High Pressure Chemistry of the Elements

Dean Goedde Literature Seminar February 27, 1997

Significant chemical changes occur in matter upon the application of pressure. As pressure reduces the distance between neighboring atoms in a solid, orbital energies increase due to electron-electron repulsion. At moderate pressures (<100 kbar; 1 bar ~ 1 atm) this effect is manifested by the formation of alloys between potassium and silver, which does not occur at ambient pressures.[1] Higher pressures (a few kbar) can induce more dramatic changes, especially in K, Rb, and Cs.[2] The heavy alkali metals have a half-filled valence s band with an empty d band lying at a slightly higher energy. It is found that as pressure increases, energy of the s band rises at a faster rate than does the energy of the d band.[3] Above a certain pressure, the valence electrons lie in orbitals of mostly d character, and the alkali metal transforms into a transition metal.[4] This crossing of bands, the so-called s to d transition, occurs for potassium near 300 kbar at room temperature.[5] Rubidium and cesium show corresponding behavior and undergo the same transition at lower pressures than potassium.[5] These results have significant implications for the composition of the Earth's core in that potassium may alloy with iron.[6]

Currently, the highest attained static pressures in the laboratory (~3.7 Mbar) are produced in the diamond anvil cell (DAC). In this device, the sample to be pressurized is placed in a circular metal gasket that is crushed between two flat diamond faces (Figure 1). Since the contact area of the diamonds is quite small (about 0.03 mm^2), only a simple hand-operated screw and lever is needed to provide the crushing force (Figure 2).

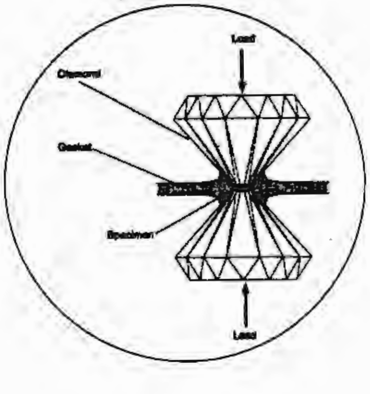

Figure 1. Diamond anvils.[7]

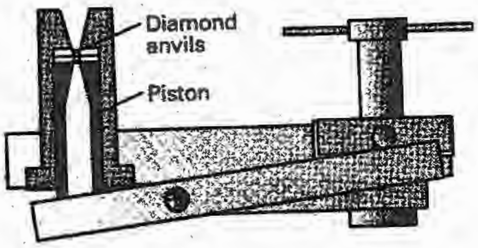

Figure 2. Hand-operated press.[8]

Under the high pressures generated by the DAC, many non-metallic elements can be metallized. Metallization occurs when band crossings put electrons into a conduction band. In 1982, Takemura, Minomura, and co-workers showed that I_2 transforms at 180 kbar and room temperature into a diatomic metal.[9] Also, silicon transforms from a semiconductor to a metal at 113 kbar,[5] and Xe shows metallic behavior starting somewhere between 1.3 and 1.5 Mbar.[5]

In 1935 Wigner and Huntington predicted that hydrogen would be converted to a monatomic metal at high pressure (250 kbar).[10] This proposal has major implications for the cores of Jupiter and Saturn, where pressures may reach many tens of Mbar.[11] The presence of electrically conductive hydrogen in Jupiter would help to explain the large observed magnetic field of this planet.[12] Wigner and Huntington sadly noted, however, that such high pressures (250 kbar) were beyond the scope of technology in their time.

As high pressure techniques developed rapidly through the last half of this century, increasing numbers of investigators have attempted to make metallic hydrogen, especially with the use of the DAC.[13] In the late 1980's Mao and co-workers pressurized hydrogen in a DAC to more than 2 Mbar.[14] At 1.8 Mbar the sample darkened slightly indicating the onset of metallization, but IR reflectance measurements contradict this conclusion. At 2.5 Mbar, hydrogen becomes very dark, and optical measurements such as IR and Raman spectroscopies become impossible. XRD is typically used as a characterization method with the hydrogen/DAC system above 1 Mbar.[13] The XRD studies clearly show that hydrogen remains diatomic even at 2.5 Mbar, although intermolecular and intramolecular distances are becoming similar.[13]

A recent paper by W. J. Nellis has described shock-wave compression of a liquid hydrogen sample to 1.8 Mbar.[15] The experimental conditions were adiabatic so that heating accompanied compression. It was found that at 3000 K the resistivity of hydrogen drops four orders of magnitude between 930 kbar and 1.4 Mbar (Figure 3). Between 1.4 and 1.8 Mbar, no further decrease in resistivity occurred. The minimum resistivity reached in this experiment was 500 μΩcm, which is comparable to that of Rb and Cs at 2000 K.[16] Although hydrogen is a good electrical conductor at these temperatures and pressures, it is unclear whether hydrogen has actually been metallized. It is possible that it is a semiconductor instead, with low resistivity arising from thermal population of a low-lying conduction band.

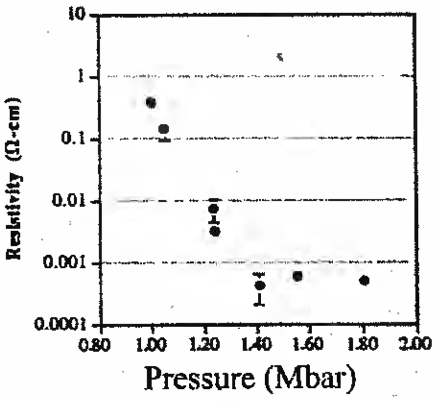

Figure 3. Resistivity of hydrogen as a function of pressure at 3000 K.[16]

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