The Oxidation State of Iron at High Pressure

Fe(III) reduces to Fe(II) in solids at high pressure; the process is reversible.

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I. Introduction

Mössbauer resonance is a convenient tool for studying the electronic behavior of iron in various environments. High pressure Mössbauer studies in this laboratory (*1–7*) have shown that, in a wide variety of compounds, ferric ion reduces to the ferrous state with increasing pressure, and that this is a reversible process. Before describing and analyzing these results, it will be useful to review briefly the relevant features of the Mössbauer effect, to outline some aspects of ligand field and molecular orbital theory and to mention the results of some high pressure optical studies which will be helpful in the interpretation of the experiments discussed in this paper.

II. Mössbauer Resonance

There are available excellent expositions of the principles of Mössbauer resonance (*8, 9*) so that we confine ourselves to a short discussion of those features important in determining the oxidation state of iron. When a free atom decays emitting a gamma ray, it recoils to conserve momentum. As a result of energy conservation, the energy of the emitted gamma ray no longer corresponds exactly to that of the nuclear transition, and, in addition, the energy spectrum is Doppler broadened. A similar argument applies to the absorption of a gamma ray by a free atom. If the atom is fixed in a crystal where the lowest quantum of vibrational energy (lowest phonon energy) is large compared to the recoil energy, an appreciable fraction of the decays are recoilless. Since the atom vibrates around an equilibrium position, the peak is not Doppler broadened and presents a very nearly monochromatic measure of the energy difference between the ground and the excited states of the nucleus. This difference (the isomer shift) is measurably affected by the electronic wave functions having non-zero amplitude at the nucleus (*s* electrons). Changes in the environment are reflected in the isomer shift through changes in occupation of the 4*s* levels and changes in the degree of shielding of the 3*s* orbitals by the 3*d* electrons. The ferrous ion nominally has six 3*d* electrons and the ferric ion five. Therefore these two states typically exhibit distinctly different isomer shifts and are easily distinguishable in a Mössbauer spectrum.

An electric field gradient at the nucleus interacts with the nuclear quadrupole moment to split the state of spin 3/2 and give two peaks in the spectrum. In the usual "ionic" complex, according to Hund's rule, the 3*d* states are occupied in a manner which gives maximum multiplicity (high spin). The aspherical distribution of the six electrons of the ferrous ion gives a significant electric field gradient at the nucleus, and thus a large quadrupole splitting. The spherically symmetric ferric state exhibits small quadrupole splitting. This effect also helps to distinguish the two states.

In very covalent compounds with a very strong ligand field, such as potassium ferricyanide the iron ions tend to pair their spins. For these low spin materials, the difference between the Mössbauer spectra of the ferrous and ferric states is less spectacular, but the determination can still be made. In the first order, the relative areas under the two sets of peaks give a reasonable measure of the amounts of ferrous and ferric ion present.

III. Transition Metal Ions in Crystals

The energy states of a 3*d* electron on a free transition metal ion are fivefold degenerate. The separation between the ground and excited states is due to the repulsion among the 3*d* electrons, and can conveniently be expressed in terms of the Racah parameters *A*, *B*, and *C* which we here consider as established empirically. When the ion is placed in a crystal where the field is less than spherically symmetric, the degeneracy is partially removed. We shall phrase this discussion in terms of an octahedral field, although the ideas are not qualitatively different for other symmetries. [Nor is the reduction of Fe(III) to Fe(II) which is the main theme of this paper.] The 3*d* levels split into two states, a triply degenerate level labeled t_{2g} and a doubly degenerate level of higher energy labeled e_g. The energy difference is commonly called 10 Dq or Δ. Optical absorption peaks of moderately low intensity in the near infrared and visible spectrum measure 10 Dq as well as the values of *B* and *C* in the crystal. These latter parameters are generally lower in the crystal than in the free ion by an amount that depends on the type of ligand. With pressure, the crystal field parameter 10 Dq increases because of the increased field of the ligands, roughly as predicted by

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theory. The Racah parameters B and C decrease with increasing pressure. This can be attributed to spreading of the $3d$ orbitals, including an outward movement of the radial maximum, which reduces the interelectronic repulsion. We shall refer to this phenomenon in our later discussion.

Generally, energy levels in a complex can be best described in terms of a molecular orbital diagram as shown in Fig. 1. The predominantly metallic antibonding levels t_{2g} and e_g, as well as their separation 10 Dq, are marked. As shown, it is possible for the t_{2g} orbital to form a pi bond with excited ligand orbitals which tends to stabilize it (i.e., lower its energy) by a modest amount. This fact will also be of use to us later.

In addition to the absorption peaks mentioned above, there appear very intense peaks centered at about 3–4 eV (24,000–32,000 cm^{-1}), with tails which may extend through the visible region. These correspond to ligand-to-metal charge transfer. In Fig. 1 such transfer is indicated from the non-bonding ligand t_{2u} level to the metallic t_{2g} state. These peaks shift to lower energy by as much as an electron volt in 100 kilobars. There are at least two apparent causes for this red shift. In the first place, the pi bonding tends to increase with pressure faster than the sigma bonding, lowering the energy of the t_{2g} level vis-à-vis the ligand levels. The calculations of Lewis (*3*) show that this is a factor, but probably not the dominant one. In the second place, the spreading of the $3d$ electrons mentioned above lowers the energy of the $3d$ states substantially. This, in fact, is probably the major contribution (*3, 10*).

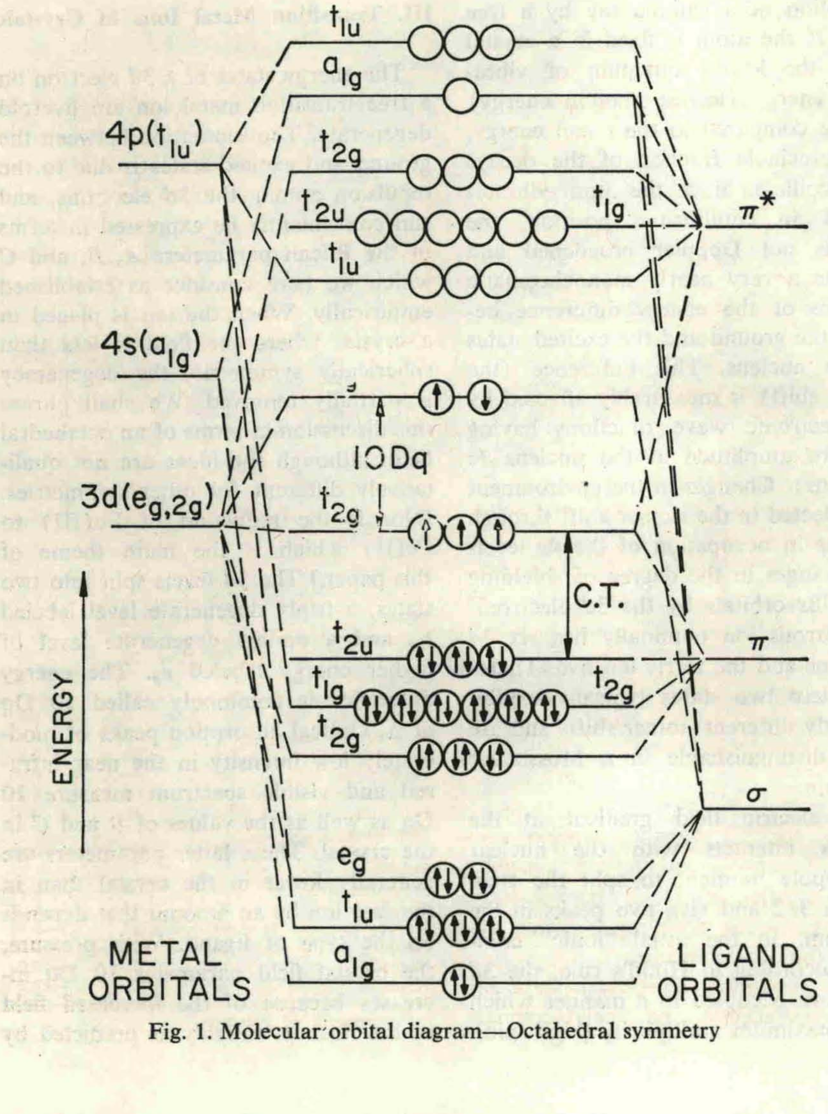

Fig. 1. Molecular orbital diagram—Octahedral symmetry

IV. The Reduction of Ferric Ion

As mentioned in the introduction, it has been found that the reversible reduction of Fe(III) to Fe(II) with increasing pressure is an ubiquitous phenomenon. We shall discuss first a few examples, together with an analysis of the process, and then present some special cases of unusual interest.

Fig. 2 shows conversion data for $FeCl_3$, $FeBr_3$, and $KFeCl_4$. The first two compounds have slightly distorted octahedral symmetry, while in $KFeCl_4$ the iron is in a tetrahedral site. The equilibrium constant

$$K = \frac{C_{II}}{C_{III}}$$

where C_{II} and C_{III} are the concentrations of Fe(II) and Fe(III) sites including the ligands. The linear relationship between ln K and ln P is very general. Constants A and B for the equation $K = AP^B$ are listed in Table 1 for a large number of compounds. There is clear evidence that these results represent equilibrium and not the result of slow kinetics. In the first place, consecutive runs at the same pressure gave essentially identical results. In the second place, when pressure was increased, as soon as a spectrum became resolved on the oscilloscope (5–15 minutes) the increased conversion was evident and remained constant with time, although complete runs took 8–48 hours or longer.

One can present a straightforward thermodynamic analysis:

$$K = \exp\left(-\frac{\Delta \overline{G}}{RT}\right) \qquad (1)$$

$$\frac{\partial \ln K}{\partial \ln P} = \frac{P\Delta \overline{V}}{RT} = \frac{P(\overline{V}^{III} - \overline{V}^{II})}{RT} = B \qquad (2)$$

where $\overline{V}^{III}$ and $\overline{V}^{II}$ represent the partial molar volumes of the Fe(III) and Fe(II) ions with their associated ligands. A slight rearrangement of Eq. 2 gives:

$$\frac{\partial \ln C_{II}}{\partial \ln P} = \frac{P(\overline{V}^{III} - \overline{V}^{II})}{RT} C_{III} \qquad (3)$$

The fractional increase in concentration of reduced sites per fractional increase in pressure is proportional to the concentration of sites available for conversion. The coefficient of proportionality is the work to convert a site measured in thermal units (units of RT). It is perhaps surprising that this is independent of pressure, i.e., that the volume change accompanying reduction is inversely proportional to the pressure, and this may be true only within our limits of accuracy. The pressure range over which its validity has been established is 10–200 kilobars. Also, conversions less than 6–7% or