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"The Chemistry of Materials Under Extreme Conditions Including Ionizing Radiation, High Vacuum, High Pressure, and High Temperature"

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13. ABSTRACT

This report covers a broad spectrum of work in such areas as the high pressure synthesis of metals made of the Group II, III, IV and V chemical elements, the synthesis of polymers by the ionizing photolysis of hydrocarbons, the interactions due to d electrons and the unusual valencies of metal atoms in compounds with general formulas such as $(M_6X_8)^{+4}$, $(M_6X_{12})^{+2}$ and $(M_3X_{12})^{-3}$, the chemistry of planetary atmospheres, the growth of diamond crystals, the energy transport in large conjugated molecules such as cobalt and iron phthalocyanine, and the catalytic action of such compounds as $SrTiO_3$ and $LaCoO_3$.

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I PURE CHEMISTRY

HIGH PRESSURE METALS

We continue our work on the high pressure systhesis of metals. Our work during this period has succeeded in producing the first case of a retainable metal from a new class made of Group II and Group V elements namely Cd_3As_2 cadmium arsenide. Below 150°K it is possible to remove this metal from the press without its reverting to the ordinary non-metallic phase (H. Katzman, T. Donohue, and W. F. Libby, Phys. Rev. Letters 20, 442-(1968). The high-pressure phase was discovered earlier by Jayaraman et al (A. Jayaraman, T. R. Anantharaman and W. Klement, Jr. J. Phys Chem. Solids 27, 1605-(1966)). Pressures of 30,000 atmospheres and temperatures of 1,000°C were used to complete the conversion. Liquid nitrogen then was used to cool the press and the pressure removed. The sample recovered was found to be metallic. No superconductivity was found from temperatures above 1.1°K. On the basis of our success in producing the metallic form of cadmium arsenide Cd_3As_2 it is clear that the metallic nature of high pressure polymorphs are not restricted to the Group IV elements and compounds with an average of four electrons per atom, the Cd_3As_2 average being three and one-fifth electrons per atom.

Therefore, it seems that we find evidence of a more general principle, namely that non-metallic systems may in general tend to become metallic at high pressures. If this is completely true it would have important significance for the physics of planetary interiors. Such a general theorem may well be justified. In fact others, in particular Dr. Drickamer at Illinois, have given results of similar bent. Theoretically, it may be that the natural ordering of atoms in the non-conductive solid, in which all the valence electrons are tied neatly into bonds, is disturbed by compression in order to form the high pressure polymorph. This disturbance follows from the fact no atom can form more than six or eight bonds and the densest packings require twelve. This very disturbance causes the electrons to have choices of various bond positions and it is, we suggest, this fact that leads to a kind of analogue of the situation in benzene where six pi electrons end up belonging to the entire molecule instead of forming either possible set of three double bond structures called the Kekulé structures. In other words graphite, which is in a sense the analogue of benzene carried to two dimensional infinite extreme, is a metal. This is known to be so experimentally and one can understand the metallic characteristic of graphite theoretically in this manner. We suggest that this principle may be at the base of a more general phenomenon, that at high pressures solids in general are inclined to be metallic. This may be extremely important in terms of planetary interiors.

CHEMISTRY OF IONIZING RADIATION

A. BENZENE

(F. H. Field, P. Hamlet, and W. F. Libby. J. Am. Chem. Soc., 89, 6035-(1967): 91, 2839-(1969)). On the general subject of the chemistry of hydrocarbon ions produced with ionizing radiation we have found that the aromatic benzene cation does not react rapidly with benzene at elevated temperatures, or rather that the equilibrium between the ion and the benzene cation dimer favors a free ion at temperatures above 100°C. The enthalpy of dissociation, the heat of formation of the dimer from the monomer and from the ion and free benzene was found to be -15 kilocalories per mole and the entropy of formation change to be -23 entropy units. This entropy change is a very reasonable one corresponding to the disappearance of one mole of gas. The heat is a reasonable one also but could hardly be predicted. It compares well however with a recent spectroscopic value for the dimer ion in the condensed phase. (B. Badger, B. Brocklehurst. Nature 219, 263-(1968)). However, the fact that their value of 14.8 agrees closely with our value of 15 may not be significant. Badger and Brocklehurst consider their dimer ion to have the sandwich structure as did Edland et al (O. Edland, P. Kinell, A. Lund, and A. Shimizu. J. Chem. Phys. 46, 3679-(1967)) who found that the ion which formed from benzene cation and benzene absorbed on silica gel is of the sandwich type. In view of all of this we guess that the dimer cation found in the gas phase has the sandwich structure.

The ionizing photolysis of methane (Jensen and Libby. J. Chem. Phys. 49, 283-(1968)) with ionizing light yields primarily ethylene and a polymer as yet uncharacterized with very small amounts of other products. It appears the majority of the polymer is formed by the ions whereas the ethylene appears to be formed by the neutral fragment CH. The quantum efficiency for ethylene is about .08, whereas the quantum efficiency for the yield of hydrogen is .45. It seems therefore that a polymer must be formed with a quantum efficiency of about .3. Ethane is observed at quantum efficiencies of about .001. Acetylene is absent. Propane also is absent. Very small amounts of isobutane are found followed by increasing amounts of longer chain hydrocarbons. Nothing longer than C 30 was seen in the polymer. The highest yield was around C 20.

Thus it would seem that pure ionizing radiation gives very different products from non ionizing photolysis where ethane is a principal product (R. Gorden and P. Ausloos. J. Chem. Phys. 46, 4823-(1967)) and no evidence of polymer is reported. Our figure for the yield of polymer may be questionable since it is based on the assumption of 70% ionization efficiency for 584 Angstrom light.

The mechanism of formation of the polymer may well have been similar to that found earlier in our work on solid methane with cobalt 60 gamma radiation. (D. R. Davis, W. F. Libby, and W. G. Meinschein. J. Chem. Phys. 45, 4481-(1966)) The situation is not completely clear, however, in view of later experiments in in other systems. But the work on the ionizing photolysis and that in the gamma radiolysis of solid methane do seem to agree in so far as the necessary data for comparison are available.

THE LONG RANGE INTERACTIONS DUE TO d ELECTRONS

A. METAL ATOM CLUSTERS - W. F. Libby, J. Chem. Phys, 46, 399-(1967)

Metal atom cluster compounds have been known for some years and appear to involve strange valences for the constitutent metal atoms. These compounds are formed from the transition elements and so our interest in d electron chemistry led us to consider the nature of the bonding. For example, one type of cluster compound considered had the general formula $[M_6X_8]^{+4}$. The M atoms which may be either tungsten or molybdenum are located at the corners of the octahedra with halide ions located above the center of each octahedral face. Now this structure can be well enough explained by ordinary valence theory with a covalent bond between each of the metal atom pairs accounting for twenty-four electrons, eight electrons being accounted for by the halogens and four electrons being required to be rejected to space to give four units of positive charge. However, other metal atom clusters cannot be so explained.

For example, a second class is $[M_6X_{12}]^{2+}$ with Nb or Ta atoms at the corners of octahedra and halides ions lying in the planes bisecting and perpendicular to each edge and forming a square around each M. For this the metal metal covalent bonds would require 24 electrons and thus the 30 available are inadequate for the twelve halogens and the two units of positive charge. In fact the metal structure must be bonded with only 16 electrons. Similarly a third class $[M_3X_{12}]^{-3}$ where M is Re and the M atoms form an equilateral triangle and nine of the halide ions are more tightly held to the three Re atoms than are the other three leaves 12 electrons for the three metal metal bonds which in a sense is acceptable as three double bonds, perhaps.

Now alternative to the theory of covalent bonding, between metal atoms, which seems to work in some but not in all of these cluster compounds, is another approach. Namely, to assume, that as in the case of the simple theory of ordinary metals, that the electrons act much as though they were gaseous particles in a three dimensional box. We suggested (W. F. Libby. J. Chem. Phys. 46, 399-(1967)) that this could be the situation for these compounds and that they were indeed metallic in nature and that the numbers of electrons required were determined by the energy levels for electrons in a box. For a cube the successively higher energy levels require 2, 8, 14, 20, 22, 34, 40, 46 and 52 electrons respectively. (H. Mueler. J. Chem. Phys. 49, 475-(1968)) found an error in our original paper so the numbers here reflect this correction). Other sets of numbers obtain for shapes different from cubes. For instance for a flat box with the height one half the base edge length the numbers 2, 6, 8, 12, 16, 18, 22, 26 and so on result, and a square column twice as tall as wide gives 2, 4, 6, 10, 12, 14, 16, 20, 22, 24 etc. The numbers of electrons that are free to roam in the cavity of the three compounds mentioned would be 24, 16 and 12. These numbers would give energy minima. Thus it seems that the electron in box theory can help in understanding metal atom cluster compounds. Cotton and Haas (J. Chem. Phys. Inorg. Chem. 3, 10-(1964) have given a molecular orbital theory with similar results.

B. HEMOGLOBIN

(A. Minton and W. F. Libby. Proc. of Nat. Acad. Sci. 61, 1191-(1968)) The hemoglobin molecule contains four subunits each of which is built around a heme platelet containing an iron atom at its center. When exposed to oxygen it absorbs one oxygen molecule for each iron atom making oxyhemoglobin. A strange mystery is connected with the fact that it takes a higher pressure of oxygen to put the first oxygen on the first heme than it does on any of the subsequent three. This is called the interaction between the subunits in hemoglobin. It amounts to about one tenth of an electron volt in free energy and appears to be symmetrical with respect to all of the four hemes, although this point is by no means completely settled expermentally. The heme platelets are arranged so that their centers, even of the closest two pairs, are 25 Angstroms apart. The other four pairs are at longer distances but the entire structure is roughly that of a distorted tetrahedron. Around each of the heme discs, which strangely enough are oriented so that for the closest pairs they are parallel, are wrapped around with long protein polypeptide chains some 140 to 150 amino acids in length. These are so constituted that the polyfunctional amino acids which leave charged groups on the polypeptid chain lie on the outside of the entire structure so that they are located on the interface between the aqueous phase and what proves to be a largely hydrophobic interior. Now our point of interest was to answer the question whether there could be bonding between the hemes themselves, which was much stronger in the hemoglobin form than in the oxyhemoglobin form. It is a strange and intriguing fact that hemoglobin is paramagnetic to the maximum extent conceivable, in that four d electrons on each of the irons are unpaired. In oxyhemoglobin however, there is no paramagnetism left, even that which is normal to oxygen gas itself is eliminated. It was our suggestion and approach that possibly the fundamental change in bonding involved when oxygen was assimilated would eliminate a long range interaction which was strong enough to amount to one tenth of an electron volt of energy. Theoretical calculations show that this would require that an electronic polarizability with several tens of thousands of cubic Angstroms magnitude exist in the hemoglobin form of the subunit and that this would be reduced to a small fraction on oxygenation.

Our experiment consisted in directly measuring the electronic polarizability of hemoglobin at high enough frequencies so as to avoid the effect of movement of heavy atoms and therefore to reveal the true electronic polarizability. The result we obtained was a complete rejection of the theory. We showed that the interaction between the subunits in the hemoglobin could not be due to a Van der Waals type of electronic polarizability interaction, similar to that which occurs on close contact between ordinary molecules and causes them to condense at their boiling points. It was an approach which was marginal and was unlikely to be successful in the first case. However, our long experience with the pervasive nature and remarkable behavior of d electrons led us to try and to test this theory. (A. Minton and W. F. Libby. Proc. of Nat. Acad. Sci. 61, 1191-(1968))

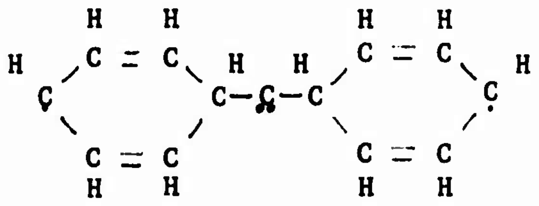
HIGH TEMPERATURE CHEMISTRY

C VAPOR CHEMISTRY

(J. Sprung, J. Quinn, and W. F. Libby) Our efforts to discover the chemistry of thermal carbon atoms using a resistance heated carbon rod as reported previously (J. L. Sprung, S. Winstein, and W. F. Libby. J. Am. Chem. Soc. 87, 1812-(1965)) have continued.

The general and major conclusion is that with benzene the major product is a polymer just as was found earlier (A. Schrodt, and W. F. Libby. J. Am. Chem. Soc. 78, 1267-(1956); and T. Rose Ph.D. Thesis, Yale, 1968. "A. Crossed Beam Study of a Simple Ion Molecule Reaction. B. Reaction of Free Carbon Atoms with Cyclic Hydrocarbons") with radioactive hot carbon atoms reacting at the ends of their tracks. It seems abundantly clear now that there must be a major reaction induced by even a single carbon atom to form substantial sized polymers. We suggest that this product may be the result of coupling to the pi systems two adjacent benzene rings to form

(A)



which polymerizes with additional benzene to form a polymer. In fact Voigt (A. F. Voigt Abstracts 152 Meeting Am. Chem. Soc. New York 1966 Abstract 46R) reports 3.6% diphenyl methane which would be a rearrangement product of compound A. Extensive tests with many different solvents even with benzene itself have failed to dissolve enough for analysis. Elementary analysis gives compositions between $C_6H_8O_{1.3}$ and $C_6H_5O_{1.4}$.

Mass spectral analysis of the products of pyrolysis by Dr. K. Bieman of MIT (J. L. Sprung Ph.D. Thesis UCLA 1966 "Reactions of Carbon Atoms with Benzene") showed that the three predominant ions were $C_6H_4^+$, $C_6H_6^+$, and $C_7H_7^+$ which can reasonably be derived from benzene and carbon atoms. Perhaps the polymer is a reaction product of air with the polymer made from compound A.

The procedure was to coat an evacuated glass bulb immersed in a liquid nitrogen bath with benzene solid by admitting benzene vapor and to flash a carbon rod suspended at the center of the bulb. This was repeated many times by pumping any absorbed benzene off the carbon rod before flashing. The characteristically brown colored polymer formed at liquid nitrogen temperature as seen through the glass wall. At the end the liquid nitrogen was removed, the benzene and volatiles removed for analysis, and finally air was admitted to the flask and the brown polymer scraped off for study. It would not form unless there was direct line of sight access to the carbon rod as shown by the shadow cast by the metal post supporting the carbon rod.

Pyrolysis by heating from 25°C to 500°C for 20 minutes in helium followed by analysis in the mass spectrometer (Kindly measured by Dr. K. Bieman of MIT.) showed peaks due to:

$C_{13}H_{12}O_2$

$C_{13}H_{11}O_2$

C_7H_7

C_7H_8

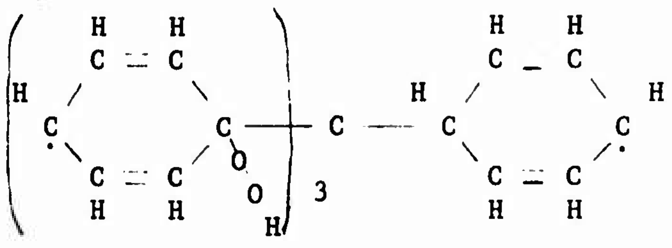
$C_{18}H_{26}$

$C_{18}H_{20}$

The presence of 18 carbon atoms in some of the products of pyrolysis indicates that the polymer probably contains at least three benzene molecules. The reaction with oxygen on exposure to air without noticeable color change could follow from compound A or a large polymer made by attaching more benzene rings to the central carbon because these molecules are free radicals with which oxygen reacts rapidly to form peroxy radicals RO_2 which react in turn with saturated C-H bonds to form C-O-O-H and release the free radical.

Thus compound B might be produced

B)



which might have the right color as well as the right empirical formula $C_6H_{5.8}O_{1.4}$. These unit compounds obviously could combine with one another to form larger molecules.

II CHEMISTRY OF THE PLANETS AND THEIR ATMOSPHERES

A. JUPITER'S RADIO SIGNALS

Some years ago it was discovered that Jupiter gives strong signals at frequencies ranging from some 40 megacycles per sec. down to the ionospheric cut off at around 10 megacycles. The total intensity is large, the planet being next to the sun the strongest source of radio signals in the sky. It is not clear how far below the ionospheric cut off the Jupiter radio broadcasts extend in frequency range. This will be one of the most interesting observations remaining for satellite receivers to make. The most remarkable thing about the planet is that most of the radio signal is controlled by one of its several moons, the moon Io. And the signals have two sharp maxima occuring when Io is at 90° and 240°, when 0° is on the Earth-Jupiter line and directly behind Jupiter. These two positions, 90° and 240° longitude are symetrical, if one supposes that the actual effect causing the radio transmission occurs some 15° ahead of the planet's location, as though there were a kind of forward wake or more properly a fan shaped proboscus reaching some 15° ahead to give 105° and 255° as the actual excitation longitudes. The moon Io's orbit is some six Jupiter radii above the planet and if the disturbance travels down the magnetic lines of force to the polar ionosphere and then excites emissions in the plane tangential to the surface of the planet at the point of contact the emissions will intercept the earth at these two positions.

We developed a theory of the cause of the moon's stimulation of the planetary emission from the observation of these two positions of maximum intensity suggesting that the turbulence was caused by the moon's lying in the inner Van Allen belt of the planet Jupiter. We (L. Marshall and W. F. Libby. Science 214, 126-(1967)) suggested that since the planet rotates in ten hours as compared to forty hours or so for the moon and since the magnetic poles of the planet are not coincident with that of the rotation the Van Allen belts must rotate with the same period as the planet and thus will move rapidly past the moon and thus hit it from the rear and cause a turbulent proboscus to preceed the moon, we estimate by some 15°. It, according to our theory, is this turbulence which is shaking the magnetic lines of force and causing the emission of radiation at the surface of the planetary ionosphere.

Our theory went one step further in suggesting that the radiation was linked to the fact that the planetary atmosphere was reducing and therefore subject to ionizing radiation effects which would make free radicals. We take it as being a remarkable coincidence that the range of radiosignals matches the strength of the Jupiter magnetic field and the range of strength of the magnetic dipoles of organic free radicals. For example, the Jupiter field being about 10 gauss at the surface of the ionosphere, we get 28 megacycles per-second for a one Bohr magneton magnetic dipole, that of the free electron. Therefore, the wide range of wavelengths seen might well be due to the richness of the free radical chemistry of the planet. It is a fact that we have noted for years that reducing systems are all much more subject to permanent change by ionizing radiation than are oxidizing systems and it was our suggestion that magnetic dipole transitions are caused by the shaking of the lines of force and that this is the source of the Jupiter signals. Others (P. Bender. Science <u>158</u>, 1487-(1967)) have questioned that this would be of inadequate intensity and have suggested one or more alternative explanations none of which have a chemical input but rest on one or another of the standard plasma physics theorems.

It is difficult at this point in time to assess the situation on Jupiter. It would appear however, that the interaction of the moon with the magnetic lines of force must be involved in the triggering and that this part of the theory probably is correct.

However, we have proceeded further and have studied in detail the phenomenology of the emission and have found another source which appears not to be controlled by Io. So there may indeed be another way of exciting the radio emission at least for part of the signals. (R. G. Wilson, J. W. Warwick, G. A. Dulk and W. F. Libby. Nature <u>220</u>, 1218-(1968); R. G. Wilson, J. W. Warwick and W. F. Libby. Nature <u>220</u>, 1215-(1968). This source lies in the frequency range between 11 and 28 megacycles per second whereas the Io controlled sources lie above this in frequency. Furthermore, the non Io controlled source occurs between 210° and 340° longitude of central meridian, in other words on about one half of the 360° total. None of the other moons affect this or the Io controlled sources. Whatever stimulates the low frequency radiowaves characteristic of this new source which we have called the Fifth Source must be different and not connected with the satellites. As yet no theory for this source has been advanced. However, the data seem to establish its existence beyond doubt. There are possibilities of extending our magnetic dipole free radical theory into this range but this work has not as yet been completed and does not belong in the report for this period.

B. FREE RADICALS IN THE HIGH TERRESTERIAL IONOSPHERE

The study of the Jupiter radiosignals described above led us to suggest that perhaps the earth itself would also be capable of stimulated magnetic dipole radiation since we know that certain of the atmospheric species have magnetic dipoles. The free electron is the first that comes to mind but a host of others are present such as atomic oxygen, atomic hydrogen and atomic nitrogen and the ions made by ionization of these constituents and those of molecular oxygen and nitrogen. We therefore undertook to see whether the earth would not, under appropriate conditions, behave in a way similar to that in which the planet Jupiter behaves when the moon Io stimulates it.

We approached the Canadian group which manufactures and operates the topside ionospheric sounder Alouette II. The satellite is in a nearly polar orbit with maximum in altitude at 3,000 kilometers and minimum at 500 kilometers and thus always remains well above the main part of the ionosphere. The satellite contains both a transmitter and a receiver which simultaneously sweep from 0.2 to 14 1/2 megacycles per second during each 30 second interval. At the beginning of each interval the transmitter emits a 100 microsecond pulse of 16 kilocycles width and after a delay of 2 microseconds there follows a receiving period of 33 milliseconds, then a transmitter emits a second pulse of continuous higher frequency followed by another listening period and so on. This sequence is repeated 900 times during the 30 second interval as the frequency increases from 0.2 to 14 1/2 megacycles per second. The pulse length and power and the receiving period remain constant. For each interval an ionogram displays the frequency of any detected signal, its time of arrival, its intensity and the real time.

Our purpose in approaching the Canadians was to see whether magnetic dipole radiation stimulated by the broadcast might not be reflected. We realized, of course, that the fundamental frequencies of the ionospheric plasma, namely the plasma frequency itself, which was being most carefully studied and was the main purpose of the topside sounder program from which determination of the density of electrons is made, the cyclotron frequency determined by the local magnetic field, and the hybrid frequencies made up of combinations of the plasma and the cyclotron frequencies would certainly be observed and therefore we must seek for free radical radiations of lower frequencies in the spectrum. We looked, therefore, for reflected radiations lower in frequency than would correspond to any of the ionospheric plasma phenomenon described and were gratified to learn immediately from the Canadian scientists, that there were indeed reflections seen at frequencies below the electron cyclotron frequency, the plasma frequency and below the hybrid frequencies. These seemed to be erratic in intensity and to come from rather near the space ship in that the time delay is very short indeed. We immediately tested our notion of the magnetic dipole reflection and were pleased to see that the frequencies found correspond with likely free radicals. Question was raised about our theory and this question is the same as that was raised in connection with the Jupiter theory, namely that the strength of magnetic dipole radiation may be too low since it is 10,000 times more difficult to induce than electric dipole. Also there was a question about the possibility of its being reflected directly back. At the present moment we feel this second point may be moot because the sources obviously lie within one wavelength of the spaceship. Planewave considerations would seem not to be rigorously applicable and it seems that it is more likely that the ringing of a cavity containing the space ship is a better approach. In any case, further study has shown that the phenomenon is real and apparently is not due to instrumental artifacts, because we have seen a strong day and night effect which causes the relative intensities or probabilities of occurrence of the various reflections to vary in a systematic way between day and night. Particularly prominent are the reflections at g values of 1.20 and 1.33 (g is the gyromagnetic ratio which is 2.0 for the electron). The 1.20 reflection is stronger at night and the 1.33 reflection is stronger during the day. It is possible to rationalize, if not rigorously explain this, in the following way: The first excited state of atomic nitrogen $^2D_{3/2}$ has 1.33 g value in one of its three hyperfine levels and the ground state of atomic nitrogen NI $^4S_{3/2}$ as well as the long lived first excited state of oxygen ion OII $^2D_{5/2}$ both have the 1.20 value. Thus we are led to suggest that photoexcitation by sunlight enhances the 1.33 peak which after sundown fades. The excited state of atomic nitrogen has the natural lifetime of 10^5 seconds.

Much further research needs to be done on these studies, but our work nearly convinces us that we are on the right track, and that there is a real radiobroadcast phenomenon from magnetic dipoles which occur in Jupiter and can be observed by the topside sounders on the earth. Laboratory work and testing of this whole theory is very much in order although it is extremely difficlut to design experiments to demonstrate or test the approach. In many ways the ionosphere is a better laboratory than any we can devise on earth for reasons of the high concentration of free radicals in the lower terrestrial atmosphere and in laboratory equipment.

C. THE CIRCULATION OF THE STRATOSPHERE OF THE EARTH

Studies of radioactive fallout from thermonuclear weapons of sufficient strength to deposit the radioactive particles and gasses in the stratosphere were made and we like others tend to the general conclusion as to the residence time being about 1.6 years with an innerhemisphere mixing time of about 3.3 years. In 3.3 years the difference between the two hemispheres will have dropped to 1/e of the value it had in the beginning and in 1.6 years the concentration of strontium 90 or any other particular radioactive isotope will have dropped to 1/e of the value it had in the beginning. We have learned from this work (P. Fabian, W. F. Libby, and C. E. Palmer. J. Geophys. Res. 73, 3611-(1968)) and from work with radioactive hydrogen (tritium) produced in the explosions that the fine particulate (less than 0.1 micron) matter and gaseous matter travel in about the same way. The residence time for tritium in the stratosphere and for strontium 90 are essentially identical and other work has shown that this is true also for radiocarbon [(J. Leventhal, and W. F. Libby. J. Geophys. Res. 73, 2715-(1968) ; (R. Berger, and W. F. Libby. VI Radiocarbon 9, 477-(1967) VII ibid 10, 149 (1968) VIII ibid 10, 402-(1968)]. These results are of course of considerable importance in matters of atmospheric circulation and worldwide meteorolgical phenemona and of direct signification to matters of air pollution.

D. THE EARTH'S MAGNETISM IN TIMES PAST

(W. F. Libby, NATO Advanced Study Institute on Planetary and Stellar Magnetism, held in 1965 at the School of Physics, the University, Newcastle-upon-Tyne) It has developed that the radiocarbon dating method, the initial work on which was supported in major part by the Air Force Office of Scientific Research at the University of Chicago in the late forties has come to be an important and substantial method of studying the earth's magnetic field in times past. The reason is simple, the earth's magnetic field shields away a certain part (about half at the present time) of the cosmic radiation which generates the radiocarbon. So if in a certain interval in past times the field had been turned off or reduced in strength the production rate of radiocarbon would have been increased and for trees and other organic matter produced in that time the radiocarbon date would be falsely young. Thus by calibrating with materials of historically known age it is possible to say whether the radiocarbon production was or was not abnormal at any given pasttime, over the intervals where we possess accurate historical records and thus can calibrate radiocarbon. Recently, and fortunately, this interval has been substantially increased by dendochronological tree ring dating of a particular Bristlecone Pine forest in the southern Sierra Nevadas where trees as old as seven thousand two hundred years have been dated both by radiocarbon and by tree rings and the resulting comparison gives a detailed curve for the appreciable deviations of the radiocarbon dates from the absolute dates, presumably due to variations in the production rates.

There are several factors which may account for the deviations. For example, the sun might increase its intensity and the solar wind which flows past the earth would shield away more cosmic rays and thus compete with strengthening variations in the earth's magnetic field. An intense study has been underway for some years to sort out these two -- the effects of the solar constant from those of the earth's magnetic field. The work is only partially completed. It involves many scientists in many many laboratories in many countries but it promises to give geophysics and astronomy new facts to work with.

We continue to work in this field with radiocarbon dating both as a geophysical as well as an archaeological tool and put it in this final report proudly, because the Air Force Office of Scientific Research helped us in the beginning days develop the method.

E. VENUS

Our principle work on the chemistry of the atmosphere of Venus has turned on the question of whether there can be oceans on this planet. At first we were persuaded that the high CO_2 content of the atmosphere fairly well demonstrated that liquid oceans and dry land cannot exist because $CaCO_3$ would precipitate as on earth until something like the present atmosphere concentration were reached.

On earth nearly all carbon is oxidized and occurs as carbonate with only a miniscule fraction remaining reduced as coal and oil. On Venus the situation would seem to be somewhat similar in that the total CO_2 (~100 atom) is commensurate with our limestone ($CaCO_3$) and dolomites ($MgCO_3$) beds, the ratio being about five or less. In the face of the large uncertainty about the extent of the terrestial limestone ($CaCO_3$) and dolomite deposits, we suggest that the geochemistry of the planet Venus and that of the earth are very similar. Taking this point of view, we then say the atmosphere and oceans are derived entirely from volcanos on both planets.

Why on Venus does CO_2 stay in the air? Why on earth does it precipitate as $CaCO_3$ and $MgCO_3$?

At first our answer was that it might be collected at the poles as giant ice caps (W. F. Libby. Science <u>159</u>, 1097-(1968) <u>160</u>, 1474-(1968) <u>161</u>, 916-(1968)). More recently (W. F. Libby. Marfa Texas Meeting, Astronomical Union, October 1969) we have come to realize that acid liquid oceans at the poles are not only conceivable but probable. The essential point is that the high temperatures of the equatorial land masses (400 to 500°C) make rivers nearly inconceivable and consequently there is no mechanism for transporting salts into the polar seas. This means that only volatiles and leachables from the sea bottom can contribute to polar sea salts. Experiment and theory both agree that this gives acidic oceans which are incapable of precipitating carbonates.

Of course, this does not prove there are oceans on Venus but it does keep the possibility alive.

Finally we have found a species of primitive algae which thrives on a CO_2 atmosphere in warm acidic water. Thus we think there is a possibility of life on Venus (The algae experiments are to be printed in the Marfa Volume.).

FINAL REPORT

January 15, 1969 to November 30, 1970

AF Grant AFOSR 1255-67 Mod. B and Mod. C

"The Chemistry of Materials under Extreme Conditions, Including Ionizing Radiation, High Vacuum, High Pressure, and High Temperatures"

I. Intramolecular Electrostatic Electron Traps (Jai Mittal, W. F. Libby. Nature 220, 1027-(1969)).

Sometime ago we suggested (W. F. Libby. J. Chem. Phys. 46, 399-(1967)) that certain compounds known as metal atom clusters could be explained as being bonded by electrons which sat in the clusters as though it were a box. Recently a new series of compounds, the cyclic perfluoro compounds, has emerged as important electron acceptors. It seems very unlikely that these molecules would have low lying vacant molecular orbitals. We therefore have suggested that the fluorine atoms in these compounds may constitute a negatively charged electrostatic wall within which the electron can fit. According to our theory the straight chain compounds should not trap electrons. It has been noted (L. A. Rajbenbach. J. Amer. Chem. Soc. 88, 4275-(1966); J. Chem. Phys. 47, 242-(1967)) that only cyclic perfluoro compounds trap electrons. We tested this experimentally further using the fact that Geiger counters are very sensitive to electron trapping. The point is that the electrons so trapped impart a negative charge to the trapping molecule which causes it to slowly be accelerated into the vicinity of the central wire long after the discharge should have been over. When it reaches the high field near the wire the electron is lost, by tunnelling presumably, and then proceeds to initiate another discharge. So it is characteristic of gases such as air in which the O_2 molecule is an electron trap that the Geiger discharge is repeated ad infinitum almost and this is a very sensitive test for electron trapping capabilities. Thus we showed that normal perfluoro butane could be added to 1 or 2% concentration to a good Geiger counter gas, (helium with about 1% by volume of isobutane at a pressure about one third of an atmosphere) without altering the discharge voltage time curve as seen on a fast oscilloscope. With cyclic perfluoro butane however the pattern consisted of a multitude of small repetitive pulses which would normally have been diagnosed as counter breakdown. Air gave a similar pattern due to O_2^- formed by electron capture.

This adds more evidence to the earlier evidence in the literature which had cited not only perfluoro cyclo butane but perfluoro methyl cyclohexane and a perfluoro cyclo octane. It would seem that a general principle is involved here and that with considerable certainty we can conclude that we are dealing with an intramolecular electrostatic electron trap. One of our group, Dr. Allen Minton, has done a quantum mechanical calculation indicating that this is reasonable in terms of the likely wave functions for fluorine and carbon in perfluoro carbons and the resultant electrostatic charges. However, a more sophisticated calculation is needed to complete the theory.

Fehsenfeld (J. Chem. Phys. 54, 438-(1971)) has reported that neither of the reactions $SF_6^- + C_4F_8 = SF_6 + C_4F_8^-$ nor $C_4F_8^- + SF_6 = C_4F_8 + SF_6^-$ are rapid. This observation indicates that there is a block to electron transfer of substantial magnitude. The intramolecularly trapped electron cannot be moved unless a minimum activation energy is available. This recalls an earlier discovery of analogous nature. Namely that highly hydrated ions are inhibited in electron transfer rates (ferrous and ferric Fe^{++}, Fe^{+++} in aqueous solution have an electron exchange lifetime of several seconds at room temperature) whereas the same ions when chelated or complexed to repel the aqueous environment as in $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ exchange in a few millions of a second. This was explained (W. F. Libby. J. Phys. Chem. 56, 863-(1952); and H. C. Hornig and W. F. Libby. J. Phys. Chem. 56, 869-(1952)) at the time as being due to the requirement that the electron transfer only after the two ions had achieved essentially identical geometries so the ferrous iron would not be left in a ferric environment and the ferric ion in a ferrous. We suggest that Fehsenfeld's observation has a similar explanation in that the ion will undoubtedly be larger than the neutral molecule and that transfer would necessarily leave the newly formed neutral swollen beyond its natural ground state size and the newly formed ion too small. Both must release energy to relax and thus will be trapped against the electron transfer process and require energy of activation.

II. Polymer Production in the Gamma Radiolysis of Methane in Liquid

Argon (W. F. Libby, Peter Hamlet, Jai Mittal, and Jeffrey Moss. J. Am. Chem. Soc. 91, 258-(1969); plus thesis research of Michael Sheridan as yet unpublished.)

γ radiolysis of solid methane produces a polymer which in the condensed phase has an average molecular formula $C_{20}H_{40}$ (D. R. Davis, W. F. Libby, and W. G. Meinschein. J. Chem. Phys. 45, 4481-(1966)). A study of the mechanism by using the ionization caused by electron transfer from methane to argon ions in liquid argon has been made. The γradiolysis of liquid argon-methane solutions shows that in mixtures containing as little as 0.15 mole % methane, a polymer averaging about $C_{22}H_{42}$ is produced with a G value of 0.084 or 1.85 for methane conversion to the polymer. These G values are calculated on the total energy absorbed by the solution and their large values indicate efficient electron transfer from methane to the argon ions. It had been suggested by us earlier that the polymer is formed by condensation of the dense blob of methane fragments which could be formed by the Auger electrons emitted following inner-shell ionization. Such ionization would be highly localized around the atom suffering inner-shell ionization and the ions on neutralization would produce a cloud of fragments which could be expected to react with each other to form the polymer and a distribution of lighter hydrocarbons.

In order to test this Auger Theory for polymer production by the γ - radiolysis of methane in liquid argon, a number of additional experiments have been performed.

Ethane, irradiated in concentrations of .15 mole % in liquid argon, gave the same polymer as methane, with a G value for loss of ethane to polymer of 2.0 compared to 1.9 for methane. Molecular weight, NMR, and IR spectra were very similar for the two polymers. Distillable (40°C, vacuum) hydrocarbons probably between C_{15} and C_{18} constituted 50% of the total product, the polymer 37%, and n-butane 8%. Methane was 2% and propane 1.6%.

Ethylene, which can polymerize by a chain reaction, would be expected to have a considerably higher G value for polymer production. It was found that $G(-C_2H_4$ to Polymer$) = 4.3$ in a 0.21 mole % solution of ethylene in liquid argon. The polymer is very similar to that produced from methane and ethane with the exception that about 1% unsaturation was seen in the NMR spectra. The polymer was 53%; $C_{15}= C_{18}$, 26%; methane 2%; ethane 5%; propane 3%, n-pentane 7% and cis-2-butene 6%.

Experiments with mixtures of the hydrocarbons in liquid argon have been made and the results are compatible with the ranking order according to ionization potential $CH_4 > C_2H_6 > C_2H_4$ i.e. in a solution of these three in liquid argon ethylene will be ionized and attacked first with ethane and methane following in order. The product distributions from the three ternary solutions are changed somewhat with respect to the binaries with slightly more of the branched and unsaturated compounds seen. However, the remarkable preference for producing light straight chain over branched hydrocarbons which is so marked in the binary solutions still holds for the ternary.

Our present view of the mechanism is as follows:

(1) Ionization of the solute with lowest ionization potential (IP) occurs by electron transfer to the argon ions and the subsequent ion molecule reactions and neutralizations produce fragments and radicals: H, CH_3, CH_2, CH and possibly others.

(2) The fragments and radicals react with the solute hydrocarbon but mainly with themselves and the products, with the exception of methane, ethane, and ethylene, precipitate and are removed to form a thin film floating on the surface of the cold liquid (87°K). Thus the products are formed within whatever short period of time, τ, precipitation requires. Normally in the presence of ionizing radiation super saturation would be unexpected.

The low yields of light branched hydrocarbons and light olefins indicate that there is some opportunity for these light products to act as electron donors and thus to be involved more than once in the disruptive ionization experience (The IP's of olefins and branched hydrocarbons are lower than those of normal straight chain aliphatics.). At our dose rate of 0.25 Megarad per hour and at an average yield of about ten carbon atoms carried into polymer and heavy hydrocarbons per 100 electron volts absorbed, the rate corresponds to a steady production of $8 \cdot 10^{14}$ precipitated C atoms per cc* per second, nearly independent of the concentration and nature of the solute light hydrocarbon. Thus, if the time of reaction and precipitation is τ seconds, the steady state concentration of reacting fragments is $8 \cdot 10^{14}\,\tau$ per cc for an average distance of separation of $\frac{1000}{\tau^{1/3}}$ angstrom units or about $\frac{300}{\tau^{1/3}}$ argon atoms apart. It is not difficult to estimate the diffusion coefficient for this system using the Eyring Method ($D = \lambda^2 \frac{kT}{h} e^{-\frac{\Delta E_{vap}}{3RT}}$ where ΔE_{vap} is the heat of vaporization ($\approx 25 \times 87$, according to Trouton's Rule) and λ is the mean separation of solute atoms, $3.4 \cdot 10^{-8}$ cm.) At 87°K, the boiling point of liquid argon which was the temperature of our experiments, this gives $3 \cdot 10^{-5}$ cm^2/sec. Thus the mean random walk diffusion distance in time τ, $\sqrt{2D\tau}$ is $8 \cdot 10^{-3}\sqrt{\tau}$ cm. or $2 \cdot 10^{5}\sqrt{\tau}$ solvent atoms. Thus it is clear that for τ values of one second or so abundant opportunity for reaction seems to be assured. The greater diffusion coefficient and abundance of atomic hydrogen seems to guarantee saturation in the products as observed.

The main polymer product is highly branched with CH_3:CH_2:CH ratios of about 1:1:1 as seen by NMR. This fact indicates that τ probably cannot be long enough for a second ionization to occur

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*Liquid argon has the density 1.8.

with the polymers because it most likely would tend to destroy the branched units as it does for the light hydrocarbon fractions. If we estimate that electron transfer is limited to something like 30Å or ten argon diameters, this being a reasonable figure for a tunneling transfer, a solute molecule's chance of being ionized is approximately $10^{-5}\ \tau$. This calculation also indicates that the lighter hydrocarbons produced probably precipitate less rapidly and have larger τ values and thus are purified of olefins and branched species by reworking.

Thus we conclude that the concentrated cloud given by the Auger Mechanism probably is not necessary to the polymer formation. The earlier work of Davis et al in solid methane apparently can be interpreted similarly since rotation and atomic hydrogen diffusion are known to occur in solid methane at 77°K, the temperature used.

It was recently reported that a polymer was formed by the action of $HFSO_3$ - SbF_5 on methane (George A. Olah, Gilles Kalpman, and Richard Schlossberg. J. Am. Chem. Soc. 91, 3261-(1969)). If that polymer was the same as that produced by γ - radiolysis, the mechanism in the Auger theory would be seriously in question. We repeated the experiments altering the pressure of CH_4, the concentration of $HFSO_3$ and SbF_5, the temperature, and the duration of reaction. A solid material was formed, but it was not a hydrocarbon. It was soluble in methanol and is believed to be chiefly SbF_3, formed by reduction of SbF_5 by the hydrogen liberated in the reaction. It has now been shown that a hydrocarbon polymer is not, in fact, formed in this system (Personal communication with Dr. George A. Olah).

Dr. Michael Sheridan received his doctorate degree for this work.

III. High Pressure Chemistry

(A High-Pressure Superconducting Polymorph of Cadmium Tin Diarsenide. H. Katzman, T. Donohue, W. F. Libby, H. L. Luo and J. G. Huber. J. Phys. Chem. Solids 30, Pergamon Press, 1909-(1969).

A High-Pressure Superconducting Polymorph of Cadmium Germanium Diarsenide. H. Katzman, T. Donohue, W. F. Libby and H. Luo. J. Phys. Chem. Solids 30, 2794-(1969).

The Heat Capacity of Indium Antimonide II. H. Katzman, J. Moss, and W. F. Libby (To be published).

Sintered Diamond Compacts Using Cobalt as a Binder. H. Katzman and W. F. Libby. (To be published)).

A superconducting polymorph of $CdSnAs_2$ prepared at about 60 kbar and 250 to 450°C has been retained at atmospheric pressure and room temperature. Its crystal structure is B1(NaCl) with a lattice constant of 5·679-5·695Å depending on the temperature at which it was prepared. The superconducting transition temperature is also a function of the preparation temperature and varies from 1·79° to 2·29°K. This new metal can be handled at room temperature but reverts between 25°C and 100°C.

In an attempt to further study the high-pressure behavior of $A^{II}B^{IV}C_2^{V}$ compounds, we turned to $CdGeAs_2$. The low-pressure semiconducting form of $CdGeAs_2$ has an energy gap of 0.53 eV and the chalcopyrite crystal structure with a =5.942Å and c/a = 1.889. We have found that under pressure it undergoes a phase transition to a more-dense super-conducting metal.

The samples were pressurized to 60 kbars and then heated to the desired temperatures. It was found that at least 300°C was needed in order for the samples to convert to the high-pressure form. Samples heated to lower temperatures showed no change from the as-cast material in X-ray diffraction patterns. The same high-pressure polymorph was formed at all temperatures in the 300°-800°C range in either boron-nitride or niobium capsules. After heating for approximately 20 hrs, the samples were slowly cooled at a constant pressure of 60 kbars and finally at room temperature the pressure was released. The product is a metastable metallic-looking form which we have been able to retain for months at room temperature and atmospheric pressure. The isolation and retention of similar metastable metals sometimes requires liquid-nitrogen temperatures (A. J. Darnell and W. F. Libby. Science 139, 1301-(1963)).

The density was measured to be 6.3 gm/c.c. corresponding a 23.4 percent reduction in volume with respect to the low pressure nonmetal. The lattice was tetragonal with cell constants, a=4,632 ± .008 and c = 5.307 ± .008 Angstrom units.

We have found that the molar heat capacity at constant pressure of InSb(II) between 80°K and 100°K is similar to that of β-Tin. This indicates that the lattice dynamics of $A^{III}B^{V}$ compounds and the corresponding Group IV elements are very similar in the metallic state. Similarities in the semiconducting forms have already been noted.

Our long six year search for a material with which to build a megabar (million atmosphere) press may have succeeded. Recently, Stromberg and Stephens (H. D. Stromberg and D. R. Stephens, Bull, Amer. Ceramic Soc. 49, 1030-(1970)) and H. T. Hall (H. T. Hall, Science 169, 868-(1970)) have reported synthesizing a polycrystalline diamond compact, carbonado, at high pressures and temperatures. We have discovered a method for sintering diamond powder (also at high pressures and temperatures) using cobalt as a binder, analogous to its role in cemented tungsten carbide. In comparison with the published reports (H. D. Stromberg and D. R. Stephens, Bull, Amer. Ceramic Soc. 49, 1030-(1970) and H. T. Hall, Science 169, 868-(1970)) on synthetic carbonado, it appears that this new material is easier to make and can be made in larger, more nearly uniform specimens. It is harder than cemented tungsten carbide and thus promises to be useful in many scientific and industrial applications as a replacement for it.

The starting materials were commercially available diamond powder of either 0-2μ, 1-5μ or 10-20μ size and cobalt powder of 0-5μ size and 99.9 + % purity. The powders were dried, weighed and mixed and then packed into tantalum containers for sintering. Pressure was generated in a piston-cylinder apparatus with appropriate modifications to allow us to work in the 60-65kb range (J. C. Haygarth and G. C. Kennedy, Rev. Sci. Inst. 38, 1590-(1967), J. C. Haygarth, E. C. Getting and G. C. Kennedy, J. Appl. Phys. 38, 4557-(1967) and J. C. Haygarth, H. D. Luedmann, I. C. Getting and G. C. Kennedy, J. Phys. Chem. Solids 30, 1417-(1969)). The samples were heated by means of an internal graphite heater and the temperature was monitored with a Pt-Pt 10% Rh thermocouple. The thermocouple emf was corrected for the effect of pressure (I. C. Getting and G. C. Kennedy, J. Appl. Phys. 41, 4552-(1970)) and the correction corresponded to an addition of 15°C to the temperature values obtained directly from the standard tables.

We chose 62kb as a convenient pressure at which to work and then determined experimentally the temperature range in which the sintering occurred. Samples had to be heated above the cobalt-diamond eutectic temperature, but not so high as to graphitize the diamonds. At 62± 1kb the samples showed partial graphitization when heated above 1610° ± 10°C. This temperature is well below the 1700°C which is reported as the diamond-graphite equilibrium temperature at 62kb by Bundy, et al (F. P. Bundy, H. P. Bovenkerk, H. M. Strong, and R. H. Wentorf, Jr., J. Chem. Phys. 35, 383-(1961)) and calculated by R. Berman (R. Berman, in In Physical Properties of Diamonds, R. Berman, Ed. (Clarendon Press, Oxford 1965), pp. 371-

393). Recently, John Haygarth (J. C. Haygarth, Private Communication.) has used piston-cylinder apparatus similar to ours to determine a diamond-graphite equilibrium point at 51.8± 0.2kb and 1335°C. Using this point and Berman's slope (R. Berman, in In Physical Properties of Diamonds, R. Berman, Ed. (Clarendon Press, Oxford 1965) pp. 371-393) of 30.4°C/kb, one can calculate an equilibrium temperature of 1645°C at 62kb which is much closer to the value that we find. Both Stromberg and Stevens (H. D. Stromberg and D. R. Stephens, Bull, Amer. Ceramic Soc. <u>49</u>, 1030-(1970)) and H. T. Hall (H. T. Hall, Science <u>169</u>, 868-(1970)) report working at higher temperatures at similar pressures to sinter diamonds, but they have no cobalt present to dissolve and reprecipitate the metastable diamonds as stable graphite and can therefore use higher temperatures. Below 1570°± 10°C, which is apparently the cobalt-diamond eutectic temperature at 62kb, no strong compacts were formed.

Therefore, 1590°C and 62kb were chosen as the sintering conditions. The samples were maintained at these conditions for about 20 minutes and were then cooled to room temperature in about an hour. As the samples were cooling, the pressure was slowly released in order to minimize the residual strains in the product but care was taken so that the samples were always kept within the diamond stability region.

The sintered samples were grayish, metallic looking, slightly ferromagnetic cylinders, ~6.3mm diameter and 2.5 to 9.0 mm long. Their properties were determined by X-ray diffraction, scanning electron microscope, electron microprobe, density and Knoop microhardness measurements.

The microhardness results are shown in Table 1 for various sintered samples.

TABLE 1

Knoop Microhardness of Various Samples

STARTING MIXTURE	KNOOP MICROHARDNESS (Kg/mm^2)
Co 20%*, Diamond 1-5μ	3000 ± 300
Co 20%, Diamond 1-5μ	2900 ± 300
Co 20%, Diamond 0-2μ	2900 ± 300
Co 20%, Diamond 1-5μ 60%, Graphite 20%	2800 ± 400
Co 20%, Diamond 10-20μ	2700 ± 100
Co 25%, Diamond 10-20μ	2200 ± 200
Co 16%, Diamond 1-5μ	2100 ± 200
Co 12%, Diamond 1-5μ	1600 ± 100
Ni 20%, Diamond 1-5μ	2200 ± 200
Tungsten Carbide - 15%* Co	1700 ± 50
Tungsten Carbide - 20% Co	1500 ± 50

*by volume (± 1%)

The values are averages for indentations over one or more polished cross-sections of a given sample. The relatively large deviations are a result of the difficulty in measuring the small indentations. The indentations were made with a force of 2kg and were about 100μ in length. Since the grain size of the samples is much smaller than 100μ these values are believed to reflect the hardness of the compact, not the hardness of only the diamonds. For comparison, the Knoop microhardness of diamond is 7000 kg/mm^2 (Handbook of Chemistry and Physics, 46th edition, R. C. Weast, Ed. Chemical Rubber Company, Cleveland, Ohio 1966 , p. F15.), cubic BN has a value of 3800 kg/mm^2 (General Electric Data Sheet on Boron Nitride, Ser. #SMD-1-B-6, Specialty Materials Department, Worthington, Ohio.) and cemented WC varies from 1400 to 1800 kg/mm^2 (Handbook of Chemistry and Physics, 46th edition, R. C. Weast, Ed. (Chemical Rubber Company, Cleveland, Ohio 1966), p. F15), depending on the amount of cobalt binder present. We tested two samples of cemented WC and the results are also shown in Table 1.

The samples containing 20% by volume of cobalt could be polished on fine-grained diamond wheels to a good metallic luster. Microscopic examination showed no signs of any diamond particles torn from the matrix during polishing. One could see the polished surfaces of the individual diamond grains indicating that they were indeed bound by the cobalt. Other indications of the strength of the material were that the polished surfaces could not be scratched with a tungsten carbide scribe and also that the Knoop diamond indentor required replacement after about 20 indentations into these surfaces.

The electron microprobe and scanning electron microscope showed that the diamond particles were well distributed in the cobalt matrix and that some diamond grain growth had occurred. A microprobe photograph of a sample containing 20% cobalt and starting with 1-5μ diamond powder is shown in Figure 1. In the photograph, the darker areas are cobalt and the lighter ones are diamond. There were some diamond grains with diameters as large as 6-8μ in the samples in which the starting diamond powder was 1-5μ. Also many diamond grains appeared to be fused together into clusters. These results suggest that the cobalt cleans the diamond surfaces of any adsorbed gases that might prohibit or retard grain growth or fusion, thereby making unnecessary the surface cleaning and degassing procedures described by Stromberg and Stephens (H. D. Stromberg and D. R. Stephens, Bull, Amer. Ceramic Soc. 49, 1030-(1970)). The grain growth very likely occurs when some of the diamond particles dissolve in the cobalt and then reprecipitate on other grains, indicating that the molten cobalt wets the diamond surfaces.

As can be seen from Table 1 the optimum amount of cobalt for "cementing" the diamond powder is 20% (± 1%) by volume. Microscopic examination of samples with less cobalt content showed regions of unwet diamond particles even after sintering for 2 hours

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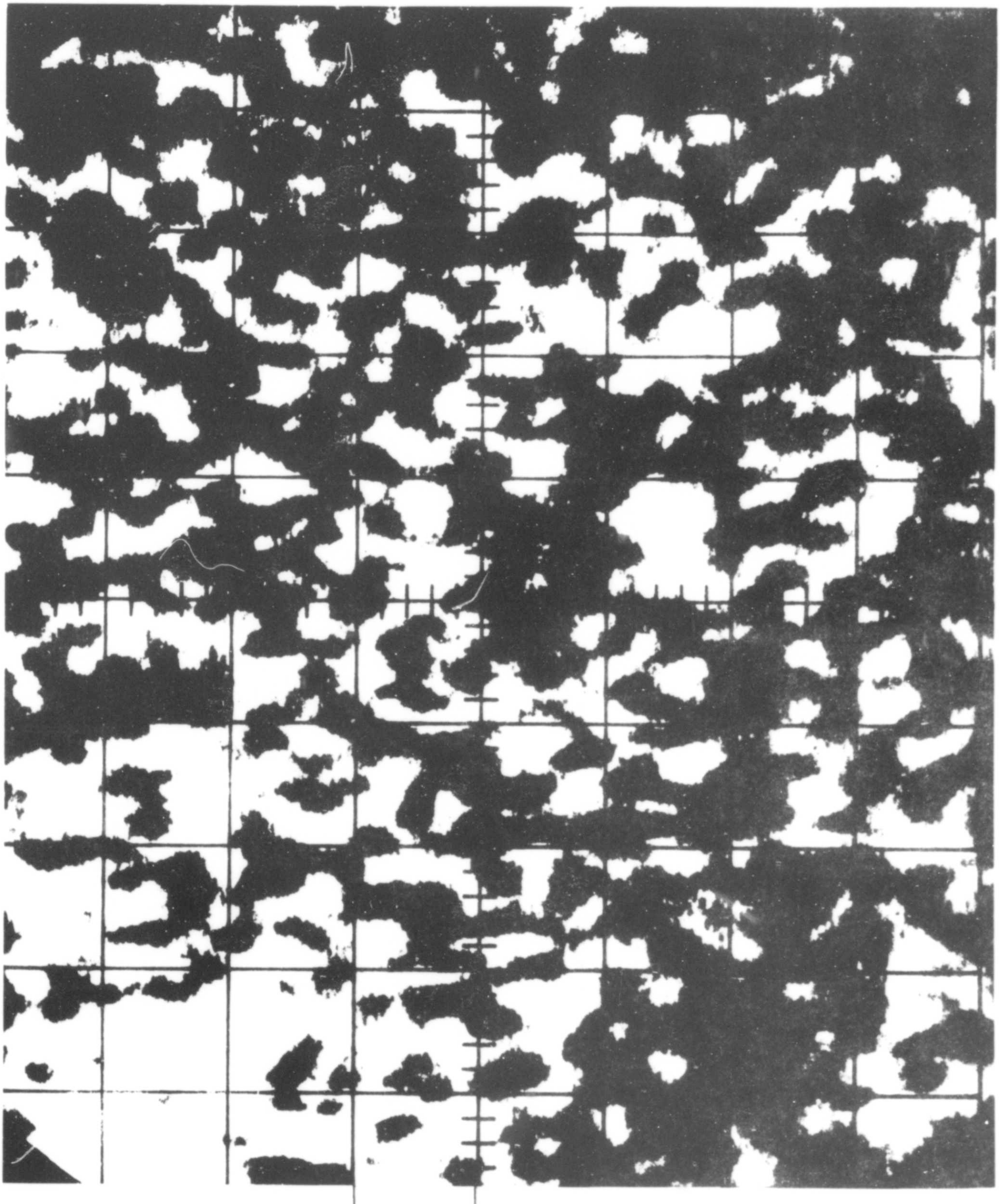


Figure 1

indicating that 20% cobalt is needed to wet all of the diamond surfaces. Samples with greater than 20% of cobalt are softer. An attempt to substitute nickel for cobalt under identical sintering conditions also led to a softer material.

The diamond particle sizes of 1-5μ and 0-2μ appear to result in harder compacts than the 10-20μ size particles. In one run we replaced ~ a quarter of the 1-5μ diamond powder with graphite powder and it was entirely converted to diamond under the sintering conditions leading to a large and non-uniform increase in the diamond grain size. It appears that more graphite can easily be substituted for diamond but that the resulting compacts may be a little softer due to the larger and less uniform diamond grain size.

The X-ray diffraction patterns on the samples with cobalt showed the presence of only fcc or β-cobalt which is stable above 450°C at atmospheric pressure (G. C. Kennedy and R. C. Newton, in Solids Under Pressure, W. Paul and D. M. Warshauer, Ed. (McGraw-Hill Book Co., Inc., New York 1963), pp. 176-177). No hcp or α-Co reflections were present. The density of each sample was found to be at least 98% of that of the theoretical density and most samples had densities greater than 99%.

In order to determine how well our new material would perform as a cutting tool and as a "truer" for grinding wheels, we did the following test. We weighed both our compact and a silicon-carbide, resin-bonded grinding wheel and used the compact to turn off some silicon carbide from the grinding wheel. We then reweighed both and determined a ratio of the weight losses. For a comparison, we also tested a commercial diamond truer and a piece of tungsten carbide under identical conditions. The weight-loss ratios for the diamond truer, our compacts with 20% Co and 1-5μ diamond powder, and tungsten carbide (10% Co) were 18,000:1, 9,500:1, and 1.5:1 respectively. Since the compacts with 20% by volume of cobalt contain only ~ 60% by weight of diamond, the compacts perform about 85% as well as pure diamond on a weight for weight of diamond basis.

In conclusion, we have synthesized a very promising new material which should have many commercial possibilities; for example, as a cutting tool or as a "truer" for grinding wheels. The procedure for its production is relatively simple and is economically feasible since inexpensive diamond dust along with graphite may be used as starting materials.

Dr. Howard Katzman has been granted his PhD for this work in high pressure chemistry.

IV. High Temperature Chemistry: Carbon Vapor (John Quinn,
Jeffrey Snapp and W. F. Libby)

Our earlier work on the reactions of carbon vapor from an electrically heated carbon rod with solid benzene (Reaction of Thermal Carbon Atoms. Jeremy L. Sprung, S. Winstein, and W. F. Libby. J. Am. Chem. Soc. 87, 1812-(1965)) has been followed by

the techniques of evaporation of a carbon filament with a pulsed laser. The results with H_2 gas were:
95% acetylene and 2.5% ethylene, 1.5% methane at 5 atmospheres or less and 68% acetylene and 26% ethylene and 6% methane at 20 atmospheres. These agree with Taki et al (J. Am. Chem. Soc. 91, 2153-(1969)) who got 95% acetylene with a similar technique. With the exploding wire technique Spangler et al (Chem. Comm. 1966 842-) showed that the acetylene produced in a 50:50 mixture of H_2 and D_2 is completely scrambled to give 25:50:25 for the amount of C_2H_2, C_2HD, and C_2D_2 thus strongly suggesting that the acetylene is formed from atomic carbon by $C + H_2 = CH + H$ and $CH + CH = C_2H_2$. In other words we are working with atomic carbon.

Our effect of pressure to convert to ethylene about one quarter of the acetylene can be understood by $CH + H_2 = CH_2 + H$ followed by

$$CH_2 + CH_2 \rightarrow H_2C{=}CH_2$$

Table I

$C + H_2$ at 5 atm or less

	% CH_4	% $H_2C = CH_2$	% $HC{\equiv}CH$
C + 1 atm H_2 # 1	1.8	2.8	95.4
C + 1 atm H_2 # 2	1.3	2.7	96.0
C + 1 atm H_2 # 3	1.5	2.9	95.6
C + 1 atm H_2 # 4	1.3	2.6	96.1

Table II

$C + H_2$ at 20 atm

	% CH_4	% $H_2C = CH_2$	% $HC \equiv CH$
C + 20 atm H_2 # 1	8.4	26.5	65.1
C + 20 atm H_2 # 2	4.4	28.2	67.4
C + 20 atm H_2 # 3	3.6	23.6	72.8
Avg	5.5	26.1	68.4

Further work has been undertaken with carbon vapor evaporated on to solid aniline held at 77°K. A heavy polymer is obtained with formula $C_{12}H_{12}O_{1.6}N_{1.2}$. It is soluble in 50% sulfuric acid at room temperature; has a brown color; its infrared spectrum is similar to that of aniline; its nuclear magnetic spectrum shows both aromatic and aliphatic protons; and the sulfuric acid solution is colorless. The molecular weight has not been measured as yet.

There are several possible formulas. The presence of oxygen must be due to reaction on exposure to air. Quinhydrone-like compounds would have the proper color and might be formed from metastable intermediates produced at the liquid nitrogen temperatures. Further research is underway.

V. Energy transport in large conjugated molecules-cobalt phthalocyanine. Mossbauer spectroscopy of Auger events (S. Hargrove, Amar Nath and W. F. Libby)

It has been shown through extensive researches (for example, A. R. Kazanjian and W. F. Libby. J. of Chem. Phys. 42, 2778-(1965)) that molecules are literally blown to bits as a consequence of Auger ionization. In an Auger event (the ionization of an inner shell electron), several electrons are ejected from the molecule and the resultant positive charges are driven to the extremities of the molecule due to electrostatic repulsion. Thus Coulombic repulsion virtually explodes the molecule, leading to the formation of several fragments. This picture, in which the molecule is blown to bits is pretty well established for gaseous substances. However, little is known about the phenomenon in solids.

The electron capture decay of a cobalt-57 atom necessarily triggers an Auger event resulting in the loss of several electrons from the molecule in which it is incorporated. The following 14.4 keV Mossbauer emmision from the product iron-57 conveys information regarding the chemical forms in which the daughter iron-57 atom is stabilized within 10^{-7} sec following electron capture. During this time complete charge neutralization occurs and several tens of electron volts of energy is deposited in the molecule. We had earlier found that the ethylenediamine tetraacetate, bis-salicylaldehyde triethylene tetramine, acetylacetone, and idenyl chelates fragment in a large majority of events, resulting in the formation of degraded ionic Fe^{2+} and Fe^{3+}. On the other hand, highly conjugated compounds such as cobalt phthalocyanine and Vitamin B_{12} appear to escape fragmentation in nearly 100% of the Auger events. Apparently, the large amount of excitation energy (about 30 to 40 eV) deposited in the molecule as a consequence of charge neutralization is very rapidly (in less than 10^{-13} sec) dispersed. It is a novel phenomenon.

We dispersed Co-57 labeled Vitamin B_{12} in foreign matrices like sucrose and polyethylene oxide in the proportion 1:100 by weight and observed their Mossbauer spectra. The Vitamin B_{12} molecule shows no sign of fragmentation as a consequence of Auger ionization. In view of the above, we conjecture that the molecule is getting rid of its 30 to 40 eV energy by optical emission rather than by phonon interaction. For this large amount of energy to be dispersed in less than 10^{-13} sec, one will have to assume emission of one or two energetic UV photons. We are presently trying to detect these photons by using a platinum coated spherical mirror to focus the emissions and photographic film as detector. This set-up is housed in a vacuum chamber as air absorbs these radiations. Vitamin B_{12} labeled with cobalt-57 is very expensive and we will be using labeled tris-dipyridyl Co(III) perchlorate instead, which is under preparation.

VI. Mossbauer Spectroscopy of Polymorphs of Iron (II) Phthalocyanine

(Steve Hargrove, Mary Hobson, Amar Nath and W. F. Libby.)

The Mossbauer spectra of Fe (II) phthalocyanine have been reported by Epstein (L. M. Epstein. J. Chem. Phys. 36, 2731-(1962)), Hudson (A. Hudson and H. J. Whitfield. Inorg. Chem. 6, 1120-(1967)), Drickamer (A. R. Champion and H. G. Drickamer. Proc. N. A. S. 58, 876-(1967)), Moss (T. H. Moss and A. B. Robinson. Inorg. Chem. 7, 1692-(1968)), Williams (B. W. Dale, R. J. P. Williams, P. R. Edwards and C. E. Johnson. J. Chem. Phys. 49, 3445-(1968)), and Gorobschenko (I. Dezse, A. Balazs, B. Molnar, V. D. Gorobchenko and I. I. Lukashevich. J. Inorg. Nucl. Chem. 31, 1661-(1969)).

Phthalocyanines are known to exist in two different crystal forms α and β but none of these workers mentioned whether they have studied the α or β polymorph. They apparently have assumed that since α and β polymorphs differ only in the packing of molecules in the crystal, that the two polymorphs are not expected to exhibit any differences in their Mossbauer spectra. Our preliminary investigations show that this assumption is incorrect, and we get slight differences in the quadrupole splittings and isomer shifts. We attribute these small differences to the interaction of the iron atom with the nitrogen atoms, in the octahedral positions, belonging to the two neighboring molecules in the case of β-polymorph. In α-polymorph the nitrogen atoms of the neighboring molecules are not situated just above and below the iron atom but further removed.

Over and above these finer differences in the spectra which we have observed, Drickamer and we have found an extra pair of quadrupolar split peaks which we suspect arise by virtue of adsorbed oxygen which is absorbed much as in hemoglobin the α form doing so more tenaciously than the β. Drickamer apparently also observed this extra pair of peaks in the α-polymorph.

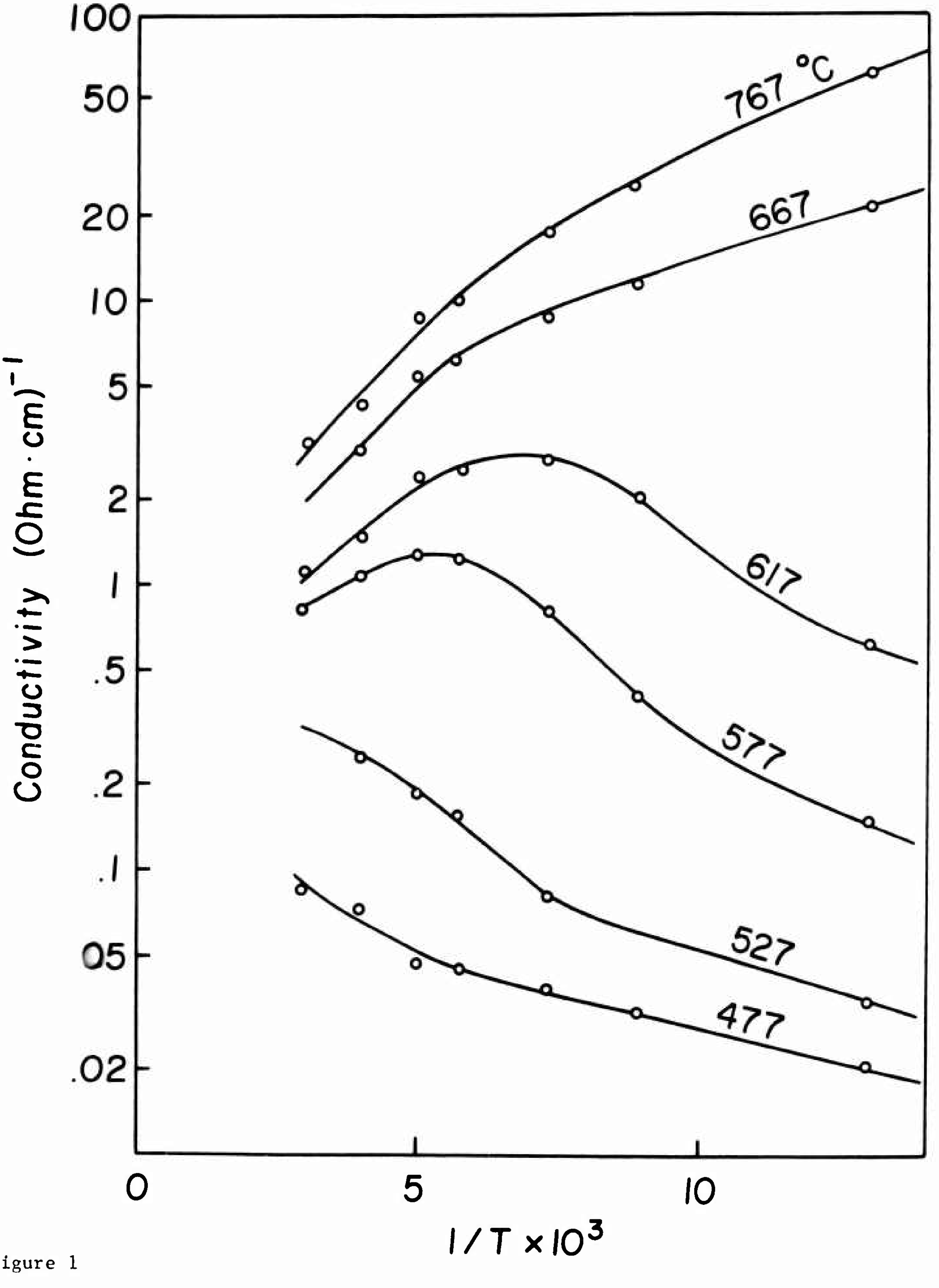
VII. Catalysis by d Band Solids (W. F. Libby, Simon Aegerter and Paul Feng)

I. Introduction

The fact that most heterogenous catalysts are transition elements or compounds suggests that the d electrons are involved in a critical and essential way in catalysis. Recently it has been found that the tungsten bronzes (M_xWO_3 where M is nearly any metal including hydrogen and x is some number less than unity) are active fuel cell catalysts (B. Broyde. J. of Catalysis 10, 13-(1968)). It has been known for some time that they catalyze the ortho-para hydrogen reaction and the hydrogen deuterium exchange (F. T. Jones and E. M. Loebl. J. Phys. Chem. 73, 893-(1969)). These is another family of transition element oxides which behave similarly to the tungsten bronzes in many physical aspects so we have tested them for catalytic activity and we find that they indeed are active. The family is the perovskites, e.g. $SrTiO_3$, which have cubic lattice with the Ti atom at the center, Sr. on each corner, and an oxygen at the center of each face. In the tungsten bronzes the structure is the same except there are no atoms on the corners except when doped (x > 0). The basic structure is that of WO_3 and doping introduces atoms such as Na on the corners. As the amount of Na is increased the crystal becomes metallic and nearly any element from hydrogen upward in the electromotive force table will serve to dope WO_3 and give a metallic system.

Most of the phenomenology of the tungsten bronzes and perovskites are to be understood probably, in terms of the empty d bands made by the tungsten or titanium d orbitals. These bands avidly take electrons from the donor doping metals turning the crystal blue and imparting metallic character.

$SrTiO_3$ behaves very similarly to WO_3 except that hydrogen is the best dopant. The extent of doping rises with temperature and the blue color imparted and the metallic conductivity similarly increase. About the lowest practical doping temperature for a crystal a few millimeters on edge is 500°C. Most of our tests have been restricted to the range 500°C to 1000°C. Fig. 1 shows the conductivity vs doping temperature. Whereas in the case of WO_3 the doping atom can easily be accomodated on the corners of the structural cube, we are forced to suggest lattice imperfections or the oxide ions as the proton sites for $SrTiO_3$. The diffusion coefficient for hydrogen in $SrTiO_3$ is low but definitely measurable (we measure it to be $0.135e^{-17,250/RT}$ cm^2/sec^2), corresponding to about 1 micron in one day at room temperature, and thus the proton must have to sit in a hole of some depth, about 0.8 e.v. The



100
50
20
10
5
2
1
.5
.2
.1
05
.02
Conductivity (Ohm·cm)$^{-1}$
0
5
10
1/T × 10^3
767 °C
667
617
577
527
477

Figure 1

technique used for measuring the diffusion coefficient and its temperature coefficient was to observe the conductivity of a single crystal of thickness d (cm), much smaller than its length or width. Gold contacts were welded to the flat faces. The temperature was elevated to a constant value in an inert atmosphere and the conductivity measured at a fixed voltage. The gas supply then was switched from argon to hydrogen and the increase in conductivity measured versus time. As long as the diffusion depth $\sqrt{Dt}$ is small compared to d the conductivity should change as $\sigma = \frac{2\sigma_o\sqrt{Dt}}{d}$

σo = conductivity at equilibrium
D = diffusion constant
t = time of exposure to H_2 (seconds)
d = crystal thickness (cm)

The temperature coefficient was obtained by using various temperatures.

Boudart (M. A. Vannice, M. Boudart, and J. J. Fripait. J. of Catalysis 17, 359-(1970) recently has measured the analogous quantity in hydrogen doped WO_3. He obtained a lower activation energy. This seems reasonable in view of the free corners in the WO_3 lattice.

As an alternative one might imagine oxygen vacancies as accomplishing the doping. (The electrons so freed then occupying the d bands.) Our evidence favors hydrogen intrusion but the matter requires further investigation.

Hall effect (D. Parker and J. Yahia. Phys. Rev. 169, 3-(1968);

H. P. R. Frederikse and W. R. Hosler. Phys. Rev. 161, 3-(1967); O. W. Tufte and P. W. Chapman. Phys. Rev. 155, 3-(1967)) measurements place the number of electrons per c.c. at about 10^{18} for a substantially doped crystal say at 700°C.

The d bands in $SrTiO_3$ lie close in a nearly continuous set. The absorption spectrum (Optical Density vs Wave legth) for a crtstal 0.2 mm thick doped with hydrogen at 700°C to 10^{18} per cc given as Fig. 2 shows a strong absorption in the infrared trailing off into the visible red leaving the blue color. Thus we see that the band is at most 1.5 e.v. wide. In the undoped faintly yellow crystal, the optical window stretches from 0.4μ to 6μ whereas in the doped the crystal is black from 0.65μ to 10μ. The strongest absorption occurs at about 2μ and below corresponding to energies of 1/2 e.v. and less in a continuum. Since each Ti gives 5 3d orbitals and each Sr 5 4d's we have two sets of d band each of which can be broken into two subsets with the cubical symmetry raising the $x^2 - y^2$, and z^2 orbitals above the diagonal xy, yz, xz by some amount. Apparently this splitting in the lower band system cannot exceed 1.5 e.v.

We tested this conclusion by goldplating opposite faces of a single crystal of $SrTiO_3$ mm thick applying 300 volts potential between the faces and exposing to both X and gamma rays. In both

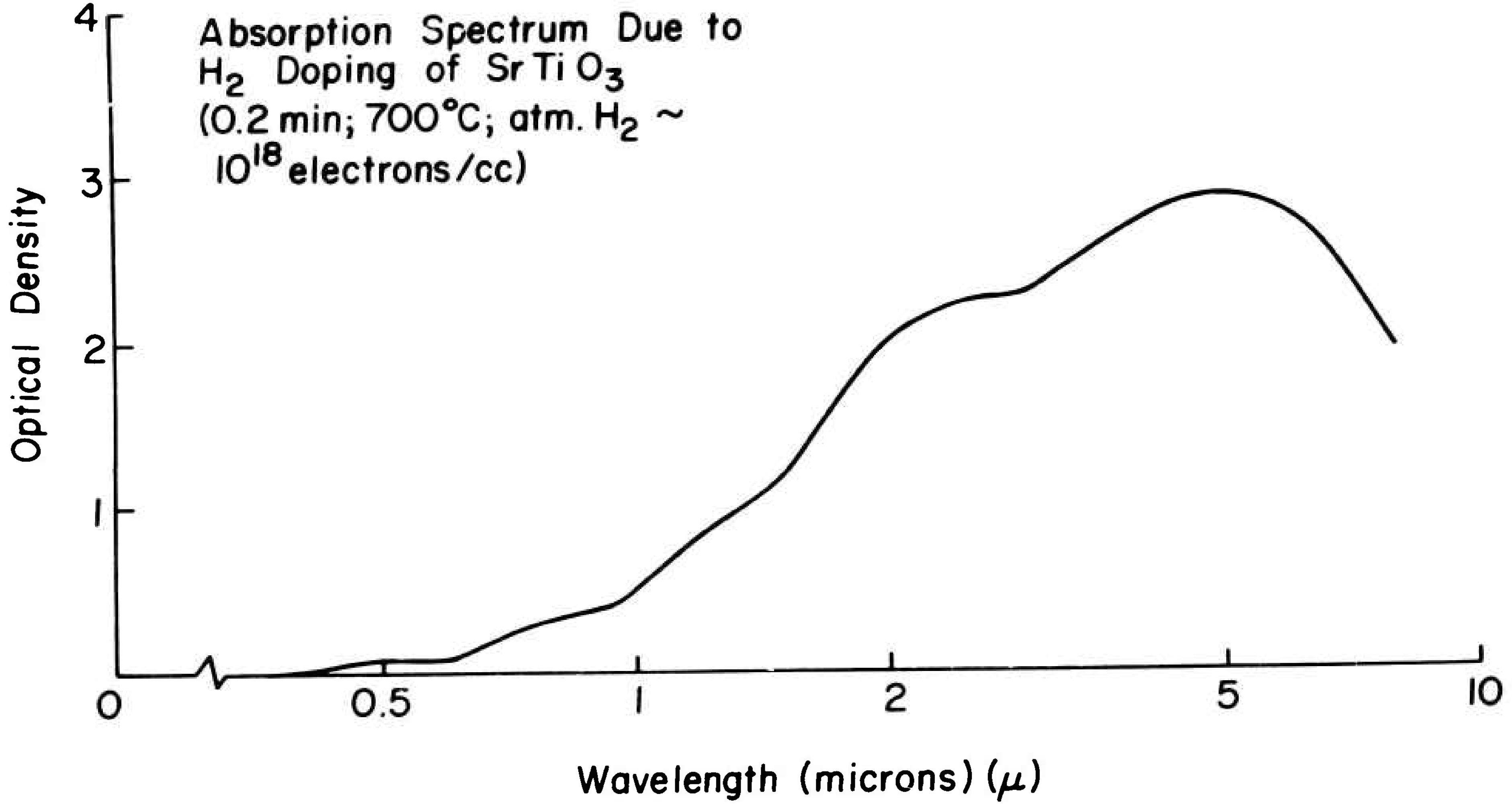

Absorption Spectrum Due to
H_2 Doping of $SrTiO_3$
(0.2 min; 700°C; atm. H_2 ~
10^{18} electrons/cc)
Optical Density
4
3
2
1
0
0.5
1
2
5
10
Wavelength (microns) (μ)

Figure 2

cases a current directly proportional to both the radiation flux and the applied voltage was observed. An ionization chamber of high fidelity and capable of dealing with very high radiation fluxes thus was found. Presumably undoped WO_3 would do as well. $SrTiO_3$ is known to be a solid most resistant to radiation damage, probably because of the curative properties of the empty d bands for restoring electrons to positive centers, much as in metals which characteristically are resistant. It is used for handling the radioactive isotopes Sr^{90} which in this form has a self dose of about four million megarad per year.

In further application of our H_2 doping theory -- namely that the H atoms enter the crystal rather than O atoms leaving to make water -- we heated a previously hydrogen doped crystal in air and then sliced it into two symmetrical pieces. The heating in the air was carried to the point that a colorless layer some 3 mm thick underlay all exposed surfaces. Then the sliced pieces when gold plated on opposite faces constituted a diode with a large discrimination in the two directionsof potential. Fig. 3 gives the data. If the potential is positive on the doped side current can flow because the protons can hop into the depleted volume. With the opposite direction the electrons have to travel by themselves and thus create an unrelieved space charge barrier.

An attempt was made to locate the protons in doped $SrTiO_3$. A fresh $SrTiO_3$ crystal 860μ thick was heated in water vapor for

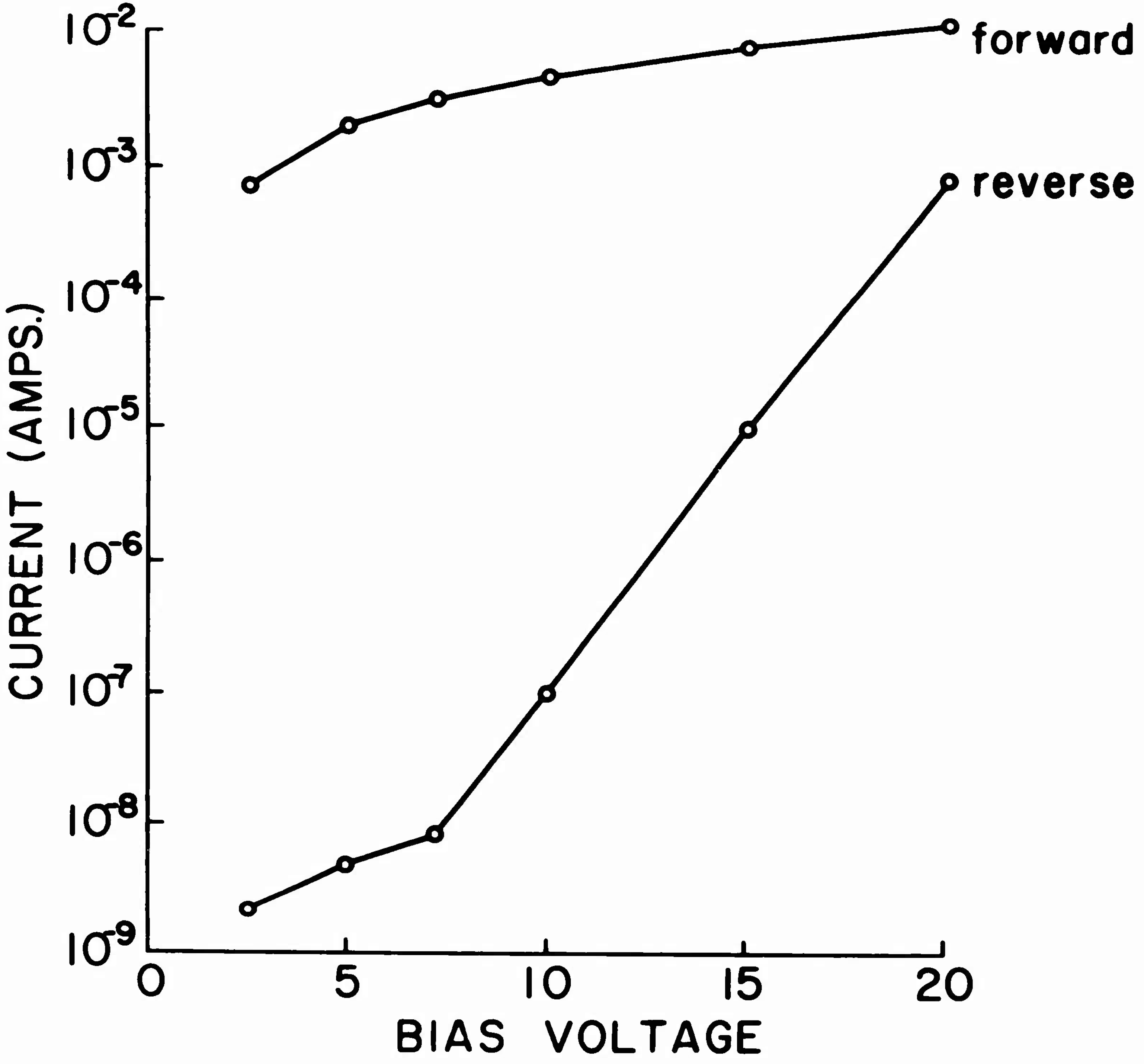

10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
CURRENT (AMPS.)
0
5
10
15
20
BIAS VOLTAGE
forward
reverse

Figure 3

one hour at 760°. The IR spectrum showed a definite signal at 3500 cm^{-1} with an amplitude of about .035 O. D. units (optical density). The crystal then was ground to 500μ thickness. This reduced the absorption to 0.019 O. D. The crystal then was heated for one hour at 760°C in D_2O vapor. The OH band disappeared ($<$ .003 O. D.) and the OD band at 2580 cm^{-1} now showed .015 O.D. units. The crystal then was ground to 400μ and the OD signal was about the same. The data are give in Table I. They prove that hydrogen enters the interior of the crystal and the protons sit on the oxide ions to make hydroxide ions. The grinding away of the surface diminished the absorption proportionally to the thickness decrease showing that the concentration was uniform throughout the crystal and it was not surface adsorption.

Table I

WATER INCURSION INTO $SrTiO_3$ LATTICE

Treatment	cm^{-1}	OD
$SrTiO_3$ 860μ thick	2580	0
heated in 1 atom H_2O one hour at 720°C	3500	.035
Ground above to 500μ with SiC, Al_2O_3 and H_2O.	2580 3500	0 .019
Above heated in D_2O 1 hr at 720°	2580 3500	.015 0
Same ground to 400μ	2580 3500	.015 0

An attempt (by Dr. E. R. Chock) was made to detect the proton NMR in an hydrogen doped crystal. None was found but the sensitivity probably was too low. Further attempts are underway.

II. Catalytic Data

A. Catalytic Activity of $SrTiO_3$

Now if H_2 molecule can be torn apart and absorbed in $SrTiO_3$, why cannot an H atom be removed from a hydrocarbon and the resultant free radical be left on the crystal surface to react?

Thus we were led some time ago to experimentally test for catalytic activity. Our results are affirmative so we add the perovskites to the tungsten bronzes and other transition element compounds as a new family of catalysts. We suggest that all solids with incompletely filled d bands may be active to varying degrees.

$SrTiO_3$ and $BaTiO_3$ have been found to be active isomerization, hydrogenation, hydrogenolysis, synthesis and cracking catalysts. In Table II we give data for a $SrTiO_3$ sample of about 2 to 3 m^2/gm surface area with contact times of one third second. At about 100°C isomerization of c-2-butene to t-2-butene and butene-1 are observed with no other reactions. The gas mixture used contained two percent c-2-butene in hydrogen at 1 atmosphere total pressure. The solid was 0.3 gms spread on a supporting glass frit separately shown to be inactive catalytically. Assuming the packing porosity to be about 1/2 and the mean density to be 2 the pore volume is calculated to be .07 c.c. At the flow rate used of 1/5 c.c./sec. the residence

TABLE II

$SrTiO_3$ as Catalyst

Preliminary Data for c-2-Butene in Excess H_2

(0.3g of ~ 3m^2/gm; 1/3 second)

° T(c)	c - 2 Butene	t - 2 Butene	1 Butene	n Butane	Methane & Ethane	Propane	Butadiene	2 -Me Butene 2
~100	96%	2.8%	1.0%	0%	0	0	0	
~200	57%	33%	10%	0.3%	0	0	0	
~300	45%	34%	20%	0.6%	2%	0.3%	0	
~400	31%	31%	20%	4.1%	12%	2.0%	0.5%	0.3%

Note: Some coking occurs above 200°C

time, t, in the powder was 1/3 second. Assuming a unimolecular law the mean lifetime τ for the c-2-butene molecule to isomerize while in the catalyst pack at 100°C is found to be 8 seconds. At 3 m^2/gm the amount of c-2-butene passing through the pack at any instant is about one hundredth mono-layer. At higher temperatures the isomerization equilibria appear to have been completely established during the 1/3 second contact time.

At 200°C .32 percent of the isomeric olefine mixture is reduced to n-butane. Thus taking the equilibrium olefines as a homogenous reactant, the unimolecular mean time for reduction would be 100 seconds. At 300°C this unit time for reduction was seen to drop to about 50 seconds and at 400°C to 7 seconds, with cracking and hydrogenolysis to form lighter hydrocarbons occurring as well. Some 16% of the olefine was converted to ethane (and possibly methan Our chromatograph would not separate them.) and some 2.5% to propane. Some heavy synthesis occurred to convert some 0.3% to 2 Me-butene-2 or c or t 4 Me-butene-2 and some 0.6% butadiene or 3 Me-pentene. These heavy peaks remain to be completely identified. Coke also was observed as a darkening of the solid reversible in air.

The solid was prepared by mixing an alkaline solution of Sr^{++} with (NH_4OH or dilute NaOH) with an hexane solution of titanium tetra isopropyl in a nitrogen atmosphere with rapid stirring and drying in hydrogen at about 150°C.

Extended (36 hours) exposure to H_2 at 450°C appears to inactivate the catalyst completely. A rinse with aqueous 6NHCl at room temperature followed by thorough washing and drying appears to restore most of the activity.

$BaTiO_3$ shows similar activity. The substitution of argon for hydrogen has dramatic effects. Table III gives some data for catalyst dried at 200°C in argon and then used first with argon as diluent gas followed by hydrogen as diluent.

Table III

Effects of Hydrogen vs Argon on

Catalytic Activity of $SrTiO_3$ to Produce Methane

(1 gm; flow rate 1cc/min)

Temperature °C	Methane Yield With Argon	Methane Yield With Hydrogen
160	1.7%	0.09%
300	2.0%	0.10%
350	2.1%	0.20%
400	2.5%	0.40%

B. Catalytic Activity of $LaCoO_3$

Recently (D. B. Meadowcraft. Nat. 226, 847-(1970)) an exciting new example of a strongly catalytically active partially filled d banded solid, $LaCoO_3$, was described. It appears that this material may rival platinum for the reduction of O_2 in batteries and fuel cells. This raises the hope (W. F. Libby. Science, to be published) that a practical catalyst for automobile exhaust may be derived from the enormous numbers of solids belonging to the general family of partially filled d banded solids. Tests with our standard 2% c-2-butene in H_2 at 1 atmosphere gave the remarkable results in Table IV showing substantial reduction at room temperature.

III Discussion

There seems to be little doubt that the d bands in $SrTiO_3$ are very attractive to hydrogen and will strip it from H_2, H_2O and hydrocarbons to put at least some of the protons on oxide ions making OH^- and thus create a neutralizing charge to allow the electron to go into the d band and roam throughout the doped region. These dissolved H atoms then have a certain fugacity which allows them to react with olefines and surface adsorbed radicals to hydrogenate and split them into smaller hydrocarbons by hydrogenolysis. The heats of adsorption for olefines and hydrocarbons were found to be approximately 0.8 e.v.

The dissembly of hydrocarbon apparently can continue to the coking stage with the hydrogen being removed and dissolved in the crystal. Our most active powders normally coked perceptibly at 400°C in a few hours.

Further work should make quantitative measurements of our qualitative observations to date.

TABLE IV

Catalytic Activity of $LaCoO_3$

(1.7 grams of 1.4 square meters per gram)

- \+ indicates peak(s) present but not computed
- * indicates peak areas estimated
- \# identification uncertain
- o overlapping peaks

T°C	Flow Rate cc min^{-1}	Mole Percent								
		CH_4	C_2H_6	#C_2H_4 or C_3H_8	n-C_4H_{10}	1-butene	trans-butene	cis butene	butadiene	
25	feed gas	-	-	0.002	1.133	0.888	3.727	94.246	-	
25	4.5 - 6.6	-	-	0.004	4.033	2.455	6.803	86.703	-	
50	4.5	-	-	0.003	8.687	5.983	12.992	72.333	-	
75	4.5	-	-	0.001	13.144	6.242	14.590	66.021	-	
100	6.0	-	-	0.005	21.770	10.462	25.271	42.467	-	
200	6.6	0.782	0.403	*1.960	69.024	0.777	9.152	17.897	+	
300	5.7	°23.013	*°7.378	8.987	36.657	°0.932	4.677	18.349	+	+
375	8.4	°36.400	°16.158	10.535	21.550	°2.370	4.895	8.086	+	+

Sinfelt (J. H. Sinfelt. Catalyst Reviews 3, 175-(1969)) speaks at length of the role of the d character of the metallic bond in correlating the specific activity of metallic catalysts for hydrogenolysis of ethane to give methane.

It is clear that our system essentially disassembles c-2-butene and puts it together in various ways adding hydrogen in some. Actually it is decidedly unclear as to whether one atmosphere (the pressure used in our experiments) of hydrogen is serving to poison. Further work at lower H_2 pressures is needed to see whether the well known (J. H. Sinfelt. Catalyst Reviews 3, 175-(1969)) fact that many hydrogenolysis catalysts show increased activity at lower hydrogen pressures in true here. It seems likely to be so from our present meager knowledge.

On the other hand Jones & Loebl (F. T. Jones and E. M. Loebl. J. Phys. Chem. 73, 893-(1969)) report that the sodium tungsten bronzes Na_xWO_3 $(0 < x \leq 1)$ have their maximum activity when x is about 0.7 and that hydrogen is not a poison under these conditions. They were studying different reactions, however, the ortho-para conversion of H_2 and the H_2, D_2 exchange.

VIII. Tritium Hydrology (J. S. Leventhal and W. F. Libby. "Tritium Fallout in the Pacific United States". J. Geophys. Res. 75, 7628-(1970)).

Tritium has been measured in rain and surface waters since the last large atmospheric nuclear explosions in 1961-1962. In

1963 on the Pacific Coast the concentrations found were high (natural tritium would amount to about 2 Tritium Units in these regions). Over the years following the levels fell (cf W. F. Libby. J. Geophys. Res. 68, 4485-(1963) J. S. Leventhal and W. F. Libby. J. Geophys. Res. 73, 2715-(1968)) as mixing with surface waters took place.

A special study was made of Crater Lake because its hydrology is so well known. It is a nearly circular body about 9 km. in diameter with steep walls 180 to 300 meters high above the water. These steep walls define the basin. The lake is very deep, 325 meters average. The area of the lake itself is 53.2 km^2, and of the drainage area 14.6 km^2. The average annual rainfall is 1.75 meters giving a total input of $1.1 \cdot 10^8$ m^3 with evaporation rate of $0.32 \cdot 10^8$ m^3 and seepage loss of $0.8 \cdot 10^8$ m^3.

Thus knowing the tritium content of the rain it was possible to calculate the total for the lake and by periodic measurement of the concentration of the surface water to determine the mixing rate. The result was a mixing time of about four or five years taken as an exponential dilution of the surface water. In 1967 the concentration was only slightly above that expected for complete stirring.

VIII. Students

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R. Protsc
H. Cheng
P. Farrell
M. Zetin
J. Severeid
H. Chn

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