurrent</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sim 5)</td>
<td>+30</td>
<td>-80</td>
<td>-110</td>
<td>+1.1</td>
<td>+5.5</td>
<td>(-0.1)</td>
</tr>
<tr>
<td>(10^0)</td>
<td>+85</td>
<td>-115</td>
<td>-200</td>
<td>+4.0</td>
<td>+19.0</td>
<td>(-0.15)</td>
</tr>
<tr>
<td>(10^{-1})</td>
<td>+15</td>
<td>-165</td>
<td>-180</td>
<td>+5.5</td>
<td>+20.0</td>
<td>(-0.22)</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>+30</td>
<td>-150</td>
<td>-180</td>
<td>+5.0</td>
<td>+25.0</td>
<td>(-0.19)</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>-30</td>
<td>-165</td>
<td>-135</td>
<td>(\sim +12)</td>
<td>+17.0</td>
<td>(-0.25)</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>+40</td>
<td>-120</td>
<td>-160</td>
<td>+7.0</td>
<td>+19.0</td>
<td>(-0.15)</td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>+80</td>
<td>-95</td>
<td>-175</td>
<td>+2.0</td>
<td>+40.0</td>
<td>(-0.10)</td>
</tr>
<tr>
<td>(10^{-6})</td>
<td>+30</td>
<td>-115</td>
<td>-145</td>
<td>+3.0</td>
<td>+14.0</td>
<td>(-0.25)</td>
</tr>
</tbody>
</table>

Table 4.20 Some potentials and currents of HgS electrodes in \(N_2\)-purged pH 7 0.1M NaNO\(_3\), previously irradiated in potassium iodide of indicated molarity.
potentials vs calomel and the relative photopotential are not greatly affected by the extent of darkening; (ii) a "degree of darkening" is necessary for optimum photocurrent production, resulting from an iodide concentration of $10^{-2}$ to $10^{-3}$M; and (iii) the relative photocurrent onset potential is about -0.20V for each darkened HgS electrode. One may conclude that darkening of red HgS can improve photocurrent production, and attempts to qualify this are discussed in Chapter Five.

The investigation of red HgS in solutions of thiocyanate, chloride, bromide, and iodide of various concentrations leads to the conclusion that each HgS-electrolyte junction must be treated as a unique system. The only general observation is that potentials adopted by HgS versus calomel become more negative as the ion concentration increases, but even this is not always true. The negative ion undergoes adsorption and makes the Helmholtz potential more negative, approximately following the Nernst equation [4-1] - see p.133. The reduced form of a redox couple is present, [oxidised form] = 1, so equation [4-1] becomes:

$$E = E^\circ - \frac{2.303 RT}{nF} \log_{10} [\text{anion}]$$  \hspace{1cm} [4-10]

The pre-logarithmic term is modified as before, since $n=1$ (see p.133), $\log_{10}[\text{anion}]$ is expressed as in equations [4-6] to [4-9], so equation [4-10] simplifies to:

- **either** $E = E^\circ + 0.059 \ pSCN$  \hspace{1cm} [4-11]
- **or** $E = E^\circ + 0.059 \ pCl$  \hspace{1cm} [4-12]
- **or** $E = E^\circ + 0.059 \ pBr$  \hspace{1cm} [4-13]
- **or** $E = E^\circ + 0.059 \ pI$  \hspace{1cm} [4-14]

Equation [4-11] is obeyed for potassium thiocyanate only for dark voltages of an electrode after irradiation, but the other voltages have no Nernstian dependence. This has been mentioned earlier and a change
in adsorptive characteristics of the thiocyanate ion, due to its irradiation, is proposed. A valence bond representation of SCN$^-$ is [\(\overset{3}{S} = C = \overset{1}{N}\)], with the negative charge on nitrogen. Resonance canonicals may be written:

\[\overset{3}{S} = C = \overset{1}{N}, \quad \overset{3}{S} = C = \overset{1}{N}, \quad \overset{3}{S} = C = \overset{1}{N}\]

negative charge on N

negative charge on S

negative charge distributed over S, C, and N

The contribution of these to the ground state of the thiocyanate ion will be determined principally by the electronegativities of S, C, and N, and by solvation. The presence of an HgS surface, and illumination of this and the ion, has unknown effects, but may alter the thiocyanate's adsorption (via N or via S) and the strength of the adsorptive interaction, which would in turn cause changes to the Helmholtz potential and band-bending. Both these changes are seen for SCN$^-$. The change in band-bending is reflected by the relative photovoltage variation of \(-64 \text{ mV.pSCN}^-\) (figure 4.16), the change in sign of zero bias photocurrent, and the onset (table 4.13). The lower two lines of figure 4.15 intersect at a concentration of \(10^{-1}\text{M} > [\text{KSCN}] > 10^{-2}\text{M}\). To the right of the intersection, 'positive' or downward band-bending exists, since the illumination potential lies positive of the final dark potential. To the left of the intersection, the illumination potential is negative of the final dark potential - meaning irradiation has shifted the bands back towards the non-equilibrium state or flat-band potential (see figure 1.9, p.18) - i.e. 'negative' or upward band-bending originally existed. On figure 4.16, the point of zero relative photovoltage is found for \(10^{-1}\text{M} > [\text{KSCN}] > 10^{-2}\text{M}\), approximately the same
as the intersection point afore-mentioned on figure 4.15. The downward and upward band-bendings correspond to positive and negative relative photopotentials of figure 4.16 - and the 'dark potential after irradiation' slope of +66 mV.pSCN⁻¹ and 'relative photopotential' slope of -64 mV.pSCN⁻¹ are close enough to confirm this.

Equation [4-12] is not obeyed by any of the potentials in chloride shown in figure 4.18. The adsorption of Cl⁻ on red and darkened HgS is different, and not consistent. Positive band bending occurs in near-saturated KCl (3.8M) to give the positive relative photovoltage and anodic onset potential, but it is unclear how this comes about and how the relative photopotential in figure 4.19 varies by approximately -52 mV.pCl⁻¹.

Equation [4-13] is obeyed to an extent by dark potentials in bromide electrolyte, but the influence of Br⁻ on illumination potentials is uncertain, especially at [KBr] > 10⁻²M (see figure 4.20). Bromide does undergo adsorption on red and darkened HgS, but its effect on band bending is uncertain, since the optimum relative photopotential occurs at the same [KBr] (≈ 10⁻²M) as the largest zero bias photocurrent and most negative onset potential (figure 4.21 and table 4.17). Bromide is likely oxidised, so the presence of bromine and a local surface redox couple will invalidate equation [4-13]. This is particularly true for the 'potential on illumination' line of figure 4.21, where bromine may have been produced.

The comments on bromide apply to potassium iodide electrolyte - equation [4-14] disregards any iodine present - although some dark potentials fall on a line of +82 mV.pI⁻¹ (figure 4.23). Iodine is more easily oxidised than bromine, so deviations for measurements on illumination will be greater. Nevertheless, iodide has a profound
effect upon red HgS; it does adsorb, and induces rapid darkening and solublisation.

The presence of the oxidised reducing agent at HgS may be responsible for positive photovoltages and negative photocurrents at zero bias. Photogenerated electrons may be captured by the oxidising agent and cause the current flow cathodically or induce a positive photopotential. Band bending may be unaffected by these ions in this case. It is impossible to state the mechanism of anomalous photoeffect generation from the results obtained.

4.3.3 Red HgS in non-aqueous electrolytes

Hydroxyl ions are considered to be oxidised on illumination of red HgS under current conditions, so the supporting solvent - water - participates in the photoelectrochemistry by virtue of its self-ionisation. It was thought worthwhile to investigate HgS in a non-aqueous system. Pyridine was chosen as it readily dissolves lithium salts, in particular LiNO₃.

Pyridine was doubly distilled from KOH pellets at 114°-116°C under normal pressure and distilled a third time immediately before making up the electrolyte. Five different salts were employed. LiNO₃ is 'Alfa Ultrapure' (anhydrous), and was kept in drying pistols at 80°C under vacuum for four hours immediately before use. LiCl is anhydrous and is similarly further dried. LiBr, Lil, and SnCl₂ were found to melt in drying pistols, so they were used as received (in anhydrous form, and fresh bottles). The experimental details are as before, except that all precautions were taken to exclude moisture from the cell - incoming nitrogen was passed through a glass tube, 20" × 1", containing fresh silica gel.
Table 4.21 summarises the results of red HgS in pyridine solutions of lithium nitrate, chloride, bromide, iodide and stannous chloride. The photo-effect/time plots for all pyridine systems are similar to those seen for aqueous nitrate, except that the response is faster and no current overshoots are seen. For initially-red HgS, the relative photopotential is about -140 mV in all electrolytes, in line with aqueous systems, although potentials vs calomel are controlled by the salt. Relative photocurrents and the onset are different for each system. LiNO₃ has a positively-shifted flat-band potential compared to NaNO₃/H₂O. The halides generate a lower photocurrent than in water, but the photocurrent onset potential becomes more negative from chloride to iodide. For LiBr, a dark current of +75μA obtains at +0.5V - the Br⁻ oxidation current - and a similar I⁻ oxidation current is seen for Lil at +0.1V. The increasing zero-bias photocurrent from LiCl to Lil suggests bromide and iodide are oxidised on illumination. For SnCl₂, a white precipitate coated the electrode on storage but did not appear to inhibit photo-effects. The results are analogous to those for aqueous SnCl₂ in that an undeterminable, negative onset potential for photocurrents is seen. Interferences in the atomic absorption determination meant no reliable mercury concentrations in the used electrolyte could be obtained. In the halide range, mercury solubilisation occurred as with an aqueous electrolyte - but no blackening took place.

An electrode previously darkened in aqueous potassium iodide was investigated in 0.1M LiCl (C₅H₅N) and exhibited a larger relative photopotential, larger relative photocurrents, and a more negative photocurrent onset potential than red HgS in chloride-water. However, solubilisation of mercury was observed; this has not been noted for
<table>
<thead>
<tr>
<th>Electrolyte Salt (0.1M in C,H,N)</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃</td>
<td>+220</td>
<td>+75</td>
<td>-145</td>
<td>-4.0</td>
<td>&lt;0</td>
<td>+4.0 &amp; +0.5V</td>
<td>-0</td>
<td>215</td>
</tr>
<tr>
<td>LiCl</td>
<td>+30</td>
<td>-125</td>
<td>-155</td>
<td>0.8</td>
<td>+0.4</td>
<td>+1.7</td>
<td>+2.7</td>
<td>+6.2</td>
</tr>
<tr>
<td>LiCl</td>
<td>-60</td>
<td>-410</td>
<td>-350</td>
<td>+10.0</td>
<td>+25.0</td>
<td>+16.0</td>
<td>+18.0</td>
<td>+22.0</td>
</tr>
<tr>
<td>LiBr</td>
<td>+60</td>
<td>-105</td>
<td>-165</td>
<td>0.2</td>
<td>+1.3</td>
<td>+1.9</td>
<td>+4.0</td>
<td>-</td>
</tr>
<tr>
<td>LiI</td>
<td>-280</td>
<td>-420</td>
<td>-140</td>
<td>+1.6</td>
<td>+3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>-170</td>
<td>-305</td>
<td>-135</td>
<td>+1.0</td>
<td>+3.0</td>
<td>+4.0</td>
<td>+2.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.21 Photo-effects generated by 'Fisons' red HgS in pyridine containing various dissolved salts. The counter electrode is a platinum wire, 0.5 mm in diameter.
blackened HgS in aqueous chloride. Nevertheless, the response of HgS in LiCl/C₅H₅N is superior to that of some similar electrodes in aqueous electrolytes.

Trace amounts of water may be responsible for photo-effects, and similarities do exist between results in aqueous and non-aqueous systems. However, certain conclusions can be drawn: (i) aqueous ions which cause darkening of HgS have no such effect in pyridine solutions (for a comparable irradiation time); (ii) solubilisation and darkening are not concurrent processes in pyridine; (iii) the darkened sulphide surface is influenced differently to red HgS by chloride in pyridine, and the effect of aqueous chloride is different yet again. This implies solvation plays an important rôle in ion adsorption and its influence on the Helmholtz potential and band bending of HgS.

4.4 Discussion

Red mercury(II) sulphide, in natural or synthetic form, is known to exhibit photoconductivity. Natural cinnabar shows photoconductivity and luminescence [218], and work on synthetic crystals illustrates the onset of photoconduction is about 600 nm, equivalent to the band gap [219]. Natural red HgS is more photosensitive than the synthetic sulphide [220], and in all these publications it is postulated that energy levels exist within the band gap. N-type conduction predominates in cinnabar, as determined by the measurement of the Hall effect [221]. (The Hall effect is observed when, in a conductor carrying a current, a magnetic field is applied at right angles to the direction of current flow. The charge carriers are deflected and a force acts to restore the flow direction of the carriers. This restoring force is the Hall voltage and the sign of this voltage determines if electrons or positive
holes carry the current.) P-type conduction is possible, as the wave­
length of exciting light can determine the charge carrier sign [222].
This explains the generation of a positive relative photovoltage at
sub-band gap wavelengths, noted in section 4.3.1.3 (p.134).

There is some work reported in the literature for illuminated red
HgS in contact with solutions. In an acid electrolyte, a photopotential
of -1 to -2µV was obtained with HgS made in situ from Na₂S, H₂SO₄, and
Hg, using a 60W mercury lamp [223]. Phenolphthalein is absorbed to a
very much greater extent on illuminated red HgS than in the dark [224].
It is postulated that mobile electrons in HgS upon illumination
increase its absorptive power, but no such electrons exist in the dark
and reduce absorbtion. This will have implications for specific ion
adsorbtion (as well as any absorption) mentioned earlier in this
chapter. Red HgS acts as catalyst in some photochemical reactions:
hydrogen peroxide is obtained from aqueous phenol [29]; oxidation of
Fe²⁺ and reduction of Fe³⁺ can be effected [225]; hydrogen peroxide is
produced from oxygenated distilled water [226]. In Grossweiner's
papers, it is suggested that light induces electron-hole pair separa­
tion in HgS, with hydroxide ions then oxidised to HO⁻ (adsorbed) at the
positive hole. H⁺ is formed on HgS by electron injection into H⁺, and
these species can react with O₂ to give H₂O₂, or with Fe²⁺/Fe³⁺. No
solublisation of HgS occurs, and no reactions take place at wavelengths
longer than those corresponding to the band gap energy. In another
publication, Grossweiner proposes that hydrogen peroxide formation is
controlled by the valence-conduction band transition, meaning the con­
duction band is placed to favour H⁺ reduction and the valence band to
favour OH oxidation [227]. This means that the band edges of red HgS
may be favourably placed for water photoelectrolysis - see figure 1.20,
Red HgS photosensitizes the methylation of mercuric acetate in aqueous acetic acid solution [228]. On irradiation, HgS solublises in the presence of Hg$^{2+}$ ions, sulphur precipitates and polymerises to sensitize the reaction:

\[(\text{CH}_3\text{COO})_2\text{Hg} \xrightarrow{\text{hv}} (\text{CH}_3\text{COO})\text{HgCH}_3 + \text{CO}_2\uparrow\]

No mercury methylation or HgS solublisation occurs in the absence of Hg$^{2+}$ ions or in the dark. Thus the presence of a specific ion controls the photo-stability of HgS.

Published work on mercury(II) sulphide illustrates its behaviour as photoconductor and photocatalyst and indicates it is not necessarily unstable. Literature reports of darkening in red HgS are mentioned in Chapter Five.

The results presented here reflect the n-type conductivity of red HgS, since the photo-induced voltage is negative. The response to light of different wavelengths illustrates that the band gap controls generation of photo-effects. Hydrogen may be the gas evolved at the counter electrode, and oxygen at HgS; if this is so, then the band edges are suitably placed to assist water photoelectrolysis. Grossweiner's work on hydrogen peroxide production gives encouragement to this. It is of importance, therefore, to calculate the energies of the valence and conduction bands and compare them with energies of solution redox couples.

The energy of the conduction band relative to the vacuum level can be calculated from the atomic electronegativities of mercury and sulphur using equation [1-19] on p.12. Atomic electronegatives ($\chi$) are obtained as the arithmetic mean of the element's first ionisation
potential (IP) and electron affinity (EA). For mercury, IP = 10.43eV and EA = 1.54eV, and for sulphur, IP = 10.36eV and EA = ~2.1eV [229].

Thus \( \chi_{\text{Hg}} = \frac{1}{2}(10.43 + 1.54) \)
\[ = 5.98 \]
and \( \chi_{\text{S}} = \frac{1}{2}(10.36 + 2.1) \)
\[ = 6.23 \]
The molecular electronegativity is the geometric mean of atomic electronegativities:

\( \chi_{\text{HgS}} = (5.98 \times 6.23)^{\frac{1}{2}} \)
\[ = 6.10 \]
So \( \text{EA HgS} = 6.10 - \frac{1}{2}(2.0) \) (eqn 1-19 for HgS, where \( \text{Eg} = 2.0eV \))

The conduction band base (\( E_{\text{CB}} \)) lies 5.10eV below the vacuum level. Redox potentials are given in volts vs SHE and \( E_{\text{CB}} \) needs to be expressed as a potential on this scale. On the SHE scale, the vacuum level lies at -4.73V (equation [1-15], p.10). \( E_{\text{CB}} \) lies 5.10eV below the vacuum level, so it will adopt a value of (-4.73 + 5.10) volts on the SHE scale. \( E_{\text{CB}} = +0.37V \) vs SHE, and \( E_{\text{VB}} = +2.37V \) vs SHE, as the band gap is 2eV.

The Fermi level of red HgS must now be obtained. Using equation [1-18] on page 11, \( E_{\text{F}} \) in the dark is the potential of the HgS electrode versus the calomel reference electrode. Sodium nitrate electrolyte is inert towards HgS and the dark potential at pH 7 is close to 0.0V vs SCE. At pH 7, \([\text{H}^+] = [\text{OH}^-] \), and a simplified equation for \( E_{\text{redox}} \) is [230]

\[ E_{\text{redox}} = \frac{1}{2}(E_{\text{ox}} + E_{\text{red}}) \quad [4-15] \]
where \( E_{\text{redox}} \) is the solution Fermi level, and \( E_{\text{ox}}, E_{\text{red}} \) are the potentials at pH 7 for the oxidation and reduction reactions, respectively.
For 0.1M NaNO₃ at pH = 7, equation [4-15] becomes

\[
E_{\text{redox}} = \frac{1}{2}(E_{O_2/H_2O} + E_{H^+/H_2})
= \frac{1}{2}(+0.815 - 0.413)
= +0.2\text{V (vs SHE)}
\]

or \(-0.04\text{V (vs SCE)}\)

Thus at pH 7 on the SCE scale, the solution Fermi (redox) energy is \(-0.04\text{V}\). In the dark, the HgS and solution Fermi energies equilibriate, so this value is taken for \(E_F(HgS)\). The dark potential (and hence \(E_F\)) shifts by \(-0.059\text{V.pH}^{-1}\) (figure 4.6). At pH 0 on the SCE scale, \(E_F = +0.37\text{V}\) or \(+0.61\text{V vs SHE}\).

The onset of relative anodic photocurrent and the potential obtained on illumination of HgS adopt similar values in a given experimental system - see Table 4.22. In other aqueous electrolytes, a correlation

<table>
<thead>
<tr>
<th>pH of electrolyte</th>
<th>Potential on illumination in V vs SCE</th>
<th>Onset potential in V vs SCE of relative photocurrent</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>-0.35</td>
<td>-0.35</td>
</tr>
<tr>
<td>7.0</td>
<td>-0.33</td>
<td>-0.35</td>
</tr>
<tr>
<td>1.5</td>
<td>+0.16</td>
<td>+0.23</td>
</tr>
<tr>
<td>2.9</td>
<td>+0.14</td>
<td>+0.13</td>
</tr>
<tr>
<td>3.8</td>
<td>+0.05</td>
<td>+0.04</td>
</tr>
<tr>
<td>4.6</td>
<td>-0.02</td>
<td>-0.03</td>
</tr>
<tr>
<td>6.9</td>
<td>-0.20</td>
<td>-0.18</td>
</tr>
<tr>
<td>8.2</td>
<td>-0.24</td>
<td>-0.22</td>
</tr>
<tr>
<td>9.1</td>
<td>-0.28</td>
<td>-0.28</td>
</tr>
<tr>
<td>10.0</td>
<td>-0.31</td>
<td>-0.35</td>
</tr>
<tr>
<td>11.0</td>
<td>-0.40</td>
<td>-0.50</td>
</tr>
<tr>
<td>12.0</td>
<td>-0.53</td>
<td>-0.55</td>
</tr>
<tr>
<td>12.9</td>
<td>-0.60</td>
<td>-0.63</td>
</tr>
</tbody>
</table>

Table 4.22 Illumination potentials and photocurrent onset potentials for red HgS in deoxygenated 0.1M NaNO₃.
between these two potentials is noted - see Tables 4.8 and 4.9. Now the condition to observe zero relative photocurrent is obtained when no effective electron-hole pair separation after generation by light, occurs. This condition is either that of band-flattening or of the carrier-pair generation rate equalling the recombination rate, with a small space-charge layer still operative. A maximum potential upon illumination will also be obtained under this condition. This has been observed: successive dilution of the heat/UV filter to allow higher illumination intensities has not resulted in any increase in relative photovoltage. Thus the Fermi level has been raised to its highest value and an increase in light intensity can raise it no higher. For the purposes of constructing a band model of HgS, the onset potential/illumination potential will be taken as the flat-band potential - i.e. the Fermi level before establishment of an electrolyte-semiconductor junction. (An attempt to obtain the flat-band potential by capacitance using the circuit on p.24 was unsuccessful. Results indicated the semiconductor was exhibiting infinite capacitance or a short-circuit was operating.) Thus $E_F(HgS) = \sim -0.25V$ vs SCE at pH 7, or $+0.40V$ vs SHE at pH 0.

The proposed levels on the SHE scale of red HgS are: $E_{CB} = +0.37V$; $E_{FB} = +0.40V$; $E_{VB} = +2.37V$; and the redox electrolyte has a Fermi energy of $+0.61V$. The band edges may vary by as much as $\pm 0.3V$ due to (i) the uncertainty in sulphur's electron affinity, (ii) the uncertainty in the absolute energy of $E_{H2/H+}$ - the quoted value of 4.73eV is the most recent calculation but 4.48eV is often used [90]. However, a rough guide to interpreting the photoelectrochemical properties of red HgS is provided by this model - see figure 4.27. The levels labelled 'Ed' represent potentials for the decomposition reactions [231]:

-207-
Postulated energy levels of red HgS at pH 0 expressed in volts. Some solution redox couples are indicated, but the HgS-liquid junction is not at equilibrium.
HgS + 2e = Hg + S^{2-} \quad \text{Cathodic decomposition} \\
E_F^{\text{(CATHODIC)}} = -0.7V \\

\text{and} \quad \text{Hg}^{2+} + S + 2e = \text{HgS} \quad \text{Anodic decomposition} \\
E_F^{\text{(ANODIC)}} = +1.05V \\

E_F, \text{ the Fermi level, is also the flat-band potential, as the junction shown in figure 4.27 is not at equilibrium.} 

From the energy level model the following can be deduced. (i) All reducing agents with \( E^\phi \) negative of +2.37V may be theoretically oxidised by light-produced holes in the valence band of HgS; (ii) all oxidising agents with \( E^\phi \) positive of +0.37V may be theoretically reduced at the counter electrode by conduction band electrons that have travelled the external circuit and remained at the same energy; (iii) HgS is susceptible to anodic oxidation on illumination (equation [4-3], p.139) since \( E_F^{(ANODIC)} \) lies at an energy such that the valence band's positive hole can capture electrons liberated in anodic oxidation; (iv) HgS is not susceptible to cathodic decomposition, since conduction band electrons are of lower energy than \( E_F^{(CATHODIC)} \). Experimental results indicate some reducing agents are oxidised, instability of HgS is linked to electrolyte species and cannot be labelled 'cathodic' or 'anodic', and reduction of the oxidised half of the redox couple has not been proved or disproved. Instability of semiconductors has been discussed in Chapter One (pp.37-44), and red HgS is kinetically stabilised against anodic oxidation by redox couples with \( E^\phi \) negative of \( E_F^{(ANODIC)} \). Kinetic factors therefore override thermodynamics and this explains how some reducing agents, but not others, are oxidised at illuminated red HgS. All of the reducing agents tried in section 4.3.2.1 are theoretically oxidisable, so kinetics must determine the reaction that occurs. One crucial factor noted from
Figure 4.27 is that conduction band electrons are energetically incapable of reducing H⁺ to H₂. However, a gas (presumed hydrogen) has occasionally been seen at the counter electrode at zero bias, which can be rationalised only if one assumes electrons 'accumulate' at this electrode and raise its Fermi energy until the H⁺ reduction level is reached. This has been postulated for TiO₂ [91]. Artificially raising $E_{F(\text{Platinum})}$ is achieved by positively biasing HgS, and cathode gas evolution is more often seen under these conditions. The theoretical minimum bias for this is +0.37 V, the difference between $E_C$ and $E_{H^+/H_2}^\circ$.

Figure 4.27 is somewhat artificial, as pH 0 corresponds to an electrolyte of one molar acid, where HgS behaves unreliably. It has the advantage that tabulated standard redox potentials can be quoted. In figure 4.28, the band edges are shown at pH 7, on the calomel scale, as would be practically encountered. The decomposition levels are assumed to be invariant with pH but the valence and conduction band increase in energy with pH, and move upwards by -59 mV.pH⁻¹. This is justified from results on varying the electrolyte pH (section 4.3.1.3); and a constant relative photopotential with pH means band bending is unaltered by pH, so $(E_F - E_{\text{REDOX}})$ remains constant. In figure 4.28 $E_{O_2/H_2O}$ is negative of $E_{D(\text{ANODIC})}$. Water oxidation is the principal half-reaction occurring at HgS on illumination, and it should quench anodic oxidation, even if other reducing agents compete for holes. In terms of thermodynamics and kinetics, the stability of HgS is explained. However, $E_{I_2/I^-}$ lies above $E_{D(\text{ANODIC})}$, so HgS should be stable in an iodide electrolyte too. This is not found in practice. Furthermore, mercury(II) sulphide solubilises in a KI suspension where the photo-electrochemical anodic oxidation reaction cannot occur. No electron flow is possible in a suspension, so solubilisation here is a photo-
Fig. 4.28
Postulated energy levels of red HgS and some solution redox couples expressed in volts at pH 7. The junction is not at equilibrium.
chemical process.

The results from varying the concentrations of Cl\(^-\), Br\(^-\), I\(^-\) and SCN\(^-\), and from other potential reducing agents, indicate the presence of particular ions and their adsorption gives photo-properties that are not explained by the band-model. The simple notion of an ion injecting an electron into a light-created valence band hole of red HgS to cause a positive photocurrent does not always obtain. For nitrate, water or hydroxyl ions are oxidised at HgS and protons are reduced at the platinum counter electrode if the sulphide is suitably biassed. The energy to effect these redox reactions comes from light and an input potential. This fits neatly into the 'band edge theory'. For other electrolytes, ion adsorption causes properties not explainable by the band model, and the effect is not understood.

In evaluating the performance of red mercury(II) sulphide as an electrode for harnessing optical energy, the following criteria have been established:

(i) Red HgS is n-type in that negative photo-induced voltages are produced.

(ii) The flat-band potential is about -0.25V vs SCE at pH 7, varying by -0.059V.pH\(^{-1}\).

(iii) The photoelectrolysis of water may be achieved with visible light if oxygen is absent from the counter electrode and a positive bias is applied to HgS. (See figure 1.17, p.28 - the bias is needed since \(E_{O^+/X^+}^{\text{Red}}\) lies above the metal Fermi energy.) If oxygen is present, photovoltaic operation is found (see figure 1.16, p.27). The theoretical conditions for optimum water photo-electrolysis noted on p.37 are not all fulfilled by red HgS, as \(E_{H^+/H_2}^{\text{Red}} > E_S\) and \(EA > 4.73\text{eV}\).
(iv) The band gap energy controls carrier generation, and allows usage of visible light.

(v) Theoretically, HgS is completely stable to cathodic decomposition and can be stabilised against anodic decomposition with suitable solutions.

(vi) In practice, electrolyte species control stability and often the photo-properties of HgS.

It is clear from figures 4.27 and 4.28 that only a small amount of band bending, equal to \((E_F - E_{\text{redox}}) - 0.2V\), occurs in red HgS. This is shown in figure 4.29. The small band bending means a weak space-charge

**Volts vs SCE**

![Diagram showing band bending in red HgS](image)

*Fig. 4.29*

Band bending (= 0.2V) in red HgS. Band edges and redox potentials are for pH = 7.
layer exists with inefficient carrier separation. The dependence of
the photovoltage on intensity indicates recombination results from
this [figure 4.11(b)]. No optical to chemical/electrical conversion
efficiencies have been worked out for an HgS photo-anode, as short-
circuiting would render such calculations meaningless. The small
potential drop across the space-charge layer will make a major contri-
bution to the intrinsic inefficiency of red HgS, let alone effects of
short-circuiting. It is surprising that any photo-effects have been
observed at all. The HgS-Pt junction appears to be rectifying; the
work function of platinum is 5.7eV [232] and that of HgS is 5.13eV
(\(\equiv E_f\) on the vacuum scale). A junction like that in figure 3.9(b),
p.119, will be obtained.

The band bending shown in figure 4.29 is that obtained at open
circuit (voltage conditions). Under current conditions, \(E'_F(\text{HgS})\) is
controlled by the applied bias. At, for example, zero bias, \(E'_F(\text{HgS}) = 0.0V\), and at +0.5V bias, \(E'_F(\text{HgS}) = +0.5V\) (vs SCE). Band bending is
therefore controlled potentiostatically when the HgS electrode is
incorporated in the current-measuring circuit. The value of \(E'_F(\text{HgS})\)
shown in figure 4.29 is very close to 0.0V vs SCE, so there will be
little alteration in band bending when the electrode is in a current-
measuring circuit and at the same potential as the saturated calomel
reference electrode. Band bending will be increased when a positive
bias is applied to HgS.

An electrolyte with a more positive \(E_{\text{redox}}\) would produce more band
bending. This electrolyte must be non-aqueous, but the results
obtained in pyridine indicate little improvement on water. It is
unwise to conclude that more efficient charge separation cannot be
induced in HgS as only a limited range of reducing agents in two
solvents has been investigated. Replacing the platinum conductive carrier by some material that gives a better junction may also improve current and voltage output. It is unknown why titanium or carbon fibre failed to work as they, in theory, should form an ohmic junction to HgS. Interesting, and as yet, inexplicable, phenomena have been observed with aqueous electrolytes containing species with $E^{\theta}$ lying between $+0.5V$ and $+1.1V$. These species may interact with energy levels within the band gap, and the presence of some, (e.g. SCN$^-$, Fe(CN)$_6$)$^{3^-}$ alter the properties on illumination, cause solublisation, and induce darkening. These properties can, at present, be commented on only in terms of 'specific ion adsorption'. Darkening improves the response to light and is, therefore, of great interest. It is dealt with in detail in the following chapter.
CHAPTER FIVE

THE EFFECT OF POTASSIUM IODIDE ON RED MERCURY(II) SULPHIDE, AND AN INVESTIGATION OF THE BLACKENED MATERIAL
CHAPTER FIVE

5.1 Introduction

A number of electrolytes have been shown to solubilise and/or blacken illuminated red HgS, and the darkened sulphide produces larger photocurrents than the red form. In this Chapter, 'controlled' blackening in aqueous potassium iodide is dealt with, along with the basic photoelectrochemical properties, mechanism of formation, and nature of darkened red HgS.

5.2 Controlled Blackening in Aqueous Potassium Iodide

It was established that potassium iodide must be in aqueous solution to act as blackening agent; dry KI crystals and red HgS were sealed in a clear polythene bag and left close to a 500 W mercury lamp for 24 hours. No visible colour changes occurred.

The controlled blackening experiments were performed with sulphide-coated platinum mesh electrodes, using the same experimental system as in Chapter Four. A number of parameters in the system were altered in turn, and the blackened electrode was washed, dried and investigated in nitrate electrolyte. The magnitude of photoeffects it generated were used to measure the 'degree of darkening'. Results in Table 4.20 of the previous Chapter indicate the molarity of potassium iodide controls darkening and hence photocurrent production in nitrate. [KI] is the first parameter to be discussed.

5.2.1 Variation of Iodide Molarity

Between 0.025 g and 0.030 g of red HgS coat the electrodes employed, which are illuminated in a current-measuring circuit for 60 minutes,
<table>
<thead>
<tr>
<th>[KI] in mol. cm(^{-3})</th>
<th>Colour of HgS after irradiation in KI</th>
<th>Relative photovoltage in mV (in nitrate)</th>
<th>Relative photocurrent in µA (in nitrate) at given bias vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^0)</td>
<td>Black</td>
<td>-160</td>
<td>+ 3.5  +11.0  +15.0  +15.0</td>
</tr>
<tr>
<td>(10^{-1})</td>
<td>Black</td>
<td>-195</td>
<td>+18.5  +21.0  +28.0  +28.0G</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>Dark red</td>
<td>-180</td>
<td>+ 9.5  +24.0  +28.5  +11.0</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>Dark red</td>
<td>-130</td>
<td>+10.0  +28.0  +20.0  +20.0</td>
</tr>
</tbody>
</table>

G = gas evolved at counter electrode (platinum wire)

**Table 5.1** Photoeffects produced in deoxygenated alkaline 0.1M NaNO\(_3\) by HgS electrodes previously irradiated for 60 minutes at 0.0V vs SCE in solutions of various KI molarities
held at 0.0V vs SCE. Table 5.1 indicates photoeffects obtained with blackened electrodes in pH 11.5 0.1M NaNO₃ (N₂-purged). Relative photopotentials are not greatly affected by iodide concentration, but lower photocurrents are noted where 1.0M KI has been used. This suggests "over-blackening" from using too high [KI] can diminish photoresponses, and an "optimum blackening" must exist.

5.2.2 Variation in Irradiation Time

Conditions are as in 5.2.1, with a 0.1 KI electrolyte throughout. Table 5.2 presents some results. The relative photovoltage reaches an optimum for a 60 minute irradiation in iodide, and drops significantly for times exceeding 240 minutes. Photocurrents do not follow the same trend, but become larger for a longer blackening time. These results conflict with earlier conclusions: in section 5.2.1, photovoltages are not significantly affected by the "extent of blackening", but here, prolonged irradiation (5-6 hrs) - and presumably more extensive "iodide-treatment" - has diminished photopotentials. Thus, the means of inducing darkening appears as crucial as the extent of darkening. Once an electrode is wholly black, 'colour' is an obsolete description, and variations in photoeffects for such electrodes must be characterised by the method of darkening.

5.2.3 Variation in Light Intensity

The red HgS electrodes are successively held at 0.0V vs SCE in a 0.1M KI electrolyte, and irradiated for 60 minutes with different neutral density filters in the light path. The filter transmission is the variable parameter and results are shown in Table 5.3. The photon flux at HgS should, ideally, be the parameter in question, but since the light is not monochromatic it is not possible to quote this.
<table>
<thead>
<tr>
<th>Time of irradiation in minutes</th>
<th>Colour of HgS after irradiation in KI</th>
<th>Relative photovoltage in mV (in nitrate)</th>
<th>Relative photocurrent in μA (in nitrate) at given bias vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Dark red</td>
<td>-150</td>
<td>+13.5 + 20.0 + 21.0 +12.0</td>
</tr>
<tr>
<td>30</td>
<td>Red/black</td>
<td>-195</td>
<td>+15.0 + 45.0 + 33.0 +19.0</td>
</tr>
<tr>
<td>45</td>
<td>Black</td>
<td>-190</td>
<td>+12.0 + 39.0 + 31.0G +37.0G</td>
</tr>
<tr>
<td>60</td>
<td>Black</td>
<td>-195</td>
<td>+18.5 + 21.0 + 28.0 +28.0G</td>
</tr>
<tr>
<td>120</td>
<td>Black</td>
<td>-140</td>
<td>+16.0 + 36.0 + 33.0 +20.0</td>
</tr>
<tr>
<td>180</td>
<td>Black</td>
<td>-140</td>
<td>+27.0 + 48.0 + 21.0 +12.0G</td>
</tr>
<tr>
<td>240</td>
<td>Black</td>
<td>-110</td>
<td>+29.0 + 70.5 + 28.5 +13.0</td>
</tr>
<tr>
<td>300</td>
<td>Black</td>
<td>- 65</td>
<td>+ 9.0 + 23.0 + 35.0 +35.0</td>
</tr>
<tr>
<td>360</td>
<td>Black</td>
<td>- 80</td>
<td>+30.0 +123.0G +150.0G +85.0G</td>
</tr>
</tbody>
</table>

G = gas evolved at platinum wire counter electrode

Table 5.2 Photoeffects obtained in deoxygenated alkaline 0.1M NaNO₃ by HgS electrodes previously irradiated at 0.0V vs SCE in 0.1M KI for various periods of time
<table>
<thead>
<tr>
<th>Colour of HgS after irradiation in KI</th>
<th>Relative photopotential in mV (in nitrate) at given bias vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark red</td>
<td>+ 6.6 + 13.0</td>
</tr>
<tr>
<td>Dark red</td>
<td>+ 6.5 + 8.0</td>
</tr>
<tr>
<td>Dark brown</td>
<td>+ 6.4 + 11.0</td>
</tr>
<tr>
<td>Black</td>
<td>+ 70 + 8.0</td>
</tr>
<tr>
<td></td>
<td>+ 100 + 8.5</td>
</tr>
</tbody>
</table>

Table 5.3  Photoeffects obtained in deoxygenated alkaline 0.1M NaNO₃ with HgS electrodes blackened with light of different intensities
Lower photo-induced potentials obtain for a lower % transmission, but
the effect on photocurrents is not clear. The zero bias photocurrent
is the same for 11%, 24%, and 48% transmission, and currents produced
at +0.2V do not increase with a higher % transmission. The photo-
currents at +0.4V and +0.6V for an electrode blackened using an 11%
transmission filter were very small and non-reproducible. No explana-
tion is suggested for these results, but an important conclusion is
that feebly blackened electrodes do not behave desirably in nitrate.
'Under-blackening', as indicated by the red-brown colour of electrodes
obtained with lower light intensities, may be responsible for the
inexplicable photocurrent trend; this is further evidence that
optimum darkening of HgS is necessary to promote optimum photoeffects
in an inert electrolyte.

5.2.4 Variation in Light Wavelength

Experimental conditions are as before, and the wavelength is varied
as in section 4.3.1.3. The photoeffects of HgS thus blackened are
shown in Table 5.4. The largest photo-induced potentials are obtained
with electrodes blackened by light of wavelength 500 to 570 nm, i.e.
slightly shorter than the wavelength corresponding to the band gap
(619 nm). Relative photocurrents follow no such trend, and appear
unrelated to the wavelength. The very high photocurrents, and
corresponding gas evolution at the cathode, for the electrode blackened
at 460 nm, are among the largest seen in an 'inert' electrolyte, and
illustrate the importance of qualifying/quantifying the blackening
process. Unfortunately, no qualification of photocurrent production
in terms of wavelength appears possible.
<table>
<thead>
<tr>
<th>Light wavelength in nm</th>
<th>Colour of HgS after irradiation in KT</th>
<th>Relative photopotential in mV (in nitrate)</th>
<th>Relative photocurrent in µA (in nitrate) at given bias vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0V</td>
</tr>
<tr>
<td>423</td>
<td>Crimson</td>
<td>-40</td>
<td>+8.0</td>
</tr>
<tr>
<td>460</td>
<td>Black</td>
<td>-90</td>
<td>+46.0</td>
</tr>
<tr>
<td>510</td>
<td>Black</td>
<td>-145</td>
<td>+9.5</td>
</tr>
<tr>
<td>565</td>
<td>Black</td>
<td>-145</td>
<td>+18.0</td>
</tr>
<tr>
<td>610</td>
<td>Black</td>
<td>-100</td>
<td>+8.0</td>
</tr>
<tr>
<td>650</td>
<td>Dark red</td>
<td>-130</td>
<td>+25.0G</td>
</tr>
</tbody>
</table>

G = gas evolution at platinum with counter electrode

Table 5.4: Potentials and currents obtained with illuminated HgS electrodes in deoxygenated alkaline 0.1M NaNO₃, that have been blackened in 0.1M KT, by illumination for 60 minutes at 0.0V at the indicated wavelength.
5.2.5 Variation of Bias of HgS Electrode

This will indicate if the magnitude of the photocurrent passed while blackening is significant. Some results are shown in Table 5.5. The resultant colour of the HgS electrode is affected by the bias; a more anodic applied potential produces a greater degree of darkening. However, the magnitude of photoeffects does not correlate with the colour. Larger relative photocurrents are seen when the electrode has been irradiated at closed circuit in iodide, and 0.0V vs SCE bias appears the optimum potential. The passage of a photocurrent while inducing blackening gives a better electrode than one contained in an open circuit; the lower relative photopotential of -165 mV for such an electrode supports this idea. A better parameter than 'photocurrent passed while blackening' is 'number of electrons passing the H_2O/HgS interface while blackening', since the latter does not contain 'time', already known to have an influence. Figure 5.1 shows the relationship between electrons passed during blackening and the zero-bias relative photocurrent in nitrate of the darkened electrode. There is a connection between the two, but it is not apparent that an optimum number of electrons exists. A larger photocurrent in nitrate is obtained when a greater charge has passed the HgS/KI interface. However, an electrode blackened at open circuit generates photocurrents in nitrate, yet no current flowed through the HgS while darkening.

5.2.6 Variation of HgS Thickness

In Chapter Four, it was noted that lower photoeffects were observed with heavier, thicker coatings of red HgS on the platinum mesh. Electrodes bearing different weights were blackened by irradiation in 0.1M KI, at 0.0V vs SCE, for 60 minutes. The darkened electrodes were
<table>
<thead>
<tr>
<th>Conditions at red HgS electrode while blackening</th>
<th>Colour of HgS electrode after illumination in KI</th>
<th>Relative photovoltage (in nitrate)</th>
<th>Relative photocurrent in μA (in nitrate) at given bias vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open circuit: HgS vs calomel</td>
<td>Dark brown</td>
<td>-165</td>
<td>+ 5.0 +10.0 +13.0 +17.0</td>
</tr>
<tr>
<td>Closed circuit: HgS @ 0.0V vs SCE</td>
<td>Dark brown</td>
<td>-230</td>
<td>+18.0 +31.0 +36.0 +17.0</td>
</tr>
<tr>
<td>Closed circuit: HgS @ -0.5V vs SCE</td>
<td>Light brown</td>
<td>-250</td>
<td>+ 5.8 + 8.0 +14.5 +18.0</td>
</tr>
<tr>
<td>Closed circuit: HgS @ +0.2V vs SCE</td>
<td>Black</td>
<td>-215</td>
<td>+11.0 +17.0 +17.0 +14.5</td>
</tr>
</tbody>
</table>

Table 5.5 Photoeffects obtained in deoxygenated alkaline 0.1M NaNO₃ with HgS electrodes irradiated for 30 minutes in 0.1M KI at given conditions
Figure 5.1
Correlation between number of electrons passing the 0.1M KI/HgS interface upon illumination to induce blackening, and the photocurrent obtained with this electrode at zero bias in deoxygenated 0.1M NaNO₃ (pH 11.5).
investigated in alkaline nitrate, and results are shown in Table 5.6. There is no significant lowering of photo-responses for heavier coatings, indeed darkening has improved the performance of thicker electrodes compared to red ones. 'Weight of coating' is not a parameter that can be used to qualify darkening.

The conclusions drawn from sections 5.2.1 to 5.2.6 are as follows: (i) an iodide concentration of $10^{-1}$ M induces optimum blackening; (ii) an irradiation time of 60 minutes gives an optimally blackened electrode, when the balance between diminishing photovoltages and improving photocurrents with increasing time, is considered; (iii) low light intensities should be avoided, as 'under-blackening' is not desirable; (iv) the light wavelength is preferably between 500 and 570 nm; (v) a bias of 0.0V should be maintained between the red HgS electrode and the calomel reference electrode; (vi) the amount of HgS covering the mesh is immaterial, for coatings between 8 and 60 mg. Thus the conditions to produce an electrode of optimum blackening are that it should be irradiated by a 1.8 kW xenon lamp via an 11 cm path-length of cooled 0.3M (approx.) aqueous CuCl$_2$, in 0.1 M potassium iodide for 60 minutes at zero bias vs SCE, with a platinum counter electrode. Ideally, one should characterise the electrode itself, as well as quoting experimental conditions. This calls for precise surface measurements, for which the instruments were not available.

The basic photoelectrochemical properties of optimally blackened red HgS are discussed in section 5.4.

5.3 Mercury Solublisation in Potassium Iodide

In Chapter Four (p.139) a 'suspension experiment' was described to investigate the photochemical stability of HgS. This is extended here
<table>
<thead>
<tr>
<th>Wt. of blackened HgS in g on the mesh</th>
<th>Relative photopotential in mV</th>
<th>Relative photocurrent in μA at given bias vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.0V</td>
</tr>
<tr>
<td>0.007164</td>
<td>-205</td>
<td>+17</td>
</tr>
<tr>
<td>0.030218</td>
<td>-145</td>
<td>+35</td>
</tr>
<tr>
<td>0.042760</td>
<td>-190</td>
<td>+19</td>
</tr>
<tr>
<td>0.068324</td>
<td>-185</td>
<td>+21</td>
</tr>
</tbody>
</table>

G means a gas is evolved at the platinum counter electrode.

Table 5.6 Photoeffects produced in deoxygenated 0.1M NaNO₃ (pH 11.5) by electrodes bearing different weights of HgS, darkened as in text.
to potassium iodide electrolyte, and the darkening/solublisation of the sulphide is investigated as a function of electrolyte concentration, amount of HgS in the suspension, and irradiation time. Experiments are performed with electrolyte and HgS contained in a gas jar, and a water-cooled, pyrex-jacketed, 125W medium pressure mercury lamp (Hanovia) is immersed in the suspension. The HgS suspension is constantly stirred with a magnetic bead, and used electrolytes are filtered and analysed by atomic absorption spectroscopy for mercury.

5.3.1 Solublisation as a Function of Iodide Concentration

2 g of red HgS are dispersed ultrasonically in 500 ml of potassium iodide electrolyte and the suspensions are irradiated or left stirring in the dark for five hours. The iodide concentration is varied from $10^{-4}$ M to $10^0$ M, and detected mercury versus [KI] is plotted in figure 5.2. Darkened HgS is recovered from irradiated suspensions for electrolytes of concentration above $10^{-3} \text{-} 10^{-2}$ mol. dm$^{-3}$, with blackening more pronounced at higher [KI]. No blackening occurs for suspensions left in the dark. Potassium iodide at molarities of $10^{-1}$ M or greater does cause solublisation in the absence of light. This implies darkening and dissolution are not concurrent, although it is more prudent to suggest they proceed at different rates; the commencement of photo-solublisation and darkening at approximately the same iodide concentration may be coincidence. [Red HgS on a platinum electrode darkens at [KI] = $10^{-5}$ M when photocurrents are obtained - see Table 4.19, p.191.] Filtered used electrolytes are clear and colourless, and no iodine is detected by the starch test.

5.3.2 Solublisation as a Function of Irradiation Time

Experimental details are as before, with a 0.1M KI electrolyte. The
experiment without irradiation revealed about 5 \mu g/ml\(^{-1}\) of mercury is solubilised for whatever length of time the suspension is left, but figure 5.3 shows an increase in \([\text{Hg(SOL)}]\) with time. A straight line has been suggested as the plot, indicating a linear solubilisation rate of about 4.4 \mu g/ml\(^{-1}\) hr\(^{-1}\). The colour of recovered HgS from irradiated suspensions ranges from 'red/brown' after 10 hours, 'brown' after 30 hours, 'dark brown' after 50 hours, to 'black' after 80 hours. No means of quantifying the colour by reflectance spectroscopy was available. No iodine was detected in used electrolytes.
Figure 5.3
Mercury solubilisation from 2g of red HgS irradiated in 500 ml of 0.1M KI.

Slope = 4.4 μg ml⁻¹ hr⁻¹ (approx)
5.3.3 Solubilisation as a Function of HgS Weight

Experimental details are as before, and the amount of HgS in the suspension is varied. Figure 5.4 indicates less mercury is detected for lower weights of sulphide used, but mercury solubilisation does not increase for larger amounts of HgS. The irradiated suspension of 8 g in 500 ml yielded brown HgS, and the colour of recovered material became blacker as the starting weight of sulphide decreased. This is evidence that solubilisation and darkening proceed at different rates; a suspension containing 8 g will reduce the light intensity reaching HgS particles - hence less blackening occurs - yet solubilisation is as great as in a 'thinner' suspension where more light reaches the particles. Therefore, solubilisation is less dependent on illumination than is blackening. Again, no iodine was detected in used electrolytes.

The principle conclusions drawn from the suspension experiments are: (i) light-induced darkening is controlled by iodide concentration and irradiation time; (ii) light-induced solubilisation of HgS is similarly controlled, with a linear dependence on time; (iii) darkening and solubilisation are not necessarily concurrent processes. Figure 5.3 postulates solubilisation is linear with irradiation time and the plot is of the form:

\[ y = mx + c \]

\[ \text{i.e. } [\text{Hg(SOL)}] = kt \]  \hspace{1cm} [5-1]

(where \( k \) is the slope of 4.4 \( \mu g/ml^{-1} hr^{-1} \)).

5.4 Properties of Blackened Red Mercury(II) Sulphide in Sodium Nitrate Electrolyte

Platinum mesh electrodes were coated with red HgS and blackening was performed under the optimum conditions deduced in section 5.2. The
Figure 5.4
Mercury solubilisation from 500 ml of 0.1M KI irradiated for five hours with differing weights of red HgS.
darkened electrode was then investigated using the experimental procedure employed for red HgS, as in Chapter Four.

5.4.1 Properties under 'Standard Conditions'

'Standard conditions' are described in section 4.3.1.1 (p.125). The relative photovoltage is similar to that obtained with red HgS, namely -100 to -250 mV, and potential-time plots are of comparable shape, except that photovoltage attainment and decline are faster. Photocurrents are larger with the blackened form - figure 5.5 shows the photocurrent-voltage plot - and current-time plots are similar to those in figures 4.3 and 4.4. The difference between the performance of red and blackened HgS is in the larger photocurrents obtained with the latter. This is attributed to an increased sensitivity to light which results in greater electron-hole pair generation, and hence a larger photocurrent flow. The photopotential is not augmented by the increased charge-carrier concentration, as it is restricted by the amount of band-bending in HgS (see figure 4.29, p.213). Illuminated blackened electrodes frequently cause gas evolution at the platinum counter electrode; this is dealt with in some detail in section 5.5.

5.4.2 Effect of Varying Electrolyte pH

Figure 5.6 shows potentials in the dark and on illumination for a blackened electrode in a sodium nitrate electrolyte of different pH values. As for red HgS, potentials vs calomel become more negative as the pH increases, but relative photovoltages are invariant. However, the plots here have a slope of -40 mV.pH^{-1}, compared to -58 mV.pH^{-1} for the red form. The relative photocurrent onset potential varies by -0.032 V.pH^{-1} (see figure 5.7), which is about half that noted for the red form (namely -0.072 V.pH^{-1}, figure 4.7). Photocurrents at zero
Figure 5.5
Photo-induced current vs bias for blackened red HgS in pH 7 0.1M NaNO₃ (deoxygenated).
Figure 5.6
Variation in dark potential (X) and illumination potential (O) for blackened red HgS with 0.1M NaNO₃ electrolyte pH.

Slope = $-40 \text{ mV} \cdot \text{pH}^{-1}$
Figure 5.7
Variation of relative photocurrent onset potential of blackened red HgS with electrolyte (0.1M NaNO₃) pH.

Slope = 0.032 V pH⁻¹
bias increase anodically as electrolyte pH increases, (see figure 5.8), but negative relative photocurrents are not obtained as with red HgS (see figure 4.8). Thus, a difference in behaviour for the two forms is seen when electrolyte pH is altered.

It is proposed that $H^+$ and/or $OH$ have different adsorption characteristics on blackened HgS, such that they influence its Helmholtz potential to a smaller degree. Potentials versus calomel, and the relative photocurrent onset potential, are pH-controlled by $-30$ to $-40$ mV per pH unit, but for red HgS, this control amounts to $-58$ to $-72$ mV.pH$^{-1}$. Hence $OH^-/H^+$ are potential-determining by about
half the extent for the blackened sulphide. Comparison of figures 4.8 and 5.8 shows the photocurrent increase with pH is greater for the darkened form; the increased photosensitivity of blackened HgS may be solely responsible for this.

5.4.3 Wavelength Response

The incident light wavelength is varied as in section 4.3.1.3. Figure 5.9 shows the action spectra; comparison with figure 4.9 indicates (i) the maximum response is blue-shifted by 50 nm; (ii) no positive relative photovoltages are seen; (iii) there is an extension in photoresponse to wavelengths longer than 600 nm. A colour change from red to black implies a shifting to longer wavelengths of light absorption. This is reflected in the extension of spectral response beyond 600 nm, but the peak response lying at a shorter wavelength is contradictory to this. It is probable that the fundamental absorption edge of red HgS at 619 nm still controls photoeffects, but the influence of darkened material is unclear.

5.4.4 Light Intensity Effects

Results identical to those for red HgS were obtained, namely the relative photocurrent increased linearly with light intensity, and the relative photopotential showed a linear dependence on \( \sqrt{\text{intensity}} \). These are shown in figure 5.10 and the same comments as in section 4.3.1.4 apply.

5.4.5 Stability

The stability of red HgS while producing photocurrents was not resolved in Chapter Four (p.141) as blackening often took place during the experiments. A darkened electrode was therefore employed to promote photocurrents at biasing potentials between 0.0V and 0.5V.
Figure 5.10(a)  
Dependence of photo-induced voltage of blackened red HgS on \(\sqrt{\text{intensity}}\).

Figure 5.10(b)  
Dependence of relative photocurrent of blackened red HgS on light intensity.
(vs SCE) for several hours. The total number of electrons passed anodically on illumination was $1.2 \times 10^{19}$. The theoretical mercury concentration in the electrolyte after passage of this charge, based on equation [4-3]:

$$\text{HgS} \xrightarrow{2h\nu} \text{Hg}^{2+} + \text{S} + 2e$$

is calculated below.

1.2 x 10^{19} electrons have been passed anodically

\[ 6 \times 10^{18} \text{ mercury atoms/ions should be solubilised} \]

\[ 6 \times 10^{18} \text{ Hg atoms/ions weigh } \frac{6 \times 10^{18} \times 200 \text{ g}}{6.022 \times 10^{23}} \]

i.e. 1990 μg.

150 ml of electrolyte was employed, so the mercury concentration should be \( \frac{1990 \text{ μg.ml}^{-1}}{150} \)

i.e. 13.2 μg.ml\(^{-1}\).

No mercury was detected in the used electrolyte by atomic absorption analysis; this is taken as evidence for the photoelectrochemical stability of mercury(II) sulphide, at least for the time irradiated (31380s). The 13.2 μg.ml\(^{-1}\) theoretical mercury concentration is close to the reliable detection unit of 7.5 μg.ml\(^{-1}\) (see Appendix II). To provide a larger theoretical mercury concentration, a second stability experiment was performed, with a total of \(9.47 \times 10^{18}\) electrons passed anodically upon illumination. This corresponds to a theoretical solubilisation of 1572 μg of mercury. The electrolyte was reduced in volume to about 20 ml, and diluted to 25 ml. The theoretical mercury concentration is now \( \frac{1572}{25} \) or about 63 μg.ml\(^{-1}\). No mercury was detected. This supports the photoelectrochemical stability of HgS.
Mercury(II) sulphide could decompose according to:

\[
\text{HgS} + 4\text{H}_2\text{O} \xrightarrow{\text{hv}} \text{HgSO}_4 + 8\text{H}^+ + 8\text{e}^- \tag{5-2}
\]

Mercury sulphate would dissolve and allow possible Hg detection by atomic absorption analysis. A major objection to this process is the involvement of water. Table 4.21 (p.201) indicates red and blackened HgS decomposes in halides in pyridine, where water is absent. Thus equation [5-2] is unlikely to describe any photo-instability.

The 'permanence' of the surficial black layer is unknown. It may alter with time, either becoming deeper or slowly reverting to the red form. Immersion of a blackened electrode in concentrated Na\textsubscript{2}S solution causes an immediate disappearance of the black coating, exposing the red sulphide. It is not known if Na\textsubscript{2}S dissolves the black material quicker than it dissolves the red, or if the action of sodium sulphide causes a black-red transformation. It proved impossible to investigate this by weighings, as Na\textsubscript{2}S readily dissolves red HgS. On one occasion, a blackened electrode lost its dark colour on standing in 0.1M KBr overnight, but this has never been repeated. Thus the stability of the blackened material, with respect to the red, rather than with respect to dissolution, is unknown.

5.4.6 Effect of Varying Thickness of Mesh Covering

Some results are given in Table 5.7. Relative photocurrents follow a similar trend as for the red sulphide (see Table 4.3, p.146), although relative photopotentials for darkened HgS are essentially uniform for electrodes bearing different coatings. A possible explanation is that light penetrates to a much greater depth in the blackened form, offsetting the effect of higher internal resistance in thicker
<table>
<thead>
<tr>
<th>Wt. of HgS coating in g</th>
<th>Dark Potential in mV vs SCE</th>
<th>Potential on Illumination in mV vs SCE</th>
<th>Relative Photopotential in mV</th>
<th>Relative Photocurrent in μA at given bias vs SCE</th>
<th>Onset Potential in V vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.007464</td>
<td>-95</td>
<td>-300</td>
<td>-205</td>
<td>+17</td>
<td>-0.25</td>
</tr>
<tr>
<td>0.030218</td>
<td>-115</td>
<td>-275</td>
<td>-160</td>
<td>+35</td>
<td>-0.30</td>
</tr>
<tr>
<td>0.042760</td>
<td>-65</td>
<td>-255</td>
<td>-190</td>
<td>+19</td>
<td>-0.30</td>
</tr>
<tr>
<td>0.068324</td>
<td>-110</td>
<td>-295</td>
<td>-185</td>
<td>+21</td>
<td>-0.25</td>
</tr>
</tbody>
</table>

G means gas evolution at platinum counter electrode

**Table 5.7** Some photoeffects obtained with darkened red HgS electrodes in pH 11.5 0.1M NaNO₃ (N₂-purged), with differing weights of material on the platinum mesh.
electrodes, and causing larger photo-responses than with a red electrode of equivalent loading.

5.4.7 Effect of adding Alcohols to the Electrolyte

Aliphatic alcohols are known to induce 'photocurrent doubling' at TiO₂ (see p.57), and a blackened HgS electrode was investigated with various alcohols included in the nitrate electrolyte. Results are given in Table 5.8. The 'alcohol-free (first run)' shows the results for the freshly blackened electrode in nitrate alone. Addition of various alcohols has not caused improvements in the photocurrents, in fact the electrode becomes worse with time, and the 'alcohol-free (last run)' readings for nitrate electrolyte alone after the experiments have been done, indicates a deterioration in performance. Alcohols have a deleterious effect on HgS - and mercury was detected in the used alcoholic electrolytes.

5.4.8 Output power characteristics

The circuit shown in figure 1.6(c) [p.16] was employed, using a blackened HgS/mesh semiconductor electrode and platinum wire counter electrode. The load is varied from zero to 18.0 Ω, and the photo-induced voltage noted for each resistor. The photo-induced current flowing through the resistance was obtained from Ohm's Law, and the photovoltage vs photocurrent is shown in figure 5.11. A very unsatisfactory plot is seen - far removed from the ideal rectangular shape - indicating little driving power in promoting a photocurrent through a series load. Many factors contribute to the power loss: bare platinum at the HgS electrode; a weak space-charge in HgS (see figure 4.29); and the likely high internal resistance of HgS.
<table>
<thead>
<tr>
<th>Electrolyte*</th>
<th>Relative photocurrent in µA at given bias vs SCE</th>
<th>Onset potential in V vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol-free (1st. run)</td>
<td>+3.1    + 8.0    +14.0 +35.0G</td>
<td>-0.20</td>
</tr>
<tr>
<td>0.1M C₂H₅OH</td>
<td>+0.3    +14.5    +21.0G +28.0G</td>
<td>-0.20</td>
</tr>
<tr>
<td>1.0M C₂H₅OH</td>
<td>+1.7    + 3.5    +11.0 +14.0</td>
<td>-0.15</td>
</tr>
<tr>
<td>0.1M (CH₃)₂CHOH</td>
<td>+2.9    + 3.4    + 7.0 +12.0</td>
<td>-0.25</td>
</tr>
<tr>
<td>1.0M (CH₃)₂CHOH</td>
<td>+0.9    + 2.0    + 4.0 +11.0</td>
<td>-0.20</td>
</tr>
<tr>
<td>1.0M (CH₃)₃COH</td>
<td>+0.1    + 1.5    + 3.2 + 8.0</td>
<td>~ 0</td>
</tr>
<tr>
<td>Alcohol-free (last run)</td>
<td>0.0     + 1.5    + 6.6 + 8.5</td>
<td>~ 0</td>
</tr>
</tbody>
</table>

G means gas evolution at the counter electrode

* Alcohols are contained in pH 7 0.1M NaNO₃ (N₂-purged)

Table 5.8 Effect on photocurrents at blackened HgS of aqueous alcohols
5.4.9 Variation in Cathode Material

As for red HgS, platinum mesh, platinum wire, platinised platinum wire, and carbon fibre were used as cathode materials. No change in photocurrent was seen for any of these, indicating the HgS electrode is current-determining/limiting in the system.
5.5 Photo-induced Gas Evolution at the Counter Electrode

This phenomenon has been referred to a number of times in the preceding pages, and generally occurs when a blackened electrode delivers currents in excess of +30 μA upon illumination. Further qualification of gas production at the counter electrode is now dealt with.

5.5.1 Dependence of Gas Evolution on Electrolyte and Applied Bias

A number of red HgS electrodes were optimally blackened and irradiated under normal conditions in either a one- or two-compartment cell. The latter had a glass frit between the compartments to allow electrical conductance between, but not mixing of, the electrolytes in the anode and cathode compartments ('anolyte' and 'catholyte' respectively). Nos. 1 to 5 in Table 5.9 are for one-compartment cells, and it can be seen that cathode gas evolution occurs in nitrate, sulphate, and chloride electrolytes, although results in sulphate are a little strange. Comparison of runs 1 and 4 shows that the minimum bias for gas evolution can be reduced if the nitrate pH is increased. The necessity of applying a bias to achieve gas evolution can be explained as follows, assuming the gas is hydrogen. At pH 7, $E_{\text{H}^+/\text{H}_2} = +0.41\text{V (vs SHE)}$, and the $E_{\text{CB}}$ of red HgS lies at $+0.37\text{V vs SHE}$ at pH 0 (p.205) or $+0.78\text{V}$ at pH 7. Assuming blackened HgS has the same electron affinity (and hence conduction band energy) as the red form, then $E_{\text{CB}}$ for blackened HgS will be no more positive than $+0.78\text{V}$; it should be less than this, since results in 5.4.2 show a smaller pH-dependence of potentials vs reference of the darkened material. Nevertheless, the $H^+$ reduction level lies at least 0.2V above the conduction band (and hence the counter electrode Fermi level at zero bias).
<table>
<thead>
<tr>
<th>No.</th>
<th>Anolyte</th>
<th>Catholyte</th>
<th>Minimum Bias in V vs SCE needed for gas evolution</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH 7</td>
<td>0.1M NaNO₃</td>
<td>+0.3</td>
<td>Gas evolution</td>
</tr>
<tr>
<td>2</td>
<td>pH 2</td>
<td>0.1M K₂SO₄</td>
<td>+0.3?</td>
<td>Gas occasionally evolved</td>
</tr>
<tr>
<td>3</td>
<td>pH 11.5</td>
<td>0.1M K₂SO₄</td>
<td>—</td>
<td>No gas evolved</td>
</tr>
<tr>
<td>4</td>
<td>pH 11.5</td>
<td>0.1M NaNO₃</td>
<td>0.0</td>
<td>Gas evolution</td>
</tr>
<tr>
<td>5</td>
<td>pH 11.5</td>
<td>0.1M KCl</td>
<td>0.0</td>
<td>Gas evolution</td>
</tr>
<tr>
<td>6</td>
<td>0.01M KOH (pH 12)</td>
<td>0.01M H₂SO₄ (pH 2) N₂-purged</td>
<td>0.0</td>
<td>Gas evolution</td>
</tr>
<tr>
<td>7</td>
<td>0.01M KOH (pH 12)</td>
<td>0.01M H₂SO₄ (pH 2) O₂-purged</td>
<td>—</td>
<td>No gas evolved</td>
</tr>
<tr>
<td>8</td>
<td>pH 11.5</td>
<td>0.1M NaNO₃</td>
<td>0.01M Methyl viologen in pH 7 0.1M NaNO₃</td>
<td>Reduced methyl viologen appears at 0.0V bias</td>
</tr>
<tr>
<td>9</td>
<td>pH 7</td>
<td>0.1M NaNO₃</td>
<td>0.01M Methyl viologen in pH 7 0.1M NaNO₃</td>
<td>Methyl viologen reduced very slowly at 0.0V bias</td>
</tr>
</tbody>
</table>

Table 5.9 - Effect of different electrolytes on cathode gas evolution
Electrons cannot discharge into the H⁺/H₂ level until E_F (platinum) is raised by this amount, which is effected by positively biasing the HgS electrode. The minimum bias for cathode gas evolution is +0.3V, corresponding quite closely to (E_{CB} - E_{H⁺/H₂}). At higher electrolyte pH's, larger photocurrents are produced, and there may be sufficient electrons to 'accumulate' at platinum and raise E_F this way ([91]), and discharge protons at zero bias.

A pH-gradient (no. 6, Table 5.9) between the HgS and counter electrode allows gas evolution at zero bias - this has been noted for TiO₂ [47]. If the catholyte is oxygen-saturated, no gas evolution is noted (no. 7, Table 5.9). This is because oxygen is more easily reducible than protons; larger relative photocurrents are seen in this system. If methyl viologen (MV²⁺) is included in the catholyte, gas evolution is suppressed, but the blue colour of reduced MV²⁺ (the radical cation) is seen. Methyl viologen is a redox indicator used in biological systems, with E_{red} = +0.44V vs SCE at pH 7 [233]:

\[
\begin{align*}
\text{CH}_3\text{N} & \quad \text{CH}_3 \\
\text{colourless} & \\
\text{Methyl viologen} & \\
& \text{(usually the dichloride)}
\end{align*}
\]

MV²⁺ is more easily reduced than H⁺ (E_{red} = +0.41V) so hydrogen evolution is stopped. With an alkaline anolyte, considerable MV⁺ formation is observed at zero bias, but there is only feeble blue colouration for a neutral anolyte (run 9, Table 5.9). Nevertheless, it is possible to obtain reduced methyl viologen at zero bias, which is an important observation, as it is possible to use MV⁺ to obtain hydrogen from water [95,234].
5.5.2 Collection of Gases

Figure 5.12 illustrates the cell for gas collection. 1 ml pipettes form the collection vessels and above the taps is a facility for transferring the gases to a mass spectrometer. The test electrode is a platinum mesh sealed into a rubber bung and the counter electrode is platinum wire similarly sealed. The reference electrode sits in the electrolyte reservoir, which has nitrogen blown over the surface. The mesh electrode is coated and blackened in the normal manner. The electrolyte (pH 11.5 0.1M NaNO₃) is nitrogen-purged before use, and the apparatus is placed so that the HgS electrode occupies the normal place on the optical bench.

Irradiation at +0.3V bias causes rapid gas evolution at the counter electrode and a few bubbles also accumulate on the HgS electrode. The photocurrent is about +70 μA, although it declines with time. A total of $7.93 \times 10^{18}$ electrons were passed as relative photocurrent, which should produce approximately 0.1 cm³ of gas, if Faraday's Laws are obeyed. The amount of gas collected was not measurable. The decline in photocurrent and under-production of gas was shown to be not due to sulphide decomposition, as passage of $7.93 \times 10^{18}$ electrons should lead to a mercury concentration of 26 μg.ml⁻¹; no mercury was detected. Rather, the accumulation of gas (oxygen?) at HgS may contribute to short-circuiting losses.

5.5.3 Identification of Cathode Gas

The minute quantities produced makes positive identification difficult. The gases were allowed to pass into a mass spectrometer, but identification was impossible as a lot of water vapour accompanied them. However, aqueous palladous chloride is known to precipitate palladium metal when hydrogen is bubbled through [235]. A normal one-
Figure 5.12
Apparatus for gas collection.
compartment cell with alkaline 0.1M NaNO₃, a platinum wire counter electrode, and blackened sulphide test electrode was used to obtain gas evolution. The gas would be swept out of the cell by the nitrogen-purge out-flow, so the departing gases were bubbled through 0.01M PdCl₂ in a dreschel bottle. A brown precipitate was seen immediately. The same observation was noted with hydrogen from a cylinder, but no immediate precipitate is seen when nitrogen is passed. Thus the gas evolved at the cathode is hydrogen. It was attempted to use this test to quantitatively monitor hydrogen evolution, but it was found that bubbling pure nitrogen through PdCl₂ gave a precipitate after half an hour.

5.5.4 Influence of Nature of Platinum Cathode

In studies of electrolysis, the physical nature of the electrodes can be critical in determining electrolysis currents and products. It was found that hardly any difference in photocurrents or gas evolution was observed if the cathode was a platinum mesh or wire, or if it was very close to (1 mm away) or distant from (4 cm away) the HgS electrode. Thus the determining factor is the nature of the HgS electrode.

5.6 Discussion

The darkening of red HgS is an important property of the material. Improvement in photocurrents and hydrogen evolution at the cathode are the results of blackening. The effects of darkening, along with the nature and formation mechanism of blackened HgS, are now discussed.

5.6.1 Comparison of Red and Darkened HgS Electrodes

The relative photovoltage obtained is the same for both kinds of
HgS; thus the band-bending and Fermi energy have not been altered. Larger relative photocurrents are seen for blackened HgS - this may be due to increased light sensitivity, although the possibility of a larger surface area should not be excluded. The darkened form may be doped with Hg or S, which might lower the internal resistance. The increased photocurrents may also be due to an alteration in the band energies at the electrolyte junction which would allow easier redox chemistry to occur. This could account for faster responses to light seen for the blackened sulphide - although a different surface with differing ion adsorption, as shown by the smaller pH-dependence of potentials vs calomel, may alter the availability of surface states for mediating electron-hole recombination. An improved sensitivity to light of wavelengths longer than 620 nm is noted for the dark material, but action spectra suggest the response is not much different to that of red HgS. This conflicts with optoacoustic spectra (see Appendix IV) of the red and blackened sulphide, shown in figure 5.13. The spectrum for red HgS indicates a decrease in signal amplitude for wavelengths longer than 600 nm; here little light is absorbed as its energy is below that of the band gap. The spectrum for blackened HgS shows no such decrease in signal amplitude, which implies continued absorption of light.* But photo-responses at 700 nm are minimal for a blackened HgS electrode. An explanation is that light absorption here does not lead to electron-hole pair generation. The nature of the blackened material may resolve this dilemma.

5.6.2 The Nature of Darkened Red Mercury(II) Sulphide

The blackening of red HgS has been noted throughout the ages: the oldest known occurrence is mentioned by the Roman author Vitruvius, who reported on the painting of the outer walls of a house on the Aventive

* Authentic black HgS has an optoacoustic spectrum as shown in Figure 5.14.
Figure 5.13

Optoacoustic Spectra for red and blackened red HgS.
Hill, Rome, with natural cinnabar mineral. After thirty days the red colour turned black [236].

When cinnabar is heated, it becomes black, and reverts to the red colour on cooling if the temperature has not exceeded $445^\circ$. Above $445^\circ$, a permanent black material is obtained. Allen and Crenshaw showed hardly any metacinnabar was present in the black material [237], and attributed darkening on heating to a change in light absorp-
tion. (The band gap of red HgS is strongly temperature-dependent [238]). It is now accepted that metacinnabar is the black form obtained on heating - the transformation takes place at 315°C in the presence of sulphur, and at 344°C in the presence of mercury [239]. Attempts to identify the black form obtained on irradiation were inconclusive: Cropp suggested mercury loss accompanied darkening of cinnabar ore, but failed to prove this [240]; Dreyer postulated surficial colloidal mercury is responsible for the black colour [241]; Brosset showed metacinnabar is formed when red HgS is sublimed, but no identification of the light-induced dark form was given [242]. Potter and Barnes noted that the colour of cinnabar is a function of stoichiometry [243]. The table below is taken from their abstract.

<table>
<thead>
<tr>
<th>% Reflectance at 700 nm</th>
<th>Atomic % of Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>50</td>
</tr>
<tr>
<td>34</td>
<td>48.29</td>
</tr>
<tr>
<td>19.5</td>
<td>47.57</td>
</tr>
</tbody>
</table>

**TABLE 5.10**

% Reflectance of Cinnabar with Mercury atomic %
[Note: the colour of metacinnabar is independent of Hg Atomic %]

From literature reports, one may conclude that heat-induced darkening is primarily due to a decrease in the band gap and the formation of some metacinnabar. Light-induced darkening is unresolved, and the material may be deficient in mercury or contain colloidal
mercury. To try and identify optically-darkened red HgS, the following techniques were employed to analyse the powder recovered from suspension experiments: X-ray powder photography, electron spectroscopy for chemical analysis (ESCA), optoacoustic spectrometry, and scanning electron microscopy (SEM).

X-ray powder photographs are normally used in structure elucidation, but here the technique is for 'fingerprinting' authentic red and black HgS and comparison of photographs of the blackened form with those of the authentic sulphide. X-ray powder photographs of authentic red and black HgS are quite similar, with the former showing more diffraction lines. One line, present in the metacinnabar photograph, but not in that of cinnabar, was selected as a yardstick. A sample of red HgS, blackened for 240h in 0.1M KI, showed an identical powder photograph to authentic cinnabar, with the 'yardstick' metacinnabar line absent. A photograph of well-mixed authentic red and black HgS did show up the metacinnabar 'yardstick' line. Therefore, no metacinnabar, that can be detected by X-ray diffraction, is present. This does not exclude its existence, as X-ray diffraction is not a surface technique and the colour change will occur primarily at the surface.

The ESCA results were obtained with a DuPont 650 electron spectrometer with a magnesium or aluminium anode.† Samples of red and black HgS (authentic) and red HgS blackened in 0.1M KI for 20 and 70 hours were investigated. The sample is prepared by pressing the powder onto the face of a 6.35 mm diameter circular brass disc. Table 5.11 gives

---

† Professor J. Wightman, of the Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA, performed the ESCA analysis on HgS.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Hg 4f_{3/2} BE(eV)</th>
<th>AF</th>
<th>S 2p_{3/2} BE(eV)</th>
<th>AF</th>
<th>Hg(AF) S(AF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red HgS (Authentic)</td>
<td>99.0</td>
<td>0.291</td>
<td>160.0</td>
<td>0.328</td>
<td>0.9</td>
</tr>
<tr>
<td>Black HgS (Authentic)</td>
<td>98.6</td>
<td>0.318</td>
<td>160.2</td>
<td>0.303</td>
<td>1.0</td>
</tr>
<tr>
<td>Red HgS irradiated 20 hrs in 0.1M KI</td>
<td>98.4</td>
<td>0.288</td>
<td>160.4</td>
<td>0.311</td>
<td>0.9</td>
</tr>
<tr>
<td>Red HgS irradiated 70 hrs in 0.1M KI</td>
<td>99.0</td>
<td>0.315</td>
<td>160.8</td>
<td>0.356</td>
<td>0.9</td>
</tr>
</tbody>
</table>

BE = Binding Energy;  AF = Atomic Fraction
No peaks due to I or K were seen, and no oxygen incorporation occurred.

Table 5.11  ESCA Parameters for Mercury(II) Sulphide
the binding energies and atomic fractions of the mercury $4f^{2}$ and sulphur $2p^{3/2}$ electrons. No change in valency occurs to either mercury or sulphur on blackening, which means the free elements are not present. No species have been incorporated from the electrolyte. In particular, no iodine-doping has taken place; this has been considered to cause the black colour of single crystal red HgS [244]. ESCA thus reveals no valence change has occurred, and the only plausible conclusion is that a light-induced phase-change of red to black HgS occurs on the surface.

Optoacoustic spectra were run of authentic red and black HgS, and of red HgS blackened in 0.1M KI by irradiation for 240 hours with the 125W mercury lamp. Figure 5.13(b) shows the optoacoustic spectrum of the blackened material, and should be compared with figure 5.14, which is an optoacoustic spectrum of authentic black HgS. These two spectra are very similar in the signals they exhibit between 650 and 800 nm. The light modulation frequency here is 240 Hz: this gives rise to acoustic signals from the uppermost layers of the material. Figure 5.15 presents spectra at 20 Hz, where the signals have originated from deeper within the material; the similarity in spectra between 650 and 800 nm is more marked. This is taken as evidence for the blackened material being black HgS, (metacinnabar).

Photographs from a scanning electron microscope (SEM) were obtained for red, black, and blackened mercury(II) sulphide. Figures 5.16 to 5.18 show SEM photographs for two magnifications, such that 1 cm represents distances of 0.1 mm or 10 µm. SEM photographs of authentic red and black HgS (figure 5.16 and 5.17, respectively) are very different. The former appears fine, "wispy", and with sharp, well-defined edges. The latter is quite coarse, and contains spherical

* Figure 5.15(a) gives further evidence from spectra in the IR region.
Figure 5.15
Optoacoustic Spectra of authentic black and blackened red HgS at slower light chopping frequency.

- Modulation Frequency 20Hz
- Scan Range uv-vis
- Scan Rate 200 nm/min
- Time Constant 0.5
- Band Pass 2 nm
- Sensitivity 10 mV
- Phase 230°
- Lamp Current 19A
Figure 5.15(a)
Optoacoustic spectra of red, black, and blackened red HgS in the IR region (modulation frequency 160Hz, scan rate 0.8 μm/min, time constant 2s, band pass 0.03 μm, sensitivity 10 mV, and phase angle 90°). The similarity in spectra for black HgS (metacinnabar) and blackened red HgS between 2000 and 2600 nm strongly suggests metacinnabar is present in the blackened red sulphide.
Figure 5.16

SEM Photographs of 'Fisons' red HgS.
Figure 5.17
SEM Photographs of 'Alfa' black HgS.
Figure 5.18
SEM Photographs of 'Fisons' Red HgS blackened in 0.1M KI with a 125W Hg-lamp for five hours.
elements, which are well-defined. The two sulphides are quite
distinguishable by SEM photographs. Blackened red HgS (figure 5.18)
has the basic 'fine' appearance of the red form, but there is
evidence of the larger, rounder, coarser particles seen in the photo­
graph of the authentic black sulphide. It is therefore likely that
the darkened material has a surface coating of black HgS.

It seems certain that photo-induced darkening of red mercury(II)
sulphide is caused by formation of metacinnabar, and mercury-deficiency
or colloidal mercury are not responsible for the black colouration.
However, this is not the end of the matter, rather the beginning,
since an electrode wholly coated with authentic black HgS is hardly
photo-responsive (see Table 4.5, p.149), and one coated from a
suspension containing 1.8 g of red HgS and 0.2 g of black HgS does not
produce the large photocurrents associated with darkened red HgS,
although an enhanced photopotential is noted (see Table 4.6, p.151).
A thin surface layer of black HgS, or possibly an intimate mixture/
solid solution of red/black HgS would seem responsible for augmented
photocurrents seen with darkened material. The depth of the black HgS
layer/red-black solid solution may be associated with the 'optimum'
darkening noted earlier.

5.6.3 The Darkening Mechanism of Red Mercury(II) Sulphide

It is worthwhile gathering together all the experimental data on
blackening before attempting a theoretical mechanism to account for a
light-induced change in crystal structure. These data are listed
below.

1. Solublisation often accompanies darkening.
2. Darkening is frequently seen in aqueous electrolytes with \( E_{\text{redox}} \)
   lying between +0.5V and +1.1V.
3. Darkening is not seen in pyridine containing salts that do cause darkening in aqueous solutions - yet solubilisation still occurs in pyridine.

4. Darkening occurs whether a current passes through HgS or not.

5. The extent of darkening is controlled by salt concentration, light wavelength and intensity, and irradiation time. The number of electrons passing through HgS has an influence on the colour of the material.

6. Illumination is essential to induce darkening.

Any mechanism should satisfactorily account for all of these observations.

5.6.3.1 Fundamental Properties of Cinnabar and Metacinnabar

The standard thermodynamic properties of HgS are given below, in Table 5.12. Metacinnabar is less stable than cinnabar, since it possesses a lower standard enthalpy and Gibbs energy. The cinnabar $\rightarrow$ metacinnabar transformation has $\Delta G^\circ = +0.54$ kcal. mol$^{-1}$ and is, therefore, thermodynamically unfavoured. An energy input is needed to effect the transformation; either heat, or a photon flux. The reverse transformation, metacinnabar $\rightarrow$ cinnabar, is energetically downhill.

Cinnabar has a crystal structure [245] consisting of infinite -S-Hg-S- chains running parallel to the c-axis. Each chain has constituent atoms strongly bound, with weak forces acting between chain units. The mercury atoms are in a close-packed structure. The bond angle at mercury (S-Hg-S) is 172.4°, and at sulphur (Hg-S-Hg) is 105.2°. The shortest Hg-S distance is 2.36 Å, within the chain structure, but distances vary from 3.10 Å to 3.30 Å for Hg and S atoms in adjacent chains. The structure can be considered as a distorted
<table>
<thead>
<tr>
<th>HgS</th>
<th>$\Delta H(298,\text{K})$/kcal.mol$^{-1}$</th>
<th>$\Delta G(298,\text{K})$/kcal.mol$^{-1}$</th>
<th>$S(298,\text{K})$/cal.mol$^{-1}$.K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cinnabar</td>
<td>-12.75</td>
<td>-10.94</td>
<td>19.7</td>
</tr>
<tr>
<td>Metacinnabar</td>
<td>-11.8</td>
<td>-10.4</td>
<td>21.2</td>
</tr>
</tbody>
</table>

*Table 5.12*  Thermodynamic Properties of HgS [from Ref. 239]
Metacinnabar adopts the zinc blende structure [246]. Each Hg-S bond is 2.54 Å long, with tetrahedral co-ordination - the bond angle at mercury and sulphur is about 109°. The lattice is therefore composed of mercury atoms in cubic close packing, with sulphur occupying half the tetrahedral sites.

5.6.3.2 The Cinnabar to Metacinnabar Transformation

The changes which must occur in the cinnabar-metacinnabar transformation are: (i) a decrease in bond angle at Hg, from 172° to 109°; (ii) an increase in co-ordination at S, from 2 to 4; (iii) an increase in Hg-S bond length of 0.18 Å. The almost linear S-Hg-S bond in cinnabar is a result of mercury forming two oppositely directed bonds from two sp hybrid orbitals. In metacinnabar, the four bonds, tetrahedrally disposed, are due to four sp³ hybrid orbitals of mercury. Calculations on the band structure of cinnabar have been published [247]; energies of the mercury 6s and sulphur 3p levels correspond to energies of the valence bands, and similarly for mercury 6p, and sulphur 4s, and the conduction bands. The valence band of red HgS is contributed to by S (3s, 3p) plus Hg (6s) orbitals, and the conduction band by S (4s) and Hg (6p) orbitals. For mercury to possess near-linear bonding to sulphur, as in cinnabar, a 6s-6p admixture is needed to achieve sp hybridisation. A mixing from orbitals contributing to the conduction band is necessary. For mercury to possess tetrahedrally-disposed bonds to sulphur, as in metacinnabar, a 6s-3×6p admixture is demanded. The mixing of Hg (6s) orbitals with those contributing to the conduction band [Hg (6p)] is much greater - and the energy difference between conduction and valence band should then decrease. So any means of increasing the 6p character of the sp admixture at mercury
will lead to a change in bonding directionality.

At sulphur, the bond angle hardly changes in the transformation, but the co-ordination increases from 2 to 4. In cinnabar, sulphur forms bonds to mercury with two of the four sp\(^3\) hybrid orbitals; the remaining two contain lone pairs. In metacinnabar, sulphur still forms Hg-S bonds via sp\(^3\) hybrid orbitals, but the orbitals formerly bearing lone pairs are used in bonding to mercury, as there now exists an Hg orbital of correct symmetry to overlap and cause bond formation to S. Thus the change in co-ordination at sulphur is brought about by a change in orbital symmetry at mercury; it is the latter change that is the fundamental parameter in the cinnabar-metacinnabar transformation.

**5.6.3.3 Molecular Orbital Treatment of HgS**

The linear combination of atomic orbitals (LCAO) to obtain molecular orbitals (MO) can be used to describe bonding in molecules. Figure 5.19 illustrates hypothetical energy manifolds for cinnabar and metacinnabar. The relative positions of the 6s,6p (Hg) and 3p (S) atomic orbitals are taken from figure 1 in reference 247, and the position of 3s (S) is estimated. In (a), the diagram for metacinnabar, the bonding electrons (six from sulphur - 3s\(^2\) and 3p\(^4\), and two from mercury - 6s\(^2\)) are placed in a \(\sigma\)-bonding orbital derived from a linear combination of sp\(^3\) hybrid orbitals of mercury and sulphur. In (b), the diagram for cinnabar, the \(\sigma\)-bonding orbital is derived from a linear combination of an sp orbital of Hg and an sp\(^3\) orbital of S. Two pairs of electrons occupy this \(\sigma\)-orbital. Non-bonding orbitals (n\(_1\) and n\(_2\)) result from unused atomic hybrid orbitals: the remaining four electrons are accommodated in the n\(_1\) non-bonding orbital. If the energy difference (\(\Delta\)) between n\(_1\) and n\(_2\) is 2eV, this gap corresponds to the optical band
Figure 5.19
Postulated Molecular Orbital Energy Manifolds for Mercury(II) Sulphide.
gap of red HgS. Promotion of an electron from \( n_1 \) to \( n_2 \) has not disturbed the bonding situation, nor has it placed an electron in an antibonding orbital. This would account for the stability of red HgS upon illumination.

The orbital \( n_1 \) is derived from two sp\(^3\) hybrid atomic orbitals of sulphur, and \( n_2 \) from two 6p atomic orbitals of mercury. The presence of an electron, due to excitation, in a mercury-derived orbital may initiate the necessary re-hybridisation to effect the structure change. This is the core of the proposed mechanism: occupation of \( n_2 \) by an electron promoted from \( n_1 \) by light causes a perturbation in charge density at mercury, and re-hybridisation occurs to accommodate this. The LCAO-MO treatment thus indicates non-bonding electrons are involved in the photo-conduction of red HgS and in the light-induced structure change.

5.6.3.4 The Role of the Electrolyte in Darkening

The above theoretical treatment of darkening in terms of the cinnabar-metacinnabar structural change might imply the transformation will always accompany band-gap illumination. But experimental results show blackening occurs only in aqueous solutions with some reducing agents, and \( E_{\text{redox}}^{\theta} \) of these agents lies between +0.5V and +1.1V. Experimental results also show that non-aqueous solutions of some of these ions do not induce darkening. It appears that the structural change is controlled by irradiation, reducing agent, and solvent. One must invoke strong interactions between the electrolyte and surface states within HgS's band gap to account for the dependence of darkening on solute and solvent. Surface states have been reported to exist for red HgS [218,219,220].

Solute-surface state interactions, if strong, would influence the
molecular orbitals of HgS and affect the re-hybridisation of mercury. Species which are potential-determining (e.g. I\(^-\), Br\(^-\)) must be adsorbed on the semiconductor surface, and those which are strongly adsorbed will cause greater perturbation in the electronic structure of HgS. This perturbation may be the deciding factor in causing re-hybridisation at mercury. [Solvation of the sulphide surface will also influence solute-surface state interactions.] Evidence to support this is that \( E^\Theta \) for species that induce darkening lies at values that fall with the band gap of red HgS (see figures 4.27 and 4.28, p.208 and p.211).

5.6.3.5 Summary of Darkening Mechanism

The proposed mechanism for the darkening of cinnabar is: light promotes a non-bonding electron to a higher non-bonding orbital; re-hybridisation of mercury may occur on occupation of the higher energy orbital; adsorption/interaction of solution ions and solvent molecules via surface states determines whether re-hybridisation of mercury actually transpires. The red-black structural change is an 'uphill' process, requiring an energy input. Metacinnabar is unstable with respect to cinnabar and the black form should revert to the red. This has been observed once (see section 5.4.5).

One would expect darkening to be influenced by the light wavelength, intensity, and time of illumination. No charge flow is needed, simply the presence of electrons in the conduction band. A salt which causes blackening does so by its influence on the molecular orbitals of HgS; a greater influence might be expected for a higher salt concentration, and more darkening then seen. Experimental results indicate the above expectations are indeed realised. The mechanism does not account for solubilisation which is dealt with next.
5.6.4 Solubilisation of Red Mercury(II) Sulphide

Cinnabar is quite unreactive [248]: it is sparingly soluble in water, insoluble in dilute acids, but can be decomposed by aqua regia or some boiling concentrated acids. Sodium sulphide solution of moderate concentrations will dissolve HgS. Table 4.10 on p.158 shows mercury solubilisation from suspensions in a number of salt solutions, on irradiation and in the dark. Only stannous chloride causes appreciable decomposition in the absence of light; Mellor notes this reaction to give H₂S, Cl₂, Hg and SnO₂ [248]. It is also noted that iodine decomposes cinnabar, as does a solution of iodine in potassium iodide, according to:

\[ \text{HgS} + 2\text{KI} + \text{I}_2 \rightarrow \text{K}_2\text{HgI}_4 + \text{S} \]  

[I-5-3]

Irradiation of HgS in KI solution causes iodide oxidation at positive holes, and the I₂/\text{I}^- solution initiates solubilisation. Iodine is never detected, since it ends up in the form of HgI₄²⁻, and is not incorporated in the HgS either (ESCA failed to detect it). The extent of solubilisation according to equation [5-3] will be controlled by the amount of light-generated iodine. More mercury in solution should be detected where a greater amount of iodine has been formed. This will occur at higher [KI] and longer irradiation time, and has been observed experimentally (section 5.3).

Bromine and chlorine are known to decompose HgS; solubilisation of HgS does occur on illumination in bromide, suggesting bromine is formed by photo-induced oxidation. However, no solubilisation is seen for HgS irradiated in chloride (except at high molarities); this implies no chlorine formation takes place at the positive holes, or, if formed, it diffuses away before attacking HgS. The extensive
solubilisation seen in $K_4Fe(CN)_6$, KCN and KBrO$_3$ is almost certainly
due to the oxidation products reacting with HgS.

'Photochemical solubilisation' is not a correct term to describe the
decomposition of red HgS on irradiation in certain salt solutions,
since the presence of a positive hole alone does not result in lattice
rupture. It is the species formed by oxidation at the positive hole
that can cause 'chemical solubilisation' of HgS, and this term is a
more preferable one.

There is probably no connection in mechanism between solubilisation
and darkening, even though both processes appear to be concurrent. An
'active' species that interacts chemically with HgS to cause decomposi­
tion is likely to interact equally strongly to allow the re-hybridisa­
tion of mercury and subsequent structure change. In addition, just as
the oxidised form of a redox couple, produced on illumination, can
cause decomposition, then it may be the photo-produced oxidised form
that interacts with surface states to initiate darkening.

5.7 Concluding Remarks

The aim of the research presented in the preceding pages was to find
a semiconductor that was responsive to visible light and stable under
its action when employed in an electrochemical system. Such a
material - mercury(II) sulphide, initially red - has been discovered and,
under known conditions, remains stable and assists the conversion and
storage of optical energy. In some circumstances, a black surface
layer is formed, which is metacinnabar, and this layer causes an
improvement in photoeffects, particularly the production of hydrogen
at the cathode. The full potential of HgS in harnessing solar energy
cannot be recognised from the work reported here; what can be
recognised is that such a potential exists.
APPENDIX I

The platinum mesh which supports semiconducting materials was described on page 90. Details are given below of the area receiving effective illumination.

For a platinum wire, only one half is illuminated. Half of the circumference of a circle of diameter 0.025 cm is \( \frac{1}{2}(\pi \times 0.025) \) cm or 0.039 cm. Thus 44 wires of length 1.5 cm and 22 of length 3.0 cm expose an area of \((44 \times 1.5 \times 0.039) + (22 \times 3.0 \times 0.039) \) cm\(^2\), or 5.29 cm\(^2\). But 44 x 22 intersections, of area \((0.039)^2 \) cm\(^2\), exist in the mesh weaving. The area shielded from light by the intersections is \((44 \times 22 \times 0.039 \times 0.039) \) cm\(^2\), or 1.49 cm\(^2\). The total area of interwoven wire receiving irradiation is therefore \((5.29 - 1.49) \) cm\(^2\), or 3.8 cm\(^2\).

However, a cylindrical wire, not a plane sheet, is illuminated. The diagram indicates the arc BC receives light at close to normal incidence whereas the arcs AB and CD receive light far-removed from normal incidence. It is assumed that arc BC corresponds to half the wire exposed to light, or one quarter of the circumference, and has a length of 0.02 cm. The area receiving near-normal (and normal) illumination is recalculated - \((0.02 \times 1.5 \times 44) + (0.02 \times 3.0 \times 22) - 1.49 \) cm\(^2\), or 1.15 cm\(^2\). This now represents the surface area of a platinum mesh receiving "effective illumination". When coated with a semiconductor, this area will increase by an unknown amount. 2 cm\(^2\) is taken as a minimum "effective surface area" for a coated mesh.
<table>
<thead>
<tr>
<th>Element</th>
<th>Lamp Current in mA</th>
<th>Wavelength in nm</th>
<th>Slitwidth in mm</th>
<th>Oxidant and pressure in psi</th>
<th>Acetylene pressure in psi</th>
<th>Limit of linear scale in µg.ml⁻¹</th>
<th>Lowest detection limit in µg.ml⁻¹</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>10</td>
<td>253.6</td>
<td>0.7</td>
<td>Air: 55</td>
<td>32</td>
<td>300</td>
<td>7.5</td>
<td>Gas pressures are for aqueous solutions.</td>
</tr>
<tr>
<td>Hg</td>
<td>10</td>
<td>253.6</td>
<td>0.7</td>
<td>Air: 37</td>
<td>13</td>
<td>300</td>
<td>7.5</td>
<td>Gas pressures are for pyridine solutions.</td>
</tr>
<tr>
<td>Mo</td>
<td>30</td>
<td>313.3</td>
<td>0.7</td>
<td>N₂O: 40</td>
<td>65</td>
<td>60</td>
<td>0.5</td>
<td>————</td>
</tr>
<tr>
<td>Pb</td>
<td>5</td>
<td>283.3</td>
<td>0.7</td>
<td>Air: 55</td>
<td>32</td>
<td>20</td>
<td>0.5</td>
<td>————</td>
</tr>
<tr>
<td>Sn</td>
<td>5</td>
<td>224.6</td>
<td>0.7</td>
<td>Air: 43</td>
<td>32</td>
<td>300</td>
<td>4.1</td>
<td>————</td>
</tr>
</tbody>
</table>

**APPENDIX II** Experimental conditions for electrolyte analysis for mercury, molybdenum, lead or tin with a Perkin-Elmer 360 Atomic Absorption Spectrometer.
APPENDIX III

Details of Balzers Broad Band Interference Filters

The figure illustrates the wavelengths transmitted by each filter used to vary light wavelength.

The light intensity obtained with each filter is tabulated below:

<table>
<thead>
<tr>
<th>Filter</th>
<th>Intensity in W.cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>0.018</td>
</tr>
<tr>
<td>K2</td>
<td>0.15</td>
</tr>
<tr>
<td>K3</td>
<td>0.2</td>
</tr>
<tr>
<td>K4</td>
<td>0.3</td>
</tr>
<tr>
<td>K5</td>
<td>0.3</td>
</tr>
<tr>
<td>K6</td>
<td>0.2</td>
</tr>
<tr>
<td>K7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The spectral distribution of the K7 filter is not included on the figure; light of wavelength of 700 nm ± 50 nm is transmitted by it.
Light wavelengths passed by Balzers Broad Band Interference Filters - 'K1' to 'K6'.
APPENDIX IV

Optoacoustic Spectroscopy

This is a new form of spectroscopy exploiting a long-known phenomenon. In the 1880's, Alexander Graham Bell witnessed the production of sound from a sample in an enclosed vessel when intermittently illuminated by sunlight [249]. This effect, later named the 'optoacoustic' or 'photoacoustic' effect results from light absorption by the sample (solid, liquid, or gas) and subsequent increase in temperature if de-excitation is via a radiation-less mechanism. The surrounding gas, or gas itself, increases in temperature. If the light source is chopped, then the temperature in and around the sample will also fluctuate. In a sealed system, this results in a periodic increase in pressure - sound generation occurs. A sensitive microphone can detect these sounds.

The magnitude of an optoacoustic signal (OAS) is dependent on light wavelength, intensity, chopping frequency, sample surface area and the thermal properties of the sample and surrounding gas. It has been experimentally determined [250] that the strength of the OAS is directly proportional to light power, and for a given wavelength, to intensity; inversely proportional to the modulation frequency; directly proportional to the sample surface area, and related to the thermal capacity of the surrounding gas. The wavelength dependence indicates an absorption spectrum of the sample is obtained, and those conditions which allow greatest heat generation and transfer from the solid and subsequent expansion of the surrounding gas, will furnish the largest OAS.

The greater the light intensity, the more heat will be generated,
and the longer the light illuminates the sample (i.e. at slowest chopping frequencies), then the greater the signal. The thermal diffusivity of the solid controls the time taken for heat to reach the surface; thus the delay in appearance of an OAS can be used to obtain thermal properties. A surrounding gas with a small thermal capacity will increase in temperature and expand using less heat than a gas with a large thermal capacity. In practice, air is normally used as the surrounding gas.

The spectrometer used to obtain optoacoustic spectra is the "OAS 400" built by EDT Research, London. It has a xenon lamp as continuum source and the light is chopped, passed through a monochromator and focussed onto the sample cell. A microphone is built into the sample cell, and the signal it receives is amplified, corrected for the spectrum of the xenon lamp, and presented on an X-Y recorder as 'signal amplitude' against wavelength (see figures 5.13-5.15). A large 'signal amplitude' means a large amount of light has been absorbed at that wavelength compared to a wavelength where the signal amplitude is smaller. The conditions shown on the spectra are those which give an optimum magnitude to a given signal.

Optoacoustic spectroscopy has advantages over 'conventional' absorption spectroscopy in that spectra can be obtained on solids, liquids, smears, gels - in fact, on anything that can be placed in the sample cell (a channel in an aluminium casting). Optically dense materials present no problem, nor does scattered light. In addition, layered samples can be investigated, and spectra of sub-surface or surface 'slices' may be isolated by altering the modulation frequency and phase angle [251]. The OAS 400 was delivered to Leicester in August 1979, with only one month of practical work remaining for this
Ph.D. No work was performed on the layered blackened HgS; it is intended to carry this out during Post-Doctoral work on mercury(II) sulphide.
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55. Ref. 9, p.3.


249. A. G. Bell: Phil. Mag., 11 (1881) 510-528.
