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High Pressure as a Basic Variable in Modern Science and Technology

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High pressure has become a basic variable in many areas of science, from Geophysics and Astrophysics through Chemistry and Physics to modern Biology. There are two general ways in which high pressure experimentation or theory can be used to increase our understanding of nature. In the first place, it can be applied to understanding the behavior of matter intrinsically at high pressure or to obtain states of matter or chemical combinations which are not obtainable or not stable at atmospheric pressure. In the second place, one can study the effect of pressure on the electronic states and physical and chemical properties of matter to provide a better characterization of these states and properties or to test theories concerning properties and processes occurring at one atmosphere and thus to predict what one might expect to observe under ordinary conditions by changing the physical or chemical environment. The first aspect contains many of the most novel and exciting results, but it is this second category of problems in particular which has made high pressure a variable of such broad importance to science, both pure and applied.

It is my intention to outline here some examples of each of these aspects of high pressure research, with a degree of emphasis on those parts where we have made contributions in our laboratory.

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The first category of problems includes much of experimental solid earth geophysics where major efforts are devoted to establishing the chemical combinations and crystal structures present in the mantle of the earth-- experimental technology is now approaching the point where one can also obtain firm information about the nature of the metallic core. In high pressure astrophysics one is interested in conditions in the interior of the larger planets and of stars. At present the relevant conditions of temperature and pressure are not experimentally available, so that most of the work is based on theory or gross extrapolation of experiment.

Pressure can also affect the equilibrium and kinetics of chemical reactions. Commercially practical reactions are carried on at pressures ranging from a few hundreds of atmospheres for polymers to 50,000 atmospheres or higher for diamond and cubic boron nitride. Processes like hydrostatic extrusion for improving the properties of metals occur at pressures up to several thousand atmospheres.

The area of electronic transitions has been one of great activity in physics since 1945, and more recently has had an impact on chemistry. With increasing pressure one decreases interatomic or intermolecular distance and thus one increases overlap of electronic wavefunctions on adjacent atoms or molecules. Since different electronic orbitals will, in general, have different spatial properties, they are then perturbed to different degrees. One possible consequence is that, under some circumstances the relative shift in energy of two states can be sufficient to establish a new ground state for the material with novel physical or chemical properties. Much of the work in our laboratory over the twenty year period up to the early 1970's was devoted to studying these

transitions which can have a wide variety of manifestations. Here we mention a sampling selected to give some notion of the diverse possibilities.

Alkali metals like cesium and rubidium become transition metals at high pressure as the conduction band takes on the character of the atomic d electrons. Divalent metals like calcium and strontium become semiconductors under sufficient pressure. On the other hand, pressure induced insulator (or semiconductor) to metal transitions are observed in a variety of materials. In iodine, the thallous halides, and in the crystals of some large aromatic molecules these transitions occur with no apparent discontinuity of structure or resistivity. In silicon, germanium, and related III-V and II-VI compounds the semiconductor-metal transition occurs with a large discontinuity in resistivity and a well established change of structure, while in sulfur and selenium the discontinuity in properties is evident but much smaller. Particularly interesting insulator-metal transitions have been observed in doped transition metal oxides and rare earth chalcogenides. There has been much speculation about metallic hydrogen. At present, theory would say that a transition to a metallic state should occur between three and four million atmospheres. Whether or not the metallic phase would have unusual superconducting or other useful properties is still conjectural.

There are also electronic transitions of considerable interest to chemists. In a wide variety of electron donor-acceptor complexes involving aromatic molecules at high pressure one can thermally occupy the excited state involving transfer of an electron from donor to acceptor. Greatly enhanced chemical reactivity and new types of organic structures result.

In a number of transition metal complexes, especially those of iron bound to ligands of low electron affinity, one observes through high pressure Mössbauer resonance, a reduction of the ferric ion by thermal electron transfer from the ligand. The probability of this transfer depends on the relative location and shift in energy with pressure of the highest (nonbonding) ligand orbitals with respect to the metal d levels. A second type of electronic transition observed in these complexes is a change in the spin state of the transition metal ion caused by its increased interaction with the ligand orbitals under high compression.

Some of these pressure induced electronic events mirror changes that can be brought about at one atmosphere by modifying the character or nature of dopants in a crystal, the type of ligand bound to a metal ion, or the chemical nature of a molecule in a complex, and thus the study of these electronic transitions has implications for atmospheric pressure physics or chemistry. In this way it provides a natural transition to the second aspect of high pressure science, where high pressure is used primarily to increase our understanding of atmospheric pressure processes. A few examples of this second category of problems are outlined below.

One of the more active areas concerns the effect of pressure on chemical reaction rates. From these measurements one can extract the change of volume of the system upon formation of the transition state. Using this information it is frequently possible to select unequivocally among several possible reaction mechanisms.

The investigation of the mechanism of rotational and translational motion of molecules in condensed systems, especially in liquids is also important. To make critical tests of the theories of such motions in these media, it is

necessary to measure the temperature coefficient of the processes under study at constant density, preferably at a series of densities. High pressure NMR and Raman studies have provided the information necessary to establish the areas of validity and limitations of modern theories.

Our work has concentrated on the characterization of electronic states and electronic transitions as well as on testing of theories of electronic phenomena. Our early work on optical absorption provided basic tests of ligand field theory widely used in inorganic chemistry as well as of some aspects of Mulliken's theory of donor-acceptor complexes. The Mössbauer resonance measurements mentioned above provided a direct confirmation of van Vleck's analysis of the effect of ligand field strength on the spin state of iron. High pressure investigations of the states of iron have provided useful analogies for understanding the behavior of metal catalysts dispersed on a supporting medium. Similarly, high pressure magnetic measurements have contributed to the understanding of the magnetic fields in alloys and in magnetic insulators.

Most recently we have been engaged in high pressure studies of luminescent spectra, efficiencies, and lifetimes. This work, in its early stages, has provided critical tests of theories of radiationless transition rates important to understanding phosphor efficiency, as well as of energy transfer processes central to fluorescent lighting efficiency, laser performance, and photochemical processes such as photosynthesis. We have also studied the effects of pressure on intersystem crossing and excimer formation in various organic phosphors. Many luminescent and photochemical processes in solution appear to depend strongly on solvent viscosity. The usual methods of varying this parameter, changing temperature or solvent composition, introduce a

variety of additional perturbations on the system. With pressure it is possible to vary the viscosity of a given solvent over several orders of magnitude at constant temperature, which permits an unequivocal separation of viscous effects from thermal or chemical effects.

Finally, high pressure luminescence measurements on protein molecules in solution have revealed considerable new evidence concerning changes of protein conformation and the denaturation process. High pressure investigations of the kinetics and mechanism of processes in biologically important systems have been significant in the understanding of tunneling in protein reactions, so the pressure parameter is becoming extensively used in a number of biophysical laboratories.

Of necessity, this has been only a brief outline of some of the ways that pressure has been important to the understanding of nature. The presentation has been like a mural painted with a broad brush, but it is hoped that the resulting picture is sufficiently clear and sharply focused to convey a strong impression of both the power and breadth of pressure as a parameter for understanding the structure of matter.

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