# Chapter 2

# BACKGROUND

## 2.1 Arsenic: Occurrence, Chemistry, and Health Effects

### 2.1.1 Sources and presence in the environment

Arsenic (As) has an average crustal abundance of 1.8 mg kg$^{-1}$, so significant concentrations in groundwater and surface water can occur as a result of weathering processes. However, due to variability of bedrock and soil composition as well as of weathering conditions, groundwater As concentrations vary widely both on spatial and temporal scales (Hering and Kneebone 2002).

High As concentrations in groundwater are typically caused by reductive dissolution of iron(III) solids, oxidative dissolution of sulfide minerals, geothermal sources, or evapotransporative processes. Both oxidative and reductive dissolution release As previously adsorbed to or coprecipitated on the solid matrix into the groundwater. These processes are responsible for elevated groundwater As concentrations affecting the most people, including regions of Minnesota, South Dakota, Vietnam, Bangladesh and West Bengal (reductive Fe(III) dissolution) and parts of Wisconsin and New England (oxidative sulfide dissolution) (Smedley and Kinniburgh 2002). Many geothermal waters are also high in As; geothermal springs are the primary source of As for water in Chile (Smedley and Kinniburgh 2002), the Eastern Sierra Nevada (Wilkie and Hering 1998) and the Yellowstone area. In regions with hydrologically closed water basins, such as the semiarid western United States, As can accumulate in shallow groundwater due to evapotransporation that exceeds precipitation (Welch et al. 2000).

Volcanic eruptions, which contribute 30–65% of the total atmospheric As loading (Nriagu and Pacyna 1988), are another leading natural source of As. Anthropogenic sources also contribute significant fluxes of As to the environment. Wood preservation (copper chrome arsenate), glass production, and pesticides account for most anthropogenic inputs. Inorganic As pesticides such as lead arsenate were widely applied to fruit, cotton, tobacco, and potato crops before being banned from widespread use in the 1980s and 1990s, and organic arsenicals are currently used as herbicides (Kenyon and Hughes 2001; Armbrust and Bridges 2002) and are added to the feed of poultry and swine. Arsenic is released into surface and groundwater from mining wastes and into the atmosphere from smelting, refining processes, and fossil fuel combustion. Naturally occurring As that would otherwise remain bound to iron oxides can be mobilized via reductive dissolution due to anthropogenically induced plumes of organics (Welch et al. 2000). These activities, however, rarely impact potable water supplies in the United States.

### 2.1.2 Arsenic chemistry

Arsenic can exist in several oxidation states (-III, 0, +III, +V), although +III and +V are the most common. Many organoarsenic compounds have been identified, and several are present in food, particularly fish. Organoarsenicals are also common in poultry and pork due to the supplements fed to livestock. In surface waters, methylarsonic acid and dimethylarsinic acid are the only organoarsenic forms typically present at detectable levels, and inorganic arsenite, As(III), and arsenate, As(V), dominate the total As loading. Most groundwaters contain only inorganic As(III) or As(V) (Figure 2.1).

**Figure 2.1.** Structures of (a) arsenous acid, or arsenite; $pK_{a1} = 9.23$, $pK_{a2} = 12.13$, $pK_{a3} = 13.4$; and (b) arsenic acid, or arsenate; $pK_{a1} = 2.22$, $pK_{a2} = 6.98$, $pK_{a3} = 11.53$.

Because its first acid dissociation constant is 9.2, As(III) is present in most groundwaters as neutral $As(OH)_3$, whereas As(V) is typically a mono- or dianion. Arsenic(III) has greater mobility in the subsurface environment because it adsorbs less strongly to many mineral surfaces compared to the negatively charged As(V).

Although As(III) is thermodynamically favored under reducing conditions whereas As(V) is expected under more oxidizing conditions, the kinetics of this redox transformation are slow and As is not typically in equilibrium with surrounding groundwater. Moreover, bacterially mediated reduction and oxidation reactions may influence the relative proportions of As(III) and As(V) (Cullen and Reimer 1989; Oremland and Stolz 2005). As(III) constitutes ~30% of total inorganic dissolved As in source groundwaters used by United States treatment and distribution facilities (Chen et al. 1999).

### 2.1.3 Epidemiological studies involving arsenic exposure

Correlations between drinking water with high As concentrations and adverse health effects were first observed in the 1930s in Argentina and in the 1960s in Taiwan and Chile, where groundwater As concentrations ranged from <1–9900 $\mu g\ L^{-1}$, 10–1820 $\mu g\ L^{-1}$, and 100–1000 $\mu g\ L^{-1}$, respectively (Nordstrom 2002). Exposure to As in drinking water was linked to incidence of Blackfoot disease, skin pigmentation changes, keratosis, cardiovascular problems, respiratory disease, and skin cancer. Studies conducted in later decades also found high incidence of internal cancers.

More recently, UN-sponsored drilling of wells in Bangladesh and West Bengal, India, which was designed to reduce mortality and morbidity from pathogens in surface waters, has achieved its initial goal but has inadvertently exposed tens of millions of people to high As concentrations (<0.5–3200 $\mu g\ L^{-1}$) in the local groundwater (Smedley and Kinniburgh 2002). This is the most widespread case of documented As poisoning in history; according to some estimates, As in drinking water will cause 200,000–270,000 cancer deaths in Bangladesh alone (Goyer et al. 1999).

### 2.1.4 Health effects

Since arsenate is chemically similar to phosphate, it can be substituted for phosphate by enzymes such as those that synthesize ATP. However, the As analogues of ATP and related compounds immediately hydrolyze, thus shutting down ATP-based oxidative metabolism (Winski and Carter 1998).

As(III) compounds have an affinity for sulfur that causes binding to proteins containing sulfhydryl groups. This is believed to inhibit the function of enzymes such as pyruvate dehydrogenase and 2-oxoglutarate dehydrogenase (Goyer et al. 1999).

Exposure to very high concentrations of As in a short time frame can lead to vomiting, diarrhea, anemia, damage to the nervous system, and death (Goyer et al. 1999). Arsenic has varying degrees of acute toxicity depending on its form:

$$R_3As > As(III) > As(V) > \text{methylated arsenicals}$$

where $R_3As$ is arsine gas and R typically corresponds to H or $CH_3$ (Korte and Fernando 1991). Methylated arsenicals have a range of (low) toxicity, but some are not metabolized by humans and are rapidly excreted, resulting in no significant toxicity.

Chronic exposure to As, however, is a much more wide-ranging problem. The most common symptoms are skin disorders including hyper- and hypopigmentation and keratosis, but neurological damages, hypertension and diabetes mellitus may also occur (Korte and Fernando 1991; Goyer et al. 1999). Moreover, As has been shown to cause increased risk of bladder, lung, kidney, and skin cancers (Smith et al. 2002). Lifetime excess bladder and lung cancer risks for consumption of drinking water containing 3 and 20 $\mu g\ L^{-1}$ arsenic are estimated to be 9 and 72 cases per 10,000 people (Goyer et al. 2001).

## 2.2 Effect of As Regulations on Water Distribution Systems

### 2.2.1 Drinking water standards

In light of new evidence of the toxicity and carcinogenicity of As, the U.S. Environmental Protection Agency revised the maximum contaminant level (MCL) for As from 50 μg $L^{-1}$ to 10 μg $L^{-1}$ in 2001. This new value, which meets the World Health Organization guidelines for As (WHO 2001), will be enforceable as of January 23, 2006. States have the option to set their own regulatory standards at or below the federal MCL; the New Jersey standard is 5 μg $L^{-1}$ (NJDEP 2004) and California is currently considering lowering its state standard below 10 μg $L^{-1}$.

The MCL and other regulatory standards are set as close to health standards as is technologically and economically feasible. This policy-making process interconnects regulatory, health, and analytical standards, which are described in Table 2.1. Health standards, such as the maximum contaminant level goal (MCLG) or the public health goal (PHG), are based on a maximum risk threshold (usually $\leq 10^{-5}$ extra cases). The MCLG for As and all other carcinogens is set to zero because it is assumed that there is no threshold for cancer risk, whereas California's PHG for As is based on a $10^{-6}$ excess risk of death from cancer caused by lifetime water consumption. Analytical standards such as the practical quantitation limit (PQL) are used to determine whether water systems across the United States would be technologically capable of detecting a given contaminant at a specified level.

**Table 2.1.** Regulatory, health, and analytical standards for arsenic.

| Standard | Definition | Level for As |
|---|---|---|
| ***Regulatory Standards:*** | | |
| Maximum Contaminant Level (MCL) | The highest level of a contaminant allowed in US drinking water. | 10 $\mu g\ L^{-1}$ (enforceable 01/23/2006) |
| ***Health Standards:*** | | |
| Maximum Contaminant Level Goal (MCLG) | The level of a contaminant in drinking water below which there is no known or expected risk to health, allowing for a margin of safety. | 0 |
| Public Health Goal (PHG) (California) | The level of a drinking water contaminant at which adverse health effects are not expected to occur from a lifetime (70 years) of exposure. With respect to cancer, risks are calculated at 1 extra cancer case per million people. | 4 $ng\ L^{-1}$ |
| ***Analytical Standards:*** | | |
| Practical Quantitation Limit (PQL) | The lowest analyte concentration that can be reliably measured within specified limits of precision and accuracy during routine laboratory operation conditions. | 3 $\mu g\ L^{-1}$ |

### 2.2.2 Affected systems

Approximately 4,000 of the 74,000 water distribution systems in the United States will need to implement As removal procedures to meet the new standard (US EPA 2002b). Of this affected subset, 94% of facilities serve less than 10,000 people and 75% serve less than 1,000 people (Figure 2.2).

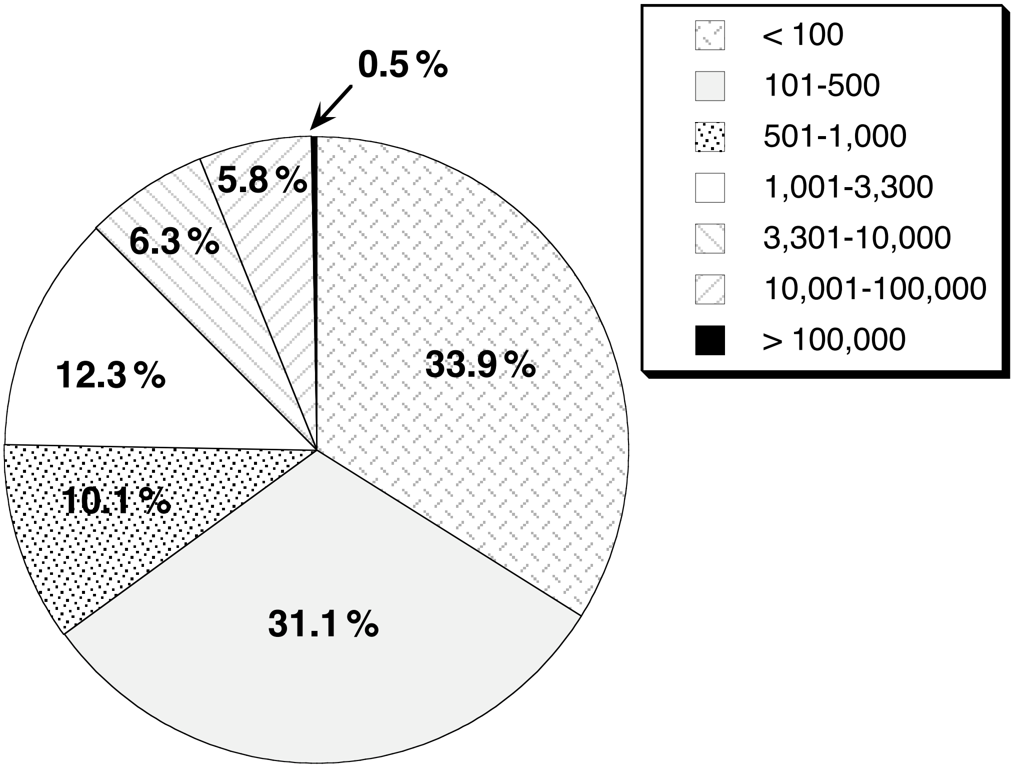

**Figure 2.2.** Breakdown of water distribution systems that will need to implement As treatment to meet the revised MCL based on the number of people they serve. Data from Focazio et al. (1999).

Small water distribution facilities, defined as those serving fewer than 10,000 people, constitute 85% of total public water supply systems and serve 10% of total community water system consumers. These facilities face disproportionate challenges in meeting the new As MCL. Due to the smaller geographic region they cover, they are less likely to have nontreatment As mitigation options such as blending high As source waters with low As source waters or refraining from using a source water high in As for all or part of the year. In addition, their funding base is smaller and capital costs are proportionally higher because economies of scale do not apply.

Because of these added difficulties, some federal aid in the form of grants and low-interest loans is earmarked for small systems. Moreover, small systems have the ability to apply for additional extensions in meeting the January 23, 2006 deadline. EPA grants states the power to offer 3-year "exemptions" to all facilities serving less than 10,000 people that can demonstrate financial hardship and that do not pose an "unreasonable risk to consumer health," allowing such systems additional time to meet the MCL. Systems serving fewer than 3,300 people may apply for up to 3 additional 2-year exemptions, potentially extending implementation of As treatment as late as January 2015 (US EPA 2002b).

Estimates suggest that thousands of water supply systems are not yet compliant with the MCL. At least 15 states, two Indian tribal programs, and the Navajo Nation have reported offering exemptions for the arsenic rule, and these bodies have collectively accepted nearly 200 applications. Historically, states have not offered exemptions to contaminants regulated under the Safe Drinking Water Act because the exemption process is complex and can give the impression that some public water supplies are less safe than others, but the arsenic problem is sufficiently widespread to merit extra options for water distribution systems. In addition, dozens of bilateral compliance agreements between states and water supply systems have been signed, and hundreds more are expected to be made in the next two months (Ware 2005). Under these agreements, the system under consideration will still be in violation of the MCL after January 23, 2006, but it will face no penalties as long as it adheres to the plan detailed in the compliance schedule. Finally, the standard monitoring schedules for systems using groundwater allow monitoring to be postponed as late as December 31, 2007 pending state approval (US EPA 2001a), and 29 states are allowing this postponement (Moller 2005).

### 2.2.3 Arsenic treatment options

Many treatment technologies, including modified coagulation/filtration, activated alumina, ion exchange, reverse osmosis, modified lime softening, and iron-based sorbents, are effective for As(V) treatment. However, only iron-based sorbents are consistently adequate for As(III) removal. When assessing technologies for As removal efficiency, the EPA assumes all As is present as As(V) and states that pre-oxidation may be necessary for source waters containing As(III) (US EPA 2001b). As(III) oxidation can be achieved by addition of chlorine, permanganate, ozone, or $MnO_2$-based media, but these approaches have varied applicability and in some cases can result in harmful disinfection byproducts. Technologies for both pre-oxidation and As removal are reviewed in more detail in Chapter 6.

There is a need for an inexpensive, low-maintenance As(III) pre-oxidation treatment that avoids the handling or production of hazardous chemicals. In this study, $TiO_2$-photocatalyzed As(III) oxidation is considered to determine whether it meets these requirements.

## 2.3 $TiO_2$ Photocatalysis

### 2.3.1 Photochemical applications of $TiO_2$

$TiO_2$ is the most widely used semiconductor photocatalyst due to its biological and chemical inertness, stability with respect to photocorrosion, and low cost. $TiO_2$ photocatalysis has been used for decades for the oxidation and reduction of organics in both liquid and gas phases. These applications typically target harmful compounds resulting from industrial processes, often achieving complete mineralization to $CO_2$, $H_2O$, and mineral acids. Its application has extended to include redox reactions of inorganics such as cyanide (Bhakta et al. 1992), chromium(VI) (Lin et al. 1993; Khalil et al. 1998; Chenthamarakshan et al. 2000), selenium(IV) and (VI) (Gruebel et al. 1995; Tan et al. 2003), and As(III).

Moreover, the photochemical properties of $TiO_2$ have recently been applied to create products with self-sterilizing, self-cleaning, or antifogging properties. The hydroxyl radicals produced on irradiated $TiO_2$ kill bacteria, viruses, and fungi by destroying their cell walls, making incorporation of $TiO_2$ into hospital, kitchen, and bathroom appliances useful. The self-cleaning and antifogging properties of $TiO_2$ stem from photoinduced super hydrophilicity. Hydrophobic molecules, which often serve as sorption sites for soot, dust, and other visible matter, are readily rinsed off the surface. A water contact angle close to zero causes uniform spreading of water rather than beading on the surface; this also prevents misting. Industrial applications of these technologies include antifogging glass for windows and mirrors, self-cleaning tiles, covers for highway lamps, paint, and spray coatings for cars (Fujishima et al. 2000).

In addition to photochemical applications, its high refractive index makes $TiO_2$ a common component in paints and pigments for cosmetics, paper, plastic, and textiles. For outdoor use, however, $TiO_2$ often must be coated with inert silica, alumina, or zirconia to prevent photooxidation of the surrounding matrix (Mills and Hunte 1997).

### 2.3.2 Properties of $TiO_2$

$TiO_2$ occurs in three polymorphic crystalline structures: anatase, rutile, and brookite. Brookite is difficult to synthesize in the laboratory, so anatase or rutile are typically used for academic and industrial applications. Anatase generally has a higher photoactivity than rutile, but exceptions exist (Hoffmann et al. 1995).

Degussa P25, the most widely used photocatalyst, is a powdered mixture produced by flame hydrolysis of $TiCl_4$ in the presence of hydrogen and oxygen, followed by a steam treatment to remove the reaction byproduct HCl. It is composed of 70–80% anatase and 20–30% rutile and has a surface area of $50 \pm 15$ $m^2$ $g^{-1}$. Particles are nonporous and cubic with rounded edges. They average 21–30 nm in diameter (Bickley et al. 1991; Datye et al. 1995), but in water they typically aggregate in clusters that measure 0.3–1.0 μm across (Cornu 2002). The point of zero charge for P25 occurs at pH 6.2–6.5 (Giacomelli et al. 1995; Hoffmann et al. 1995; Rodriguez et al. 1996) and it has a surface hydroxyl site density of $3.3 \times 10^{14}$ sites $cm^{-2}$ (Erdem et al. 2001). The photoactivity of P25 is generally greater than that of pure anatase, pure rutile, or a combination of the two pure phases.

### 2.3.3 Mechanism of semiconductor photoactivity

At ground state for an ideal semiconductor, a continuum of electron energy levels called the valence band is completely filled with electrons, whereas the higher energy conduction band, separated by a band gap with energy $\Delta E_{bg}$, contains no electrons. The values of $\Delta E_{bg}$ for anatase and rutile are 3.20 eV and 3.06 eV (Mills and Hunte 1997), corresponding to respective wavelengths of 388 and 412 nm. When radiation with energy equal to or exceeding $\Delta E_{bg}$ is absorbed, an electron is promoted to the conduction band ($e^-_{CB}$), leaving a positively charged hole in the valence band ($h^+_{VB}$):

$$TiO_2 + h\upsilon \rightarrow h^+_{VB} + e^-_{CB} \qquad (2.1)$$

These two charge carriers may recombine either in the bulk or at the particle surface, generating heat. Alternatively, they may migrate to the particle surface and be trapped by surface titanol groups:

$$e^-_{CB} + \equiv Ti^{IV}OH \rightarrow \{\equiv Ti^{III}OH\} \qquad (2.2)$$

$$h^+_{VB} + \equiv Ti^{IV}OH \rightarrow \{\equiv Ti^{IV}OH^\bullet\}^+ \qquad (2.3)$$

Trapped electrons may subsequently reduce electron acceptors (A) including $O_2$, $Ag^+$ and various organics (Reaction 2.4). Substrates may be oxidized by surface-bound hydroxyl radicals (trapped holes, Reaction 2.5) or by direct electron transfer to untrapped holes (Reaction 2.6). Figure 2.3 summarizes these processes.

$$A + e_{CB}^- \rightarrow A^- \qquad (2.4)$$

$$D + \{\equiv TiOH^\bullet\}^+ \rightarrow D^+ + \equiv TiOH \qquad (2.5)$$

$$D + h_{VB}^+ \rightarrow D^+ \qquad (2.6)$$

### 2.3.4 Approaches for examining $TiO_2$ photooxidation

In aqueous phase photooxidation, several experimental parameters affect how efficiently the substrate is oxidized, including the type of $TiO_2$ used, substrate concentration, $TiO_2$ loading, dissolved oxygen concentration, solution pH, reactor geometry, light intensity, presence of interfering species, and the flow rate or stirrer speed. The majority of mechanistic photochemical studies have used suspended $TiO_2$ in stirred batch reactors due to the relative ease with which these parameters can be

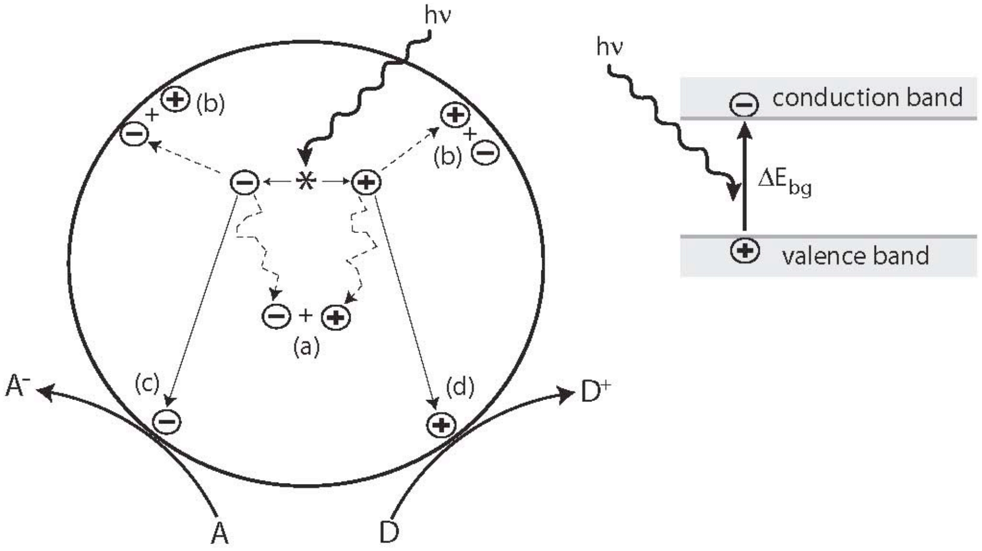

**Figure 2.3.** Schematic of semiconductor photocatalysis. After absorption of radiation of energy equal to or greater than the bandgap energy $\Delta E_{bg}$, an electron is promoted from the conduction band to the valence band. The resulting conduction band electron and valence band hole may then recombine in the bulk (reaction a) or at surface traps (reaction b). Alternatively, they can migrate to the particle surface where the electron reduces an acceptor (reaction c) and the hole oxidizes a donor (reaction d).

controlled. Slurry reactors afford relative homogeneity of an otherwise heterogeneous medium. In spite of their utility for understanding the mechanisms of the photoreaction, $TiO_2$ slurry systems are not practical for commercial application because of the difficulty of removing $TiO_2$ after treatment. Instead, flow-through, fixed-bed or fluidized-bed systems provide a more feasible alternative for treatment applications. These systems, however, can suffer from lower catalyst activity due to decreased available surface area. Many such systems also experience mass transfer limitations. Catalyst poisoning, at least for gas-solid systems, has been observed to occur more readily under flow-through conditions compared to batch reactors (Sauer and Ollis 1996).

## 2.4 Arsenic(III) Oxidation by $TiO_2$

### 2.4.1 Arsenic sorption on $TiO_2$

It is generally agreed that substrates being oxidized or reduced by $TiO_2$ first adsorb to the $TiO_2$ surface, so the interactions of As(III) and the reaction product As(V) with the $TiO_2$ surface must be considered. Bissen et al. (2001) investigated the sorption of 1.34 $\mu$M As(III) and As(V) to 0.001–0.05 g $L^{-1}$ P25 $TiO_2$. Although the percentage of sorbed arsenic increased with greater $TiO_2$ loading, it did not increase proportionally to $TiO_2$ concentration. However, the lack of reported solution pH values makes these data difficult to interpret. More recently, sorption envelopes were generated for As(V) on Hombikat UV100 $TiO_2$ (Dutta et al. 2004) and for both As(III) and As(V) on nanocrystalline $TiO_2$ (Pena et al. 2005). Both of these solids are anatase and have a higher surface area than P25. As pH increases, the extent of As(V) sorption decreases gradually at first and more sharply at pH 6.5 (133 $\mu$M As(V), 0.05 g $L^{-1}$ Hombikat UV100) or 8–11 (13.4 $\mu$M As(V), 0.2 g $L^{-1}$ nanocrystalline $TiO_2$). In the latter study, sorption of As(III) exhibited a maximum over the pH range from 6.5 to 9–11, with a gradual decrease toward more acidic values and a more rapid decrease under more basic conditions. These trends are similar to those noted for As sorption to iron oxides and oxyhydroxides. Moreover, comparable concentrations of As(III) and As(V) adsorb on both $TiO_2$ and iron solids, whereas As(III) sorption on aluminum oxides is much less than that of As(V) (Hering and Dixit 2004). Therefore, in the absence of structural information on As sorption to $TiO_2$, we consider sorption studies on iron oxides and assume that similar conditions prevail on $TiO_2$.

Both macroscopic studies and measurements using extended X-ray absorption fine structure spectroscopy have shown that As(III) participates in inner-sphere binuclear surface complexes on goethite and both inner- and outer-sphere complexes on amorphous iron oxides. As(V) forms inner-sphere complexes with both goethite and ferrihydrite (Sun and Doner 1996; Manning et al. 1998; Goldberg and Johnston 2001). As(V) complexes on ferrihydrite are mostly bidentate with a fraction of monodentate complexes (Waychunas et al. 1993; Waychunas et al. 1995), whereas complexes on goethite are binuclear (Sun and Doner 1996). Similar inner-sphere binuclear surface complexes have been observed for phosphate, an electronic analog of As(V), on $TiO_2$ (Connor and McQuillan 1999).

### 2.4.2 Redox potentials

Aerated, illuminated $TiO_2$ systems generate valence band holes, hydroxyl radicals, and superoxide anions, all of which are thermodynamically capable of oxidizing As(III) to As(V) at pH 6.0 (Figure 2.4). The reduction potential of the photogenerated hole (2.75 $V_{NHE}$) is higher than those of the hydroxyl radical and As(V), so it can oxidize $H_2O$ to $^{\bullet}OH$ and As(III) to As(V). The hydroxyl radical reduction coupled with oxidation of As(III) is also thermodynamically favored. $O_2$ can accept a conduction band electron to form superoxide, which can then be further reduced to hydrogen peroxide. This reaction coupled with As(III) oxidation is also thermodynamically favored, although the driving potential is smaller than that for direct hole transfer or reaction with hydroxyl radical.

### 2.4.3 Previous work

Yang et al. (1999) were the first to demonstrate As(III) oxidation using UV-irradiated $TiO_2$ slurries, and this system has since been examined by several other groups (Bissen et al. 2001; Lee and Choi 2002; Jayaweera et al. 2003; Ryu and Choi 2004; Dutta et al. 2005; Pena et al. 2005; Xu et al. 2005). Reaction conditions are summarized in Table 2.2. The oxidation reaction is fairly insensitive to pH over the range from 3–9 (Bissen et al. 2001; Lee and Choi 2002; Dutta et al. 2005), but increasing the $TiO_2$ loading from 0.01–0.05 g $L^{-1}$ increases reaction rate constants proportionally (Bissen et al. 2001). Addition of Fe(III) and humic acids was demonstrated to enhance As(III) photooxidation (Lee and Choi 2002; Dutta et al. 2005). In experiments using natural sunlight in place of UV lamps, complete loss of 1.33 μM and 26.7 μM dissolved As(III) occurred within 5 and 30 minutes (Bissen et al. 2001; Pena et al. 2005).

The mechanism of As(III) oxidation on $TiO_2$ is not confirmed, but potential oxidants include the valence band hole, $^{\bullet}OH$, and $O_2^{\bullet -}$. Hydroxyl radicals, which generally remain adsorbed to the solid surface (Lawless et al. 1991), are most often cited as the primary oxidants in $TiO_2$ photocatalysis systems, but direct hole oxidation has been documented for several substrates (Draper and Fox 1990; Mao et al. 1991; Carraway et al. 1994; Cermenati et al. 1997; Grela et al. 1997; Kesselman et al. 1997b; Guillard 2000; Pichat et al. 2000). Superoxide, which also remains primarily sorbed to the $TiO_2$

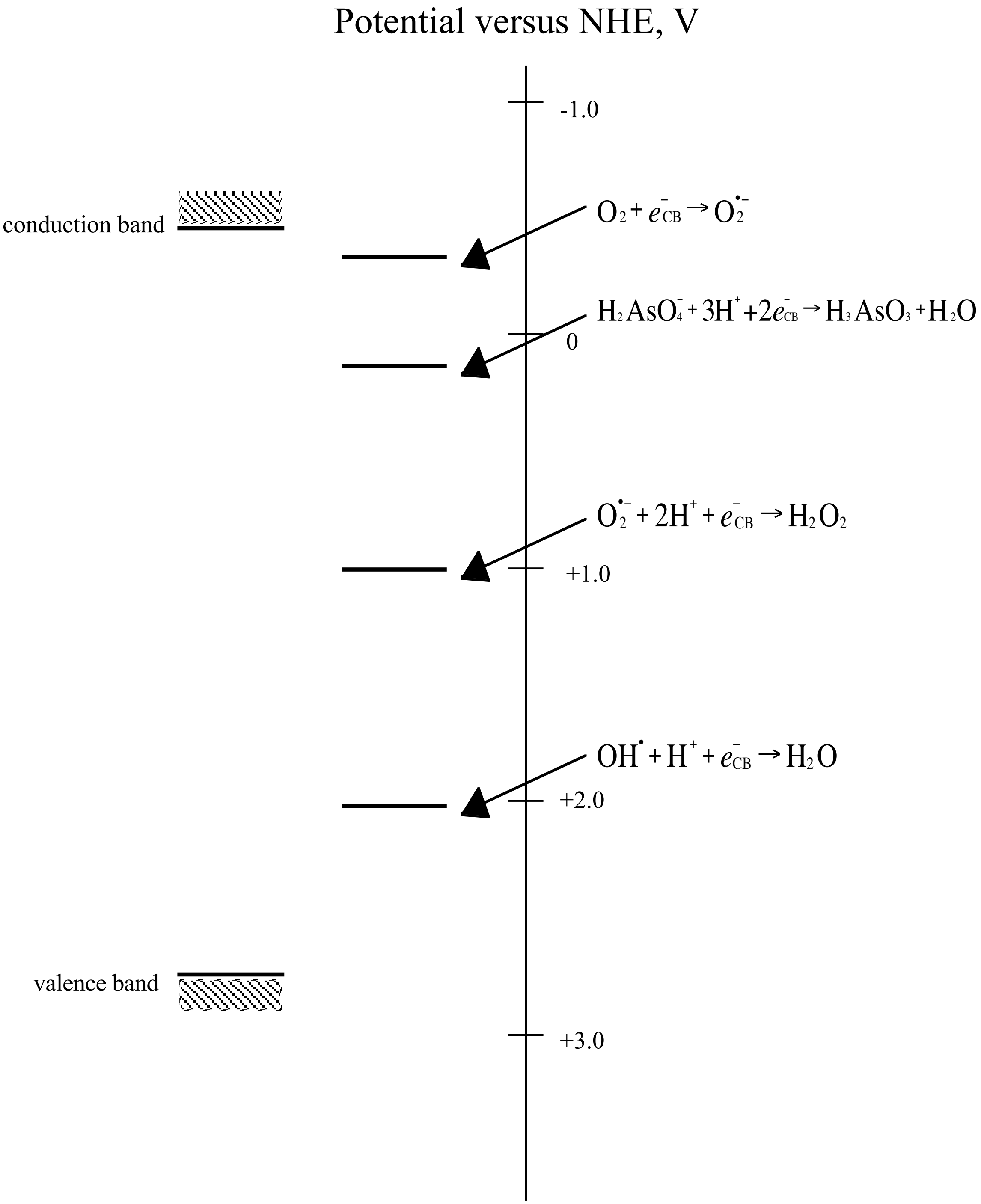

**Figure 2.4.** Potential versus normal hydrogen electrode diagram comparing the position of the valence and conduction bands of anatase $TiO_2$ at pH 6.0 with the reduction potentials of species in solution at pH 6.0 (Bard et al. 1985).