Mechanism of the Electrochemical Reduction of Persulfates and Hydrogen Peroxide

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ABSTRACT

Electrochemical studies have shown that the reduction of persulfate and hydrogen peroxide is a two step mechanism, the first step occurs by electron transfer with the conduction band and the second step by hole injection with the valence band. It could be concluded from corresponding measurements performed with a semiconductor electrode (GaP) that the electrochemical properties of these oxidizing agents have to be described by two instead of one redox (normal) potential. One normal potential is much lower (ϵ^0_1) and the other much larger (ϵ^0_2) than the theoretical value (ϵ^0) determined from thermodynamic data. These values are estimated as

$$\epsilon^0_1 \leqq 0.6\text{v};\ \epsilon^0_2 \geqq 3.4\text{v};\ \epsilon^0 = 2\text{v for } S_2O_8^{2-}$$

and

$$\epsilon^0_1 \leqq 0.6\text{v};\ \epsilon^0_2 \geqq 2.9\text{v};\ \epsilon^0 = 1.77\text{v for } H_2O_2.$$

Redox reactions with persulfates and hydrogen peroxide have been subject of several investigations. Especially the electrochemical behavior of H_2O_2 was of interest in connection with the electrochemical reduction and formation of oxygen. Bagotzky and Jablokowa (1) and Weiss (2) determined the reaction order in the reduction process of H_2O_2 on a dropping Hg-electrode and assumed a two step mechanism

$$H_2O_2 + e^- \rightarrow OH + OH^-$$

$$OH + e^- \rightarrow OH^-$$

R. and H. Gerischer (3) and Winkelmann (4) obtained the same results with a Pt-electrode and assumed also the same mechanism. Chemical properties of persulfate also are reported in the literature (5). The reaction kinetics, however, have not been studied in detail. Frumkin (5) has only postulated a possible reduction process which is similar to that of H_2O_2.

In the present paper investigations on the reduction mechanism using a semiconductor electrode (GaP) are reported. As is shown such a GaP-electrode with a large energy gap makes it possible to obtain fundamental information about the corresponding charge transfer in the reduction process.

Experimental

The electrochemical measurements were performed with single crystals of GaP as electrode material. These crystals were oriented in the <111> direction. The best results were obtained with Ga planes. In all cases the density of free carriers was about $10^{17}/cm^3$. The solutions (Merck, p.a.) were buffered to the proper *p*H values using standard phosphate and borate buffers. The electrodes were glued in araldit (CIBA) sockets (exposed area ~ 0.2 cm^2). A saturated calomel electrode was used as a reference electrode. (In the figures, however, values are plotted against the potential of the normal hydrogen electrode.)

All measurements were performed under potentiostatic conditions. In the medium *p*H range, measurements could be carried out only at cathodic potentials since $Ga(OH)_3$ layers are formed during anodic polarization (8). The interfacial capacity was determined at 250 kc by measuring the phase angle between a-c current and a-c voltage (6). The experimental arrangement for the luminescence measurements has been described previously (7).

Reduction of Simple Redox Systems

Charge transfer processes on GaP electrodes may occur via the valence or the conduction band of the crystal. As was reported (8) previously the anodic dissolution proceeds via the valence band, whereas for the cathodic hydrogen evolution conduction electrons are consumed. In the latter case a charge transfer across the interface can only occur if sufficient electrons in the conduction band are available. Consequently, in the case of n-type GaP the interfacial current rises rapidly with increasing cathodic potential, whereas with p-type GaP a very small saturation current of less than 1 μa was found (Fig. 1). Illumination of such a p-type electrode, *i.e.*, optical excitation of electrons from the valence band into the conduction band, leads to an increase of the cathodic current. The saturation current is only determined by the number of electrons excited by light. As shown in Fig. 2 it increases linearly with the light intensity.

Moreover, it was observed (8) that the charge transfer during the reduction of certain redox systems on GaP proceeds via the conduction band and in others via the valence band. This is demonstrated in Fig. 3 for ceric and ferricyanide ions in acid solutions using a p-type electrode. In the first case the current density is quite large and is not determined by the diffusion of minority carriers toward the surface, *i.e.*, the reduction of ceric ions proceeds via the valence band. In the case of ferricyanide ions the cathodic current is much smaller. Since this current may be increased by illumination of the p-type electrode it has to be concluded that electrons from the conduction band are consumed for the reduction of $[Fe(CN)_6]^{3-}$ in acid solutions.[1]

As proved by investigations with a variety of semiconductor electrodes the probability for a charge

[1] It should only be mentioned here that in alkaline solutions the reduction of $[Fe(CN)_6]^{3-}$ proceeds via the valence band. This effect is not of interest here, it was discussed elsewhere (8).

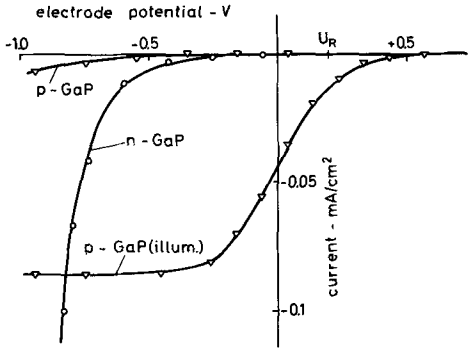

Fig. 1. Current-potential behavior of n- and p-type GaP electrodes in the cathodic region (1*N* H_2SO_4) (electrode potential against normal hydrogen electrode, NHE).

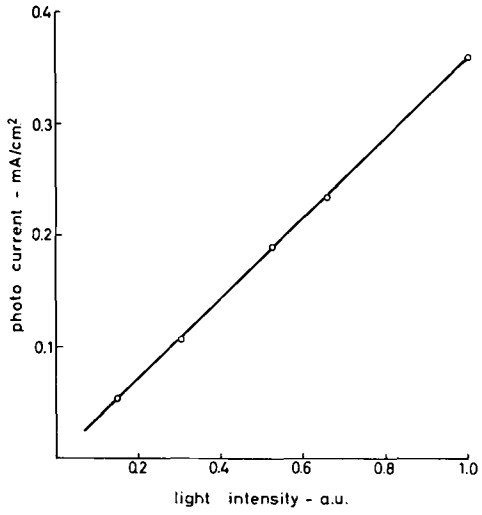

Fig. 2. Cathodic photocurrent vs. light intensity for a p-GaP electrode (1N H_2SO_4).

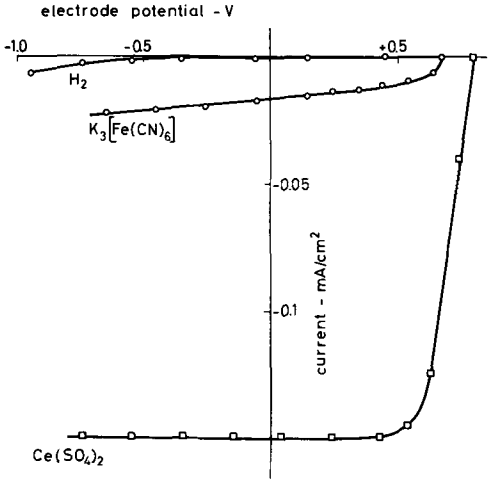

Fig. 3. Current-potential (NHE) behavior of a p-type GaP electrode in various oxidizing agents (10^{-2}M) in 1N H_2SO_4.

transfer via the conduction or the valence band depends on the redox potential of the corresponding systems (9). It was always found that the valence band process is preferred for systems with a high redox potential. This result may be qualitatively understood by the fact that an oxidizing agent is an electron acceptor. This property can be described energetically by deep lying energy levels. If we have, *e.g.*, a redox reaction of the type

$$A^{(z+1)+} + e^- \rightarrow A^{z+}$$

then the $A^{(z+1)+}$ ions represent the unoccupied and, A^{z+} the occupied electron levels. According to Gerischer's theory (10) the position of those energy levels is influenced by the solvation shell of the corresponding ions. Since the structure of the solvation shell depends on the charge of such an ion in its oxidized ($A^{(z+1)+}$) or reduced state (A^{z+}) the energy levels of $A^{(z+1)+}$ and A^{z+} differ considerably from each other. This is schematically shown in Fig. 4. According to the basic concept of this model electrons can be exchanged only between states on the same energy level (10), *i.e.*, the tunneling of an electron occurs without energy exchange with the surrounding molecules. As further shown by Gerischer the Fermi level in the semiconductor and of the redox system are equal at equilibrium conditions. Since generally we do not have an inert electrode no equilibrium is achieved, *i.e.*, one observes a corrosion potential which differs considerably from the redox potential. This

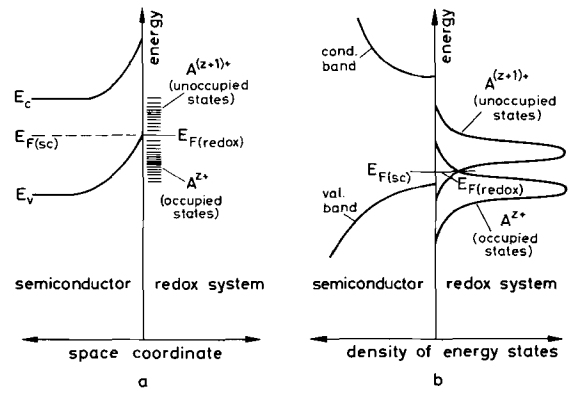

Fig. 4. Schematic energy diagram of the interface semiconductor-redox system.

model proposed by Gerischer (10) is the basis of all further considerations.

In Fig. 4 we have shown schematically a situation where the energy levels of the redox system only overlap with the valence band. In this case the electron transfer only occurs via the valence band as it was observed with ceric ions on gallium phosphide electrodes. The normal potential of this redox system amounts to 1.4v. The energy levels of redox systems with a higher normal potential have a much lower position in Fig. 4 (strong electron acceptors), *i.e.*, in this case the electron transfer is expected even more to proceed via the valence band.

We have performed corresponding measurements with persulfates and hydrogen peroxide which have a normal potential of 2.0 and 1.77v, respectively. As discussed above the reduction of these systems should occur via the valence band, *i.e.*, the reduction current should not be limited by minority carriers in p-type GaP. In contradiction to this postulation, however, we did observe a cathodic current diffusion limited by minority carriers. The results obtained with persulfates and hydrogen peroxide and the corresponding reduction mechanism are discussed next.

Reduction Mechanism of Persulfate and Hydrogen Peroxide

In Fig. 5 the current-voltage behavior is shown for a p-type GaP electrode in sulfuric acid before and after addition of $(NH_4)_2S_2O_8$ of various concentrations. It should be noted that the current scale is considerably enlarged compared with Fig. 1. As shown in Fig. 5a only a very small current increase occurs after addition of a large amount of $S_2O_8^{2-}$ ions. Similar results were also obtained with H_2O_2. As shown in Fig. 5b the cathodic current may be increased by illumination of the electrode. In this figure it is quite striking that at large cathodic potentials the current obtained for the reduction of $S_2O_8^{2-}$ is twice as large as that measured during the hydrogen evolution in H_2SO_4. As discussed in the previous section and demonstrated in Fig. 1 and 2 the saturation value of the photocurrent for the hydrogen evolution is only determined by the number of electrons excited by light from the valence band into the conduction band. Provided that this argument still holds for the reduction of persulfate we have to assume that only half of the electrons necessary for the reduction is produced by light excitation. This is possible principally because two electrons are necessary for the reduction of one persulfate ion according to

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad [1]$$

Actually, this result leads to a very simple model assuming that reaction [1] is a two step process. We can then assume that only for the first reaction step an electron from the conduction band is consumed, whereas an electron from the valence band is transferred across the interface in the second step. Conse-

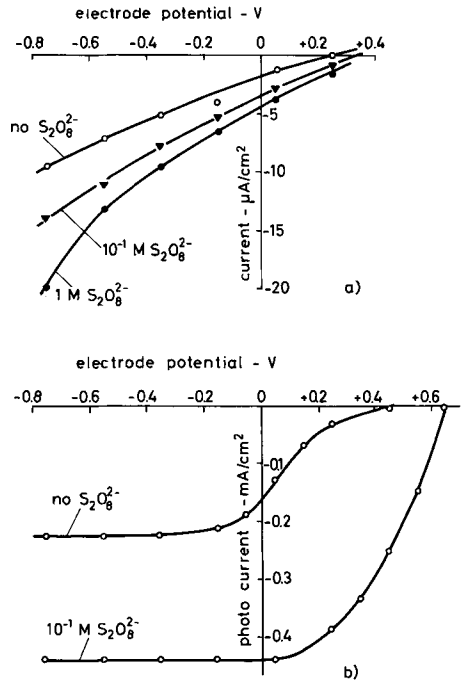

Fig. 5. Interfacial current vs. electrode potential (NHE) of p-type GaP in 1*N* H_2SO_4 with various concentration of $(NH_4)_2S_2O_8$. (a) Without illumination, (b) during illumination.

quently reaction [1] may be split up into

$$S_2O_8^{2-} + e^- \rightarrow SO_4^- + SO_4^{2-} \quad [1a]$$

$$SO_4^- \rightarrow SO_4^{2-} + p^+ \quad [1b]$$

In these equations e^- indicates an electron from the conduction band whereas p^+ is a hole injected into the valence band. Such a hole is created if an electron from the valence band is transferred to the redox system. A similar equation can be postulated for the reduction of hydrogen peroxide

$$H_2O_2 + e^- \rightarrow OH + OH^- \quad [2a]$$

$$OH \rightarrow OH^- + p^+ \quad [2b]$$

Such a current-doubling was also observed by Morrison and Freund (11, 12) for the oxidation of formic acid on ZnO. These authors also postulated a two step mechanism in which both valence and conduction band are involved. This interpretation of the current doubling, of course, is only an assumption. In the case of GaP electrodes, however, it is possible to prove this model as follows:

As mentioned above holes are injected if electrons from the valence band are consumed in the second reaction step ([1b] and [2b]). Using n-type GaP instead of p-type as the electrode material, these holes diffuse into the interior of the crystal and recombine somewhere with an electron from the conduction band. As we reported recently (7) this recombination process corresponds to a radiative transition, *i.e.*, luminescence occurs if holes are injected into an n-type GaP electrode. Such an experiment can only be performed with n-type material in order to have sufficient electrons in the conduction band for the recombination with injected holes. In the case of persulfate or hydrogen peroxide an n-type electrode has also the advantage in the luminescence experiment that the first reaction step ([1a] or [2a]) is not limited by minority carriers.

As we reported recently (7) we did observe luminescence which can only be explained by injection of holes. The same spectral distribution was also obtained with hydrogen peroxide. This result proves indeed that the second reaction step proceeds via the valence band.

pH dependence.—In a further experiment we also measured the *p*H dependence of the current doubling, as shown for hydrogen peroxide in Fig. 6 and for persulfate in Fig. 7. As a standard value we used again the cathodic photocurrent for the H_2 evolution which is independent of the *p*H value. In the case of H_2O_2 current doubling always occurs in alkaline solutions, whereas in acid solutions it depends on the H_2O_2 concentration (Fig. 6).

This *p*H dependence may obviously be related to the degree of dissociation of this molecule. Since the *p*K value of H_2O_2 is about 12 it may be concluded that the OOH^- ion is more easily reduced on a GaP electrode than the undissociated molecule itself. The *p*H dependence for $S_2O_8^{2-}$ as shown in Fig. 7 is much more difficult to understand. One possible explanation for the drop of the current doubling above about *p*H = 2 would be the assumption that hydrogen persulfate ions ($HS_2O_8^-$) exist below *p*H = 2. In general ions with a lower negative charge are more easily reduced than those with a higher charge for electrostatic reasons. Unfortunately the corresponding *p*K value is not known. Only the corresponding *p*K value for SO_4^{2-} (HSO_4^-) is tabulated which would fit to the experimental results (*p*H ~ 2). It seems to be reasonable to assume the *p*K value for persulfate to be similar. This is supported by the fact that the reduction current (saturation value) of persulfate on a Pt electrode varies in the same way in the corresponding *p*H range and remains constant at higher *p*H values. On the other hand the photocurrent on a GaP electrode increases slowly again at higher *p*H values. This may be due to the fact that $S_2O_8^{2-}$ is not very stable in alkaline solutions and decomposes partly to H_2O_2 (via Caro acid).

It would be interesting to study the *p*H dependence in the reduction of persulfate or peroxide also with n-type electrodes since then sufficient electrons are available in the conduction band. Current voltage curves have shown, however, that with n-type material practically no increase of the cathodic current

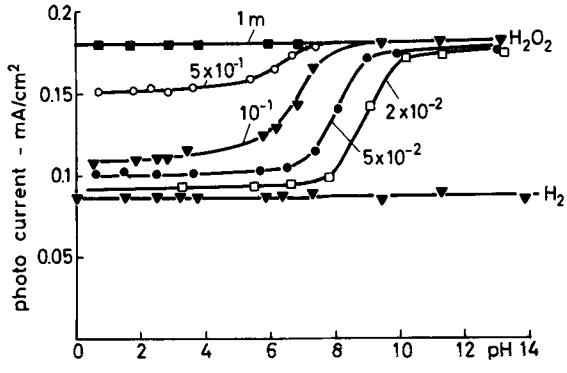

Fig. 6. *p*H dependence of the photocurrent for p-type GaP in various H_2O_2 concentrations.

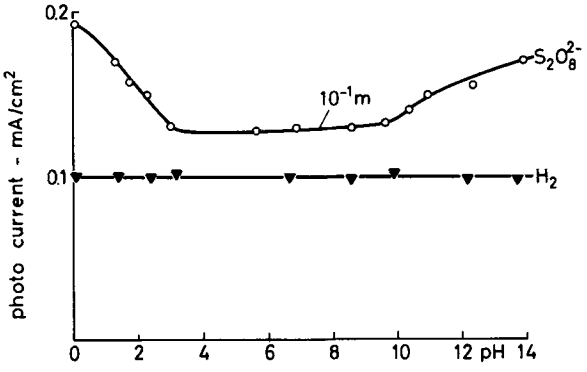

Fig. 7. *p*H dependence of the photocurrent for p-type GaP and 10^{-1}M $(NH_4)_2S_2O_8$.

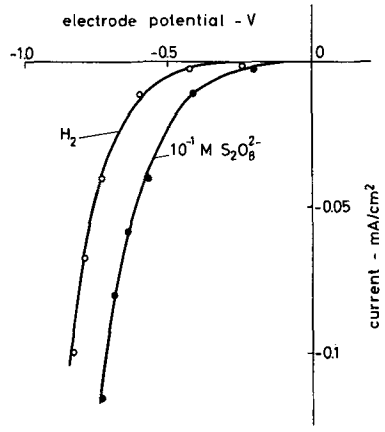

Fig. 8. Current potential (NHE) behavior of an n-type GaP electrode in 1*N* H_2SO_4 and 10^{-1}M $(NH_4)_2$ S_2O_8.

occurred after addition of persulfate to H_2SO_4 (*p*H = 0.5) (see Fig. 8). On the other hand we did already mention in connection with the luminescence experiments that holes are injected if $S_2O_8^{2-}$ ions were present in the electrolyte. From this we may conclude that obviously the reduction of $S_2O_8^{2-}$ does occur at higher cathodic potentials than for p-type electrodes. Actually, in the case of n-type electrodes the reduction of persulfate sets in at about the same potential as the hydrogen evolution. This result implies that also with n-type electrodes the rate determining step is not determined by the redox system but by charge carriers within the electrode. This prediction may easily be proved by capacity measurements as follows:

In Fig. 9 the experimental values of the space charge capacity C_{sc} are plotted *vs.* the electrode potential for n- and p-type GaP. According to this figure $1/C_{sc}^2$ varies linearly with the electrode potential, *i.e.*, the space charge capacity follows the Schottky-Mott law

$$\frac{1}{C_{sc}^2} = \frac{2kT}{e^2\ \epsilon\epsilon_0\ N_{D(A)}} \left(\frac{e\ U_{sc}}{kT} - 1 \right)$$

where U_{sc} = potential drop across the space charge layer, $N_{D(A)}$ = density of donor or acceptor states within the semiconductor, ϵ = dielectric constant, ϵ_0 = 8.854 x 10^{-12} amp·sec·v^{-1}·meter^{-1}). Such a relationship is always obtained for a depletion layer (6). Extrapolating the curves to $1/C_{sc}^2 = 0$ one obtains roughly flat band position, *i.e.*, $U_{sc} = 0$. The band bending is zero for n-type at —0.9v and for p-type at +1.2v. The difference between the two flat band positions is then 2.1v, *i.e.*, it is slightly less than the energy gap of GaP (2.25 ev). This result is expected for highly doped semiconductors provided that the potential difference applied across the interface occurs only within the space region of the electrode. From this result the band bending at the rest potential U_R = +0.35v (see Fig. 9) can be determined (13). One obtains an upward bending of 1.25v for n-type and downward bending of 0.85v for p-type as shown schematically in Fig. 10. Consequently the electron density at the surface of an n-type electrode is so small that any charge transfer from the conduction band into the electrolyte is only determined by number of electrons available at the surface. This behavior makes it also impossible to obtain any further information about the reduction of persulfate from current voltage curves with n-type GaP-electrodes.

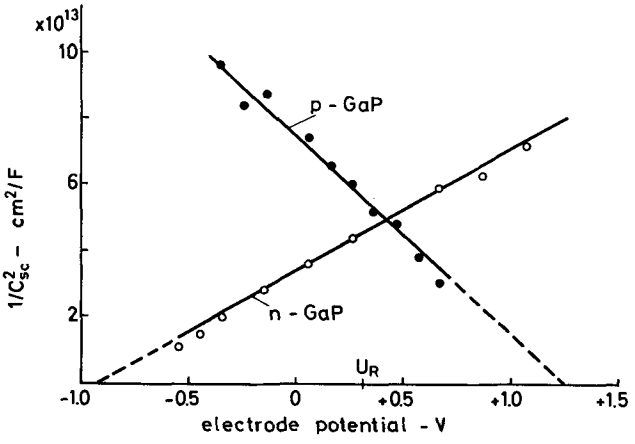

Fig. 9. Reciprocal values of the square root of the space charge capacity for n- and p-GaP electrodes in 1*N* H_2SO_4. Potential *vs.* NHE.

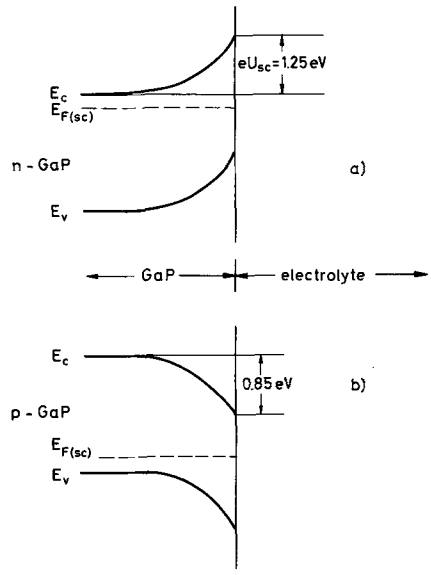

Fig. 10. Energy band bending at the rest potential U_R; (a) n-GaP, (b) p-GaP.

Normal potentials of persulfate and hydrogen peroxide.—As described in the first part of our discussion in this paper it depends on the normal potential of a redox system whether the charge transfer occurs via the conduction or via the valence band. Since the reduction of $S_2O_8^{2-}$ and H_2O_2 is a two-step mechanism in which both energy bands of the electrode are involved it follows directly from Gerischer's model (10) that the properties of these redox systems can only be described by two instead of one normal potential. This can be demonstrated again by an energy diagram (Fig. 11a) which is similar to that shown in Fig. 4b. In the case of persulfate, for example, we have now three energy states. The energy position of the

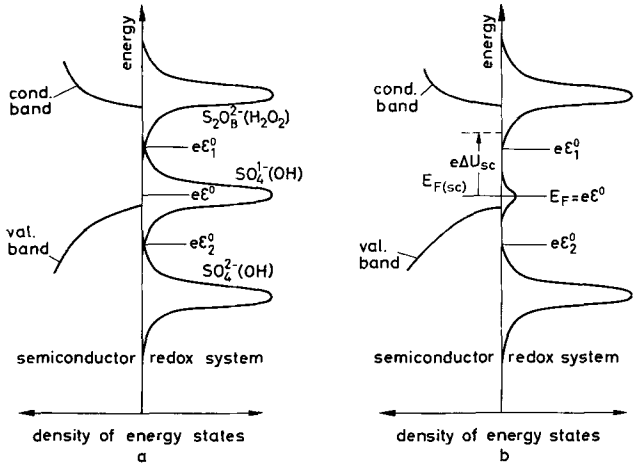

Fig. 11. Schematic energy diagram of the interface semiconductor-persulfate (hydrogen peroxide) (at equilibrium). Concentration of SO_4^{1-}: (a) large, (b) small.

intermediate state SO_4^- is just between the unoccupied $S_2O_8^{2-}$ and the occupied state SO_4^{2-}. According to Gerischer's model the density of the unoccupied ($S_2O_8^{2-}$) and of the intermediate state (SO_4^-) are equal at normal potential ϵ^0_1 for the first reaction step provided that the concentrations of $S_2O_8^{2-}$ and SO_4^- are equal. The latter condition is more or less trivial because, according to Nernst law, the redox potential is only identical with the normal potential if the concentrations are equal. In the same way also the normal potential for the second step ϵ^0_2 is determined. The effective redox potentials depend on the concentrations of the three species. The corresponding Nernst equations are given by[2]

$$e\epsilon_1 = e\epsilon^0_1 + kT \ln \frac{C_{S_2O_8^{2-}}}{C_{SO_4^-} \; C_{SO_4^{2-}}} \qquad [3]$$

$$e\epsilon_2 = e\epsilon^0_2 + kT \ln \frac{C_{SO_4^-}}{C_{SO_4^{2-}}} \qquad [4]$$

where e = elementary charge, and k = Boltzmann's constant. The free enthalpy of the complete reversible electrochemical reaction is given by $\Delta G = zF\epsilon^0$. For a two-step mechanism this free enthalpy may be split up into two values

$$zF\epsilon^0 = (z_1\epsilon^0_1 + z_2\epsilon^0_2)F \qquad [5]$$

According to [1a] and [1b] $z_1 = z_2 = 1$ and $z = 2$ so that

$$\epsilon^0 = \frac{\epsilon^0_1 + \epsilon^0_2}{2} \qquad [6]$$

i.e., the normal potential ϵ^0 of the total system is just the mean value of the normal potentials ϵ^0_1 and ϵ^0_2 defined for each reaction step (see Fig. 11a). Under equilibrium conditions the concentrations of the three species have to arrange themselves in such a way that the redox potentials are equal, *i.e.*,

$$\epsilon_1 = \epsilon_2 = \epsilon \qquad [7]$$

Since the intermediate state SO_4^- is a very unstable species its concentration is very low. Using an electrolyte containing $S_2O_8^{2-}$ and SO_4^{2-} ions in concentrations of the same order of magnitude then the effective redox potential ϵ of the complete system is almost identical with the corresponding normal potential ϵ^0 according to

$$\epsilon = \epsilon^0 + \frac{kT}{2e} \ln \frac{C_{S_2O_8^{2-}}}{C^2_{SO_4^{2-}}} \qquad [8]$$

In this case the redox potential ϵ ($\approx \epsilon^0$) is just halfway between the two normal potentials ϵ^0_1 and ϵ^0_2 and the density of energy states for the intermediate species (SO_4^{1-}) is very low as indicated in Fig. 11b.

Moreover, at equilibrium the Fermi level $E_{F(sc)}$ in the semiconductor and the Fermi level $E_{F(redox)}$ in the redox system (which is defined as $e\epsilon$) are equal (10) (Fig. 11b). Values of the normal potential ϵ^0 in this energy scale are not known. Only the corresponding normal potential ϵ^0_h relative to the hydrogen normal potential can be generally measured or calculated from thermodynamic data. In the case of persulfate $\epsilon^0_h = +2.0$v (14). Consequently, at equilibrium one would also measure an electrode potential of +2.0v provided that no corrosion etc. occurs. This is a very large potential and according to capacity measurements the energy bands even for p-type GaP would be bent upward very strongly. Consequently the electron density at the semiconductor surface would be very low, *i.e.*, at an electrode potential of +2.0v the Fermi level at the surface of the semiconductor is quite close to the valence band. This leads to the conclusion that the upward band bending has to be decreased considerably by varying the electrode potential into the cathodic direction before sufficient electrons are available in the conduction band for a charge transfer across the interface. In the energy distribution picture (Fig. 11b) this is equivalent to an upward shift of the Fermi level in the semiconductor (dotted line for $E_{F(sc)}$). According to the current voltage curves (Fig. 5b) a reduction current was actually measured below +0.75v, *i.e.*, Fermi level $E_{F(sc)}$ has to be shifted upward relative to the equilibrium value by at least 1.5v.

It is important to note that this behavior of persulfate or hydrogen peroxide not only occurs on semiconductor electrodes but exhibits a general property of these redox systems. Using a platinum instead of a semiconductor electrode a cathodic reduction current is also only observed below about +0.8v, although sufficient electrons are available even at large anodic electrode potentials. On the other hand it is also a necessary condition for a charge transfer that occupied energy states in the metal overlap with the empty states ($S_2O_8^{2-}$) in the redox system. In the case of a metal its Fermi level is also equal to that of the redox system at equilibrium. Since only energy states up to Fermi level are occupied and no higher energy levels can be filled, the overlapping between the occupied states and the $S_2O_8^{2-}$ states is very poor (Fig. 13a). Applying an external voltage ΔU the Fermi level in a metal (in contradiction to a semiconductor) cannot be shifted relative to its energy states. In this case only the potential difference across the Helmholtz double layer can be changed (Fig. 12b), *i.e.*, the energy states in the metal are shifted relative to those of the redox system as shown schematically in Fig. 13b. Since the energy difference between the unoccupied ($S_2O_8^{2-}$) and the occupied state (SO_4^{2-}) is quite large (see below) the electrode potential has to be varied considerably into the cathodic direction before a current flow is discernible.

Comparing the results obtained with $S_2O_8^{2-}$ and H_2O_2 with those of other redox systems it is possible to get a rough estimate for the values of the two normal potentials ϵ^0_1 and ϵ^0_2. This does not mean that we obtain absolute values of the potentials. We can only determine corresponding values of the normal poten-

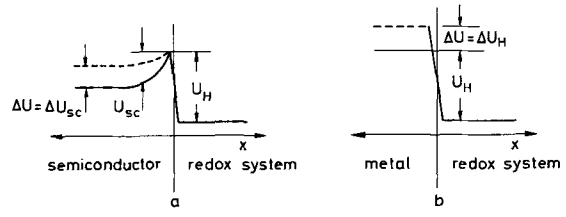

Fig. 12. Potential distribution for (a) semiconductor and (b) metal electrolyte interface. Dotted line: at cathodic polarization.

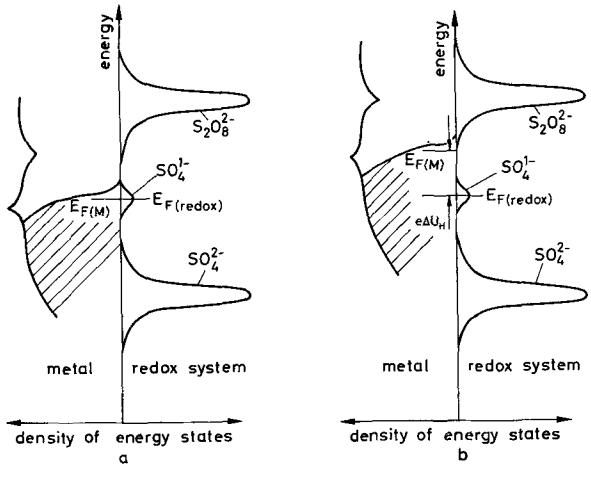

Fig. 13. Schematic energy diagram of the interface metal-persulfate. (a) At equilibrium, (b) during cathodic polarization.

[2] The reference point for the normal potentials $\epsilon^0_{1,2}$ is here not the standard hydrogen electrode. The point of zero energy is the free electron energy at infinity which is zero by definition.

tials $\epsilon^0_{1,h}$ and $\epsilon^0_{2,h}$ *vs.* a normal hydrogen electrode. As mentioned before it depends on the normal potential whether the charge transfer in a certain redox reaction occurs via the conduction or the valence band. According to Fig. 3 the reduction of Fe^{3+} proceeds already via the conduction band. Since the normal potential of the Fe^{2+}/Fe^{3+} amounts to 0.6v we have to conclude that also the normal potential $\epsilon^0_{1,h}$ for the first reaction step of persulfate and hydrogen peroxide is equal or smaller than this value. The normal potential $\epsilon^0_{1,h}$ can immediately be calculated using Eq. [6] since the normal potential of the complete system is known from thermodynamic data. One obtains for persulfate

normal potential:	ϵ^0_h	$= +2.0$v (complete system)
	$\epsilon^0_{1,h}$	$\leqq +0.6$v (1. reaction step)
	$\epsilon^0_{2,h}$	$\geqq +3.4$v (2. reaction step)
and for H_2O_2:	ϵ^0_h	$= +1.77$v
	$\epsilon^0_{1,h}$	$\leqq +0.6$v
	$\epsilon^0_{2,h}$	$\geqq +2.94$v

In the case of persulfate, *e.g.*, the difference between the two normal potentials is

$$\Delta\epsilon = |\epsilon^0_1 - \epsilon^0_2| \geqq 2.8\text{v}$$

Consequently, the energy difference between the unoccupied and occupied states is also larger than 2.8 ev.

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Capacities of Zinc-Potassium Hydroxide Interfaces

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ABSTRACT

A galvanostatic pulse current technique was employed to measure the capacitance of flat and porous zinc electrodes in 32 w/o KOH solution at 25°C. The data were obtained by operating near the hydrogen evolution potential. The electrode capacities were used to obtain the wet surface area of the zinc-KOH interface. Some exchange currents were obtained and average pore cross sections were calculated for porous zinc electrodes.

The metal-electrolyte interface exhibits a double layer capacitance which can be used to calculate the surface area. The objective of this investigation was to obtain a better understanding of the properties of the zinc electrode in the zinc-air battery. Unpublished results of investigations conducted on zinc electrodes at the Naval Ordnance Laboratory indicated that porous zinc electrodes do not seem to passivate as readily as flat zinc electrodes. Performance data is usually based on current density in terms of projected geometric area without regard for the physical structure of the surface. Since performance is dependent on the surface characteristics, the double layer capacitance technique was employed to determine the wet surface area of the zinc electrode.

Grahame (1) states that the charges (once the conditions equilibrate) do not cross the double layer because they lack the tendency to do so. The metal electrode is infinitely polarizable either (+) or (—) at the interface. The distribution of charge in the electrolyte phase at the interface may be calculated using the Gouy-Chapman theory. The original theory assumed point size charges, but this has been modified by Stern to account for finite size particles. In this theory, two double layers are assumed; the compact double layer (Helmholtz or inner double layer) is separated by the distance of closest approach from the outer or diffuse double layer.

The double layer capacity is usually measured by a galvanostatic pulse or an a-c bridge technique. The total capacitance is made up of two double layer capacitances in series. If the bulk of the capacitive nature of the interfacial system is very close to the interface then $C_{diffuse}$ is large and the total capacitance is equal to the compact capacitance. This is usually the case in strong electrolytes. It is also assumed that there is no specific adsorption of impurities which would alter the double layer. The capacitance is a function of potential. The electrode-electrolyte interface exhibits a minimum capacitance with respect to some particular potential, often referred to as the

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