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ARTIFICIAL PHOTOSYNTHESIS: QUANTUM CAPTURE AND ENERGY STORAGE

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July 1982

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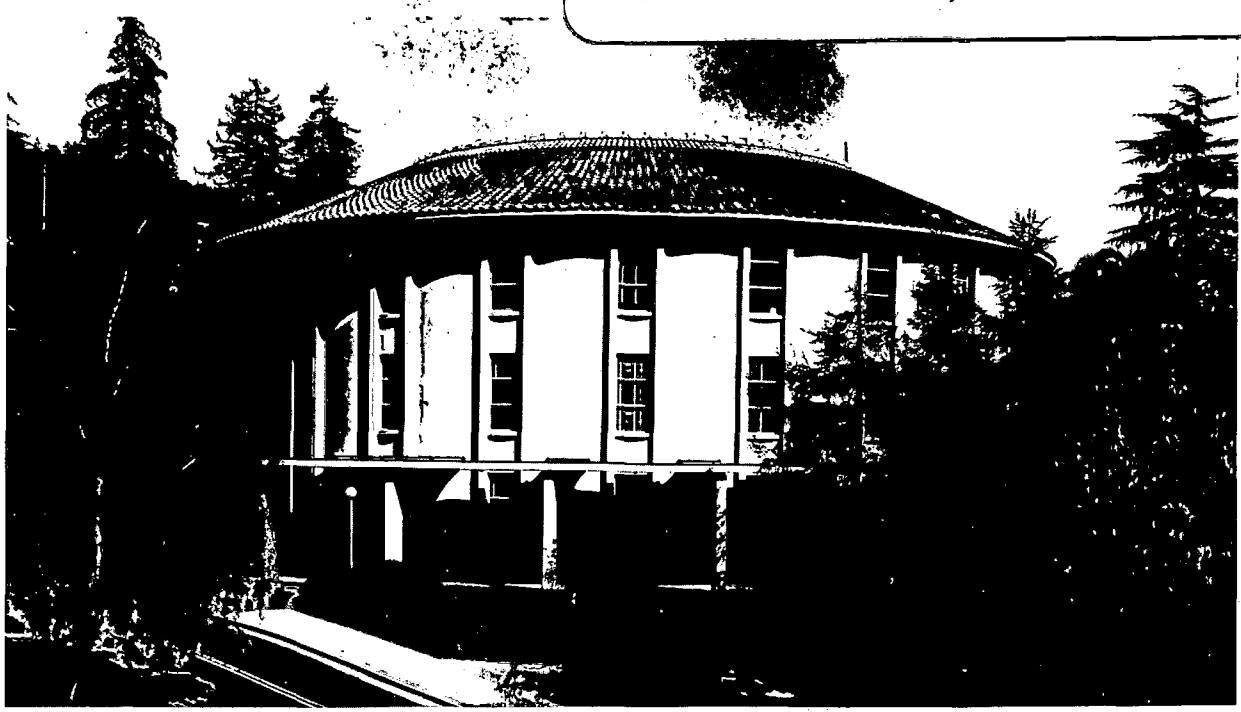

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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ARTIFICIAL PHOTOSYNTHESIS: QUANTUM CAPTURE AND ENERGY STORAGE

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ABSTRACT

Organized systems are described to achieve separation of the charges produced by quantum absorption in a sensitizer, and their stabilization in separated chemical form. These systems involve phase boundary charge separation by both membranes and charged particles, in both cases simulating the natural system.

This work was supported by the Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

In any problem in which we seek to capture and convert quanta to stored energy there is a sequence of events, each of which presents a problem that must be solved. First, there must be an electronic system to absorb the quanta in the visible region. Since we are really talking about the storage of solar energy, we must have a system that can keep the quantum long enough to do some chemistry. Then, having performed that chemistry; i.e., having produced one or more chemical objects which store the energy and therefore, by definition, are at a higher energy state with respect to the back reaction, we must prevent that back reaction and remove the chemicals that have been stored from close proximity to each other. So, there is a series of various types of physical problems which must be solved in order to successfully accomplish quantum capture and eventually quantum storage in stable chemical form.

Natural System

The photosynthetic system of green plants has learned how to accomplish this with some degree of efficiency. Efficiency is really not the critical factor, but the plant has learned how to store quanta in stable chemical form. It took several billion years to develop this capability. I would like to discuss some of the principles of green plant quantum absorption and conversion and then I would like to try and abstract from that bit of knowledge some basic principles which might be applied to a totally synthetic system, a system which does not use any part of a natural system except the principles of its structure and function.

The photosynthetic system, of course, resides in the green chloroplasts of the plant and it consists largely of a membranous structure, shown in Fig. 1, in which we can see each of the membranes being a bilipid membrane, roughly 40-60 Å thick, and they have two sides. The two sides are indicated in this figure by large protrusions on one side of the membrane and small protrusions on the other. When we examine what the apparatus in the chloroplast can do (Fig. 2) we find that it does the job in two quantum acts, one using a pigment having an absorption band at 680 nm and the second having a pigment with an absorption band at 700 nm. It raises the electron in two steps, from the oxidation level of water to oxygen, to some intermediate level which is actually higher than that of hydrogen, and then falls back through a series of electron transfer agents in the course of which it is making another central component for the photosynthetic organism, namely, ATP, to fill the hole left by the second quantum which raises the electron to a level considerably higher than that of molecular hydrogen. It then falls back through a series of electron transfer agents, including ferredoxin, eventually reducing pyridine nucleotide, which together with the ATP formed at the first stage, can reduce carbon in the carbon reduction cycle of photosynthesis. There are a number of plants which, when deprived of carbon dioxide, will generate a hydrogenase and thus develop molecular hydrogen at this point. All of the green plants develop molecular oxygen as the other component in the redox system.

The elements that are involved in hydrogenase development and in the oxygenase development are now known. We know, for example, that at this point the element is an iron, bound in an iron-sulfur complex in a protein, not a heme, which can develop hydrogen when it is reduced

sufficiently vigorously. At this end, we know a little less, we know only that manganese is involved in the oxygen development, in the development of intermediate oxidant on the way from water to molecular oxygen, and we will discuss that aspect of the reaction later. We will use two different sensitizers and go forward from that point.

We recognize that there are two quantum acts, one on each side of a membrane, which suggested that there are at least three different stages in the electron transfer process. Two of them are phase boundary transfers, i.e., first an electron from a water boundary to an oil boundary, then the electron passes through the oil phase and out again from the oil phase to a water phase. We have to abstract from this the fact that we are using sensitizers, which are surfactants; they lie at a water-oil interface on both sides, and we have to learn how to transfer an electron through an oil membrane. Finally we make use of the fact that both of these transfers are phase boundary transfers, that is, transfers of electrons across a phase boundary. Those phases can be two different liquid phases, or they can be a solid and a liquid phase (as they are in photoelectrochemical semiconductor devices). One of the early experiments in this area that was performed in Berkeley occurred when we recognized that we needed a surfactant dyestuff and something to separate the charge and made use of the surface potentials on a semiconductor, using chlorophyll as a sensitizer. (This was a mistake, as anyone who has worked with chlorophyll will know. The plant does this reaction very well because it can regenerate new chlorophyll at will, whereas our systems cannot.) We have avoided using natural materials for these studies.

Preliminary Design

I can now generalize these principles in Fig. 3 which describes the totally synthetic system which fulfills all of the demands. Vesicles, such as are shown in the upper part of Fig. 3, were first developed by an English physiologist, A. D. Bangham, and at that time, I tried to have these particles called "bangasomes." (We are really just now only realizing the debt we as scientists owe to Dr. Bangham and his discovery in the early sixties.) Dr. Bangham called the vesicles liposomes as they were made from natural phospholipids, but they can now be made from synthetic materials. These are closed bilipid vesicles, with water on the inside and water on the outside, and a hydrocarbon membrane in between. The hydrocarbon membrane is two molecules thick, roughly 40 Å thick. In order to make this system work, all reactions have to be done simultaneously; the water-oil transfer as well as the oil-water transfer, in order to make the system function. It is possible to separate the two phase boundaries, using micelles, using a donor in the water and an oil-soluble sink (hydrocarbon sink) in the micelle, or a source in the oil layer and a sink in the water layer, with a single phase boundary transfer.

After determining not to use chlorophyll, which is really a surfactant dyestuff, we developed other sensitizers and donors. A surfactant dyestuff has a hydrophilic head and a hydrophobic tail, so it will organize itself in the required location. We also need to generate acceptors and donors in place of the natural ones which can perform the required steps. The structures of the donors/acceptors/sensitizers that we have used, in principles of structure, are shown in Fig. 4. The synthetic porphyrin most resembles the natural chlorophyll, a

tetrapyrrole macrocycle, which has four R-groups on the bridging carbon atom, and the four R-groups can have a number of different substituents. However, it is very easy to make a surfactant from structures of the tetrapyridyl type, merely by changing the length of the quaternary carbon chain, so we have a single tail. This synthesis is actually not as simple as it might appear because of the complexity of the reactions which occur, creating materials which are difficult to separate. If we take one of the bipyridyls of the $Ru(bipy)_3^{2+}$ with a carboxyl group on each of two positions and then make an amide from the carboxyl with a long chain amine, we have generated a double tailed one sided surfactant sensitizer from the $Ru(bipy)_3^{2+}$. We have used mainly six sensitizers: the nonsurfactant molecule, the corresponding surfactant one, and three of the soluble porphyrins, and one surfactant one.

For acceptors, in order to generate hydrogen or something equivalent to it, the common structure that has been used for some years is dipyridyls which have been quaternized. The name for this when quaternized with two methyl groups is methylviologen and the essential feature is the dipyridinium which has the capability of accepting a single electron into the conjugate system and being a stable free radical which does not dimerize and which has a blue color, making it a good "marker" in chemical reactions. The methylviologen has another advantage because when one electron is added it becomes a monocation radical. If we start as a diplar ion (PVS^{O}) with no net charge, when an electron is added, it has the same electronic structure as before and it turns blue like methylviologen, but instead of having a positive charge it has a negative charge. Thus it starts with no net charge, and when one electron is added it becomes a negative ion. We

called this material propylviologensulfonate (PVS^{o}). It is possible to manipulate the charges and reaction characteristics of the various donor and acceptors, pretty much at will.

We used the tris bipyridyl ruthenium itself, in the +2 state, as a donor, which can move on to ruthenium-3+. Still another donor is a manganese porphyrin. When you have Mn^{3+} in the center of the porphyrin, it is not a very good sensitizer because it is paramagnetic and has a very short excited state lifetime. However, because it is manganese it is susceptible to stable oxidation-reduction. When we use zinc porphyrin or ruthenium bipyridyl as sensitizer, we can induce oxidation of manganese from +3 to +4. This becomes very important for the development of the catalytic function of the manganese in the possible production of O_2. In nature, at the far end on the reduction side was the pyridinium compound, DPN; but long before the electron got to that stage it went through several iron-sulfur complexes. These iron-sulfur complexes are ferredoxins and some of them are hydrogenases, and they have the general structure of iron-sulfur clusters; a cube with four irons and four sulfide ions, and the irons in general are suspended in a protein framework, usually by percaptide bonds from the sulfhydryl groups on the cysteines in the polypeptide. We have synthesized several of these iron-sulfur clusters in which the only thing that varies is the nature of the mercaptide. These iron-sulfur cubes can act as electron acceptors. We know electrochemically, that if they are reduced sufficiently they will generate molecular hydrogen.

I have introduced all of the molecules which we will use in our artificial photosynthesis experiments. Let us see what we can do with these molecules. The first task is to demonstrate that we can

photochemically transfer an electron through the vesicle membrane. The scheme for this process is shown in Fig. 5, using the ruthenium surfactant in a synthetic phospholipids vesicle and heptylviologen as an acceptor; we used this compound because it has a distribution between the oil and the water phase. (Methylviologen is practically all in the water phase.) For the donors we began with EDTA which upon oxidation with Ru^{+3} gives an irreversible oxidation product. We have also used water-soluble Ru^{+2} as the donor which would generate, from the surfactant Ru^{+3}, Ru^{+3} in the water phase, which has the oxidation potential to produce oxygen from water, just as heptylviologen radical has the reduction potential to produce hydrogen from water, provided in both cases a solid surface is available for the collection in one place of two electrons or the four holes in another place. One has to provide at least two kinds of donor and acceptor surfaces for the two electrons to accumulate or the four holes to accumulate. The iron-sulfur compound, however, does not require a solid surface because it has a cluster of four iron atoms in which electrons can be placed, up to three electrons. When three electrons are put onto the iron-sulfur cluster, the result is molecular hydrogen, with the concomitant reoxidation of two Fe atoms.

Photochemical Transmembrane Electron Transfer

With this type of a membrane, with the sensitizer (Ru^{+2}) on both sides of the surface, with a donor system on one side and an acceptor system on the other side of the membrane, is it possible to photochemically transfer the electron from the inside to the outside? When heptylviologen is used, the reaction goes very well; when methylviologen is used, however, the reaction goes rather slowly because there is no acceptor directly in the membrane and the excited state has to wait to find the

aqueous methylviologen to hand on the electron, and thus the back reaction begins to take over. This experiment is illustrated by Fig. 6, and in early experiments a carrier for the electron was used, in this case, quinone and also a proton carrier. This slowed the rate of reaction down because it was necessary to reduce the quinone in the membrane before the electron transfer occurred. The vesicles were made by dissolving all the components (phospholipids, synthetic phospholipids, dyestuff, carriers) you want in the membrane in an organic solvent, and everything you want on the inside in a buffer, and the organic solvent containing the organic material is injected into the buffer; shake the vessel, and the vesicles appear in the suspension. The vesicles have the same material(s) on the inside and the outside. The suspension of vesicles is poured through a gel which has pores in it just big enough to let the molecules in but not the vesicles. All the molecules on the outside are absorbed into the gel and the vesicles come through. Then it is possible to add whatever materials you want on the outside, creating an unsymmetrical system. Obviously, electron transfer has been demonstrated across the membrane. First the excited Ru^{+2} hands over an electron to the heptylviologen in the membrane, which immediately exchanges with the heptylviologen in the body of the solution, and thus the electron has been removed from the oil phase and the ruthenium has been changed to Ru^{+3}. The Ru^{+3} will exchange with the ruthenium^{+2} atoms which are present in the immediate vicinity (40 Å), so there is an electron transfer across the membrane, a tunneling phenomenon because the two energy states are identical with a slight barrier in between. The electron transfer is very rapid. We now have Ru^{+3} on the inside of the membrane. It is a strong oxidant and it can

oxidize EDTA (a reductant) irreversibly and regenerate Ru^{2+}. We also used a water soluble donor, ruthenium trisbipyridyl which could be oxidized by the surfactant Ru^{+3} to give water soluble Ru^{+3} which could then be used with ruthenium oxide to generate oxygen. All of these reactions have been done separately.

If there is indeed an electron transfer through the membrane it should be possible to change the rate by putting a potential across the membrane. To generate the membrane potential we inserted a concentration of cations on the inside made up mostly of potassium and only a slight amount of sodium. On the outside of the membrane the cation concentration was the same, so the situation was isotonic with the Na^+ and K^+ concentrations reversed. There is thus a potassium ion gradient from the inside to the outside of the membrane. If we now add to the membrane an ionophore which is specific for potassium and allows only potassium to leak through the membrane, you can see that the potassium will leak down the gradient to the outside of the membrane, leaving a negative charge on the inside and having a positive charge on the outside. The reaction can also be done in the reverse way (Fig. 7). The data for the effect of ionophore insertion into the membrane is shown in Fig. 8, showing the transmembrane potential effect on quantum yield of heptylviologen reduction in the vesicle system. We are indeed handling the electron in the way we had postulated.

Structure of Vesicles

Is it possible to determine the size and distribution of the sensitizers on the vesicles? This has been done with a Stern-Vollmer type experiment, using ruthenium and studying its quenching by iron. If you take water soluble ruthenium trisbypyridyl (Ru^{+2}) and examine the

fluorescence in the absence of any quencher (Fig. 9) and then add quencher (in this case ferric ion) the Stern-Vollmer plot is linear which means that every excited ruthenium is accessible to quenching by ferric ion, by electron extraction, and that every ferric ion can see all of the ruthenium ions in this homogeneous solution. When the same experiment is performed with a vesicle containing surfactant ruthenium and use ferricyanide as quencher, the Stern-Volmer plot is a curve, not a straight line (Fig. 10). This tells us that all of the ruthenium in that vesicle is not accessible to the ferricyanide added on the outside. From an analysis of the curve we can show that 66% of the ruthenium is on the outside of the vesicle and 33% of the ruthenium is inaccessible. We can now calculate the ratio of outer/inner surface areas and thus the vesicle size. Another experiment was performed in which the ferricyanide was placed on both sides of the membrane, and the Stern-Volmer plot is again a straight line (Fig. 11). From this data it is possible to calculate that the diameter of the vesicles is about 500 Å and the vesicle is about 25 Å thick. An additional independent measurement of the vesicle size was also performed. The vesicles were made with radioactive sucrose in the buffer and the material passed through the gel, so all the radioactive sucrose and other materials on the outside of the vesicles were held up by the gel, with the remaining material clean vesicles. The radioactivity in those vesicles was measured and it was possible to calculate the internal volume of the vesicles because the amount of radioactivity was known and it is possible to determine the internal volume of the vesicles. This confirmed the size obtained from the other experimental data.

Terminal Catalysis

Some time ago we decided that it might be possible to use manganese, which is involved on the oxygen side, directly as a sensitizer. However, this really did not work too well because the manganese is paramagnetic and does not have a longlived excited state. Then experiments were undertaken to find out how it would be possible to get the manganese to the Mn^{+4} state so it might make oxygen. The obvious method was to separate the sensitizing function from the donor function by making a membrane which had both zinc porphyrin with a tail on it and a manganese porphyrin with a tail on it, and the single unilamellar vesicle with a diameter between 200 and 500 Å, prepared by sonication, is shown in Fig. 12. The ratio is three manganese molecules for every zinc porphyrin. With that kind of a ratio and with propylviologensulfonate (PVS) on the outside of the vesicle, having a negative surface, when light is shone on this system oxidation of the manganese occurs from Mn^{+3} to Mn^{+4}, with reduction of PVS.

The kinetic model for the photo-oxidation of the manganese porphyrin with the zinc porphyrin sensitizer is shown in Fig. 13. No back reaction occurs between the reduced PVS and the oxidized manganese. This was shown by a flash photolysis experiment at 602 nm (Fig. 14), showing that the PVS is reduced and stays reduced. A confirmatory experiment using difference spectra (Fig. 15) also indicates that no back reaction occurs.

Prototype Membrane Device

We have all the parts of the membrane system (sensitizers, catalysts) and have demonstrated the transfer of electrons through a membrane of at least 30 - 40 Å. The question now arises as to whether

or not, with the information available, it is possible to construct a practical device to accomplish photosynthesis artificially using entirely synthetic materials. The first step was to transform the vesicle experiment to a membrane which can actually be handled, by the use of commercial membranes which have been developed for artificial kidneys or desalinization, for example. These hollow fiber membranes are made either of nylon or of cellulose acetate, and we used the cellulose acetate hollow fiber kidney device treated with zinc tetraphenylporphyrin to create a membrane suitable for this purpose. We performed experiments to see the effect of various sensitizers. The oil soluble porphyrin dissolved in an organic solvent (THF or DMSO) swelled the membrane, and the dyestuff diffused into the membrane with the solvent. When the water soluble solvents are washed out the zinc tetraphenylporphyrin remains in the membrane (Fig. 16) and the dyestuff is distributed throughout the thickness of the hollow fiber body of the membrane. We now have the hollow fiber membrane dyed. We now need to experiment with the dyestuffs and put them about 40 Å apart in this hollow fiber so that when the electron is transferred away from one of them on the inside there is one every 40 Å to carry it through. We then placed the hollow fibers which had been treated into a device (Fig. 17), containing about forty fibers; the inside of the fibers are connected to the tubes by sticking the batch of fibers up into the tube through an epoxy glue. So the inside of the fiber is connected to the tubes and the outside is connected to the sidearm. It is possible to get at the inside and outside separately, to perform electrochemistry or gas chemistry on these fibers. The prototype device (hollow fiber device) for photodecomposition of water has been constructed, for the membrane

device. It will be necessary eventually to put the oxygen catalyst on the outside of the fibers of this device and the hydrogen catalyst on the inside. Photochemical and electrochemical experiments need to be performed to show that electron transfer can occur through such a thick membrane, through the agency of the dyestuff inside the membrane.

Particle Systems

There is another completely different way of achieving the stabilization of the redox separation. We attempted to perform electron transfer across the interface of a water-oil emulsion leading to separation of redox products by a highly negative charged surface. We adjusted the sensitizer to be positive and the acceptor initially to be neutral, with the results shown in Fig. 18. Here we have used a 40 Å silica, colloid, highly negatively charged, together with the $Ru(bipy)_3^{2+}$ as sensitizer and PVS as acceptor. The Ru^{+2}, being positively charged, will be in the vicinity of this huge negatively charged surface, and when it is irradiated, the PVS, which is neutral and thus can approach the surface, is reduced. This system works very well. The Ru^{+3} can be regenerated back to Ru^{+2} at the negative surface without any problems; here we have used a sacrificial donor TEA. The PVS reduction using silica gel and Ru^{+2} is shown on the left hand side of Fig. 18, and it is possible to see that the homogeneous reaction, without the silica gel, goes very slowly. The reaction was also done with sodium lauryl sulfate micelles, and the reason this is slower than the reaction done with silica gel even though it is a negatively charged surface is that it is not possible to get the negative potential on the NaLS micelles that you can get on silica colloids because the silica colloids are crosslinked and the NaLS is not. If you try to build up a negative charge to a high

level with the NaLS micelles they come apart. When salt is added to the micelles, the homogeneous solution reaction returns. The right hand side of Fig. 18 is exactly the same set of experiments done with a different sensitizer, the zinc tetramethylpyridinium porphyrin, and the behavior is exactly the same. The system works as expected.

To prove that we really are inhibiting the back reaction with the negatively charged silica particle we performed a flash photolysis experiment, the results of which are shown in Fig. 19. It is possible to see the reduction of PVS and the back reaction in the homogeneous case. If the silica particles with a large charge are added, no back reaction occurs. If salt is added to the silica, to reduce the surface potential, the back reaction occurs again. If the pH is adjusted, adding protons to the negative oxygen anions on the silica surface, even the forward reaction almost stops completely.

Obviously, we can't do both things (oxidation and reduction) at the same negative surface, so it is necessary to find a way to get the electron away from the negative surface and generating hydrogen. This can be done by using PVS as a shuttle, in the same system, with ruthenium and triethanolamine. Even a negative ion can then be reduced by the propylviologen radical, here reducing a triply charged negative ion (Fig. 20). The shuttle system works very well, essentially keeping the PVS^{o} concentration high so that the reaction rate does not fall off. The data from an experiment of this type (Fig. 21) have confirmed our hypothesis, and the reactions are synergistic with the PVS shuttle.

Particle Device

Remembering that we can reduce the potential on the silica surface at will, by adding salt (Fig. 22), we can shuttle the electron back and

forth between two different negative surfaces. This gives us the design for a system which uses silica colloids in the photodecomposition of water (Fig. 23). We are generating oxygen at the strongly negative silica surface with eight negative charges per unit area, with light and PVS, Ru^{+3}. On that negative surface the ruthenium oxide catalyst is placed. Thus, the Ru^{+2} is regenerated with the evolution of oxygen. On the right hand side there is another negative surface, with four negative charges per unit area, and the platinum catalyst is placed there which allows the propylviologensulfonate radical to regenerate by making hydrogen and go back in the shuttle to the other side. This is an even simpler system than the membrane because it is possible to perform the reaction(s) in two different vessels, with a little bridge between them, just for the PVS shuttle to travel in; or it is possible to insert an ordinary membrane and the PVS can go through while the particles will not. There is a system which is actually useful and the larger scale process can be actually developed from what we know at this time from the laboratory experiments.

Catalyst Systems

However, the system would be better if it were possible to eliminate the ruthenium oxide and the platinum. To get rid of the ruthenium oxide is not too difficult. Suitably chosen manganese compounds susceptible to oxidation from the Mn^{3+} to Mn^{+4} state may be used. The Mn^{4+} has the oxidation potential not only to make oxygen, but also to perform other reactions as well. I believe that it would actually be more efficient to use the Mn^{+4} to make things other than molecular oxygen, i.e., create useful intermediate oxidants. The Mn^{+4} actually forms a manganese ion which can perform oxygen transfer

reactions with great efficiency. This we have called a "hot" oxygen atom. On the other hand, it would be useful to eliminate the platinum catalyst, substituting the iron-sulfur clusters in the place of the platinum. The iron can be in either oxidation state, ferrous or ferric, or a combination. Experiments have been performed to show that the hydrogen comes out electrochemically.

We have made four or five of the synthetic iron-sulfur clusters (tertiary butyl group, phenyl group, carboxypropyl group), but the reason why we want this substance is to replace the negative surface with the platinum with the negative iron-sulfur cubes, since we already know we can reduce the negative ion ferricyanide. We have done one of the crucial experiments. We have been able to demonstrate that these iron sulfur cubes are very efficient quenchers of the fluorescence of $Ru(bipy)_3^{2+}$. If this occurs by electron transfer from the excited Ru^{+2} to produce Ru^{+3} and reduced Fe^{+2} in the iron-sulfur cluster, we will have <u>all</u> of the separate steps necessary to construct a truly artificial photosynthetically modeled quantum capture, conversion, and storage system.

<u>Acknowledgement</u>: The work described in this paper was supported by the Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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This paper is not intended as a review of the field of artificial photosynthesis but is a description of the experiments which have been done here in Berkeley. The papers cited below are the important citations for this work and do not purport to represent a survey of the entire field of artificial photosynthesis.

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Figure Captions

Fig. 1 Electron micrograph of chloroplast lamellae

Fig. 2 Photosynthetic electron transfer scheme (Z-scheme)

Fig. 3 Structures of donors/acceptors/sensitizers used in artificial photosynthesis

Fig. 4 Photoelectron transfer scheme

Fig. 5 Scheme for photosensitized electron transfer across a lipid vesicle wall

Fig. 6 Cofactors in photoelectron transfer reactions across a membrane

Fig. 7 Generation of transmembrane potentials by valinomycin

Fig. 8 Effect of ionophores (A) and transmembrane potentials (B) on quantum yield of heptuviologen reduction in the vesicle system.

Fig. 9 Stern-Volmer plot: Luminescence quenching of $^*Ru(bpy)_3^{2+}$ by Fe^{3+} in homogeneous aqueous solution

Fig. 10 Stern-Volmer plot: Luminescence quenching of *Ru-surf in vesicle walls by $Fe(CN)_6^{3-}$ in the continuous aqueous phase.

Fig. 11 Stern-Volmer plot: Luminescence quenching of *Ru-surf by $Fe(CN)_6^{3-}$ inside and outside vesicles (PC/Ru-surf = 31).

Fig. 12 Single unilamellar vesicle with a diameter between 200 and 500 A, prepared by sonication and indicated ratio between phospholipid and photosensitizer of 86:3:1 with the PVs added outside of the vesicle.

Fig. 13 Model for photo-oxidation of $Mn^{III}TpyP-C_{16}$ with the Zn-porphyrin sensitizer.

Fig. 14 Flash photolysis experiment (pulsed dye laser using Coumarin 450) of $ZnTPyP-C_{16}$ incorporated into egg-PG membranes and PVS using the transient absorbance change at λ = 602 nm as detection technique.

Fig. 15 Difference spectra of system I ($3x10^{-5}$ M $Mn^{III}TyP-C_{16}$; 10^{-5} M $ZnTPyP-C_{16}$; 10^{-3} M PVS in egg-PG vesicle) vs system II (10^{-5} M $ZnTPyP-C_{16}$; 10^{-3} M PVS in egg-PG vesicle) after subsequent 5 min illumination at 430 $\pm$ 5 nm at 31 x 10^{-6} E/min-Cm^2 light intensity

Fig. 16 Treated hollow fiber, AnTPP (acetone) 50X

Fig. 17 Hollow fiber apparatus for photodecomposition of water

Fig. 18 Propylviologen radical, $PVS^{\overline{\cdot}}$, formation as a function of light absorbed, monitored by the increase of absorbance at ε = 602 nm. (ε = 12500 $M^{-1}cm^{-1}$).
(A) $Ru(bipy)_3^{2+}$ as sensitizer; (a) SiO_2 system;
(b) homogeneous system; (c) micellar system;
(d) NaLS micellar system with 0.1 M NaCl.
(B) $Zn\text{-}TMPyP^{4+}$ and $Zn\text{-}TPPS^{4-}$ as sensitizers;
(a) SiO_2 system with $Zn\text{-}TMPyP^{4+}$; (b) homogeneous system with $Zn\text{-}TMPyP^{4+}$; (c) SiO_2 system with $Zn\text{-}TPPS^{4-}$; (d) homogeneous system with $Zn\text{-}TPPS^{4-}$.

Fig. 19 (A) In a homogeneous aqueous phase, pH = 9.8
(B) In a 0.2% SiO_2 colloid, pH = 9.8
(C) In a 0.2% SiO_2 colloid, pH = 9.8 with added salt (NaC) = 0.1 M
(D) In a 0.2% SiO_2 at pH 4.5

Fig. 20 Schematic function of SiO_2 particles in separating Photoproducts

Fig. 21 Formation of reduced product as function of light absorbed showing synergism of shuttle

Fig. 22 Quantum yield for propylviologen, $PVS^{\overline{\cdot}}$, formation as a function of the surface potential of negatively charged interfaces (o) SiO_2 system; (●) NaLS micellar system

Fig. 23 Utilization of SiO_2 colloids in the photodecomposition of water

Fig. 1 XBB 741-7523

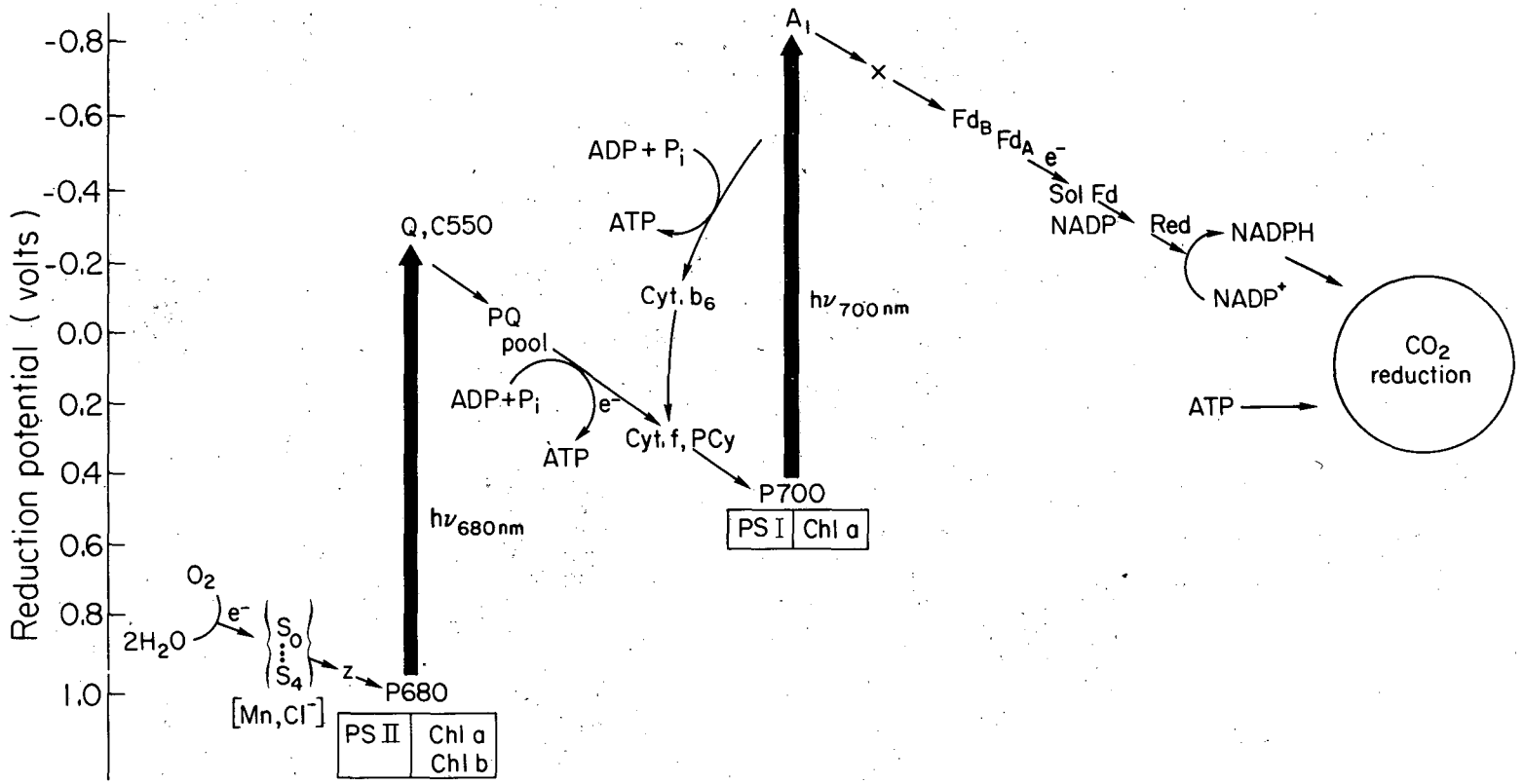


Fig. 2

XBL797-4937

PHOTOELECTRON TRANSFER SCHEME

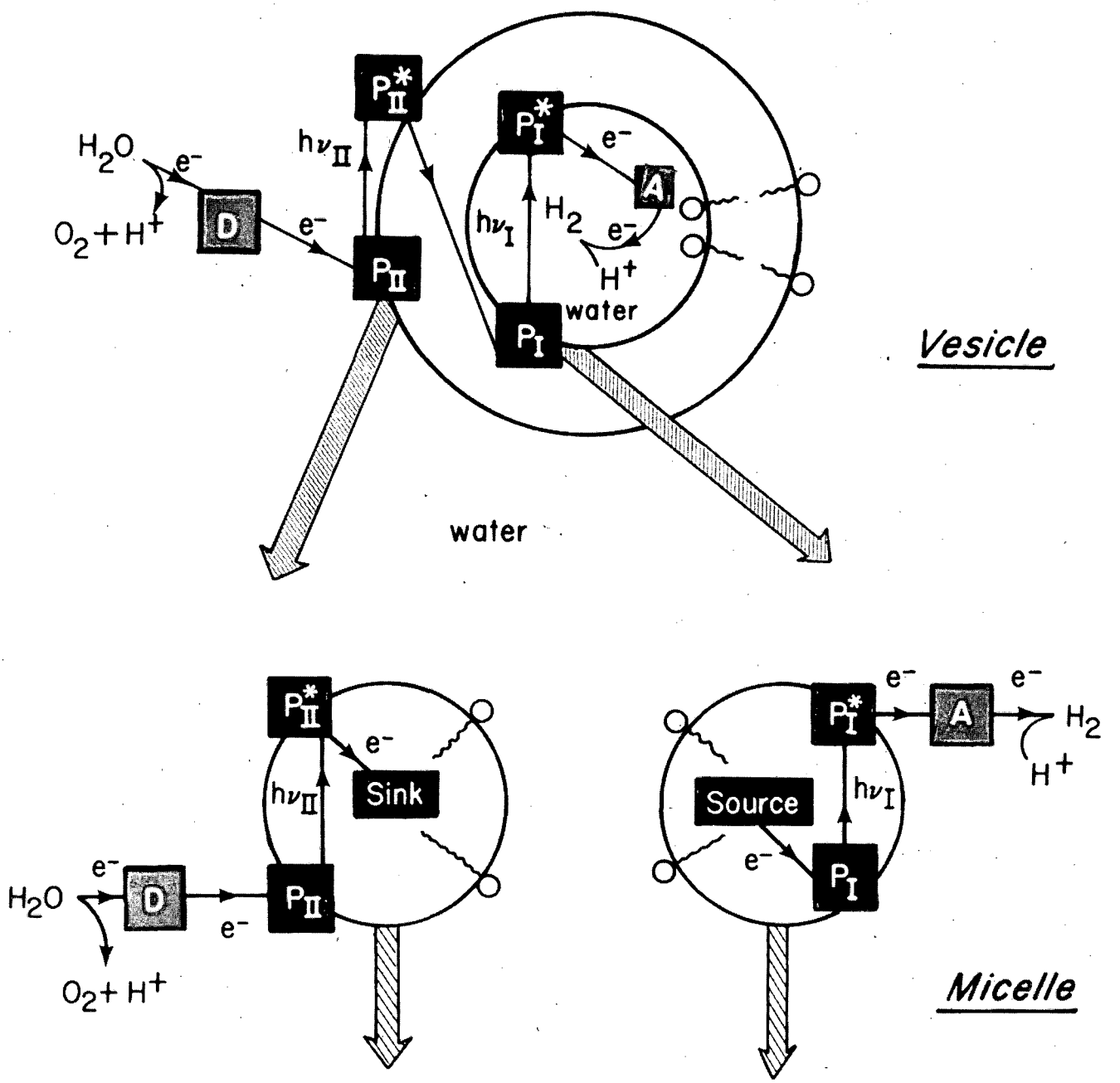


Fig. 3

BBC 774-4090

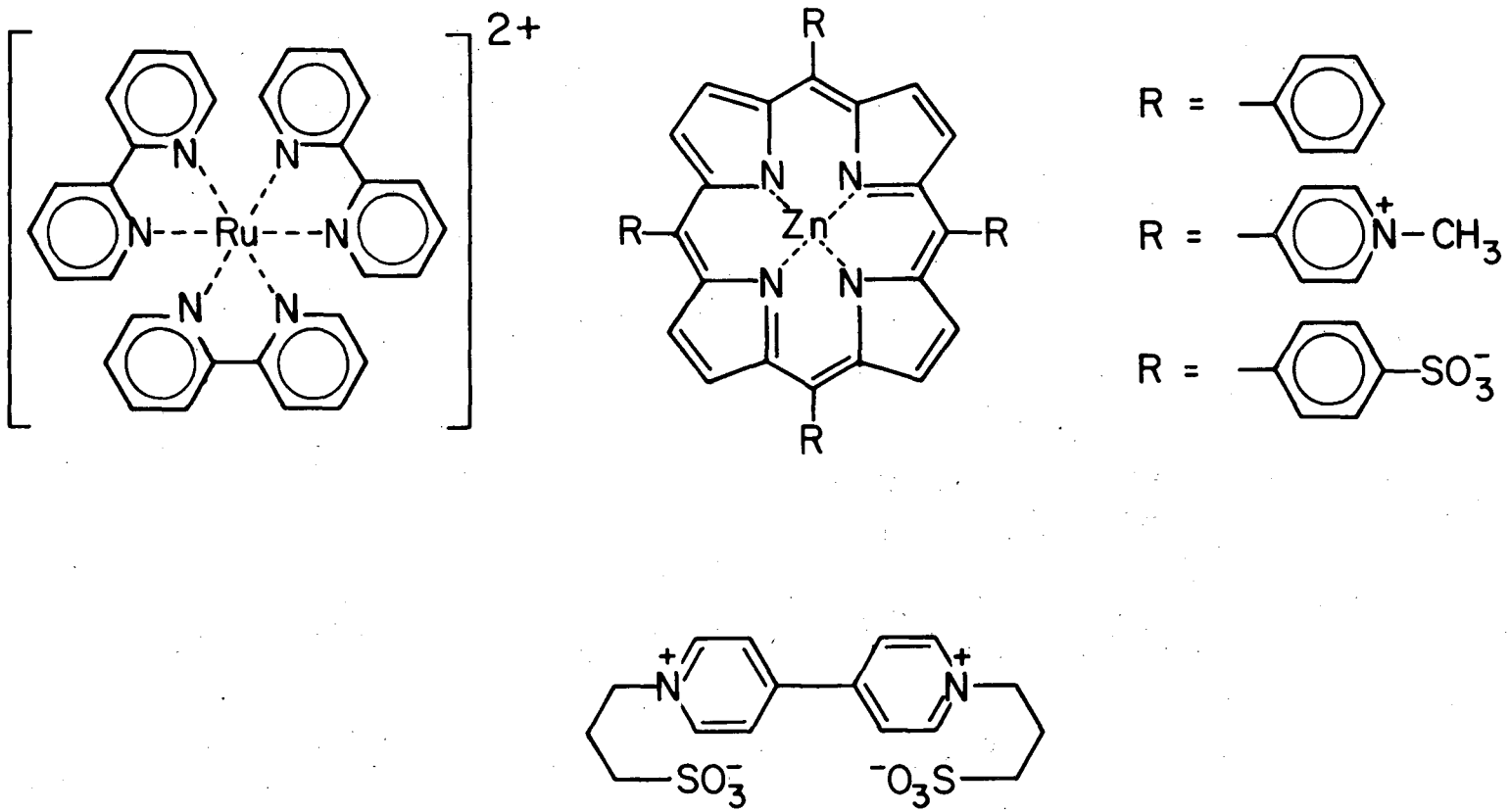


Fig. 4

XBL 814-4530

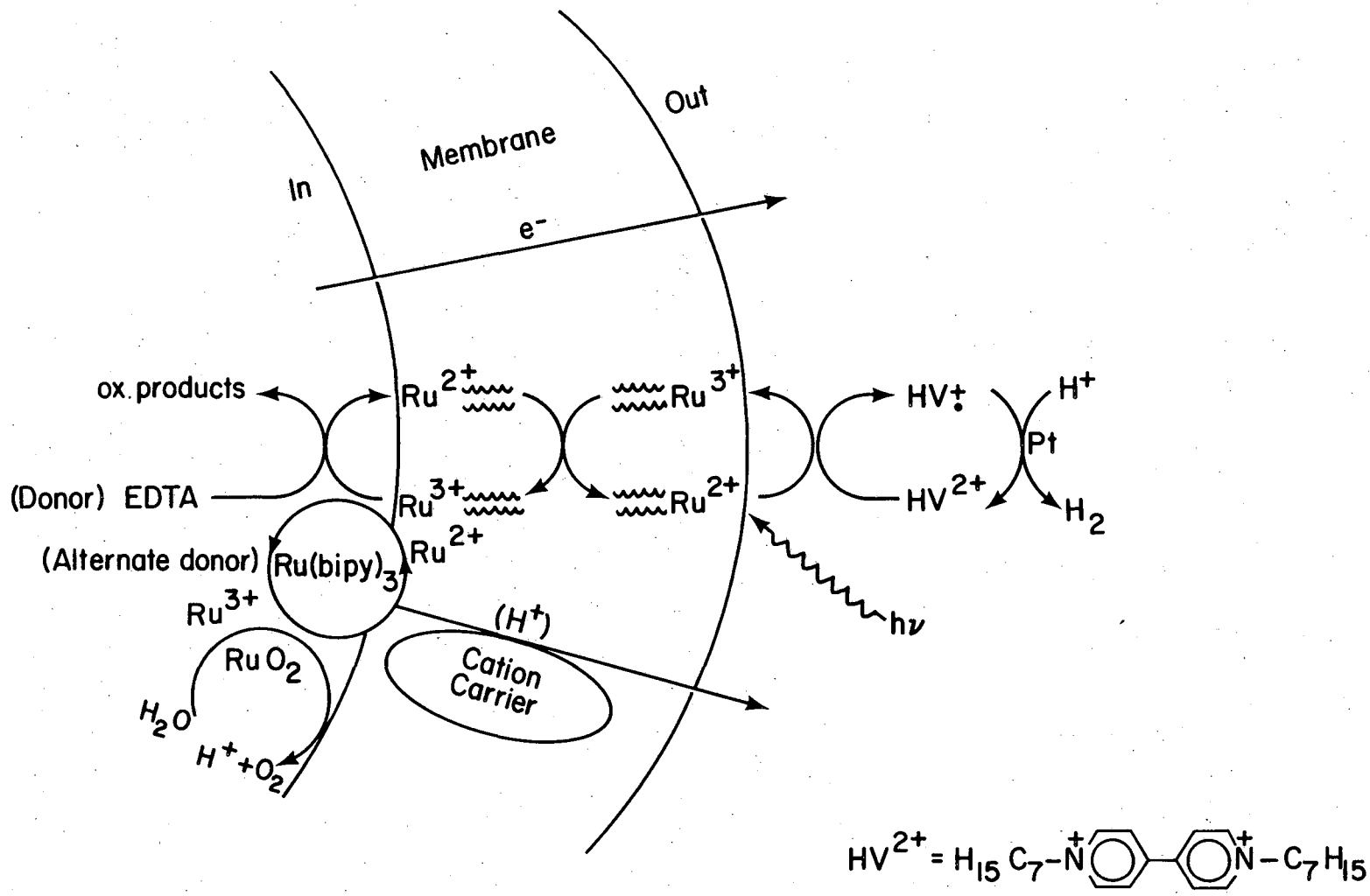


Fig. 5

XBL 821-61

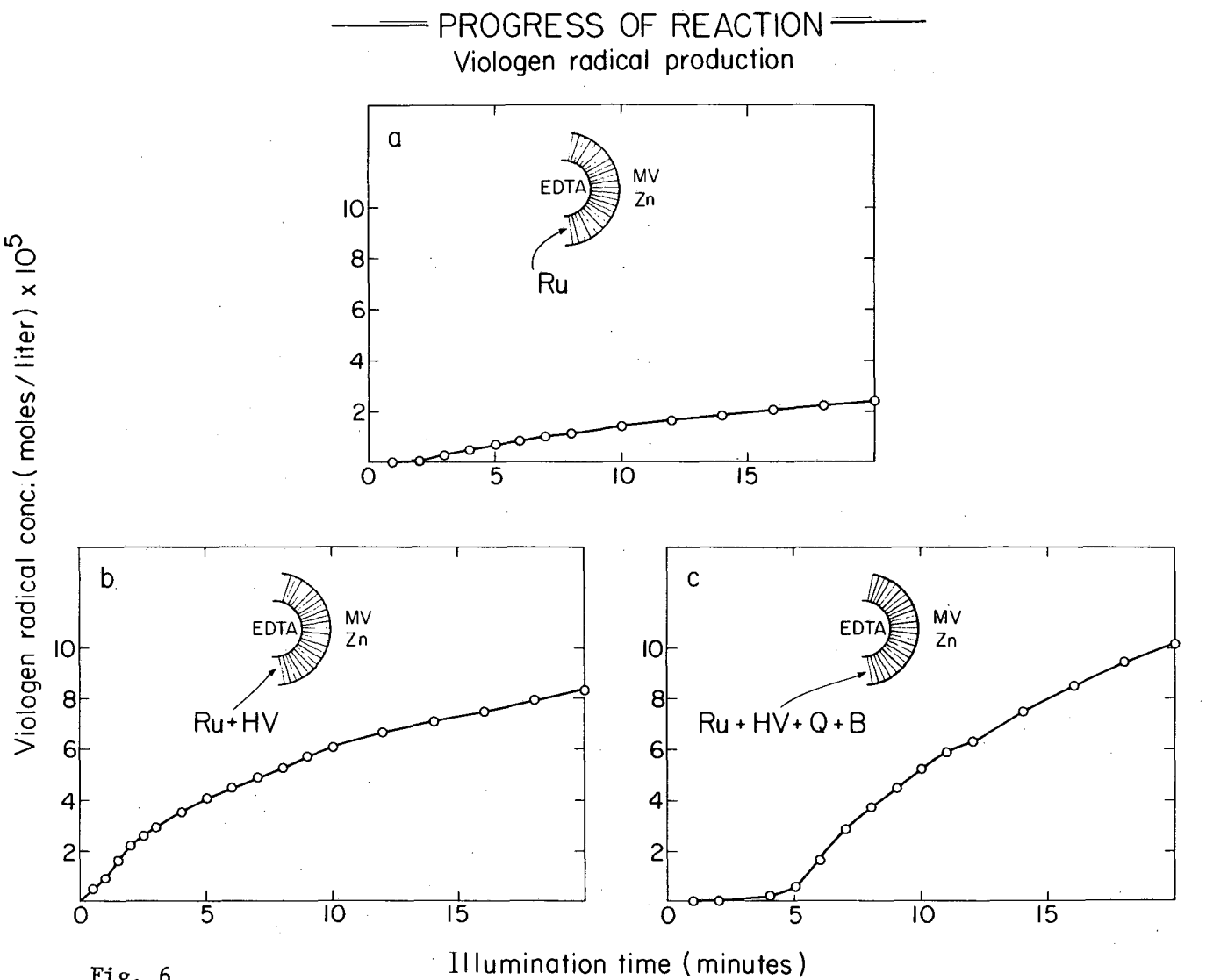


Fig. 6

XBL 791-4643

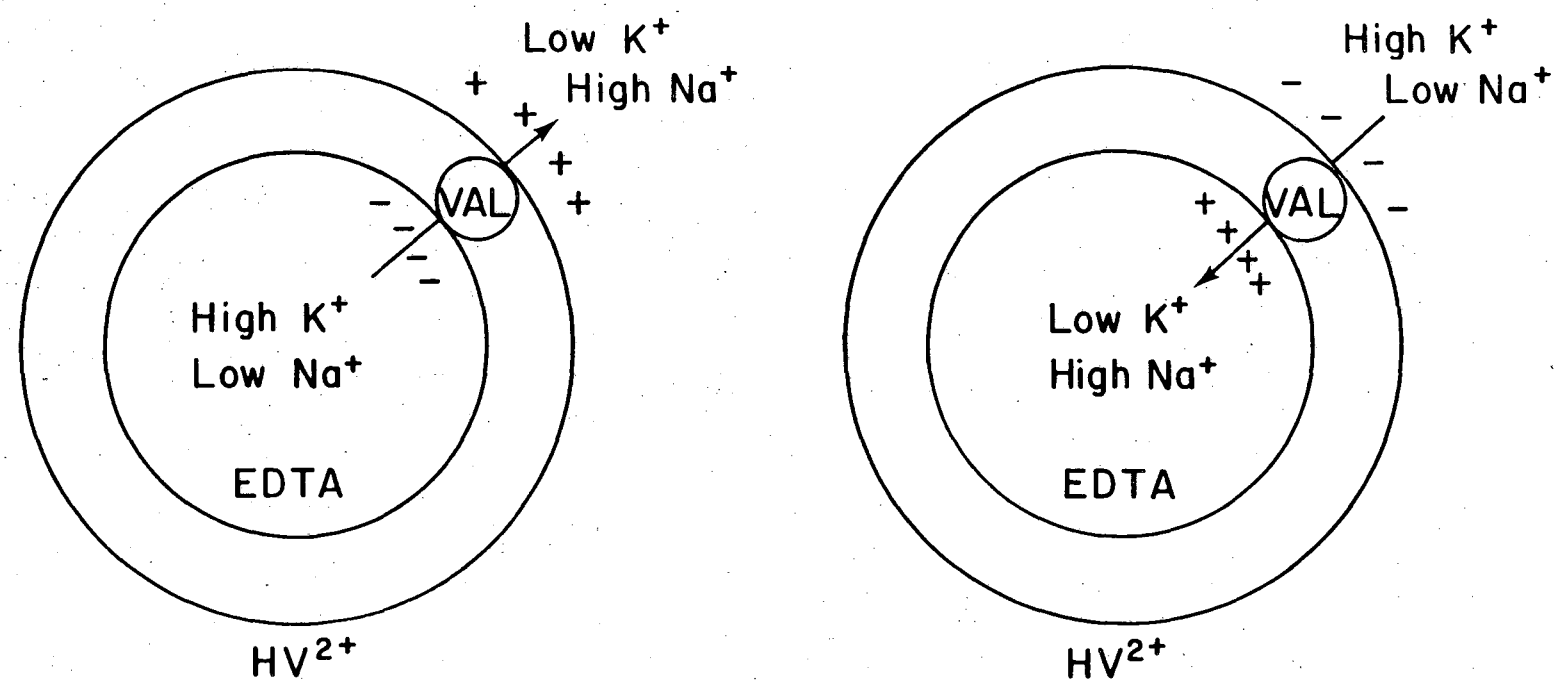


Fig. 7

XBL 812-4491

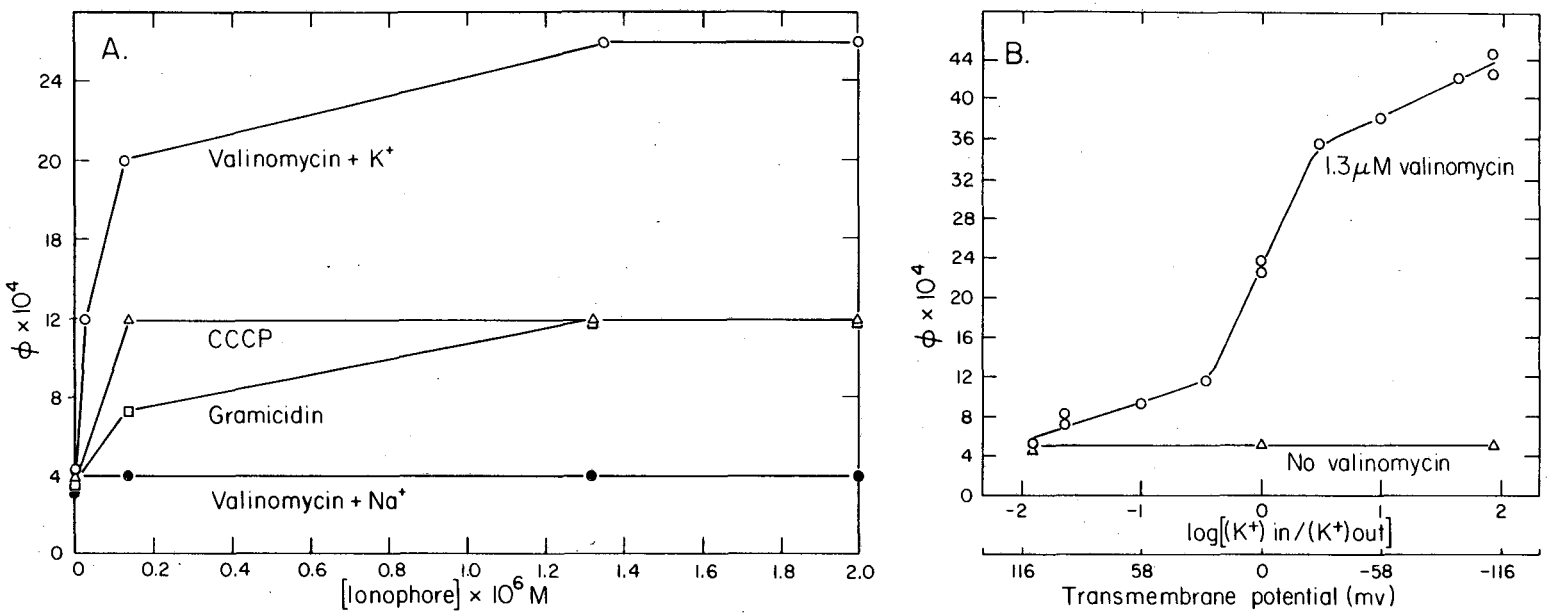


Fig. 8

XBL 814-4528

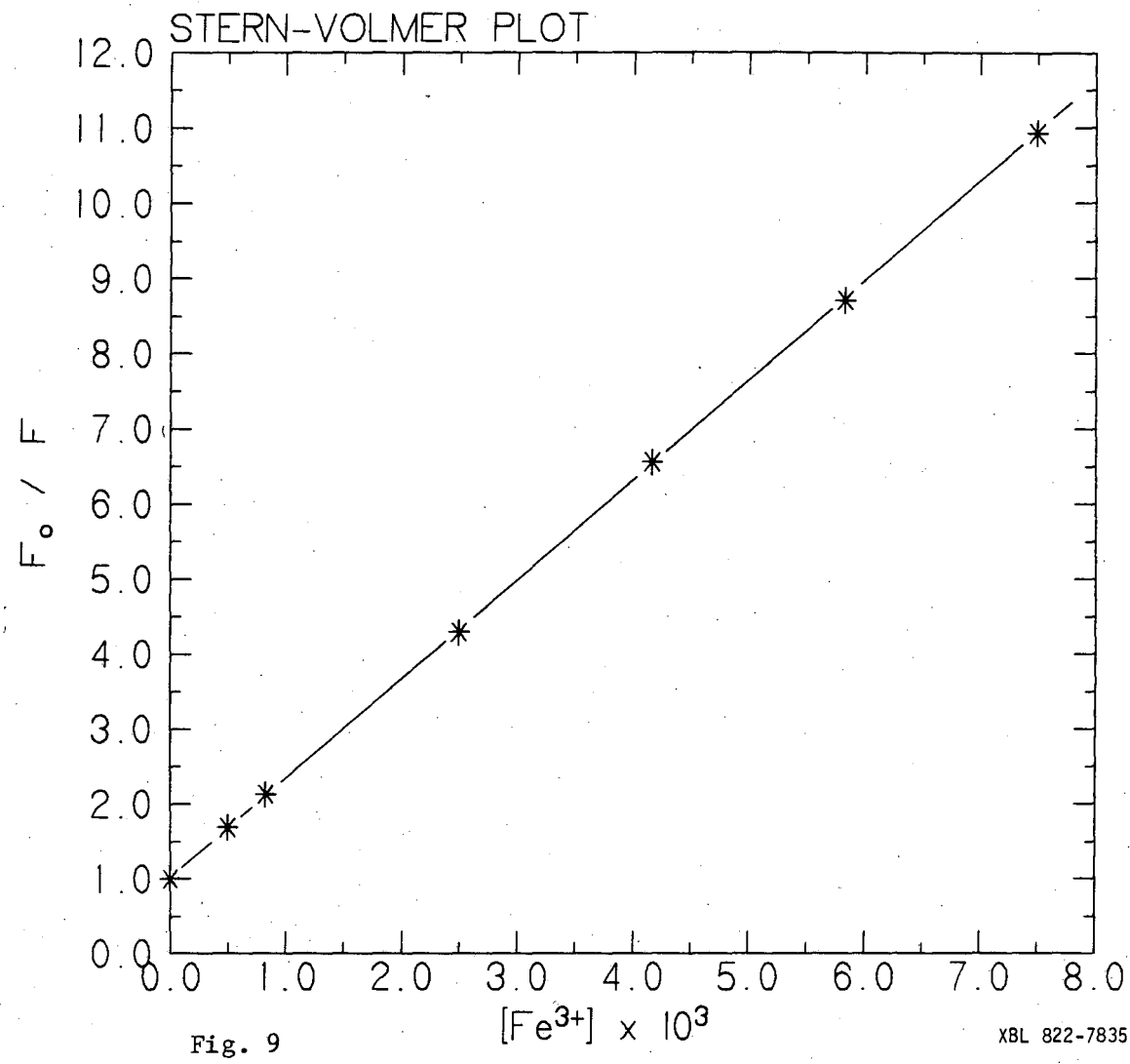


Fig. 9

XBL 822-7835

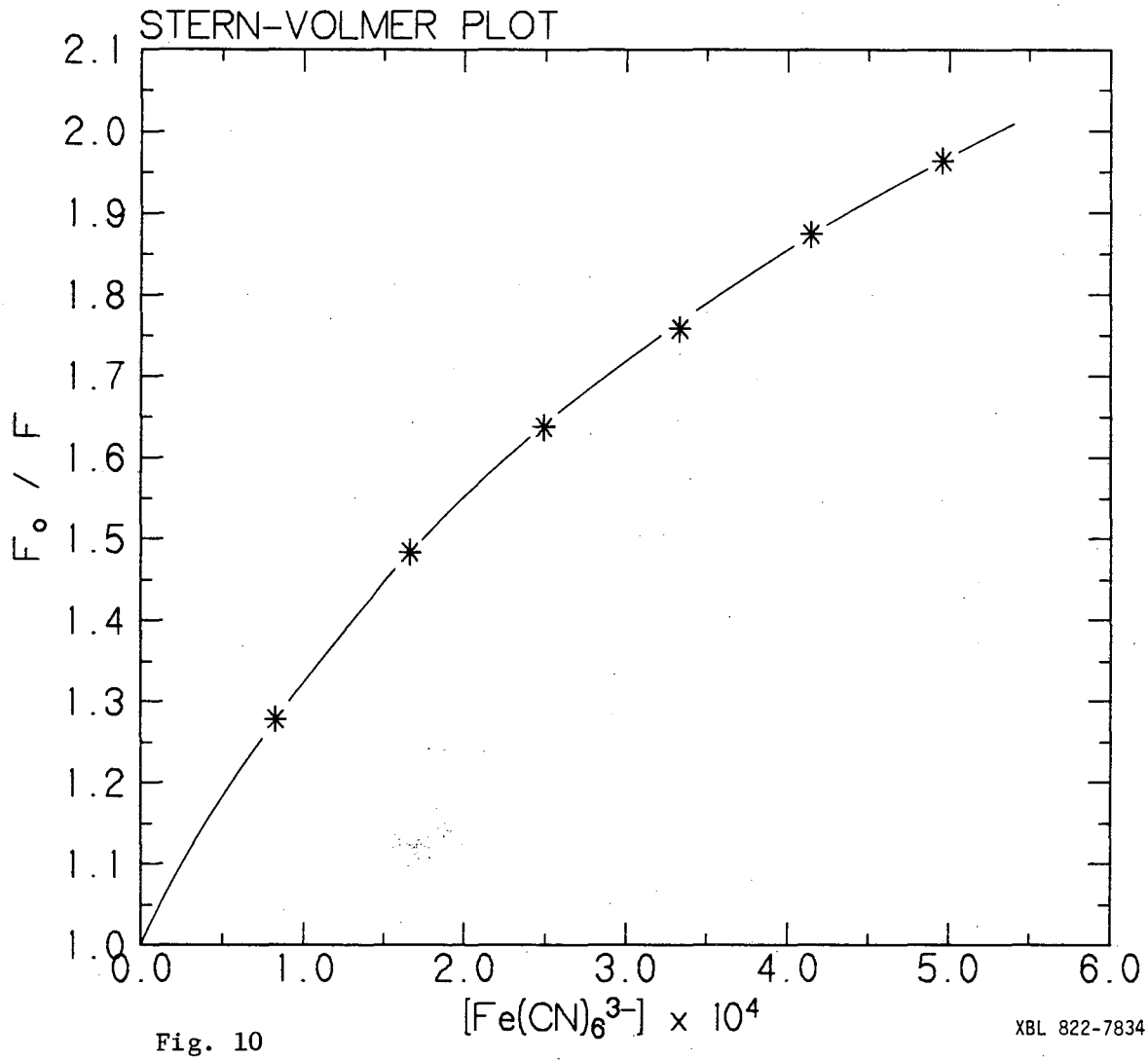


Fig. 10

XBL 822-7834

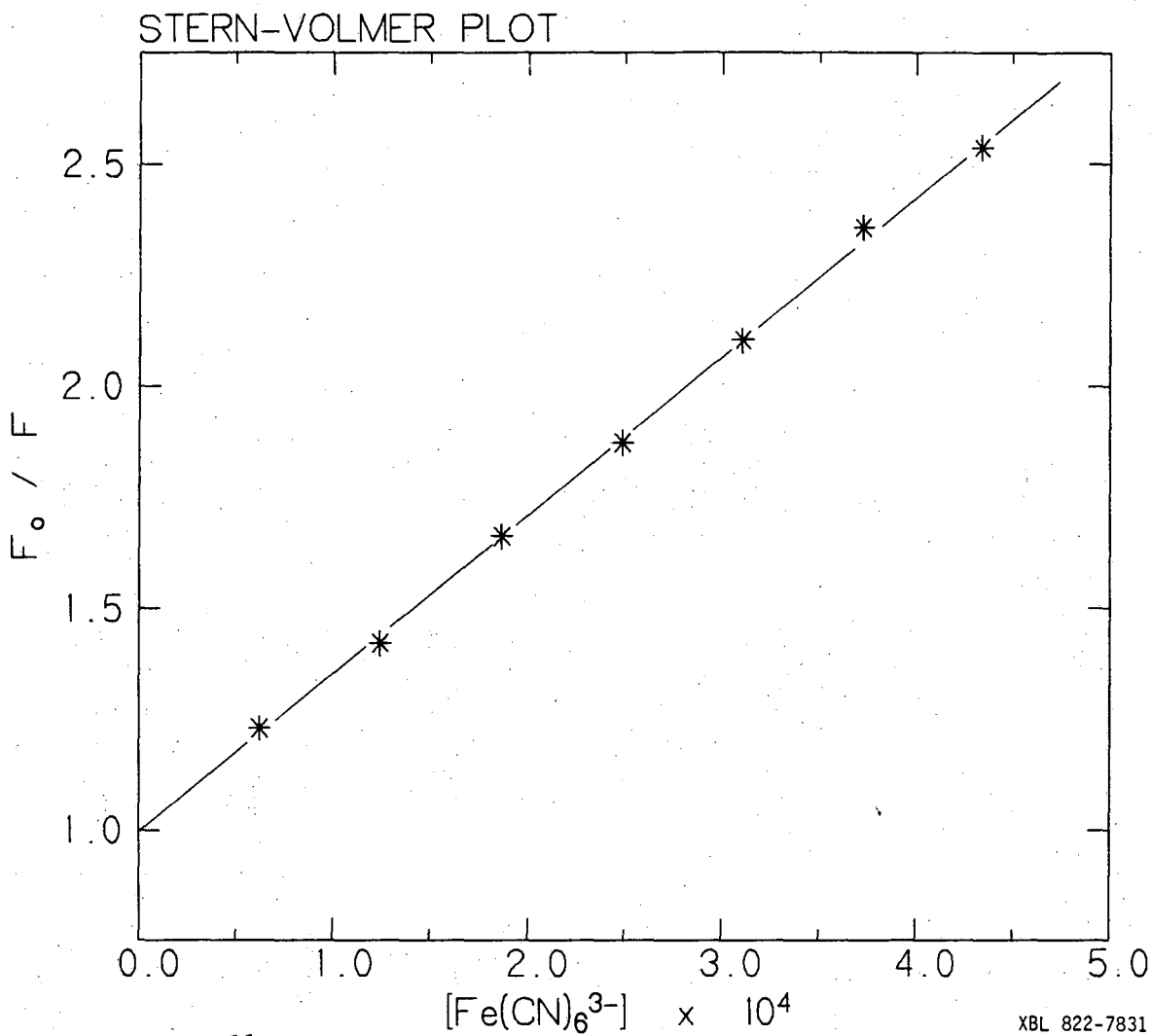
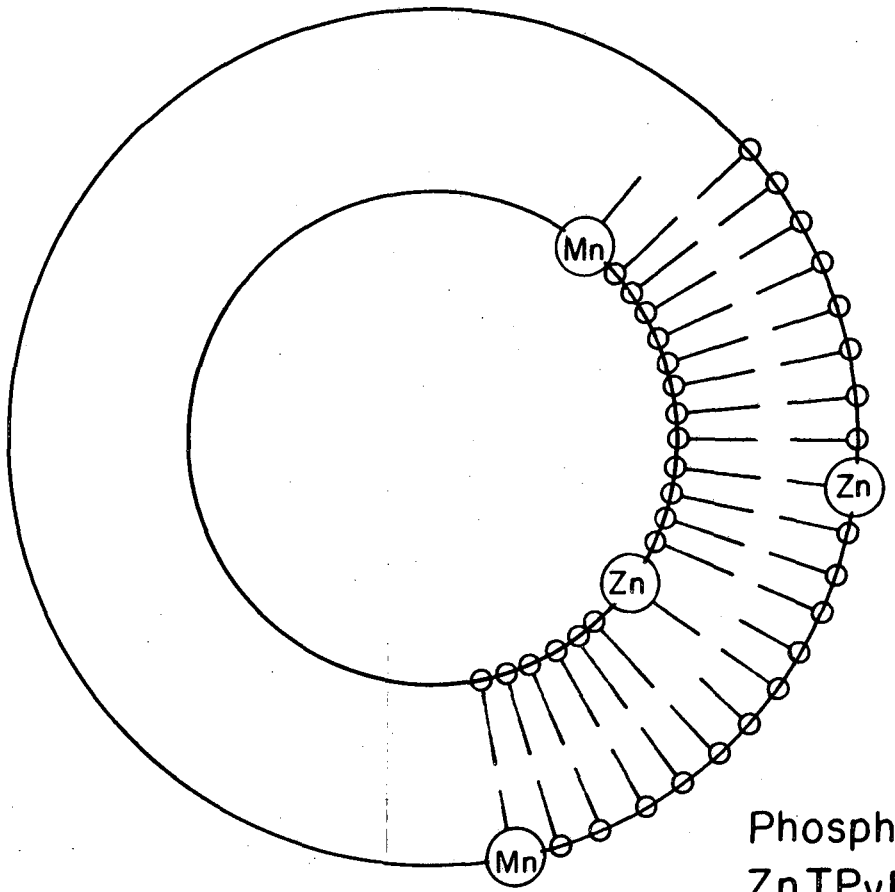

STERN-VOLMER PLOT
2.5
2.0
1.5
1.0
F₀ / F
0.0
1.0
2.0
3.0
4.0
5.0
[Fe(CN)6 3-] x 10⁴
XBL 822-7831

Fig. 11



Phospholipid: Mn TPyP-C16: ZnTPyP-C16 = 86:3:1

10^{-3} M PVS outside, pH 7

Fig. 12

XBL 824-476

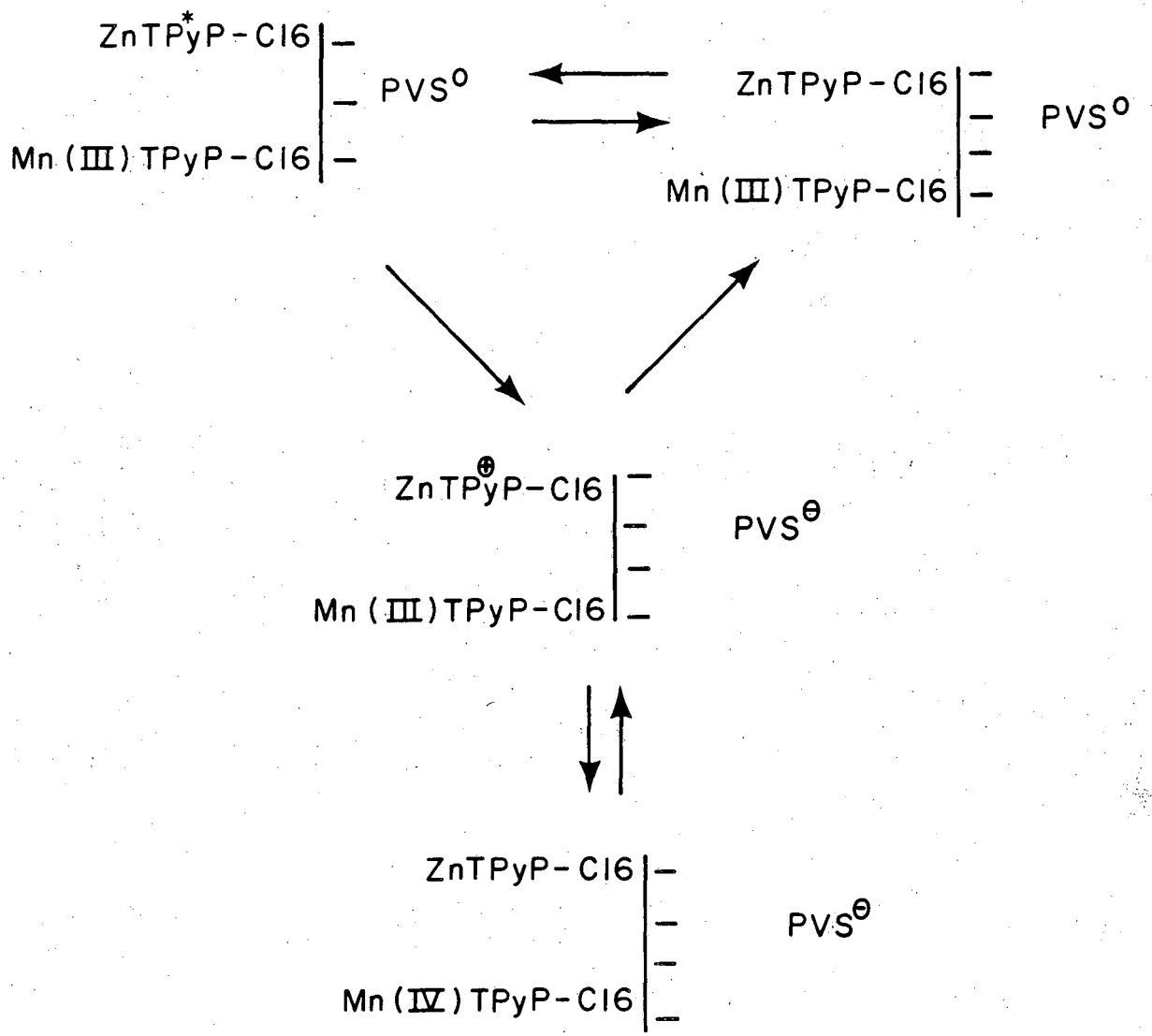


Fig. 13

XBL 824-477

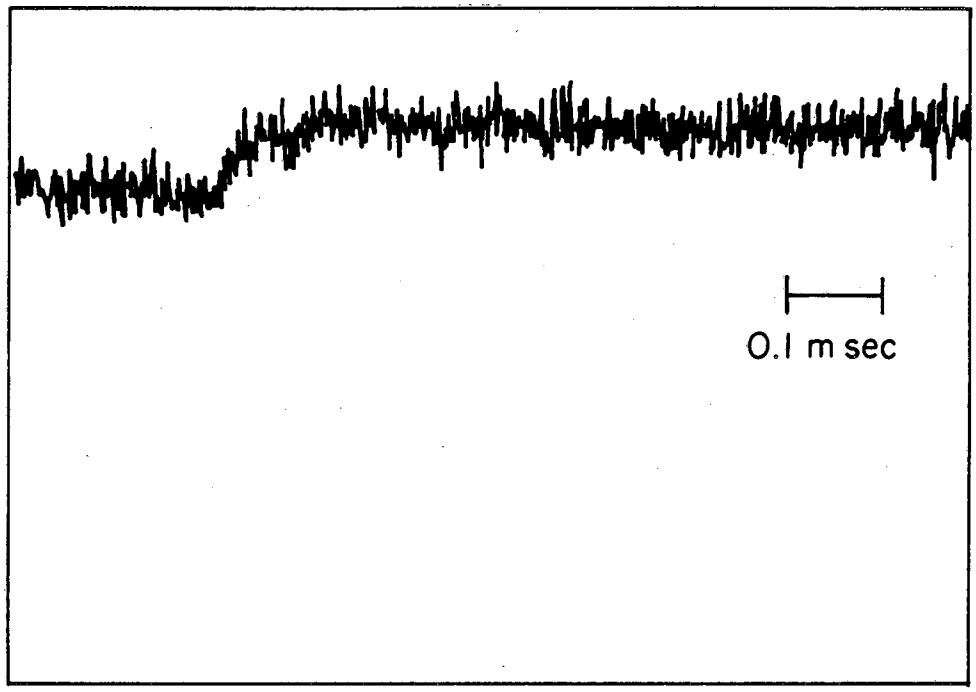


Fig. 14 XBL 824-474

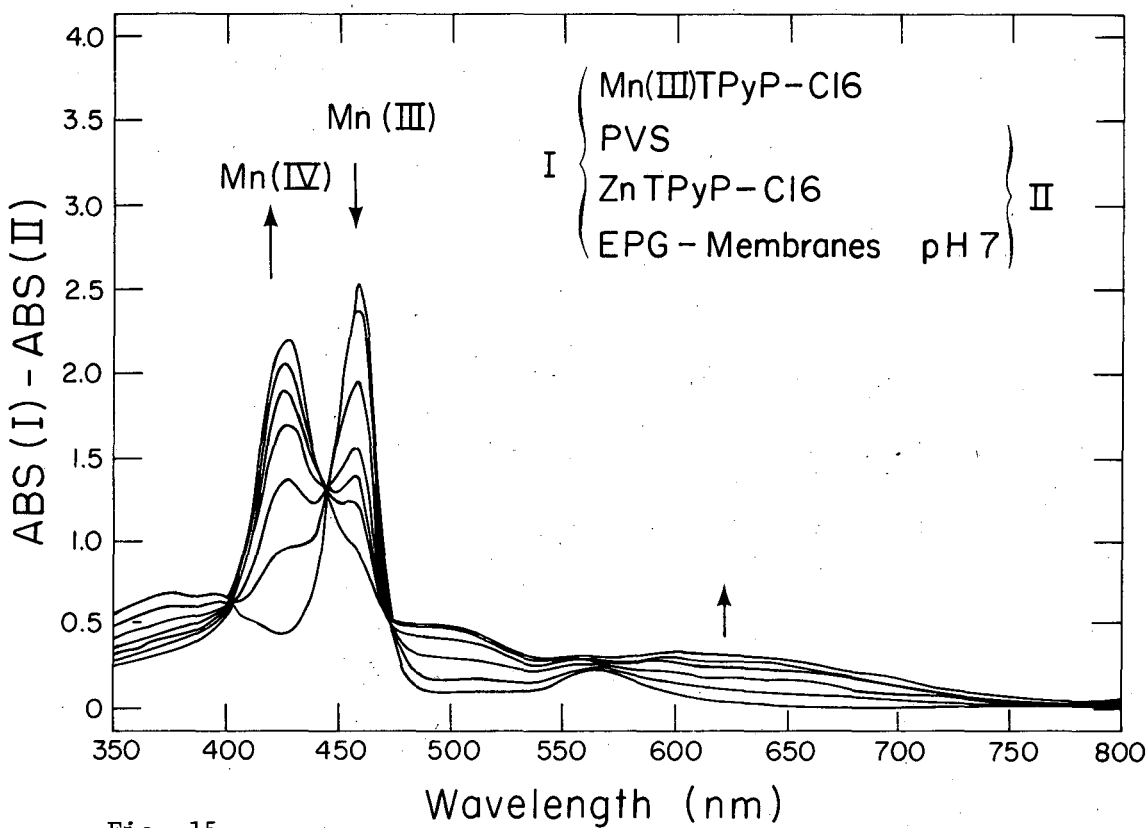


Fig. 15

XBL 824-475

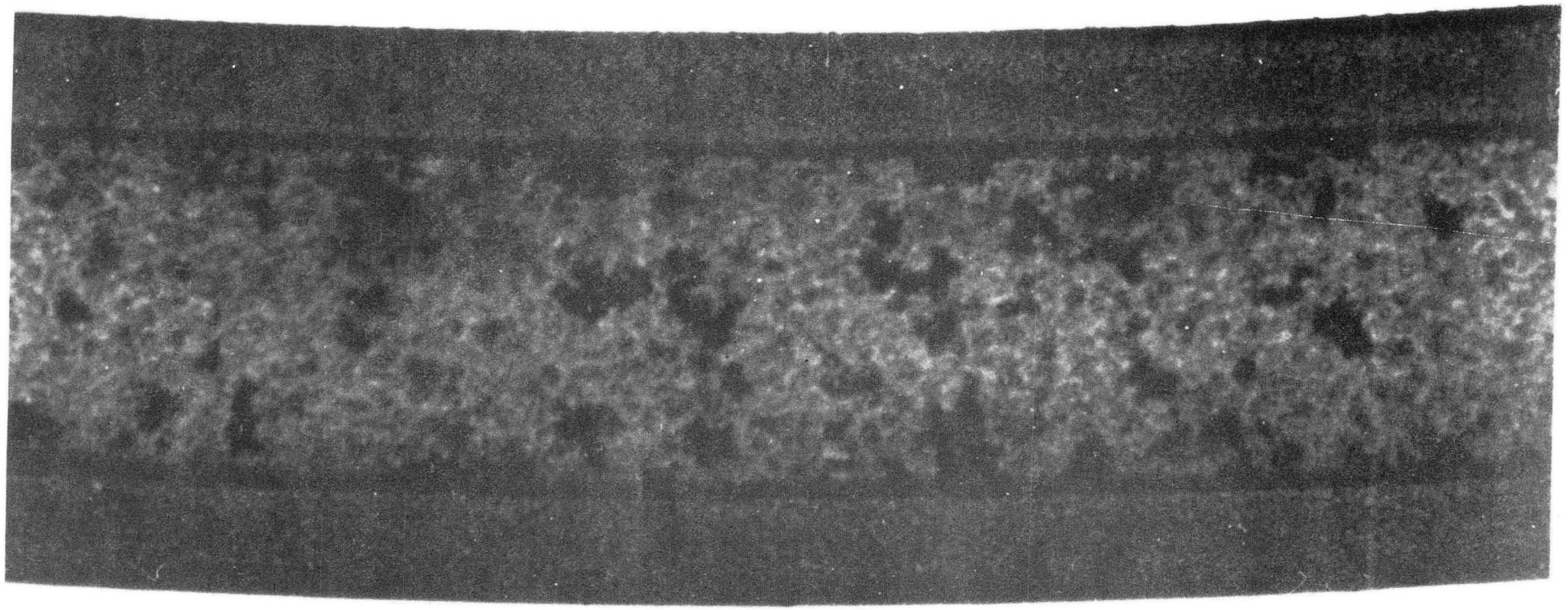


Fig. 16

BBC 813-2202

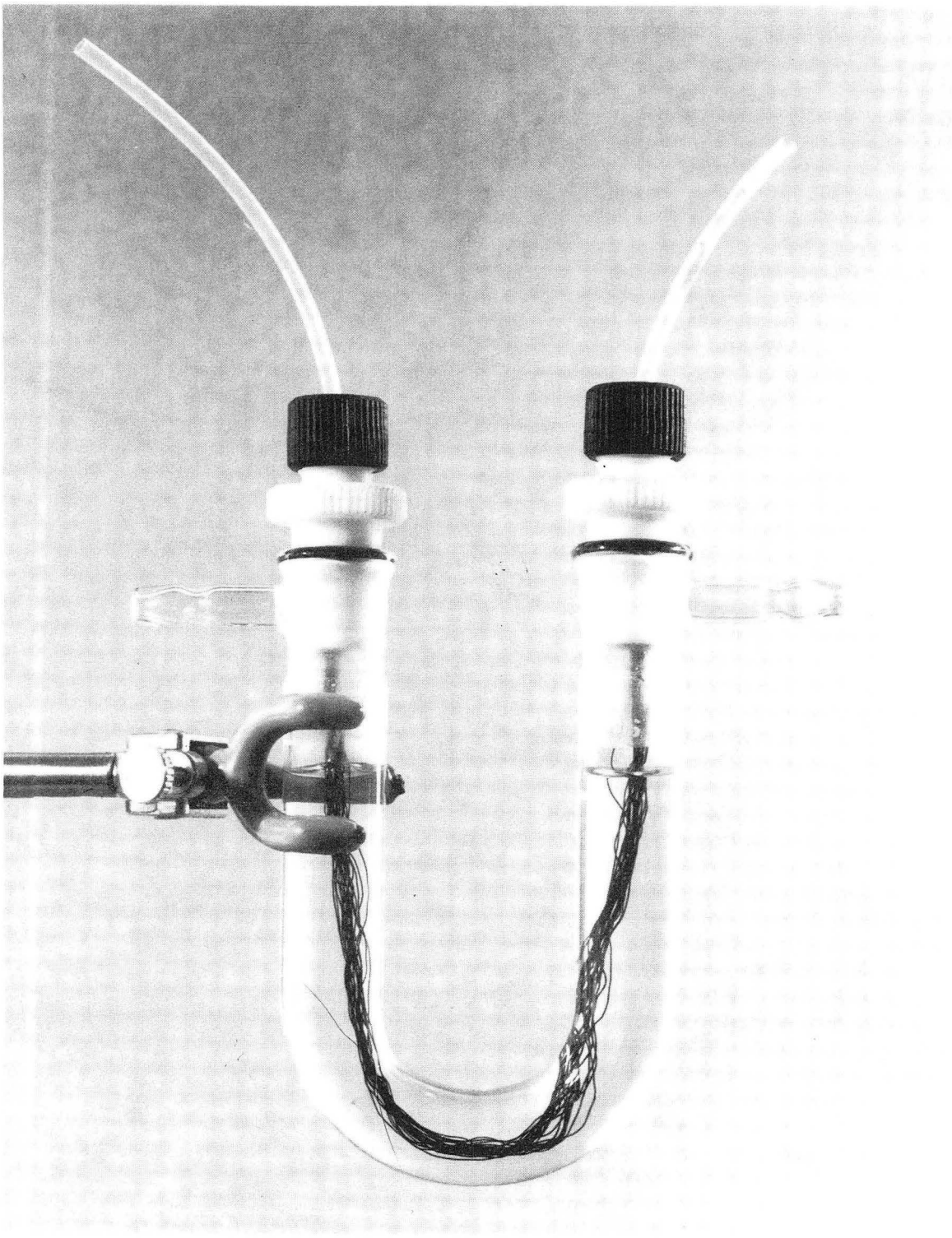


Fig. 17

CBB 814-3554

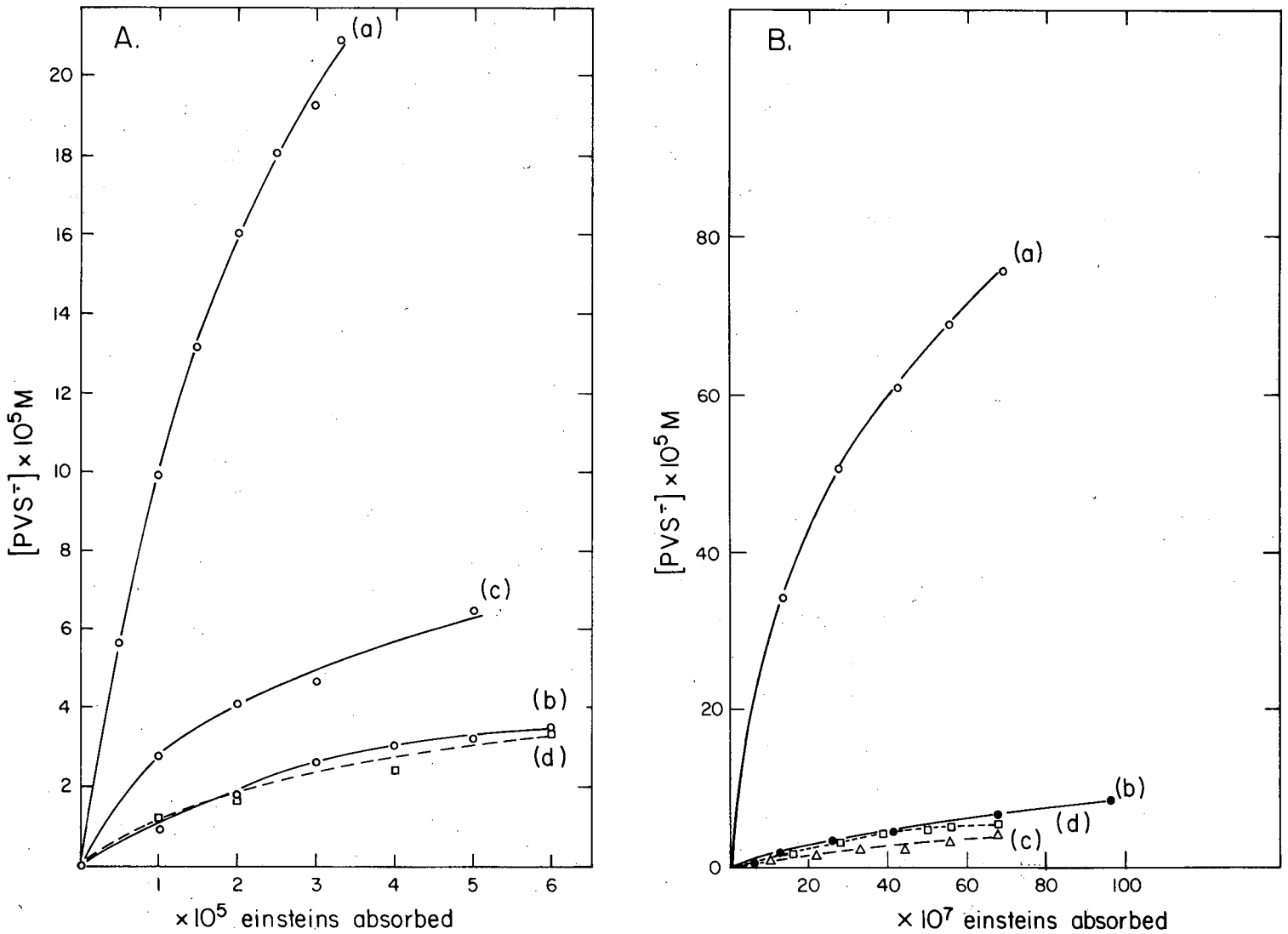


Fig. 18

XBL 814-4529

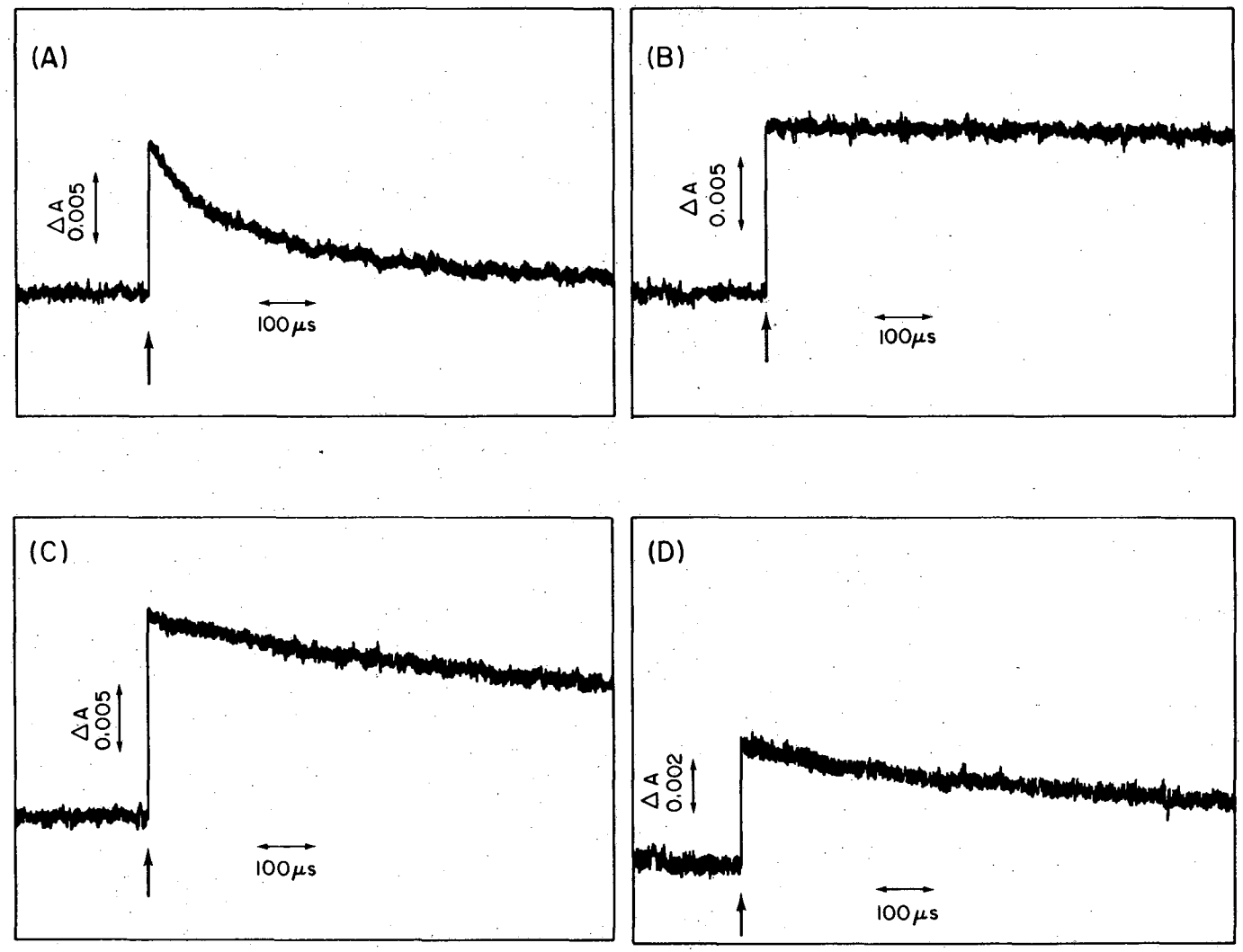


Fig. 19

XBL 814-4561A

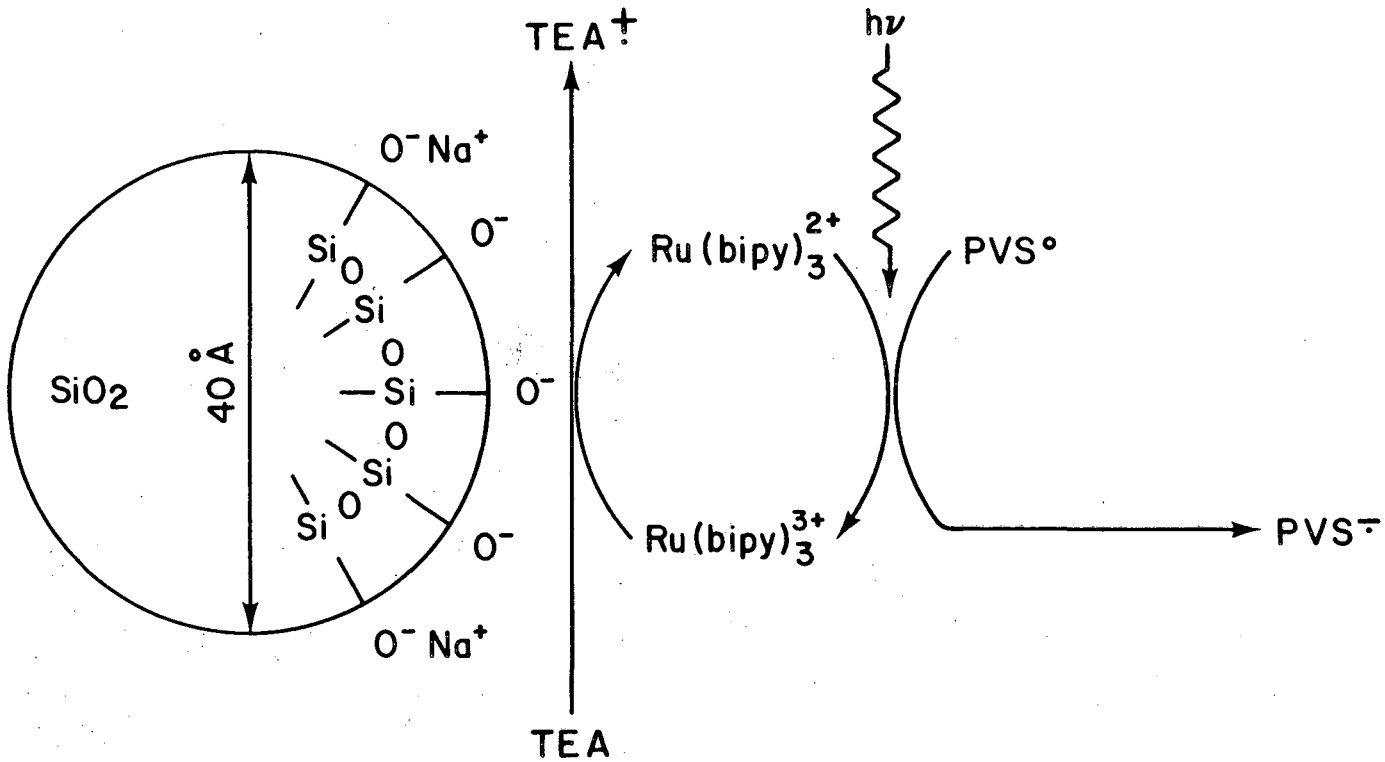


Fig. 20

XBL 811-4426

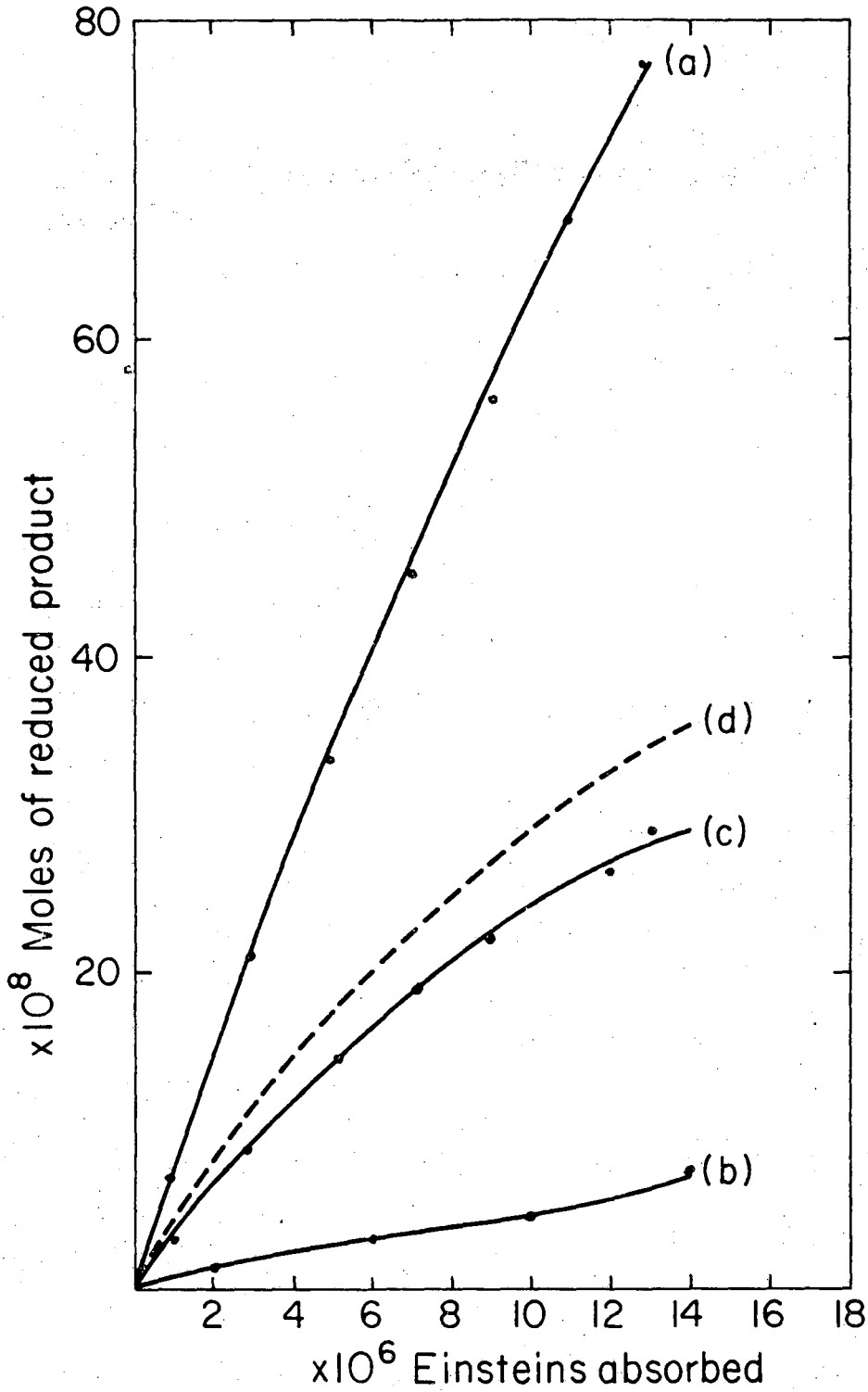


Fig. 21

XBL 818-3387

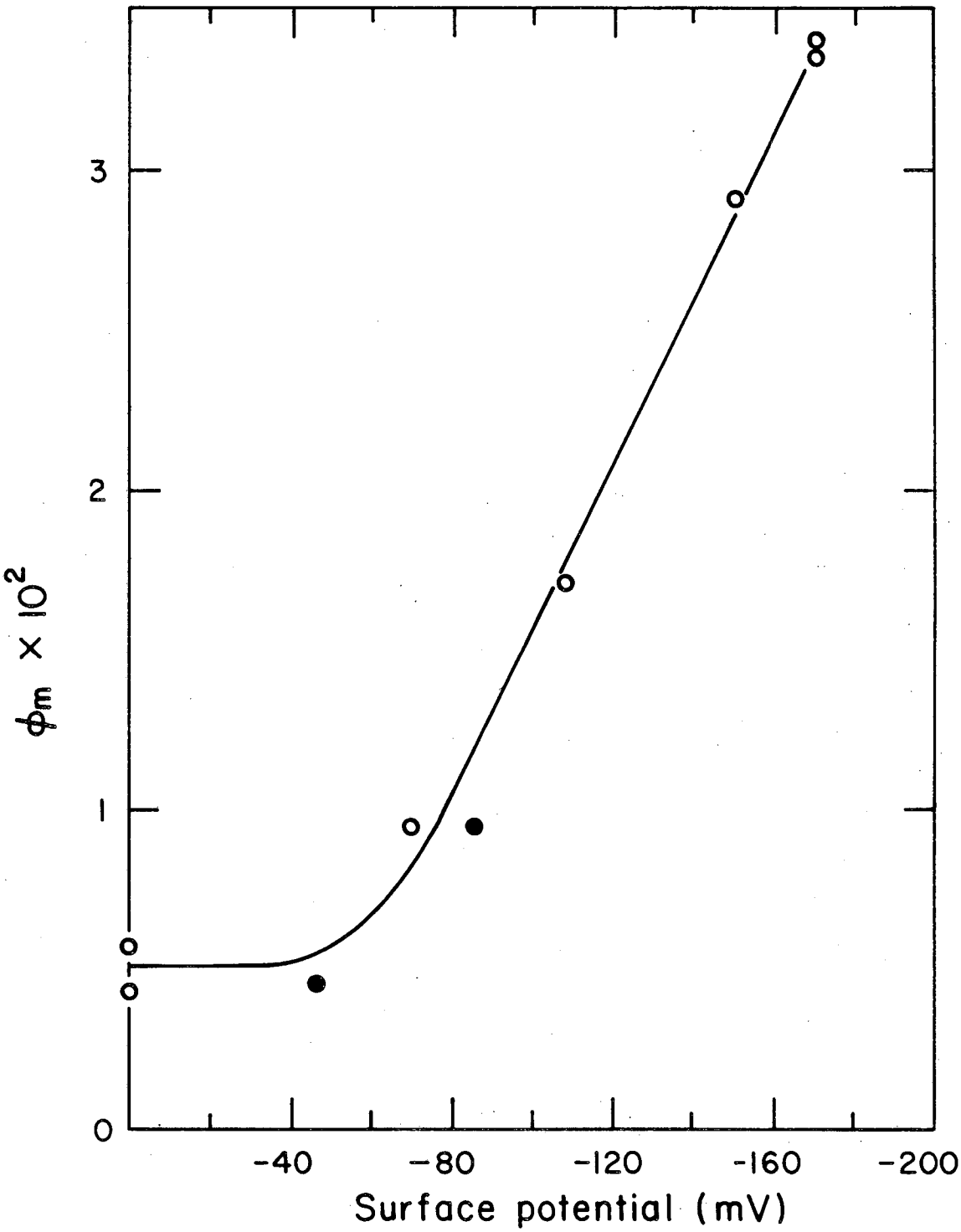


Fig. 22

XBL 811-4425

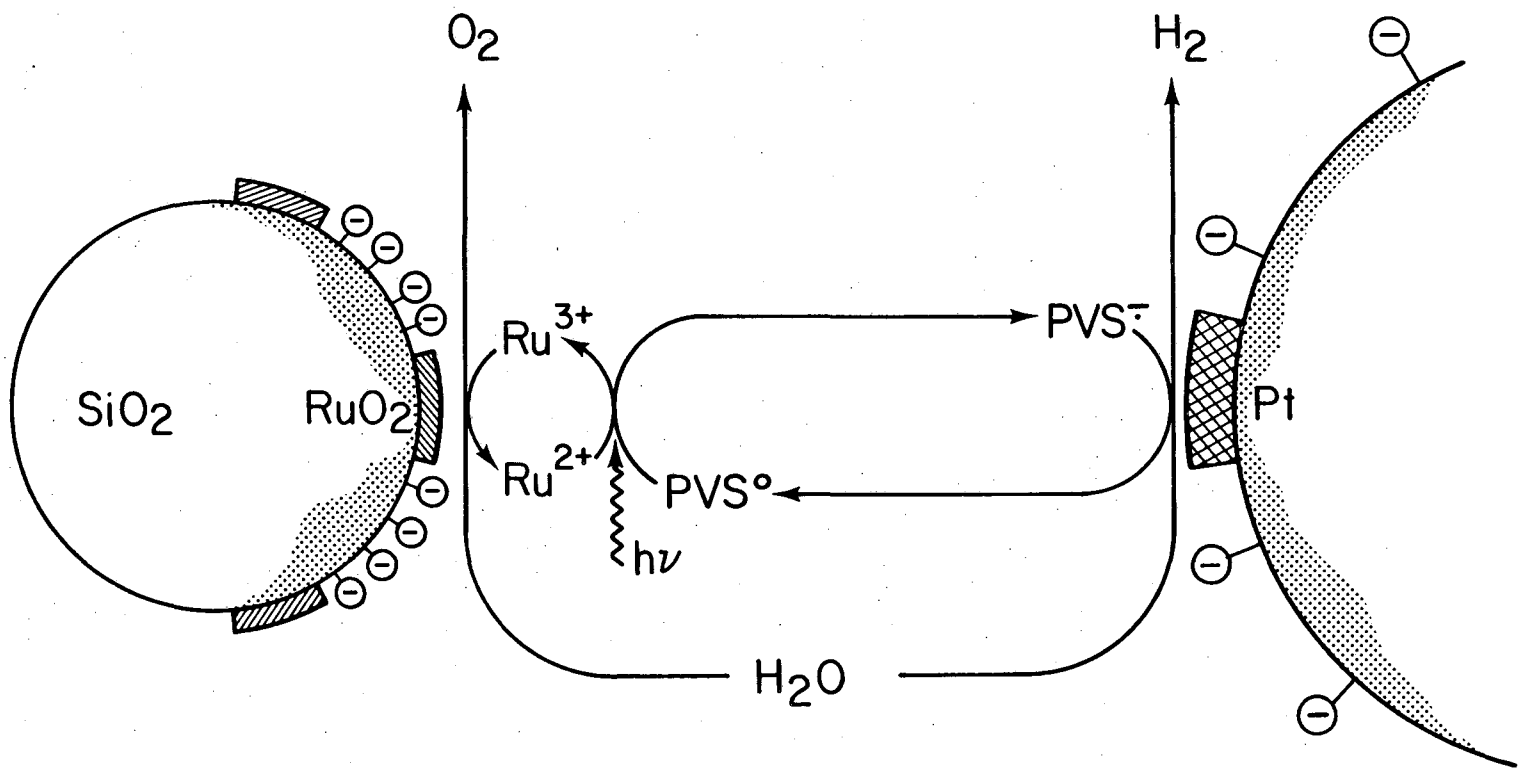


Fig. 23

XBL 812-4486

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