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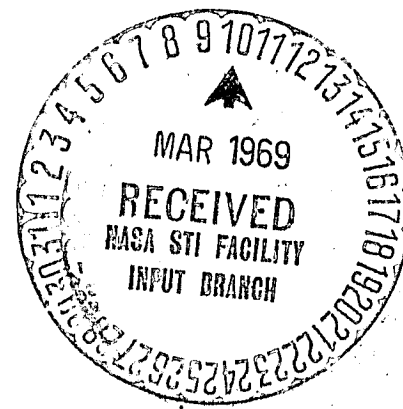
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EFFECT OF ENVIRONMENT ON THERMAL CONTROL COATINGS

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I INTRODUCTION AND SUMMARY

Degradation of thermal control coatings under combined conditions of ultraviolet radiation and vacuum is initiated by the photoproduced holes and electrons, which can undergo chemical reaction. Such chemical reactions change the structure of the coating, leading eventually to coloration. The approach we are using to prevent optical degradation is to find surface additives which act as recombination centers, alternately capturing the holes and electrons and thus removing the photoproduced carriers with no net chemical change.

The fundamental portion of the investigation, the development of background knowledge from which to predict which species should capture holes (in the reduced form) and electrons (in the oxidized form), has been brought to a satisfactory completion. The results of experimental measurements of hole and electron capture on ZnO, using an electrochemical technique, are discussed. It is concluded that an effective species should be one-equivalent (stable oxidation states separated by one electron) and should have an energy level a few tenths of an electron volt below the conduction band edge.

Tests of the effectiveness of a typical additive species (ferro/ferricyanide), using the conductance degradation measurement, on a single crystal of ZnO show that the additive is effective, reducing the degradation rate by six orders of magnitude or more in some cases. However, the action is not characterized sufficiently yet to permit accurate determination of important practical details. For example, it is not yet clear how long the protective action will be maintained, i.e., whether some of the additive will be slowly consumed. Thus this work is continuing.

Preliminary results of optical degradation in additive treated powders are reported. These measurements were made by M. J. Brown at Electro Mechanical Research, by arrangement with John Schutt of NASA. The

results are consistent with those of the conductivity degradation studies; both show marked improvement with the additive.

Early results using electron spin resonance (ESR) are reported. The objective is to determine the optimum technique for impregnating powders with the additives. The testing procedure is still under development; the present problem is to pretreat the powder with and without additives and to have well defined, equivalent initial condition before exposure to ultraviolet radiation.

The approach and a short discussion of preliminary results with oxide pigments other than ZnO are presented. Extension of the method to other pigments should be possible with a measurement of the "redox potential" of the conduction band edge, as in principle this is the only major variable. This measurement is being attempted utilizing electron injection from a mercury amalgam into a thin oxide layer.

II INTERACTIONS OF CARRIERS WITH ADSORBED SPECIES

In the preceding interim report,² two electrochemical techniques were described which we have used for studies of interactions of charged carriers in semiconductors with adsorbed species. These techniques were utilized with ZnO to study the relative hole capture cross section of surface additives in the reduced form and the relative electron capture cross section of the additives in the oxidized form. For an additive couple to be effective for the electron-hole recombination, it is required that both the hole capture and the electron capture cross section be high.

A. Electron Capture Cross Section

The measurement of relative electron capture cross section for additives in the oxidized form is made by a determination^{1,2} of the cathodic current as a function of the density of electrons at the semiconduction surface, n_s . A measurement of the electrical capacity associated with the surface depletion layer yields n_s . Then assuming

the rate of electron capture is first order in both surface state density and in electron density, the cathodic current density, J , should be related to the cross section, σ , by an expression describing capture by surface states:

$$J = e\bar{c}n_s[X]\sigma \quad (1)$$

where e is the electronic charge, \bar{c} the thermal electron velocity, and $[X]$ the surface concentration of the oxidizing agent.

In Eq. (1), J and n_s are measured quantities, \bar{c} and e are constants, and the concentration of X in solution is controlled. The relative capture cross sections for various species can be estimated by normalizing to the same concentration and by assuming that $[X]$ at this concentration varies less from species to species than σ . If no specific adsorption is assumed, $[X]$ becomes a constant.

Details of the theory and measurement of electron capture cross section are given in the attached paper, which is a preprint of a paper that has been submitted for publication. In essence the theory suggests that the energy level of the additive and hence its capture cross section should be related to the redox potential of the additive species. One can, in theory, define a "redox potential of the conduction band" such that if the redox potential of the one-equivalent additive is greater than this, the energy level of the additive is above the conduction band minimum; if the redox potential is less, the energy level is below the minimum. As will be discussed in Section II-B, several experiments have indicated that the redox potential of the ZnO conduction band is about -0.1 eV with respect to the normal hydrogen electrode.

The results of the electron capture cross section for various species, as a function of the redox potential of the one-equivalent couples, are shown in Fig. 1. This figure is reproduced from Appendix A. The capture cross section is plotted in the form of $\sigma[X]$ as calculated from the experimental fit of Eq. (1), with the concentration in solution normalized to 0.01 M.

The importance of these results in the present study is that high electron capture cross section is found for species with a redox potential between 0.1 and 0.8 eV lower than the redox potential of the conduction band.

From a theoretical point of view, this behavior can be reconciled with the surface state capture theories of solid state physics. An energy level above the conduction band edge would be ineffective in the capture of free conduction band electrons because reinjection of any captured electron would be energetically favorable. An energy level very far below the conduction band edge would be ineffective because of the large energy release; since dissipation of large amounts of energy in the form of phonons becomes increasingly difficult, σ decreases. Thus, one has a maximum of σ .

From a practical point of view, this approach permits prediction of several possible additives which are not easily tested by the methods available, but for which the redox potential is known. Also, as the theory should not be unique to ZnO, it implies that for other pigment materials, one has only to determine the redox potential of the conduction band in order to determine promising additives. Methods for this determination on other materials will be discussed in Section VI.

B. Hole Capture Cross Section

The measurement of relative hole capture cross section by the reduced form of a one-equivalent species is made by a comparison with a two-equivalent species.^{1,3,4} The two-equivalent species injects an electron following hole capture; the one-equivalent does not. The electron injection results in an anodic current increase. Thus if a solution contains a two-equivalent ion (a "doubling" agent), and a one-equivalent species is slowly added, then the current will decrease because the one-equivalent species captures a larger and larger fraction of the holes. By experimental analysis, one can then determine the hole capture cross section of the one-equivalent species relative to the two-equivalent species.

To compare a series of one-equivalent species, as is required in this program, one simply compares each species in the series to the same two-equivalent ion.

Details of the method are given in references 1, 3, and 4. Details of the theory are presented in reference 4.

Our recent results of relative hole capture cross section vs. redox potential of the additive are summarized in Fig. 2. The redox potentials were taken from Latimer.⁵ We use the redox potential to characterize the properties of the various species on the same basis as was described earlier. Each curve in Fig. 2 represents a different doubling agent. The various curves should not be the same because the capture cross section of the various doubling agents is not the same. However, the slopes should be the same, but are not. This indicates problems in either the theory or the measurement procedure.

The important qualitative feature of Fig. 2 is the apparent increase in capture cross section, σ_p , as the redox potential of the additive approaches the "redox potential" of the ZnO conduction band, about -0.1 eV. Measurements at higher redox potential cannot be made because such species spontaneously inject electrons. (This is one of the reasons that -0.1 eV is considered the conduction band potential; an energy level above the conduction band edge is expected to spontaneously inject electrons.)

In practical application, then, the optimum level for hole capture is apparently close to the conduction band edge. In studies of other oxide pigments we will use this criterion.

Theoretically, the observed increase in σ_p with higher redox potential (energy level) is best interpreted in terms of electron transfer from one localized surface level to another. Thus, we assume that the (photo-produced) hole is first captured by a surface state, viz., becomes localized on a specific oxygen ion at the surface. Then the electron from the reduced form of the additive makes the transition from its localized level to the surface state occupied by the hole. It is often found for electron transfer from one molecule to another that the

probability increases with the difference in energy. The transfer is best described using the reaction coordinate approach where the rate may decrease as the energy difference increases (see, for example, Delahay⁶). This behavior is in direct contrast to that expected if the process were free hole capture, in which case, as was described above in the discussion of free electron capture, one would have expected the cross section to decrease with higher energy level (or redox potential).

If the two-step model of hole capture is correct, it should be possible to apply it to other oxide materials (where the surface states may be similar to ZnO). It is expected, therefore, that one needs a level a few tenths of an electron volt below the conduction band edge for efficient hole and electron capture.

C. Tabulated Results

A summary of the values of the capture cross sections for holes and electrons for substances that may undergo one-equivalent oxidation-reduction processes is given in Table I, parts 1 and 2. The vertical arrangement follows an order of decreasing redox potentials (column IV). Column I lists the chemical element with its probable oxidation states. Column II gives the values of the product of the electron capture cross section, σ_e , and the surface concentration of the capturing species, $[X]$, at solution concentration of 0.01 M. Column III lists the values for the hole capture cross section relative to either Sn(II) or CH₃OH with the exception of Mn(II/III) for which the doubling agent was As(III). As was outlined in a recent publication,⁴ the hole capture cross section for a non-current-doubling substance relative to a doubling substance, σ/σ_D , is given by

$$(J_p/J_e) - 1 = (\sigma/\sigma_D)([S]/[D]) \quad (2)$$

where J_p is the hole current that is available for reaction with either the current-doubling substance, D, or the other capturing substance, S; J_e is the electron injection current which is the difference between the cell current and the hole current; and the brackets represent concentration. Columns V and VI list the experimental conditions under which the

Table I, Part 1
CAPTURE CROSS SECTIONS

I Element, Oxidation States	II Electron Capture ^a , $\log_{10} \sigma_e [X]$	III Hole Capture ^b , $\log \sigma_h / \sigma_D$ D = Sn(II) D = CH ₃ OH		IV Redox Potential ^c , E ₀
V (II/III)	<-12	Injects electrons		+0.25
Co (II, III)	<-14 <-10		4.5 3.4 3.2	-0.1
S (IV/V)			0.8 ^d	?
S (IV/V)			0.7 ^d	?
S (IV/V)		-0.8 ^d -1.1 ^d	0.5 ^d	-0.17
Cu (I/II)	<12			-0.15
Fe (II/III)	-5.7 -6.7 -7.0 -5.1	-0.8	2.7 3.1 3.4	-0.36
Ag (0/I)	-5.0			-0.37
I (0/-I)	-9.7 -9.2		1.1	-0.5
Mn (VI/VII)	-4.7 -3.2			-0.5
Mn (II/III)		-2.3 -1.5 -1.9 -1.5	D = As(III)	-1.5
Ir (III/IV)	-3.0 -2.2	-2 -2.2 -1.4 -1.4		-1.0
Fe (II/III)	-5.0	+0.2 -0.01		-1.1
Br (0/-I)			-0.9	-1.1
Ce (III/IV)	<-12 -8.2	-3.0 -3.3		-1.6 -1.4
Cl (0/-I)		<<-3	<<-3	-1.4

(a) σ_e , electron capture cross section; [X], surface concentration in numbers per unit area (J normalized to a solution concentration of 0.01 molar--see Eq. 1). (b) σ_h , hole capture cross section of element; σ_D , hole capture cross section of current-doubling agent D. (c) E_0 , redox potential under standard conditions given in W. Latimer, Oxidation Potentials, 2nd ed., Prentice Hall, 1952, (d) maybe a two-equivalent process involving capture of two holes.

Table I, Part 2

EXPERIMENTAL DETAILS FOR CAPTURE CROSS SECTIONS

I Element, Oxidation States	V Electron Capture Details				VI Hole Capture Details		
	Form of ion	pH	$\log N_D^b$	pF^c	Form of ion	pH	pD_1^f
V (II/III)	HCl ^b	0.3	17 ^c	0.3	HCl ^a		
Co (II/III)	Co(NH ₃) ₆ ⁺³	4.0 10.3	17.7 ^c 17.9 ^d	1.4 1	Co(NH ₃) ₆ ⁺²	10.3 ^d 10.3 ^d 10.3 ^d	0.0 -0.1 -0.1
S (IV/V)					C ₆ H ₅ SO ₃ ⁻	12.5 ^d	0.0
S (IV/V)					CH ₃ C ₆ H ₅ SO ₃ ⁻	12.5 ^d	-0.1
S (IV/V)					SO ₃ ⁻²	1 ^c 1 ^c 12.5 ^c	3.5 3.5 0.5,0
Cu (I/II)	Cu ⁺²	3.7	19 ^c	1.3			
Fe (II/III)	Fe(CN) ₆ ⁻³	8.7 12 9 3.8	18.9 ^c 18.6 ^d 18.6 ^d 18.3 ^d	2,3 3,4 2,3,4 2,3,4	Fe(CN) ₆ ⁻⁴	12.5 ^d 12.5 ^d 12.5 ^d 1 ^c	-0.2 -0.4 -0.7 3.2
Ag (0/I)	Ag(NH ₃) ₂ ⁺	12	17.0 ^d	1,2			
I (0/-I)	I ₃ ⁻	3.8 3.8	16.8 ^c 17.0 ^d	2,3,4 2,3	I ⁻	12.5 ^d	0.5,0
Mn (VI/VII)	MnO ₄ ⁻	4.5 8.7	18.8 ^d 18.0 ^d	2,3,4 3,4			
Mn (II/III)					OAc ^{-a}	4 ^d 4 ^d 4 ^d 4 ^d	1.3 2.4 2.5 2.5
Ir (III/IV)	IrCl ₆ ⁻²	3.8 3.8	18.0 ^d 16.5 ^d	2,3 2,3	IrCl ₆ ⁻³	1 ^c 1 ^c 1 ^c	3.5 3.3 -- 3.2
Fe (II/III)	Fe(phen) ₃ ⁺³	1.5	17 ^c	3,4	Fe(phen) ₃ ⁺²	1 ^c	4.7 3.5
Br (0/-I)					Br ⁻	12.5 ^d	0.5,0
Ce (III/IV)	NO ₃ ^{-b} SO ₄ ^{-2b}	1.5 1.5	17 ^c 18.8 ^c	3,4 3,4	NO ₃ ^{-a}	1 ^c 1 ^c	3.7 3.7
Cl (0/-I)						1,4,9,13.5 ^c	-1

(a) possible complexing agent; (b) N_D , donor density in numbers per cubic centimeter; (c) (0001) crystal face; (d) (0000) crystal face; (e) pF , $-\log_{10}$ formality of capturing species in solution; (f) pD_1 , $-\log_{10}$ initial formality of current-doubling agent

electron capture cross sections and hole capture cross sections were determined.

III CONDUCTANCE DEGRADATION ON ZnO

The conductance degradation, as measured by Lal and Arnett⁷ and by Collins and Thomas,⁸ is a sensitive measure of chemical changes of the ZnO due to ultraviolet irradiation in vacuum. If there are no chemical changes, and if sufficient time is allowed for the release of trapped carriers the conductance should be the same before and after irradiation. However, normally a significant change is observed, which the above authors have attributed to desorption and decomposition at the ZnO surface. We call this change "conductance degradation" or its inverse, "resistance degradation," in analogy with the slower optical degradation under the same conditions.

The objectives of these studies are to study the effect of surface additives in reducing the rate of degradation and to examine the theory of the behavior of the additives as recombination centers. Measurements of resistance degradation, the irreversible decrease of dark resistance caused by exposure to light, have been made as a function of time of illumination and as a function of the surface treatment of the ZnO.

In our studies we are using lithium-doped ZnO because the relative changes are many orders of magnitude larger than normal low resistivity ZnO and the features of degradation on the doped and undoped ZnO are similar. The experimental method is as follows:

(a) Pretreat the lithium-doped single crystal of ZnO either by (1) dipping the wafer in an aqueous solution of the additive to be tested, removing the excess solution by touching the edge of the sample to a piece of clean glass, and air drying, or by (2) spraying the solution on a hot ZnO crystal using an atomizer. The atomizer deposition rate was calibrated by depositing ions under standard conditions, in a tray of water, and measuring the deposition rate by the rate of conductivity increase of the water.

(b) Attach four clip contacts to the sample, mount it in the apparatus, and evacuate the system. At this point there is little resistance degradation observable, presumably because water adsorbed on the ZnO acts as a recombination center. This water will slowly come off with continued evacuation and the ZnO then becomes subject to resistance degradation.

(c) Heat the ZnO to 250°C in vacuum (about 10^{-7} torr) for two hours in the dark to drive off water. Measurements can then be made for most samples. For some very sensitive samples, however, degradation has occurred at this stage with no intentional exposure to illumination; in this case it is necessary to do step (e) before the degradation measurement, step (d).

(d) Measure the sample's dark resistance before and after a short period of illumination, taking the irreversible decrease of the dark resistance as the resistance degradation. The inverse of this is the conductance degradation, ΔG . Continue the measurements over alternating periods of illumination (measuring photoconductance) and darkness (measuring dark resistance and thus degradation). The illumination intensity has not been calibrated, but we have standardized it using a PEK 200-watt mercury lamp with quartz optics and a 2-cm aperture 30 inches from the sample.

(e) Restore the sample to its original, high, dark resistance by exposing it to 1 mm of nondried oxygen. Step (d) can then be repeated.

Typical results obtained with the dipping technique of additive application are shown in Fig. 3. Each sample was treated in an aqueous solution of the concentration shown. The curves marked "mixture" contained Fe(II)/Fe(III) in a 50/50 ratio. The saturated mixture contained solid Fe(II) and Fe(III). As can be seen in Fig. 3, the untreated sample (blank) has a rapid conductance degradation, $\Delta\sigma$. With the additives, however, the value of $\Delta\sigma$ at any exposure time is lower. Dipping the sample in a saturated solution of $\text{Fe}(\text{CN})_6^{-4}$ and $\text{Fe}(\text{CN})_6^{-3}$ leads to at least six orders of magnitude decrease in the degradation.

These results can be better understood in terms of the degradation and the rate of degradation at some given exposure time plotted as a function of treatment. Such plots are shown in Fig. 4 and 5, where Fig. 4 shows the degradation after 10^5 sec and Fig. 5 shows the rate of degradation.

There is a difference between the degradation observed during the first run, step (d), and the succeeding runs after the sample has been exposed to oxygen, step (e). This is shown in Fig. 4 (after bakeout).

Although Figs. 4 and 5 show the protection offered by the additives, the dependence on additive concentration does not follow the expected behavior. One would expect the degradation to depend inversely on, or as the inverse square of, the additive concentration.⁹ For example, with the saturated solution (~ 0.5 M) yielding $\Delta\sigma = 10^{-12}$ mhos (Fig. 4), one would expect the 10^{-2} M solution to yield $\Delta\sigma \sim 10^{-10}$ mhos. However, it is clear that the dependence observed is much stronger; 10^{-5} mhos is actually observed with a 10^{-2} M solution.

The reason for this inconsistency may be that the dipping technique does not yield adequate uniformity with low molarity solutions. As the solution dries, it forms a meniscus and the salts may follow the solution rather than depositing on the surface. Thus, some areas of the surface would have relatively low additive coverage.

This possible difficulty was taken into account in the development of the atomizer deposition technique, which is presently under study. Figure 6 shows a comparison between the dipping method and the atomizer method. The amount deposited by the two techniques was compared using a high concentration $\text{Fe}(\text{CN})_6^{-3}$ solution and visually comparing the coloration. Then the same amount of liquid was used with a dilute (10^{-2} M) solution. The results show that samples prepared by the atomizer technique provide a factor of 10^6 lower degradation than samples prepared by the dipping technique consistent with the suggestion that dipping produced a nonuniform coverage.

Measurements made after the atomizer was calibrated are shown in Fig. 7. The "blank" curve is for ZnO with no additive and represents the average of several runs. These results suggest that the degradation rate with additive is insensitive to the amount of additive for the range of surface coverage examined (1×10^{13} to 5×10^{14} cm^{-2}). Decreasing the molarity of the solution and compensating for the decrease with a longer deposition time to maintain the same surface concentration had no significant effect; therefore, these results do not appear to be influenced by nonuniformity. Since the results in Fig. 7 were all obtained on a new crystal, it is possible that the degradation observed is associated with a bulk doping effect. This possibility is being investigated.

Despite the lack of dependence on additive concentration, it appears that 0.01 monolayer of additive is sufficient to decrease the degradation rate by three orders of magnitude.

IV OPTICAL DEGRADATION RESULTS

Through the courtesy of John Schutt at Goddard and M. J. Brown at Electro Mechanical Research Company, a preliminary test of three samples at 350 sun hours exposure has been made.

The three samples were prepared at SRI by mixing ZnO and water in a ratio of 1 g/1 cc. In sample 1 no iron salt was added to the water; in sample 2 a 10^{-4} M solution in both $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ was used; in sample 3 a 10^{-3} M solution in both $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ was used. After mixing, the paste was dried, broken up, and sent to John Schutt for measurement.

Assuming $3 \text{ m}^2/\text{g}$ for the ZnO (SP-500 NJZ), sample 2 had 5×10^{12} ions/ cm^2 (0.005 monolayer) and sample 3 had 5×10^{13} ions/ cm^2 (0.05 monolayer) of Fe(II + Fe(III)). The reflectance spectra for the three samples are shown in Figs. 8, 9, and 10.

The results for sample 3 (Fig. 10) look very promising, showing negligible optical degradation. Obviously there is insufficient additive

on sample 2; improved impregnation methods would be required for this amount of additive to be effective. The results shown in Figs. 8 to 10 are consistent with the results obtained in the conductance degradation studies, but must be considered preliminary, as there are insufficient samples.

V ELECTRON SPIN RESONANCE STUDIES OF POWDERS

The objective of the ESR studies is to determine the optimum technique for impregnating powders. At a later stage the ESR technique will be applied to measure the degradation of other pigment materials.

The ESR program has been divided into three parts. The first is techniques development which is now in progress; some results are reported below. The second part will be studies of methods of deposition of additives on powders to determine the most effective conditions. The third will be application of the ESR technique with other pigment materials.

Two ESR parameters have been found to be very sensitive to the uv-vacuum exposure: the intensity of the $g = 1.96$ line and the crystal current. Both parameters in principle measure added electrons in the ZnO conduction band. Several authors¹⁰⁻¹² have associated the 1.96 line with conduction electrons and donors. The crystal current is associated with the increased conductivity of the powder, particularly intragranular conductivity.¹³

We have found that both signals change by several percent after low intensity irradiation in vacuum. However, we have also found that without such exposure the 1.96 line depends on the iron salt additive that is under test. For example, if the ZnO is heated to temperatures over 250°C in vacuum (to dry the ZnO, for example), one finds a large 1.96 line for additive-free ZnO, but no 1.96 line for ZnO with ferrocyanide and/or ferricyanide additive. This implies that the iron salts affect the natural oxidation/decomposition reactions occurring on the ZnO surface at high temperature. In order to make a quantitative

comparison between the treated and untreated ZnO, both materials must initially be similar (other than the additive variation under study); therefore, such high temperature interaction must be avoided. A short study of this "high temperature" interaction as a function of pretreatment conditions is in progress to determine acceptable pretreatment conditions.

VI PIGMENT MATERIALS OTHER THAN ZnO

As was discussed in Section II, the overall approach to the degradation problem should in principle not be dependent on the oxide material selected. The location of the energy level should be primarily dependent on the conduction band edge of the material (with respect to the redox potential scale, as was discussed above).

Thus, the research necessary to provide good additives for other oxide pigments should be much more direct than was required for the initial material, zinc oxide. The program is in two parts: first, to measure the conduction band edge of the pigment material, which will enable selection of promising additives, and second, to test the additives. At present we are planning to use ESR for testing the additives.

Two materials have been selected for study, ZrO_2 and La_2O_3 . In the work to develop the techniques for conduction band edge measurement, we have used primarily ZrO_2 because of the ease of handling.

In the case of ZnO one method adopted for measuring the conduction band edge was anodic injection by strong reducing agents. It was found that V^{+2} , Cr^{+2} , and Sr^{+2} inject, whereas $Fe(CN)_6^{-4}$, MnO_4^- , and others do not. From several techniques including the injection technique, the "redox potential of the conduction band edge" was determined to be about -0.1 eV with respect to the hydrogen electrode. The injecting species all have a higher redox potential than the conduction band edge, whereas the noninjecting species have a lower redox potential. One can also use the technique to determine the approximate conduction

band edge by using species with increasing redox potential, and determine the band edge to be between that of the highest potential noninjecting species and the lowest injecting species.

For the initial studies of ZrO_2 , the sample is a thin film of ZrO_2 on Zr, formed by anodic oxidation¹⁴ in HNO_3 to a potential of 3.5 volts. Tests on aqueous solutions showed that V^{+2} and Cr^{+2} do not inject, so the band edge is higher than this. Beyond this redox potential, aqueous solutions become unstable. Thus another "electrolyte" was sought.

Mercury is presently under study as an appropriate "electrolyte." Thus the plan is to test various amalgams for injection and to determine for which metal (Na, In, Zn, etc.) the injection ceases. Comparison of injection into zinc oxide by the same series of amalgams will then permit determination of the band edge. Initial studies have been made with a sodium amalgam, where injection is clearly expected, in order to develop sensitive techniques to identify injection.

The difference between zinc oxide and most other oxide pigment candidates is the high Fermi level in ZnO with a resulting lack of bulk trapping effects. In other materials bulk electron trapping can occur, giving rise to space charge effects which affect the potential at the surface and perhaps complicate the measurement injection.

After several exploratory studies, there are indications that the use of a low constant current may provide a sensitive test. With no sodium present in the mercury, the potential (Zr to Hg) increases linearly with time, simply due to charging of the capacity associated with the ZrO_2 . The rate of voltage increase diminishes as sodium is added. This we ascribe to leakage due to injection. The test must be examined more closely in order to test the interpretation.

When the injection is understood in more detail, other amalgams can be tested both on ZrO_2 and ZnO to establish the relative conduction band position.

VII CONTINUING STUDIES

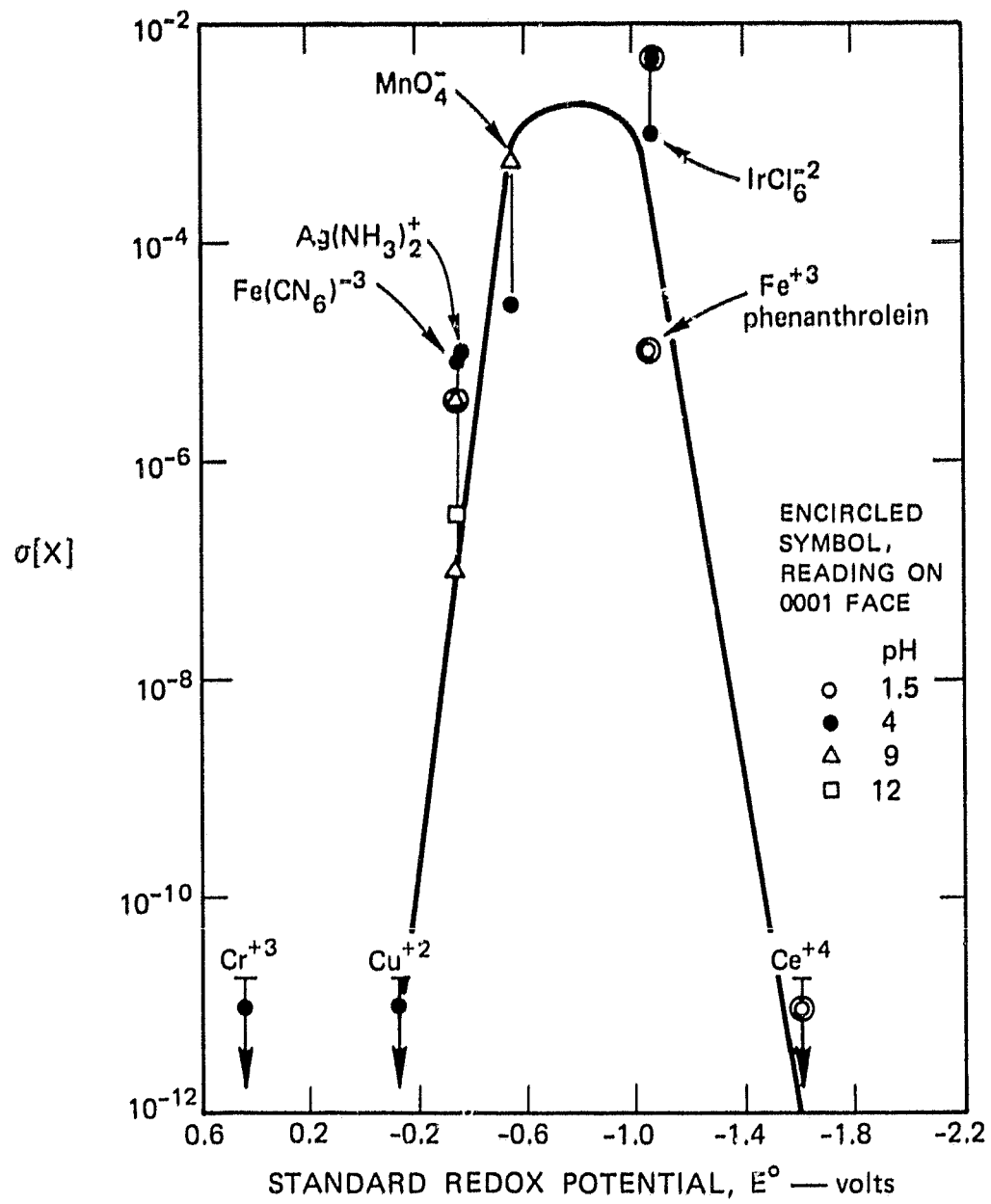
In order to determine accurately the mechanism of the surface recombination on additives, the studies will be continued on the conductivity degradation of single crystals. This is necessary to determine (a) if the additive is in some part acting in a sacrificial way and that one can, by experimental analysis, define the optimum amount and ratio of additives.

The work on additives for other materials will be continued so that a simple means can be devised to predict additives for arbitrary pigment materials.

The work on ESR will be continued, with the two objectives: (a) to define the optimum method of depositing additives on ZnO powder, and (b) to test degradation in the case of other pigment candidates.

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TA-365,522-20

FIG. 1 ELECTRON CAPTURE CROSS SECTION OF ONE-EQUIVALENT OXIDIZING AGENTS

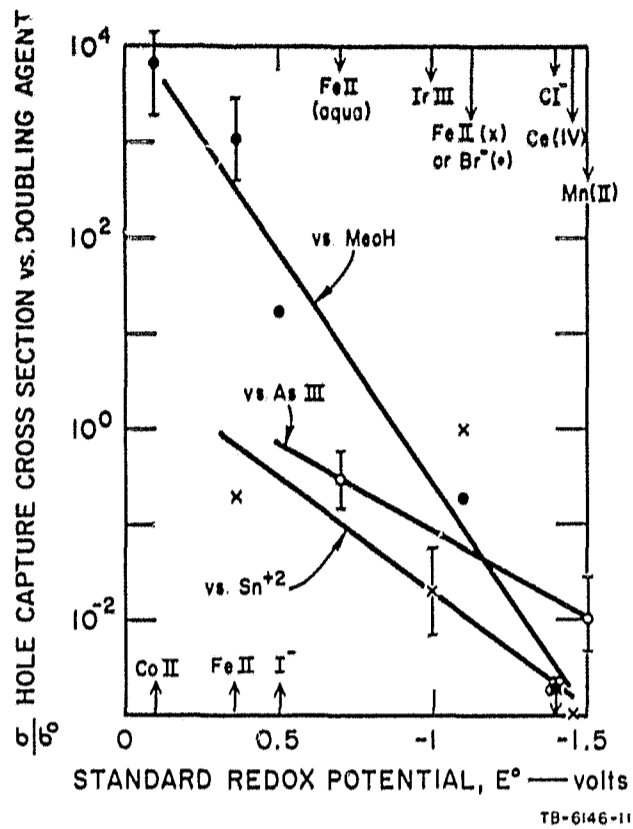


FIG. 2 HOLE CAPTURE CROSS SECTION OF ONE-EQUIVALENT REDUCING AGENTS

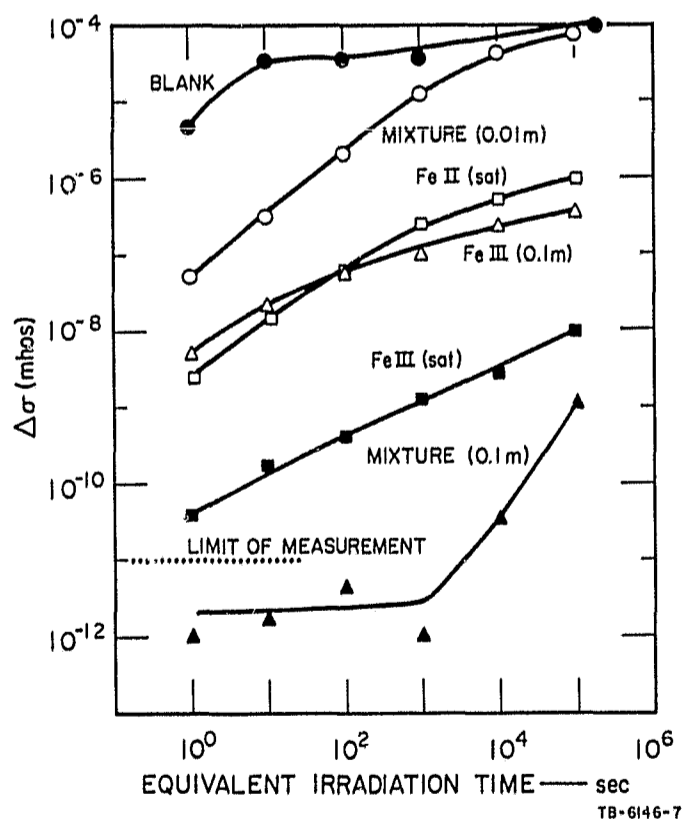


FIG. 3 CONDUCTANCE DEGRADATION VERSUS ILLUMINATION TIME (additives applied by dipping technique)

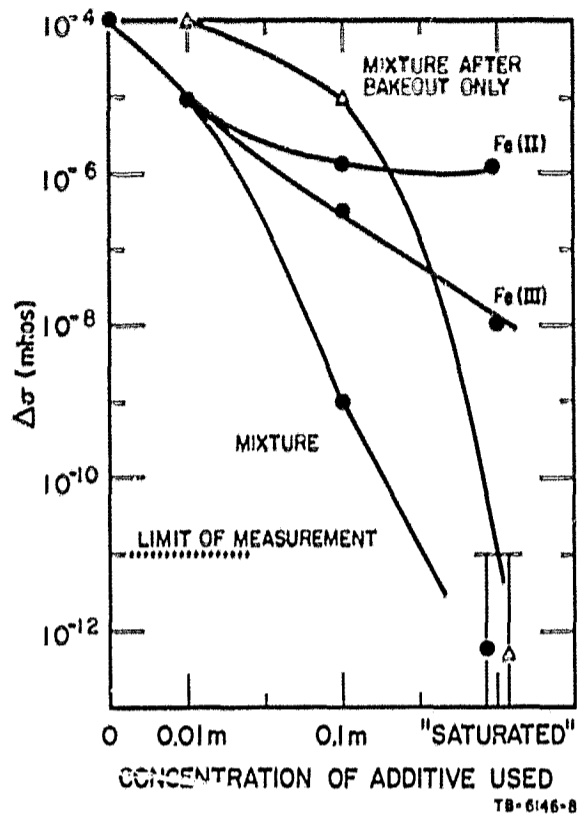


FIG. 4 CONDUCTANCE DEGRADATION AFTER 10^5 SECONDS ILLUMINATION WITH VARIOUS CONCENTRATIONS OF ADDITIVE

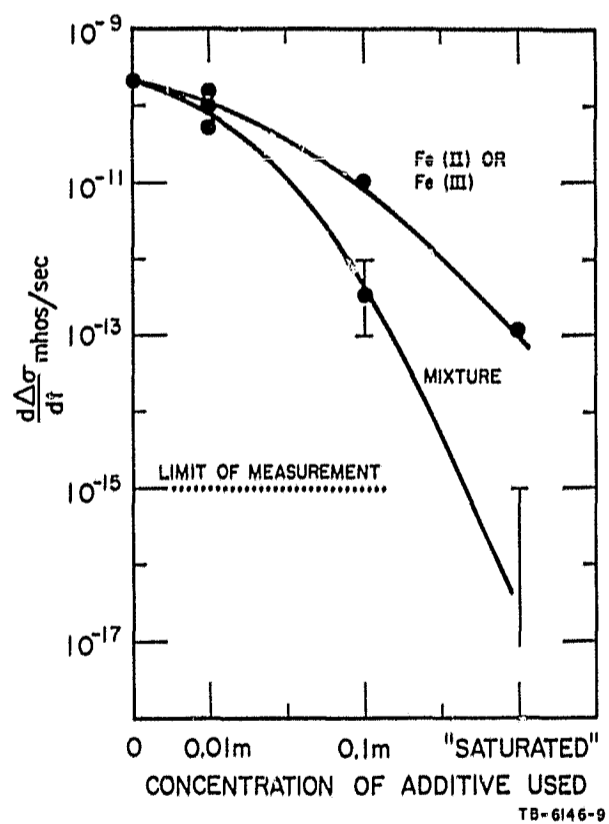


FIG. 5 RATE OF CONDUCTANCE DEGRADATION AFTER 10^5 SECONDS ILLUMINATION WITH VARIOUS CONCENTRATIONS OF ADDITIVE

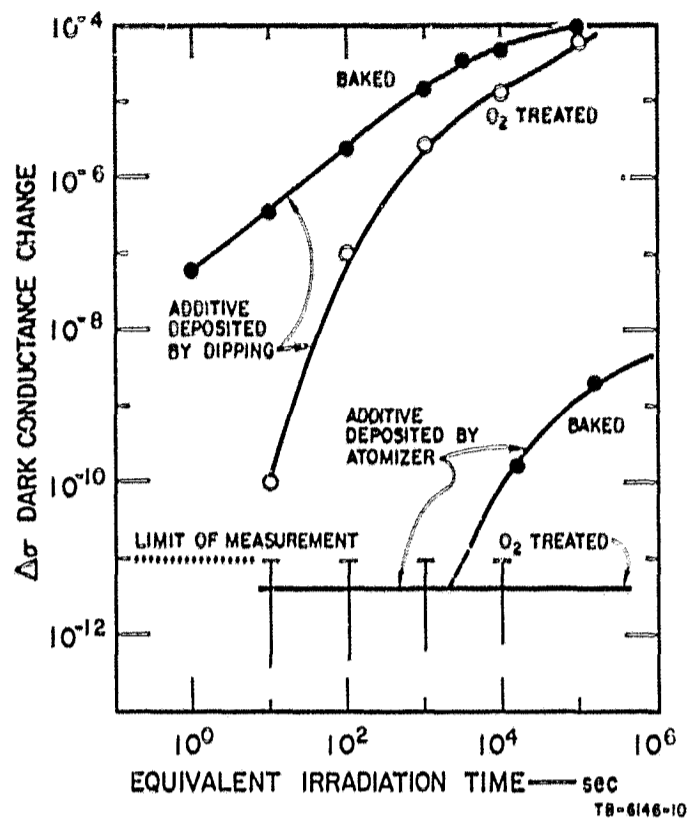


FIG. 6 COMPARISON OF CONDUCTANCE DEGRADATION AFTER DEPOSITION OF Fe(II)/Fe(III) MIXTURE USING DIFFERENT APPLICATION TECHNIQUES

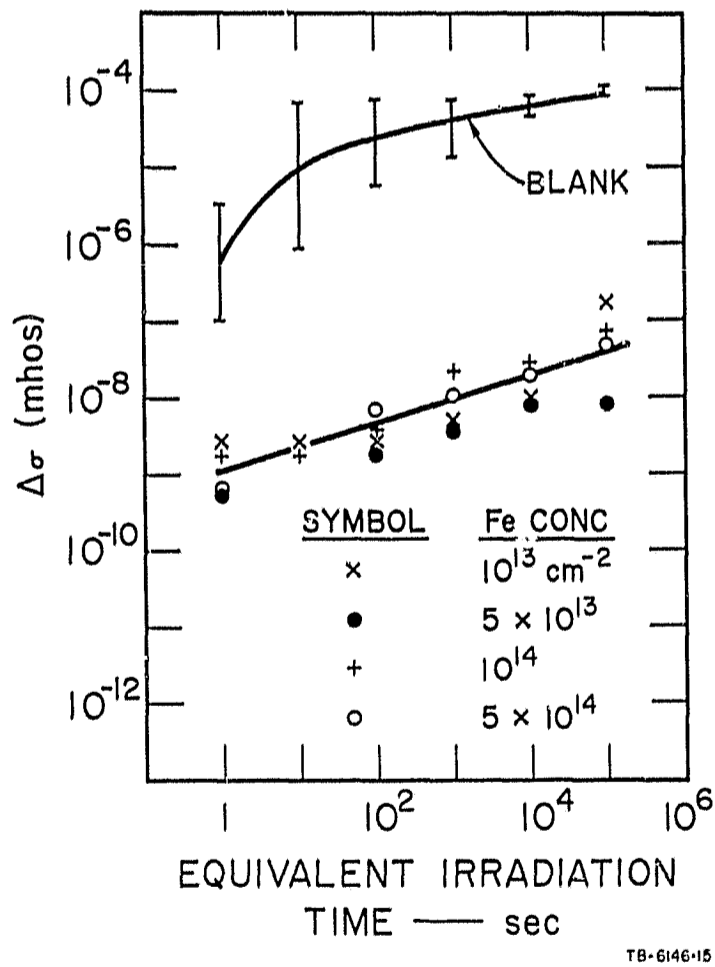


FIG. 7 CONDUCTANCE DEGRADATION VERSUS ILLUMINATION TIME (Fe(II)/Fe(III) mixture deposited by atomizer)

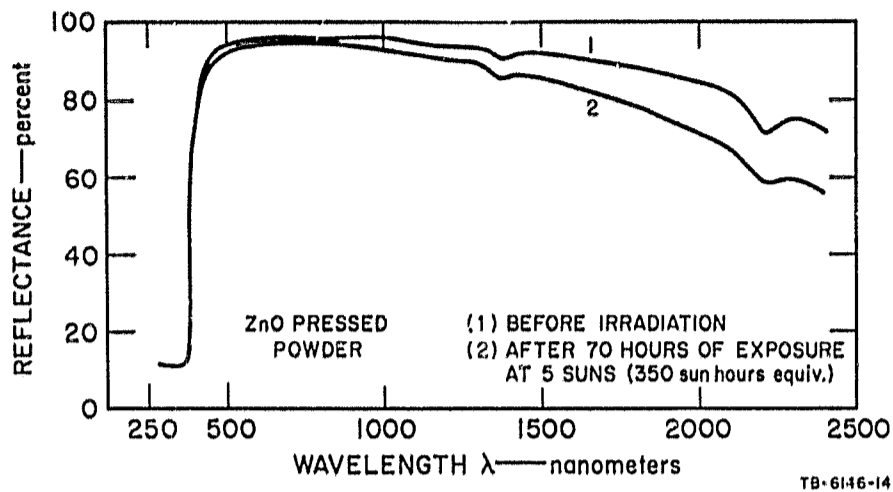


FIG. 8 OPTICAL DEGRADATION AFTER 350 SUN HOURS (blank, no iron salt added)

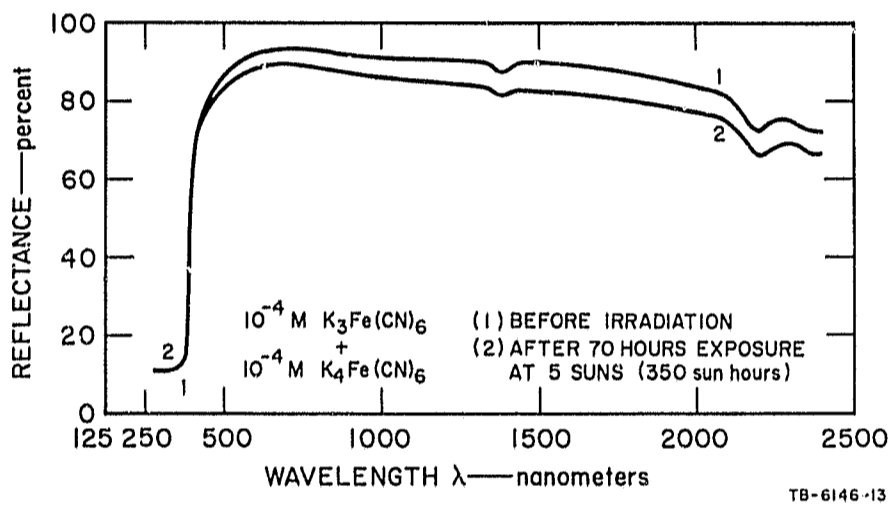


FIG. 9 OPTICAL DEGRADATION AFTER 350 SUN HOURS (surface concentration of additive $5 \times 10^{12} \text{ cm}^{-2}$)

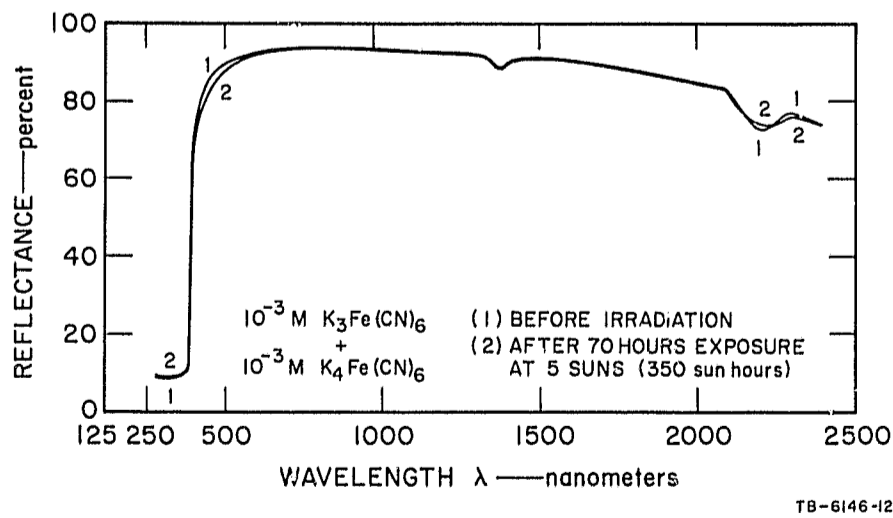


FIG. 10 OPTICAL DEGRADATION AFTER 350 SUN HOURS (surface concentration of additive $5 \times 10^{13} \text{ cm}^{-2}$)

ELECTRON CAPTURE BY ENERGY LEVELS ASSOCIATED WITH IONS IN SOLUTION*

I. CALCULATION OF ENERGY LEVELS IN SOLUTION

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ABSTRACT

To correlate the electron capture cross section of ions in solution with the energy level associated with such ions, it is necessary to evaluate the energy levels by an independent method. The standard oxidation-reduction potential is used to make such an estimate. The mathematical analysis of the reversible potential of a redox system is reformulated, separating the electrode processes into electronic transitions and chemical rearrangement, the separation based on the Franck-Condon principle. The method is restricted to inert electrodes at which only electron transfer occurs between the electrode and the solution. It is shown that the energy level of the oxidizing agent (with respect to the Fermi level at a reversible hydrogen electrode) is given, for simple one-equivalent redox systems, by the standard redox potential plus terms calculable from the equilibrium constants for various chemical rearrangements. In appendices the energy levels of two-equivalent redox systems are discussed, and by analysis of a simple electrochemical cell it is shown that there is no inconsistency between the usual theory and the present formulation.

*This research was supported by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by National Aeronautics and Space Administration under Contract NAS 7-100.

1. Introduction

The purpose of this paper is to explore further the possibility that for cathodic reduction of oxidizing agents on a ZnO electrode, the behavior can be described in terms of the theories of electron capture by surface states. Earlier work on ferricyanide¹⁾ has indicated that such a description is appropriate. In the present study the electron capture cross section is examined for a series of oxidizing agents; the electronic energy level of the various oxidizing agents is estimated, and the expected variation in cross section with energy level (from solid-state analogy) is compared with the observed experimental results.

To relate the capture cross section to the energy level of the species, we must first develop a method of estimating the energy level of the species. In this paper (Part I), a model is developed through which the electronic energy level of interest can be estimated from the standard oxidation-reduction potential of the species. This approach to energy levels in solution was initiated by Beck and Gerischer²⁾ in a qualitative way. The present discussion attempts to put the concept in a somewhat more quantitative form.

In Part II of this paper, the electron reactivity of a series of one-equivalent oxidizing agents is related to their estimated energy levels

2. Formulation of the problem

When an electron is transferred from an electrode to an ion in solution, several distinct steps occur. After each of these steps, the energy level of the electron will be different. The first problem, therefore, is to identify which of these energy levels is important in determining the capture cross section.

Consider for example an electron transferring between a metal and an oxidizing agent in solution, the electron originating at a level above the Fermi energy of the metal. There are many steps in such a process, each involving energy change. Some steps involve electron motion only

(the electron transferring, causing a change in the free energy of the metal; the neighboring electrons in the system responding to the new electrostatic configuration). Other steps involve ion motion (polarization of the ions in response to the new electrostatic configuration, hydration). Still other steps involve major chemical changes which occur following the electron capture (hydrolysis, dimerization, complex formation, etc.).

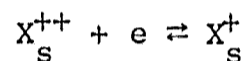
It will be the assumption of the present analysis that the energy level we wish to calculate is the energy level of the electron after the first phase, electron motion only. We will assume that the electron moves to the lowest available energy level on the ion, neglecting the possibility of "cascade" type capture (which is discussed in Part II). The subsequent changes in the energy level of the electron due to hydration or chemical reaction of the newly reduced species will not affect the capture cross section of the energy level for electrons. The designation of such a level as an important intermediate is consistent, for example, with the Franck-Condon principle, where ionic motion takes place after the electronic transition is completed. In this and in the Franck Condon case, we are relying on separation of steps on the basis of the time factor. We assume that electronic steps occur so rapidly that the ionic structure does not have time to relax, so that the factors (including energy changes) governing the electronic transition probability cannot include subsequent ionic relaxation.^{3,4)}

With the designation of such an intermediate electronic energy level as the level of interest, important in capture cross section, a simple description of the equilibrium occupation of the levels is sacrificed. It will be shown that at least two energy levels must be indicated on the band diagram;⁵⁾ the energy level dominant in the reduction process derives from the description above (corresponding to the capture of an electron by the oxidizing agent), and a level dominant in the oxidation process is determined by analogous arguments (corresponding to the removal of an electron from the reducing agent). The equilibrium occupation statistics will be shown to depend on the energy involved in the "chemical" steps.

In an attempt to use electrochemical measurements to calculate such energy levels basic difficulties are encountered. Standard electrochemical models do not, unfortunately, separate the energy of the system into chemical steps, involving ion motion, and electronic steps, which involve only electron motion. It is necessary then to reformulate the expressions of electrochemistry with parameters that differ from those normally used.

3. Electronic energy levels in solution

Consider an aqueous solution with an inactive electrolyte, such as K^+ and Cl^- , and two stable oxidation states, X^+ and X^{++} , of the species X. The overall reaction we are considering is



on an inert metal electrode. The specification of the charge on the ion is for convenience, and does not restrict the generality of the formulation. The subscript s indicates fully solvated species.

Figure 1 shows the electronic energy levels associated with the solution phase. For each ion there are many electronic energy levels, but normally only one for each species is considered active (will actively accept or donate electrons to an electrode). For example, the ion Cl^- with a Z of 17 for the chlorine atom has 18 filled electronic energy levels and an infinity of empty energy levels. The only level noted in Fig. 1 is the energy level occupied by the extra electron. Complications associated with degeneracy of the active level will not be considered here. For potassium with a Z of 19, the only level noted is the normally empty level of the nineteenth electron. The energy levels indicated will be those of the solvated species. Thus, if we take the energy of an electron at infinity to be equal to zero (the energy level of interest for potassium), E_{K^+} is the energy released bringing an electron from infinity to the level before any ionic motion or chemical change can occur. Similarly the energy level E_{Cl^-} is the energy to remove an electron from Cl^- infinity, without any ionic relaxation. The subscript

a is used if the level is normally empty in solution, the subscript d is used if the level is normally full. The use of these symbols bears some relationship to the terms acceptor and donor in solid-state terminology. In any real solution, other levels will be present (such as H_3O_a^+ and OH_d^- in aqueous solutions), which are omitted for simplicity.

In the case of the species X, there is an appreciable quantity of both filled and empty levels: both X_s^+ and X_s^{++} species. The energy E_{X^+} to remove an electron from the ground state of a filled species is not necessarily the same as the energy E_X^{++} released as an electron (from infinity) occupies the acceptor level of the X_s^{++} . The two levels associated with X are shown in Fig. 1.

In fig. 1, and in subsequent discussion, the broadening of the energy levels, discussed in detail by Gerischer⁵), is not considered. It is not clear at this time how serious this omission is. Broadening due to variations in hydration will certainly occur but will be limited in general to the kT range, which is of little interest here. It is felt that more energetic chemical processes such as hydrolysis or complex formation will cause multiple energy levels in general, rather than broadening of a single energy level. This will complicate the observed behavior of the species, but does not change the arguments to be presented for the calculation of each of the several energy levels.

3. Electrochemical potential of electrons in solution

To analyse electron transfer between the energy levels and the metal electrode, it is necessary to introduce a parameter, which we will term the electrochemical potential of electrons and which describes the occupancy of each of the energy levels.

Each of the electronic energy levels indicated in Fig. 1 has the possibility of existence in both the filled and unfilled forms. Consider, for example, a solution one molar in both X^+ and X^{++} . Each species will become solvated. In particular the species X^{++} will take on some chemical

form $R \cdot X^{++}$, where R represents all attached species of the solvation.* Then at the electrode at equilibrium we will have the reaction



which is associated with electronic transitions to and from the energy level $E_{X^{++}}$. The intermediate species $R \cdot X^+$ is the chemical form of the filled energy level, and E_{X^+} is the energy of the electron after electron movement but before ion movement. The intermediate species $R \cdot X^+$ will not be present at the concentration of one molar (unit activity); only the dominant solvated form of X^+ is present at unit molarity. At equilibrium, the principle of detailed balance⁶) demands that the forward and reverse directions of reaction (1) proceed at equal rates.

Now with an inert metal electrode, the only species which crosses the phase boundary between the electrode and the solution are electrons. Thermodynamics require that the electrochemical potential for electrons be constant across the interface at equilibrium. Thus:

$$E_F = \mu_e \quad (2)$$

where E_F is the Fermi level in the solid, and μ_e is the Fermi level or electrochemical potential of electrons in solution. However, relation (2) only begins to have significance if we can define μ_e in terms of the type and concentration of chemicals in solution. With such a definition, the properties of the solid (E_F) and the properties of the solution (μ_e) can be connected at equilibrium through (2).

There are two approaches for evaluating μ_e , each with some lack of rigor: The first approach is to apply the Fermi distribution function

*In the following discussion the subscript s is dropped, its function being replaced by the R's.

directly to the energy level E_X^{++} . Here we are focussing attention on ions deep in solution and not necessarily near an electrode. Then, the Fermi distribution yields:

$$[R \cdot X^{++}]/[R \cdot X^+] = \exp \left\{ -(\mu_e - E_X^{++})/kT \right\} \quad (3)$$

or

$$\mu_e = E_X^{++} - kT \ln \left\{ [R \cdot X^{++}]/[R \cdot X^+] \right\}$$

where the square brackets have their usual interpretation as reactant concentrations. However, for the identity to be valid, a mechanism must be supplied through which equilibrium is reached. This mechanism must normally involve the electrode, and conditions near the electrode may be slightly different from conditions deep in the solution. A second method of deriving (3) provides a slightly better understanding of the assumptions. Consider ions near the metal electrode but on the solution side of the Helmholtz double layer. These species can for our purposes be viewed as surface states if they are near enough to the metal electrode to permit electron transfer even when there is no specific adsorption. Thus they can be described by the Fermi distribution utilizing the Fermi level of the metal:

$$[R \cdot X^{++}]/[R \cdot X^+] = \exp \left\{ - (E_F - E_X^{++})/RT \right\} \quad (4)$$

Now, if we neglect the Gouy layer, the species obeying (4) are at equilibrium in all respects with ions in the bulk solution. There is at equilibrium no difference in ratio of $[R \cdot X^{++}]/[R \cdot X^+]$ between species which are, say, 5A from the electrode and those which are 5 mm from the electrode. Thus, with (4) and (2), we determine that a meaningful definition of electrochemical potential for bound electrons in the solution can be given by (3). Thus (3) is probably quite satisfactory as a first approximation, but the effect of differences in the Gouy layer is not clear.* With this minor reservation we have a quantity μ_e

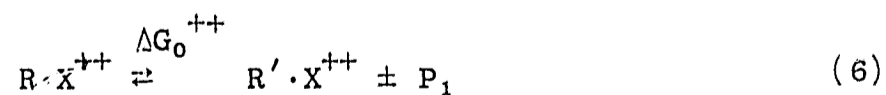
*A simple mathematical analysis of the distribution of ions in the Gouy layer⁷ leads to consistency with (4) throughout the region, viz. E_F as defined is constant, with the concentration changes and E_X^{++} changes compensating through the region of varying potential.

defined by the chemical properties of the solution which we can term the electrochemical potential of electrons in the solution. Note that the concept of electrochemical potential for electrons in solution will have meaning very similar to the Fermi level concept in the solid. In fig. 1, for example, when the energy μ_e is near the energy levels for X, then the deep levels, such as chlorine, will be filled, except for a mathematically definable quantity of chlorine gas. (This quantity may not exist in reality because the chlorine/chloride equilibrium is not attained.) If a new energy level (chemical species) is added to the solution it will attempt to reach a ratio consistent with μ_e (assuming a mechanism of electron exchange is available), and a chemical reaction will proceed. In summary, this is another way of looking at normal aqueous chemistry, a way through which the connection to the solid-state approach is clarified: When the metal electrode and the solution are placed in contact, the electrochemical potentials for electrons in the two phases must be equalized by charge transfer to satisfy (2). If the level μ_e is much lower than the level E_F initially, electrons will be transferred to the solution, forming the Helmholtz double layer, until Eq. (2) holds.

4. The determination of the energy levels of a species from the reversible potentials associated with a one-valent transition

As discussed above, for a one-valent redox process, there will be two energy levels of primary interest, the one level associated with the electron capture on some form of the oxidized species, the other level with electron injection from some form of the reduced species.

The reduction of the dominant form of the oxidized species $R \cdot X^{++}$ can be described by a series of reactions



Here the R's are molecules or ions associated with the reactants at various stages of the reaction. They could be water of hydration, protons, etc. The species $R \cdot X^{++}$ is the dominant form (unit activity assumed) of the oxidized additive; the species $R'' \cdot X^+$ is the dominant form (unit activity) of the reduced additive, and $R' \cdot X^{++}$ is the form of the oxidized reactant which we postulate exhibits the highest exchange current and whose energy level we wish to calculate. The species P are those absorbed or released from the reactant during the chemical rearrangements (6) or (8). The quantities ΔG_0 are the free energy absorbed in the forward direction of reactions (6) or (8). The subscript o on the ΔG 's refers to oxidizing agent; we are calculating the free energy changes occurring before and after electron capture by the oxidizing agent.

We will use the relations from thermodynamics governing equilibrium:

$$\Delta G_0^{++} = -kT \ln \frac{[R' \cdot X^{++}] \cdot [P_1]^{\pm 1}}{[R \cdot X^{++}]} \quad (9)$$

$$\Delta G_0^+ = -kT \ln \frac{[R'' \cdot X^+] \cdot [P_2]^{\pm 1}}{[R' \cdot X^+]} \quad (10)$$

From eq. (3), we have

$$E_{R' \cdot X^{++}} = \mu_e + kT \ln [R' \cdot X^{++}] / [R' \cdot X^+] \quad (11)$$

and using (9) and (10) to eliminate the species involving R' , we have

$$E_{R' \cdot X^{++}} = \mu_e - \Delta G_0^{++} - \Delta G_0^+ - kT \ln \frac{[R'' \cdot X^+] \cdot [P_1]^{\pm 1} \cdot [P_2]^{\pm 1}}{[R \cdot X^{++}]} \quad (12)$$

If added reactants $R \cdot X^{++}$ and $R'' \cdot X^+$ are at unit activity, and if the species P are at unit activity, we find the simple relation

$$E_{R' \cdot X^{++}} = \mu_e - \Delta G_0^{++} - \Delta G_0^+ \quad (13)$$

Normally we compare the standard oxidation-reduction potential, and the assumption of unit activity can be made with the normal caution. The assumption that P_1 and P_2 are at unit activity must be evaluated for each case. Often there are no molecules involved in the processes other than the reactants and the dielectric, and the assumption is straightforward. In other cases, if for example proton evolution is involved, justification is still straightforward with proper control.

In Eq. (13) we have not yet defined a zero of energy. We have earlier suggested the possibility that an electron at infinity be at zero energy, but this is inconvenient. In the following we will define the zero of energy as the Fermi level (the electrochemical potential for electrons) at the reversible hydrogen electrode.

With this zero, the value of μ_e to be used in Eq. (12) is the electrode potential for the couple X^{++}/X^+ relative to the standard hydrogen electrode, and the energy levels are measured relative to the hydrogen electrode reference energy.

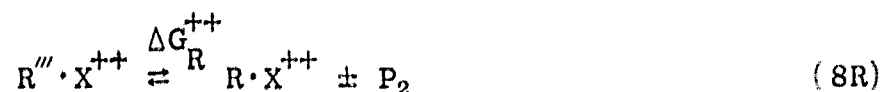
The most convenient approach is in the estimation of the energy level $E_{R'/X^{++}}$ to use Eq. (13) with the standard oxidation/reduction potential. If P_1 and P_2 do not involve protons or hydroxide ions, then the redox tables for either acid or base can be used. If P_1 or P_2 do involve protons or hydroxide ions, again either redox potential table can be used; for example, if the table for one molar base is used, Eqs. (6) and (8) can be written in terms of hydroxide ion evolution, and then Eq. 13 can be used to provide the energy level, as the P's will be of unit activity. If the table for redox potential in acid solution is used, then Eqs. (6) and (8) can be written in terms of proton evolution, and Eq. (13) can again be used. The same energy level will be obtained for the same species $R'X^{++}$, the G's in the two formulations will compensate for the change in the tabulated redox potential.

Thus in Eq. (13) we have a method of determining the energy level for electron capture by any species of interest, assuming the ΔG 's can be

evaluated. Success in applying the approach depends on the ability to postulate the form of the kinetically active species and to calculate the ΔG 's associated with forming the species from the solvated oxidizing and reducing agents.

In most cases, the kinetically active form of the reducing agent (the form from which most electrons are injected at high anodic currents) will not be the same as the kinetically active form of the oxidizing agent. For example, at a hydrogen electrode the active form of the oxidizing agent may be H_3O^+ (solvated), which would then be the species $R' \cdot X^{++}$, whereas the active form of the reducing agent may be $H\cdot$ or even H_2 , which would not correspond to $R' \cdot X^+$ in Eq. (7)

We can derive a set of equations equivalent to the above for the energy level associated with a reducing agent. We write



and obtain

$$E_{R''' \cdot X^+} = \mu_e + \Delta G_R^+ + \Delta G_R^{++} \quad (14)$$

as the energy level from which electron injection occurs.

It should be noted that as RX^{++} and $R'' \cdot X^+$ are the stable forms of the reactants, normally ΔG_0^+ and ΔG_R^{++} will be negative, while ΔG_0^{++} and ΔG_R^+ will be positive.

5. Energy of Hydration

To illustrate the calculation of the ΔG 's and for reference for Part II, it is of interest to consider the problem of hydration energies, using a simple Born approach to hydration.

The mechanism of electron capture requiring the lowest energy transition state is pre-polarization of the dielectric [Eq. (6)] followed by electron capture on the pre-solvated species [Eq. (7)]. The pre-polarization energy can be estimated on the basis of the following simple model. Consider the ion, of charge Ze , as a sphere of radius r imbedded in a dielectric medium of dielectric constant ϵ . Just outside this sphere, on the "surface" of the dielectric, resides a surface charge associated with the dielectric polarization. This surface charge⁸ is $-Ze(1 - 1/\epsilon)$. If we draw an imaginary "outer sphere" of radius a which includes this charge, it is clear that the energy to be calculated is the energy to place one positive charge on the surface of this "outer sphere," with the corresponding negative charge remaining on the surface of the grounded electrode. Thus the charge associated with the "outer sphere" changes from Ze/ϵ to $(Ze/\epsilon + e)$. We will assume the value of ϵ for water to be on the order of 80, so $Z/\epsilon \ll 1$. The energy to pre-polarize the medium becomes approximately the energy to charge a neutral sphere of radius a by one positive electronic charge:

$$\Delta G_0^{++} = e/8\pi\epsilon\epsilon_0 a \text{ e. v.} \quad (15)$$

where the ΔG_0^{++} symbol is used because the course of the reaction is along the lines of Eqs. (6) and (7). This is on the order of 0.05 eV for a about 2\AA .

6. Conclusion

Based on an electronic model of electrochemistry we have developed a method of estimating energy levels associated with ions in solution. This analysis will be used to indicate the approximate energy level of

several one-equivalent species in Part II of this paper, with the objective of relating capture cross section of species to the energy level. Because of the unknown chemistry involved at the ZnO electrode, the form of the active species is not known, so the actual energy level can only be estimated. However the correlation may be satisfactory because the electronic energy changes and the known parts of the chemical energy changes can be much larger than the unknown parts of the chemical energy changes.

7. Appendix A two-equivalent oxidation or reduction

An approach similar to that used to calculate Eq. (13) can be used in the analysis of the two-equivalent species. However it is algebraically easier, although perhaps not as instructive, to recall from the usual electrochemical arguments the relationship (17) which holds between the reversible potentials

$$\mu_e^{II} = \frac{1}{2} (\mu_a + \mu_b) \quad (17)$$

where μ_a and μ_b are the reversible potentials of the one-equivalent steps, and μ_e^{II} is the reversible potential for the two-equivalent system. Equation (17) with Eq. (13) leads to

$$\frac{E_{R \cdot X^{++}} + E_{R \cdot X^+}}{2} = \mu_{es} + \Sigma \Delta G \quad (18)$$

where the E's represent the energy levels for the first and second equivalent of electron capture, and $\Sigma \Delta G$ is the sum of four free-energy changes of changes of the type of Eqs. (6) and (8), two from each equivalent of electron capture. It is observed in Eq. (18) that the Fermi level becomes located about half way between the energy levels for electron capture, adjusted to a greater or lesser extent by the chemical energies involved in the ΔG 's. Under equilibrium conditions only one measurement is made, that of μ_{es} . It is therefore clear that the values of E's cannot be separated from this measurement.

8. Appendix B the electrochemical cell

To meet the objective of calculating electronic energy levels associated with ions, it has been necessary to approach the analysis of electrochemistry by what appears to be a new set of postulates. It is important to show that the approach is not in conflict with the normal successful theories of electrochemistry which do not separate the course of the reaction into fast (electronic) steps and slow (ionic) steps. Such discussion is instructive, but not necessary to the primary objective of estimating energy levels, so it is presented as an appendix.

To illustrate some of the differences with clarity, we will discuss the origin of the potential in a simple electrochemical cell, consisting of inert metal electrodes in solutions A and B separated by a salt bridge. In the solutions A and B we will introduce different one-equivalent chemical couples. Now the potential difference measured by a voltmeter is the difference in Fermi energy, or electrochemical potential for electrons, at the identical metal voltmeter contacts.

The first postulate of the present theory was that only electrons are transferred at all interfaces (other than the interfaces between the salt bridge and the solutions). At equilibrium, then, the Fermi level at one side of the voltmeter is equal to that at the electrode in A, and the Fermi level at the other side of the voltmeter is equal to that at electrode B. Double layers at intermetallic contacts which equalize the Fermi levels will certainly exist, but are a refinement in concept not utilized.

The most important apparent difference between the present approach and the standard approach is that in the present analysis it is concluded that the electrochemical potential for electrons is the same in solution as in the electrode, so that there is no driving force for electrons between electrode and solution. Thus the concept of a half-cell potential is no longer useful. This apparent discrepancy is resolved by noting on the one hand that our definition for electrochemical potential of electrons

is only meaningful if an electrode is present, permitting exchange of electrons. Thus a "driving force for electrons" cannot be defined for a bulk solution; a measurement requires an electrode. On the other hand it is clear that standard electrochemical analysis provides no means for measuring a half-cell potential or a solution potential, so the apparent discrepancy is avoided because in both cases the "solution potential" is simply a mathematical convenience and no physical difference is predicted.

Continuing with the analysis of the cell, we will adopt the mathematical convenience of specifying the electrochemical potential for electrons as a characteristic of the entire solution. As the electrodes are reversible with respect to the solution, the reading on the voltmeter is $(\mu_{eA} - \mu_{eB})$. The electrochemical potentials μ_{eA} and μ_{eB} for solution A and B respectively are given by Eq. (3), Eq. (12), or in standard solutions by Eq. (13). Thus, if the μ_c 's are measured relative to a common reference, the resulting expression for the open circuit potential is identical to that found by standard formulations.

It only remains to show that the μ_e 's are measured relative to a common reference, and this reference is provided by the salt bridge. At the bridge/solution interfaces there is no electron exchange, solely ion exchange, so the chemical potential of the chloride ion is constant across these interfaces. Assuming that there is no driving force for chloride ions to move from A to B, the chloride energy levels (see fig.1) must be the same.

Thus according to the present formulation, the change in electrochemical potential for electrons occurs across the salt bridge, the only point in the electrical circuit where there is a barrier to electron flow.

To summarize, the present approach utilizes the definition of a quantity which we term the electrochemical potential for electrons in solution, which is analogous to the Fermi level in the solids and expresses the reactions of interest in terms of electron reactions only, again analogous to the methods used for solids. The chemical rearrangements then become

difficult to handle. The standard electrochemical approach, on the other hand, considers that ionic species are being introduced and removed during the electrode reaction (rather than simply electrons), and this makes the chemical analysis simpler, but the analysis in terms of electronic effects becomes difficult.

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Figure Caption

Fig. 1. Energy levels of ions in solution. The symbol represents the chemical, the minus or positive signs represent the charge on the ion as normally found in solution, the symbol "a" indicates that the level considered is normally empty and may be filled during an electrode process, the symbol "d" indicates the reverse. The subscript s indicates the solvated form of the ion.

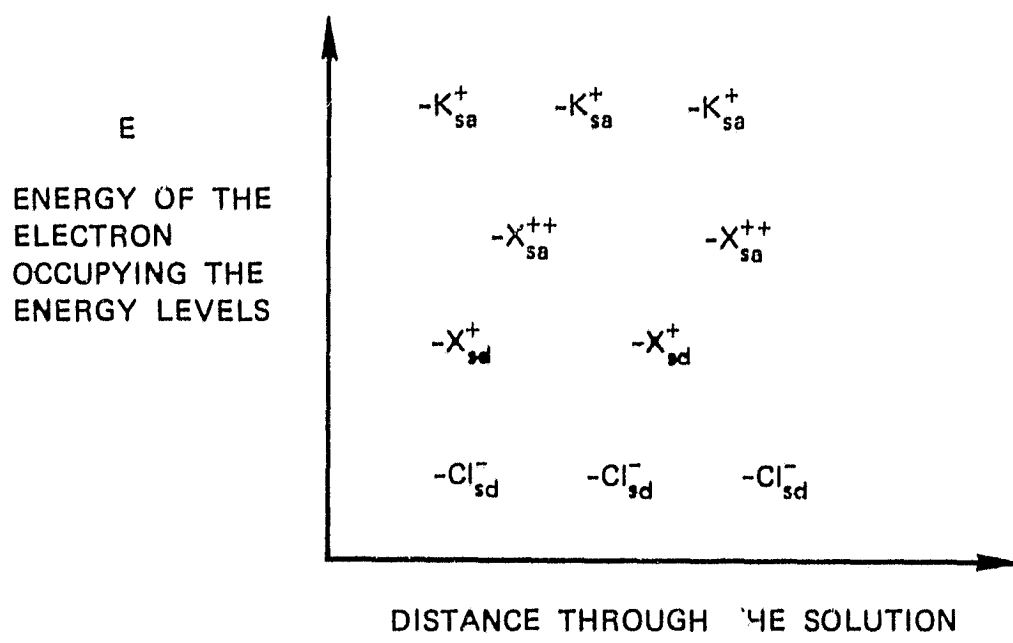


FIG. 1

ELECTRON CAPTURE BY ENERGY LEVELS ASSOCIATED WITH IONS IN SOLUTION*

II. EXPERIMENTAL OBSERVATIONS WITH ZnO

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ABSTRACT

Measurements of the electron reactivity (electron capture rate) of oxidizing agents at the ZnO surface, are presented as determined by cathodic electrochemical reduction. Because in this system the Helmholtz potential is insensitive to the oxidizing agent used, the energy level of a particular species with respect to the ZnO conduction band is not considered a variable. Thus the electron capture by (reduction of) the species can be interpreted according to surface state capture theory. The energy levels are estimated according to the model described in Part I of this paper, and the electron reactivity measured for a series of one-equivalent species is related to the energy levels of the species. A maximum in electron reactivity is found for energy levels just below the conduction band minimum, the reactivity decreasing rapidly for higher energy levels. There is some indication that the electron reactivity decreases for very low energy levels, in accordance with expectations if the process is controlled by a multi-phonon electron capture model.

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1. Introduction

In a recent publication¹⁾, the techniques and theory for cathodic reduction of ferricyanide ions at the surface of a single-crystal ZnO electrode have been presented. The present paper reports similar results on several other one-equivalent oxidizing agents, and attempts to correlate the electron reactivity of these species with their energy level in solution. The energy level is estimated from the redox potential of the ions in solution, as discussed in Part I of this paper²⁾.

The theory of electron capture by energy levels in a semiconductor has been thoroughly analyzed in the past years^{3,4)}. It has been shown that for simple phonon-aided processes, the electron capture cross section rapidly decreases the deeper the levels are below the conduction band, because more and more phonons are required to dissipate the energy. High electron capture cross sections for very deep energy levels are observed at times and interpreted⁴⁾ in terms of a model involving capture of electrons in excited states with subsequent cascading of the electron to the deep ground state energy.

The theory of electron capture from a metal electrode by ions in solution, on the other hand, has been formalized quite differently. It is clear that in this case the energy levels of the active species will tend to move often toward the Fermi level in the solid, during the formation of the Helmholtz double layer^{2,5)}. This will also be expected with semiconductor electrodes if electron exchange associated with the active redox reaction determines the Helmholtz potential^{2,5)}.

In fact, because of the dominance of Helmholtz potential effects, and of the effects associated with chemical changes between filled and empty levels (reducing and oxidizing agents) the formulation of electrochemical theory in terms of energy levels has been inappropriate.

With the ZnO electrode, however, there is evidence¹⁾ that Helmholtz

double layer effects are not dominating, and for most species of interest the Helmholtz potential is not affected by the presence or absence of these species. It has also been shown^{1, 6)} that for many common species, electron exchange is irreversible; that although the oxidizing agent of a redox couple can be reduced, electrons cannot be injected into the ZnO conduction band by the reducing agents. The latter effect can be interpreted as an indication that the filled energy level is far below the conduction band, and the former effect indicates why: the ZnO is not acting as a reversible electrode controlled by the redox couple.

If the Helmholtz potential of the ZnO does not change as the oxidizing agent is changed, then the energy of the conduction band edge in the ZnO with respect to the solution potential will be invariant, independent of the energy level of the oxidizing agent used. For example, if the energy of the conduction band edge is at -0.3 eV with respect to some arbitrary zero of energy (as discussed in Part I, we use the Fermi level of the hydrogen reference electrode as this arbitrary zero), it will remain at -0.3 eV independent of the oxidizing agent used. Then if the oxidizing agent has an energy level at -0.1 eV, it will be above the conduction band edge by 0.2 eV; if it has an energy level at -0.5 eV, it will be below the conduction band edge by 0.2 eV.

Because of this behavior of the ZnO electrode, it would appear that the electron capture cross section of ions in solution may well be controlled by their energy level in a manner similar to electron capture by energy levels in the solid. It becomes possible to analyse in these terms the electron capture cross section of various species in solution, a possibility not realizable on a metal electrode because the Helmholtz double layer compensates for differences in energy level. The experimental test of such a model using a series of one-equivalent oxidizing agents is the purpose of this paper.

2. Method

To compare the capture cross section of various species with their calculated energy level, two requirements must be met. First, it must

be shown that the Helmholtz voltage on the ZnO does not change when the species of interest is added to the solution. Denoting the energy of the edge of the conduction band by E_c and the energy level of the oxidizing agent in solution by E_x , we have

$$\Delta E = E_c - E_x + eV_H + e\Delta V_H(X) \quad (1)$$

where ΔE is the energy released by the electron transition, V_H is the Helmholtz potential with no active oxidizing agents in solution, and $\Delta V_H(X)$ the change in Helmholtz voltage when X is added. As it is the objective to show that σ , the capture cross section, varies with ΔE in a manner consistent with solid-state theory, it is clear that $\Delta V_H(X)$ should be zero for all species X, in order to yield a simple interpretation.

Second it must be shown that the electron capture process can be described by the formulations of surface-state capture used in solid-state physics. This permits identification of the quantity σ , the capture cross section.

The methods used in this work have been described in an earlier communication¹). To emphasize how the two requirements discussed above are met, a brief summary will be presented here.

Measurement is made of the voltage V of the ZnO vs. a saturated calomel reference electrode, of the cathodic current, and of the differential capacity between the ZnO and a Pt working electrode. It has been shown⁷) that with a ZnO electrode the capacity measured is the capacity of the depletion layer at the ZnO surface. With V_s the surface barrier, C the capacity, A the area of ZnO exposed to the solution, N_D the donor density, we have from the Schottky relation and the parallel plate capacity formula:

$$V_s - kT/q = \frac{1}{2} q N_D A^2 \epsilon \epsilon_0 (1/C^2) \quad (2)$$

where the other symbols have their usual meaning.

The ZnO voltage is determined by V_s , the Helmholtz voltage, and other double-layer potentials in the circuit, the latter considered constant.

$$V = V_s + V_H + \Delta V_H(X) + \text{constant} \quad (3)$$

If $d(1/C^2)/dV$ is constant, it is concluded that V_H and $\Delta V_H(X)$ are independent of V . Then we can simplify (2) and (3)

$$V - V_f(X) = \frac{1}{2} q N_D A^2 \epsilon \epsilon_0 (1/C^2) \quad (4)$$

where V_f is the "flat band potential," the potential when $1/C^2$ is extrapolated to zero. If V_f is independent of the presence or concentration of the species X , the first requirement given above is met.

In order to conclude that the electron capture process can be described by the formulations of surface-state capture, it must be shown that the capture rate (= cathodic current J) must be first order in the electron density at the surface (n_s) and first order in the density of available levels ($[X]$).

The electron density at the surface is calculated from the density in the bulk [N_D , calculated from the slope of Eq. (4)], multiplied by the Boltzmann factor associated with the surface barrier:

$$n_s = N_D \exp(-eV_s/kT) \quad (5)$$

where V_s is determined from (2).

If the current (at constant n_s) is found proportional to the concentration of X in solution, the assumption is made that the capture rate is proportional to $[X]$. This implies that the concentration (cm^{-2}) of available levels is proportional to the concentration (per cm^3) of ions in solution. It has been found that the criterion can usually be met at sufficiently low concentration.

When the requirements are found to be met, as was found for all of the results reported below, the results can be interpreted according to the normal theories of irreversible electron capture by surface states

$$J = q \sigma [X] \bar{c} n_s = q \sigma [X] \bar{c} N_D \exp(-eV_s/kT) \quad (6)$$

with σ the capture cross section and \bar{c} the mean electron velocity. In Eq. (6), J is measured, \bar{c} is estimated (we use 10^7 cm/sec), and n_s is calculated from the capacity.

From Eq. (6), a value is calculated for $\sigma[X]$, the "electron reactivity" of the species X. In the measurements below, the values are normalized to $[X] = 10^{-2}M$, and the data for $\sigma[X]$ recorded for this molarity. The parameter of interest is σ , the capture cross section of the various ions, but this is not experimentally separated from $[X]$ (the active surface concentration of the oxidizing agent when the solution concentration is $10^{-2}M$). In order then to compare σ for various species, the assumption must be made that the change in $\sigma[X]$ from species to species occurs primarily as a result of the change in σ . This assumption will be considered further under "Discussion."

The crystals, their etching, mounting, and the electrochemical cell used have been described in the earlier communication.¹⁾

The oxidizing agents studied were chosen so that reasonably well-defined one-equivalent reductions were possible. The list included $K_3Fe(CN)_6$, $(NH_4)_2IrCl_6$, $KMnO_4$, 1,10 Phenanthroline ferric perchlorate, $CuCl_2$, $Ce(HSO_4)_4$, $Ce(NH_4)_2(NO_3)_6$, VCl_3 , and $Ag(NH_3)_2^+$ from $AgNO_3$ in ammonia. For the various pH values studied the buffers were phthalate (pH3.7), acetate (pH4.5 to 5.5), borate (pH8.7), ammonia (pH12), and H_2SO_4 or HNO_3 used to reach pH 1.5.

The iron phenanthroline solution was prepared by oxidation of the ferrous form, using PbO_2 in sulphuric acid and filtering. The other salts were dissolved from stock reagents.

3. Results

Typical results plotted according to Eq. (6) are shown for various species in fig. 1. The logarithm of current per unit area exposed is plotted against the surface barrier V_s as determined from capacity. For each curve the surface barrier shown is equal to the applied voltage plus the constant V_f , determined from a plot of $1/C^2$ vs. V [Eq. (4)]. This constant V_f varies considerably with pH, to a less extent with variations of donor density⁶⁾ and slightly from unknown sources¹⁾. The results shown are those corresponding to 0.01M solutions where measurements were made at this concentration.

In all of the cases recorded in fig. 1 the current readings were observed with substantially positive V_s (bands bending up). With other measurements such as the measurements with Cu^{++} ions, or with no active ion in solution, high cathodic potentials such that $V_s \rightarrow 0$ were required in order to obtain measureable currents. In this region, where $V_s \rightarrow 0$, the value of V_s is not known; below about $V_s = 0.03$, $1/C^2$ is no longer linear in V , and estimation of the surface barrier is not reliable⁷⁾. However, a maximum $\sigma[X]$ can be estimated.

In Table I below, results are tabulated for the various ions tested. The ion concentration tested and pH are listed, together with the ZnO crystal face exposed and donor density calculated (from $1/C^2$ vs. V). The constant V_f , the "flat band potential," is recorded for each case. It is observed to be insensitive to the oxidizing agent used, although it varies considerably with pH.

From the curves of fig. 1, the values for N_D , and the molarity of the solution, the values of the "electron reactivity," $\sigma[X]$ normalized to 0.01M, can be calculated from Eq. (6) and are listed in Table I for the various species. As V_f , and hence V_s , cannot be considered accurate to better than ± 0.03 volts, the value of $\sigma[X]$ must be considered to be at best accurate to within perhaps a factor of 5 either way, so even the one figure given is not to be considered significant. For a given

Table I

Parameters for calculation of electron reactivity of various oxidizing agents

Oxidizing agent	Concentration (molarity)	pH	face	V_f (volts vs. calomel)	N_D (cm^{-3})	α_X (extrap. to 0.01M)
Ce^{+4} (in HNO_3)	$10^{-3}, 10^{-4}$	1.5	(0001)	+0.04	10^{17}	$< 10^{-12}$
Ce^{+4} (in H_2SO_4)	$10^{-3}, 10^{-4}$	1.5	(0001)	+0.04	6×10^{18}	6×10^{-9}
Fe^{+3} (phenanthroline)	$10^{-3}, 10^{-4}$	1.5	(0001)	+0.02	10^{17}	1×10^{-5}
MnO_4^-	$10^{-4}, 10^{-3}, 10^{-2}$	4.5	(0001)	-0.20	7×10^{18}	2×10^{-5}
	$10^{-4}, 10^{-3}$	8.7	(0001)	-0.38	1×10^{18}	7×10^{-4}
IrCl_6^-	$10^{-3}, 10^{-2}$	3.8	(0001)	-0.17	1×10^{18}	1×10^{-3}
	$10^{-3}, 10^{-2}$	3.8	(0001)	-0.25	3×10^{16}	6×10^{-3}
Fe^{+3} (cyanide)	$10^{-3}, 10^{-2}$	8.7	(0001)	-0.55	8×10^{18}	3×10^{-6}
	$10^{-4}, 10^{-3}$	12	(0001)	-0.5	4×10^{18}	3×10^{-7}
	$10^{-4}, 10^{-3}, 10^{-2}$	9	(0001)	-0.45	4×10^{18}	1×10^{-7}
	$10^{-4}, 10^{-3}, 10^{-2}$	3.8	(0001)	-0.20	2×10^{18}	8×10^{-6}
I_3^-	$10^{-4}, 10^{-3}, 10^{-2}$	3.8	(0001)	-0.27	7×10^{16}	2×10^{-10}
	$10^{-3}, 10^{-2}$	3.8	(0001)	-0.25	1×10^{17}	6×10^{-10}
$\text{Ag}(\text{NH}_3)_2^+$	$10^{-2}, 10^{-1}$	12	(0001)	-0.6	1×10^{17}	1×10^{-5}
Cu^{++}	$5 \times 10^{-2}, 10^{-2}$	3.7	(0001)	-0.25	10^{19}	$< 10^{-12}$
V^{+3} (in HCl)	0.5	(0.5M HCl)	(0001)	+0.12	1×10^{17}	10^{-12}

oxidizing agent, the value of $\sigma[X]$ was independent of concentration (for the concentrations studied) to well within this error. Another source of error in the calculation of $\sigma[X]$ arises because the slope of the line is not the 60 mV/decade required by Eq. (3), although always in the range 65 ± 5 mV/decade. It has been found by experience that as we have refined our techniques and improved the curves toward a 60 mV/decade slope, the low currents are seldom affected greatly. The error is normally accentuated at higher current. Thus for our calculations of $\sigma[X]$ where the slope is greater than 60 mV/decade, we have used the low current measurements.

The results indicate that perhaps there is a slightly higher electron reactivity $\sigma[X]$ on the (0001) side than on the (000 $\bar{1}$) side. The influence of pH shows no particular pattern, $\sigma[X]$ increasing with pH with MnO_4^- , decreasing or passing through a minimum with $\text{Fe}(\text{CN})_6^{-3}$.

The values of $\sigma[X]$ were in general fairly reproducible. Of the materials listed, the only one in which there appeared serious problems was the silver ion. The problems were attributed to metallic deposits during the reduction process. The current became very high if a high integrated current was permitted to pass. By keeping the current low, and the elapsed time during the measurement short, the results appeared reproducible.

A similar problem, but much less serious, was found with permanganate. The results became erratic and deposits were found on the crystal, if extremely high current ($> 10 \mu \text{ a/cm}^2$) was employed extensively. This was ascribed to reduction to MnO_2 and was avoided by using only low current values.

4. Discussion

4.1 Model

The energy level of an oxidizing agent can be assumed to be related to its standard redox potential, as has been suggested in earlier

studies^{2,8}). A species with a high redox potential is expected in general to have a high energy level, the reduced form tending to donate electrons; a species with a low redox potential will have a low energy level, the oxidized form tending to accept electrons. Qualitatively this type of behavior has been observed on germanium by Beck and Gerischer⁸).

It has been shown in this laboratory⁹) that the vanadous and chromous ions inject electrons into the ZnO conduction band, indicating an energy level above the conduction band minimum. It has also been shown¹⁰) that at times $\text{Fe}(\text{CN})_6^{-4}$ will inject electrons, but the results have not been reproducible and the critical conditions for injection have not been identified. At the gas/solid interface, it has been shown that H atoms inject electrons¹¹) into the ZnO conduction band, that Sn^0 or Sn^{+2} inject¹²), and that on the $(000\bar{1})$ plane, $\text{Fe}(\text{CN})_6^{-4}$ has an energy level about 0.15 e.v. below the conduction band¹²).

From these indications, it would appear that the bottom of the ZnO conduction band must be located in the region of the energy level of $\text{Fe}(\text{CN})_6^{-4}$, perhaps a few tenths of an e.v. above it. As most of the evidence arises from measurements in solution, the estimate should be valid with the Helmholtz double layer present.

These observations provide an estimate of where the conduction band edge is located relative to the energy levels in solution, as reflected in the redox potential. The next question is how the capture cross section should vary depending on whether the energy level is below or above the conduction band edge. The capture of electrons by the oxidized form of the various species should show a decrease in apparent cross section for species more electropositive than $\text{Fe}(\text{CN})_6^{-3}$, as capture by energy levels substantially above the conduction band minimum should be unfavorable. The decrease may be a factor of 10 for each 60 mV increase in energy level.

A simplified model shows how this factor would arise. We can assume that the cathodic current carried by ions into the solution is

proportional to the concentration of reduced species $[X^-]$ near (within the order of 20 \AA) the surface. This will be a good approximation if the removal of ions is the rate limiting step. For those levels near or above the edge of the conduction band, we will assume that the levels are in equilibrium with the surface density of conduction electrons n_s . That is, the exchange current between the conduction band and the active species is assumed to be higher than the net cathodic current when the level is near or above the conduction band. Under these conditions, the removal of ions may be rate limiting. Then the ion current is proportional to the concentration of reduced species $[X^-]$, which is given from Fermi statistics:

$$J \propto [X^-] = (n_s/N_c)[X] \exp \left\{ -(E_t - E_c)/kT \right\} \quad (7)$$

with N_c the effective density of states in the conduction band ($n_s \ll N_c$), and E_t and E_c the surface state and conduction band energies respectively. This leads, by comparison with (6), to an apparent $\sigma[X]$ decreasing rapidly as E_t increases above E_c , with a decrease of one order of magnitude per 60 mV increase in $E_t - E_c$. This model illustrates how a high energy level will decrease the effective σ by re-injection, but is simplified, as it assumes ion movement to be rate limiting and ignores the difference in energy level between the oxidized and reduced species.

Capture of electrons by species with an energy level below that of $\text{Fe}(\text{CN})_6^{-3}$ (viz. below the conduction band edge) should be favorable, but one cannot predict whether the capture cross section for stronger oxidizing agents should pass through a peak and decrease (as would be predicted by a phonon-aided capture process³) or should be maintained at a high but erratic value (as would be predicted by a cascade-aided process⁴).

5. Estimation of energy levels

To test the general features of the above model, the energy level associated with the various species must be evaluated, then the measured electron reactivity from Table I compared with the energy level. As

discussed in Part I²), the identification of energy levels in solution is somewhat arbitrary, for there is a possibility of many forms of each species, and one must assume which form is the kinetically active species.

We will make several assumptions and approximations in order to arrive at an estimate of the energy level. The first is that there is negligible specific adsorption of the active species. The second is that hydrolysis contributes negligibly to the energy for the species studied. The third is that the kinetically active species is the pre-hydrated species (as discussed in Part I), so that hydration and similar electrostatic effects contribute a small fairly constant energy correction and will be neglected. We will assume in general that the dominant species in solution (pre-hydrated) is the kinetically active species.

With these approximations it turns out from the analysis in Part I that the calculated energy level for a species is below the standard hydrogen electrode Fermi energy by an amount equal to the standard redox potential of the species. We have used for the redox potential the values given by Latimer¹³). It is clearly possible for some ions to make the small adjustments suggested by theory for hydration and hydrolysis, but the accuracy of the electron reactivity results do not warrant it at this time.

For some of the species used, more complex considerations must be evaluated. The $\text{Ag}(\text{NH}_3)_2^+$ ion is an example. In this case we have at least two possible routes for the reduction:



or



The decision regarding which route is kinetically active is somewhat arbitrary. If we assume Eq. (8) is the dominant route, an estimate for ΔG_1 must be made to determine the energy level. We will assume negligible energy release in Eq. (8b), as the reaction corresponds simply to the desorption of the ammonia, so $\Delta G_1 \sim 0$. Then the energy level for $\text{Ag}(\text{NH}_3)_2^+$ becomes the redox potential of this species in one molar NH_3 . If, on the other hand, Eq. (9) is kinetically active, the simplest approach is to use the standard redox potential of silver reduction (9b), and determine the concentration of silver by the equilibrium constant of (9a), $K = 10^{-7}$. The energy level is thus -0.69 eV, but the concentration of free silver used in estimation of $\sigma[\text{X}]$ is too high by a factor of 10^7 (the solution studied was 1 molar in NH_3). With this correction, $\sigma[\text{X}]$ when normalized must be the order of 10^2 to account for the observed reduction. This is anomalously high compared to the values for other ions and we therefore assume that Eq. (8) represents the dominant reduction route.

Similar reasoning was used in the case of I_3^- , which was found to have $\sigma[\text{X}] = 5 \times 10^{-10}$. The only route for the reduction with only one energy level involved would be first the dissociation of the ion yielding neutral iodine atoms and then the reduction of these species. Estimating the effective concentration of neutral iodine atoms, which would be very low, the value for $\sigma[\text{X}]$ normalized to 10^{-2}M in I would be anomalously high. Thus it was assumed that the iodine was reduced by a two-equivalent process, and the results therefore are not comparable to the simple model. Alternatively, strong adsorption of iodine on the ZnO surface could account for the results.

6. Correlation of electron reactivity and energy levels

In fig. 2 is shown the electron reactivity at 10^{-2} molar, $\sigma[\text{X}]$, as a function of the standard redox potential, for the various species tested, excluding I_3^- . Solid lines with a slope of 60 mV/decade have been included to permit comparison of the simplified theory with experiment.

It is clear that for these materials the electron reactivity follows the type of curve discussed above for the variation of capture cross section with energy level. The value of $\sigma[X]$ decreases rapidly for redox potential more positive than $\text{Fe}(\text{CN}_6)^{-3}$. This then provides further evidence that the energy level of the ZnO conduction band is close to the $\text{Fe}(\text{CN}_6)^{-3}$ level.

The decrease in electron reactivity for large negative values is as expected if we assume a multi-phonon electron capture process. However, there is too little data in this region of redox potential to establish confidence in this interpretation.

The ceric results are of interest not only because of the indication of low capture cross section, but also because two forms of ceric ion were studied: one the highly complex form ¹⁴⁾ as found in sulphate solutions; the other, ceric ions in nitrate, where minimal complex formation is expected¹³⁾. The ceric nitrate result is included in fig. 2. The sulphate result cannot be included in the figure because we do not know which complex is kinetically active. It is of interest, however, that the complex form shows a $\sigma[X]$ much greater than the uncomplexed form. This observation is consistent with the present model because the complexing of the ceric may produce a higher energy level²⁾. If one of the complexes has an energy level in the region of the maximum of fig. 2, the product of its high cross section and the low concentration of the complex may lead to $\sigma[X]$ of observed order of magnitude.

The data of fig. 2 are consistent with the assumption of little specific adsorption. If we make the approximation that the maximum cross section expected is on the order of 10^{-15}cm^2 , the ionic cross section, and that ions within the order of 20Å of the surface can be reduced, then with the $6 \times 10^{18}\text{cm}^{-3}$ ions available at 10^{-2}M , the maximum $\sigma[X]$ that should be measured is 10^{-3} . This estimated value compares well with the maximum value actually observed. If the assumption is correct that there is little specific adsorption, then the values for σ become more meaningful.

Finally a comment should be made with respect to the effect of pH. The variation of $\sigma[X]$ with pH, observed with ferrocyanide and permanganate, could occur due to a change in the energy level of the conduction band relative to the zero in solution because of a Helmholtz potential change at the electrode with pH. Alternately it could be associated with hydrolysis of the ion under study, changing its energy level or changing the concentration of the kinetically active species. It would be premature to attempt an interpretation of the behavior at this time.

7. Conclusions

The suggestion that there should be a relation between electron reactivity of ions in solution and electron capture theories of semiconductor physics appears to be qualitatively justified. The energy level, as estimated from the redox potential, must be slightly below the semiconductor conduction band minimum for maximum capture cross section. There is some indication that if the level becomes too deep, the capture cross section diminishes.

If this model is correct it suggests some interesting implications about selectivity in reduction of ions at such a semiconductor surface with a non-varying Helmholtz voltage. Two-equivalent reductions would almost inevitably be slow, as one of the energy levels normally would be far from the region of maximum cross section. (Experimentally we have found no clearly two-equivalent ions, out of perhaps 5 or 6 studied, with $\sigma[X]$ greater than 10^{-9} .) The relative electron reactivity of various species will be far different from that found at a metal electrode, where the semiconductor rules do not apply (here filled energy levels in the solid are available at all energies below the Fermi level). Thus some interesting new electrochemical synthesis may be possible with semiconductor electrodes.

Presumably similar concepts may be expected to apply regarding hole capture (oxidation) at the surface of p-type semiconductor electrodes. However many p-type semiconductors with a wide band-gap involve oxide

ions as the anion, and as these are easily oxidized themselves, they can complicate the behavior.

I would like to acknowledge the valuable discussions and suggestions of Dr. T. Freund during the course of this research. From his observations, the data used for the reduction of V^{+3} was obtained.

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List of Figures

Fig. 1. The variation in cathodic current with the surface barrier, for various one-equivalent oxidizing agents.

Fig. 2. The variation in electron reactivity as a function of the redox potential (the energy level) for various one-equivalent oxidizing agents.

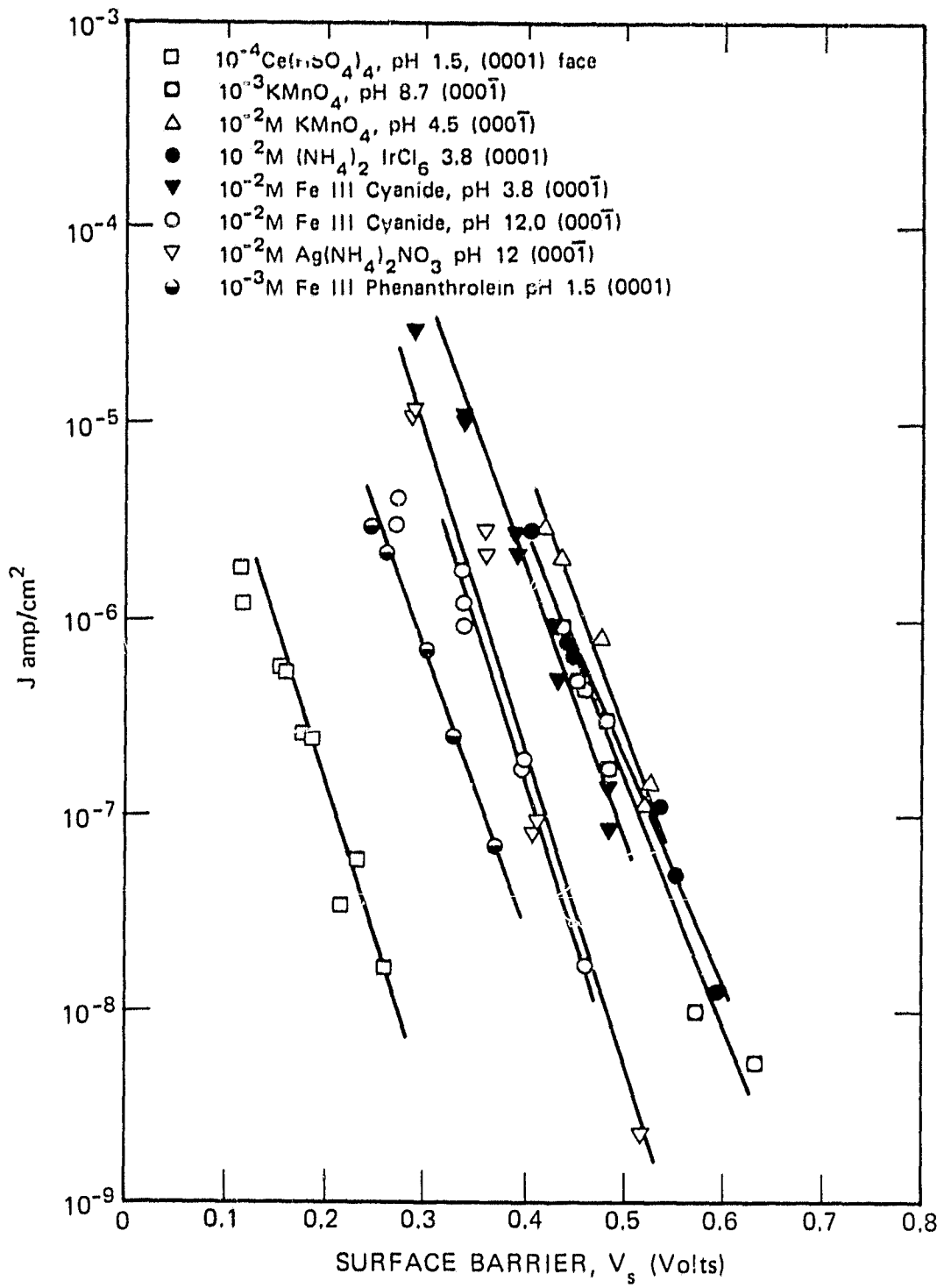


FIG. 1

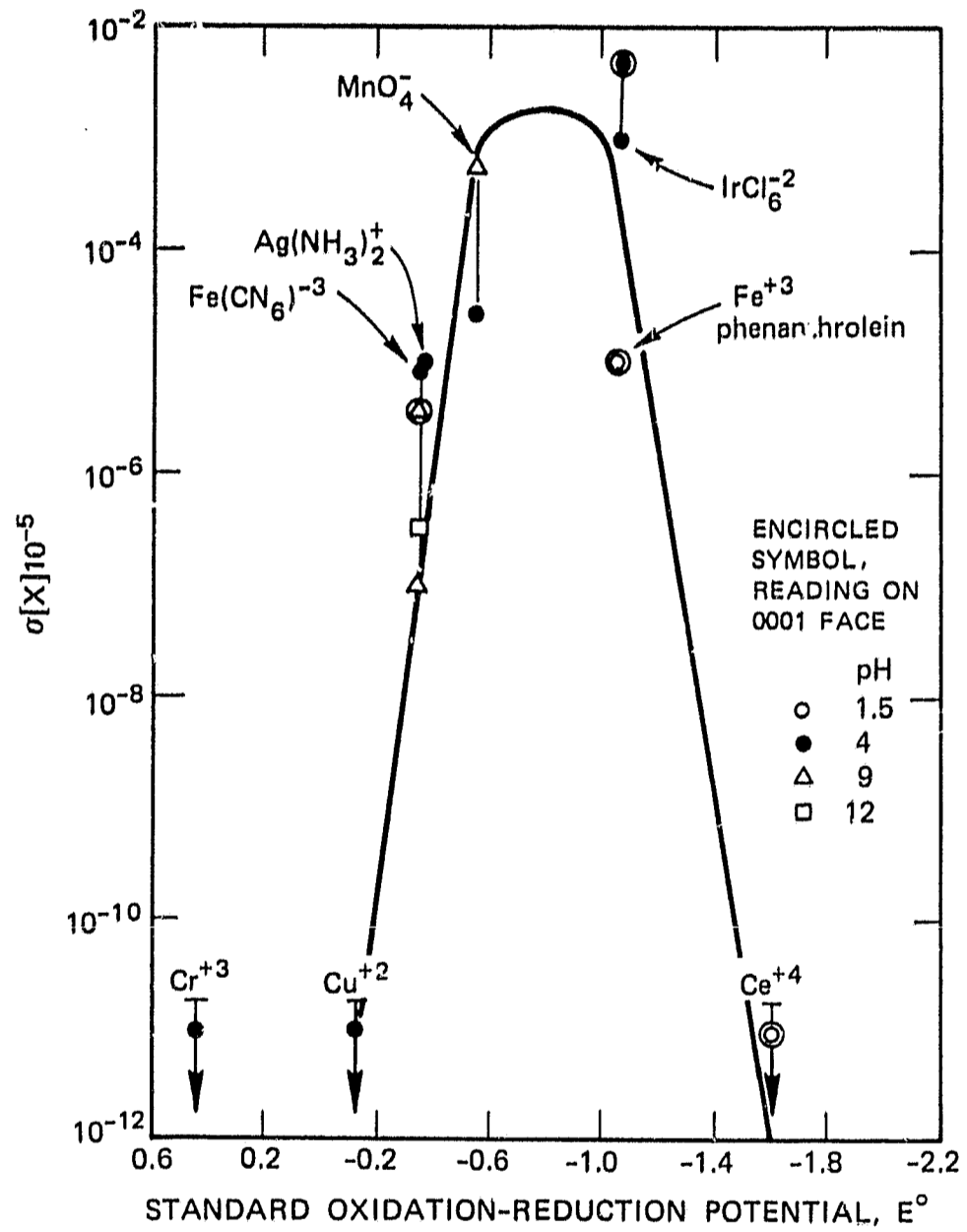


FIG. 2