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Chapter 8

Chemical Equilibrium: Acid–Base and Redox Analogies in Solids

The basic principles that apply to equilibria in solution can be used to gain insight into the behavior of important classes of solids like semiconductors and ion conductors. In this chapter we introduce the notion that traditional, wet acid–base equilibria and Nernstian redox chemistry have counterparts in the solid state. For example, doping aluminum into silicon is analogous to dissolving HCl in water, and a light-emitting diode is analogous to an electrochemical concentration cell.

The electronically and ionically conducting solids that form the basis for many of these analogies illustrate not only chemical equilibria, but the application of several other concepts, including the solutions to the Schrödinger equation for the hydrogen atom and periodic properties. Moreover, the chemical principles that govern these solids are readily connected with common devices like solar cells, light-emitting diodes, diode lasers, gas sensors used in catalytic converters, and ion sensors.

Electrons and Holes

One way of describing conductivity in a semiconductor such as silicon is to use a localized bonding picture (Figure 8.1A). In this model, the focus is on the bonds that bind each silicon atom to four other silicon atoms. Because the silicon–silicon bonds are relatively strong, the electrons are held fairly tightly and are not mobile. However, a few electrons can be excited out of the covalent bonds by absorption of thermal energy (or by light of at least band-gap energy; *see* Chapter 7), giving rise to small electrical conductivities near room temperature. A representation is shown

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in Figure 8.2, in which the arrows show electrons (e^-) that have been freed to roam throughout the silicon crystal.

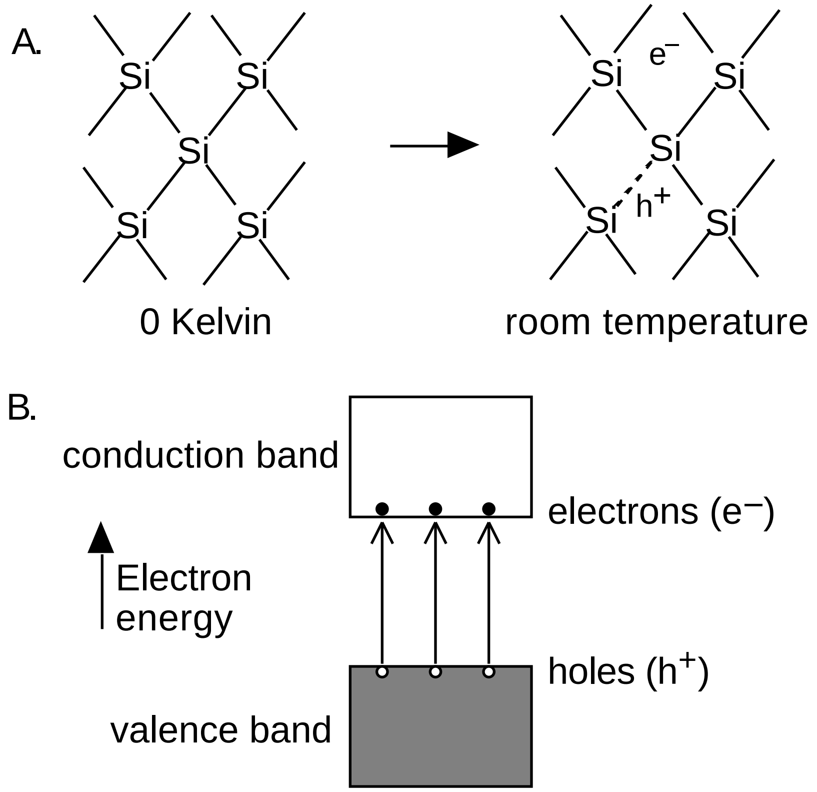


Figure 8.1. A: A localized bonding picture of a semiconductor. In the absence of heat or light, the valence electrons are localized in two-electron Si–Si bonds. However, absorption of heat or light energy produces some mobile electrons (e^-) and an equivalent number of mobile holes (h^+). The one-electron bond resulting from creation of the electron–hole pair is indicated with a dashed line. B: The band structure of a semiconductor using a delocalized bonding picture. Electrons (filled circles) may be excited from the valence band by absorption of light or thermal energy. Holes (open circles) are left behind in the valence band.

Mobile electrons and holes (*see* next paragraph) are collectively called *carriers* because they are the species responsible for the conductivity of a semiconductor. They “carry” the electric current in the semiconductor.

Equally important in this representation are the one-electron bonds resulting from the creation of the mobile electrons. One of the most powerful formalisms in discussing solids is to treat missing electrons as particles called “holes”; they are symbolized by h^+. The mobility of the holes in this localized bonding picture is illustrated in Figure 8.2, which shows electrons from adjacent two-electron bonds moving into the holes: this movement restores one-electron bonds to two-electron status, but makes an equal number of what were two-electron bonds become new one-electron bonds. This process thus conserves the number of holes and effectively moves the holes throughout the crystal.

The positively charged nature of the hole is appreciated by imagining the effect of a voltage that is applied to the sample, as shown in Figure 8.2: the negatively charged electrons that are actually moving would be attracted to the positive terminal, but this is equivalent to thinking of the holes as moving toward the negative terminal. This can be modeled in the classroom as shown in Figure 8.3.

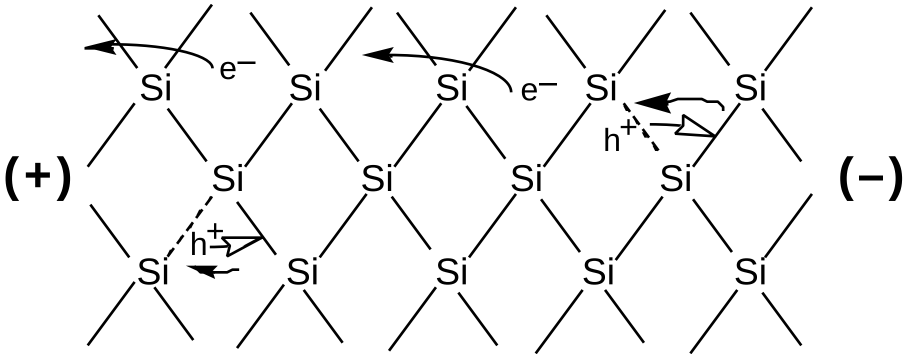


Figure 8.2. If a voltage is applied to a crystal of semiconducting material, the electrons migrate toward the positive terminal and the holes migrate toward the negative terminal. Two kinds of electron motion are illustrated. Excited electrons (e^-) move through the crystal toward the positive terminal. In addition, an electron in a bonding pair can jump into a one-electron bond (hole). This results in net motion of the electrons (dark arrows) and holes (open arrows) in opposite directions.

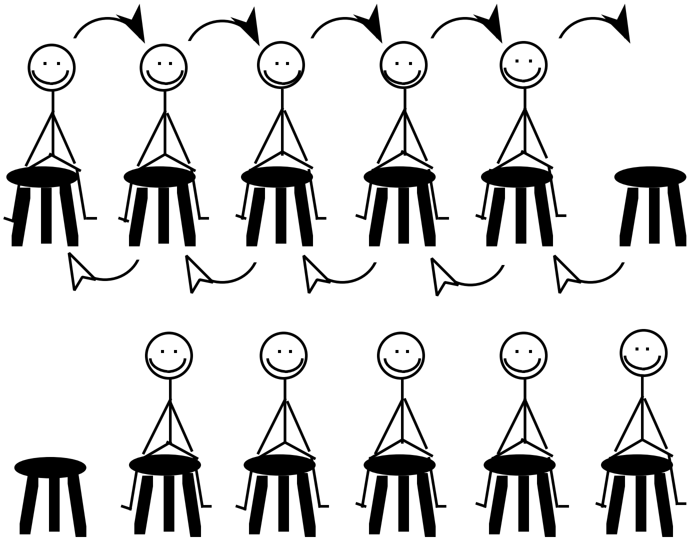


Figure 8.3. Hole mobility can be modeled by students. Five students are electrons and one empty chair is a hole. Having each student move one chair to the right (dark arrows) produces a result that is equivalent to the empty chair moving to the left (open-tipped arrows).

Another way of describing the conductivity in silicon is to use a delocalized bonding picture (Figure 8.1B). In Chapter 7, we noted that semiconductors are characterized by a filled valence band that is separated by a band gap from an unfilled conduction band at higher energy. Ambient thermal energy promotes a few energetic electrons across the band gap, and this process becomes more favorable with an increase in temperature and a decrease in band gap. Each electron promoted to the conduction band becomes a mobile electron and results in an electron missing from the valence band; a missing electron is also treated as a mobile hole in the valence band. To compare with the localized bonding picture, the promotion of electrons can be thought of as removing electrons from the delocalized bonding orbitals (the valence band) connecting the atoms in the crystal.

The energy scales of electrons and holes are inversely related. By convention, in energy diagrams the energies of electrons increase vertically upward on the page (Figure 8.1B). In contrast, hole energies decrease in the upward direction, giving rise to the analogy that holes are like bubbles in that they float or rise to reach lower energy. This effect can be demonstrated as described in Demonstration 8.1.

Demonstration 8.1. Hole Energies and Conductivity

Materials

Stoppered test tube, nearly filled with glycerine

Procedure

- Invert the test tube.
- A bubble will slowly move from the bottom to the top of the test tube. By way of analogy, holes are like bubbles in a fluid. They are the absence of something, in this case the absence of electrons. The shift in contents can be explained as a movement of the bubble or a movement of the fluid.

  The entire tube may also be viewed as a band, with the fluid being electrons and the air being holes. Inverting the tube animates the phenomenon that electrons (fluid) move to the bottom of the band (tube) to achieve lowest energy, or equivalently, holes (air) move to the top of the band (tube) to reach lowest energy.

Demonstration 8.2. A Classroom Model of Hole Conductivity

Materials

A row of chairs or desks with students in all but one of them

Procedure

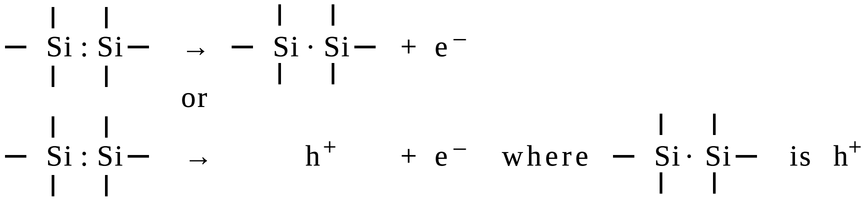
- Arrange a row of students so that the empty seat is at one end of the row (see Figure 8.3).
- Have an instructor or student stand at each end of the row, with one of these two individuals representing the positive terminal of a battery (this is the person next to the empty seat) and the other the negative terminal.
- Instruct the student in the seat next to the empty one to move into it. Then tell the next student to move into the newly empty one. Repeat until all students have moved by one seat.

In this model, the students are analogous to valence-band electrons. As the students shift seats, moving toward the individual who represents the positive terminal, it can be pointed out that, simultaneously, the empty seat is a hole that is moving toward the negative terminal. A more extensive analogy in which the entire classroom is regarded as a band (and a nearby room as an adjacent band) recently was published *(1)*.

The Autoionization Analogy

A solid like silicon can be regarded as a medium, somewhat analogous to water. Just as autoionization in water produces H^+ and OH^- ions, which can be regarded as mobile defects in the solvent, the analogous autoionization process in silicon produces a mobile electron and a mobile hole. In the delocalized bonding picture, promotion of electrons produces conduction band electrons, e^-, and valence-band holes, h^+, in equal numbers, just as dissociation of water molecules produces protons and hydroxide ions in equal numbers. In the localized bonding picture, the equations for autoionization in the two media are given by equations 1–2:

$$H:O:H \rightarrow H^+ + OH^- \tag{1}$$



$$\begin{array}{l} -\overset{|}{\underset{|}{\mathrm{Si}}}:\overset{|}{\underset{|}{\mathrm{Si}}}- \;\rightarrow\; -\overset{|}{\underset{|}{\mathrm{Si}}}\cdot\overset{|}{\underset{|}{\mathrm{Si}}}- \;+\; e^- \\ \qquad\qquad \text{or} \\ -\overset{|}{\underset{|}{\mathrm{Si}}}:\overset{|}{\underset{|}{\mathrm{Si}}}- \;\rightarrow\; h^+ \;+\; e^- \quad \text{where} \; -\overset{|}{\underset{|}{\mathrm{Si}}}\cdot\overset{|}{\underset{|}{\mathrm{Si}}}- \;\text{is}\; h^+ \end{array} \tag{2}$$

In equation 2, the symbol $-\overset{|}{\underset{|}{\text{Si}}}\cdot\overset{|}{\underset{|}{\text{Si}}}-$ represents the one-electron silicon–silicon bond—the "hole"—that results from ionization of a bonding electron. Its shorthand notation, h^+, reflects the fact that, as noted, the hole is mobile and can move away from the site of its generation.

The process of dissociation in water is countered by the very high likelihood that when H^+ and OH^- ions encounter each other in aqueous solution, they will recombine to make water molecules. A similar process, the recombination of electron–hole pairs, occurs in the solid. As shown in Figure 8.4A, when an itinerant electron encounters a one-electron silicon–silicon bond, a hole, the normal two-electron bond is restored. When a mobile conduction-band electron recombines with a mobile valence-band hole, both carriers are annihilated and no longer contribute to electrical conductivity in the solid. The delocalized bonding view of the same event is shown in Figure 8.4B:

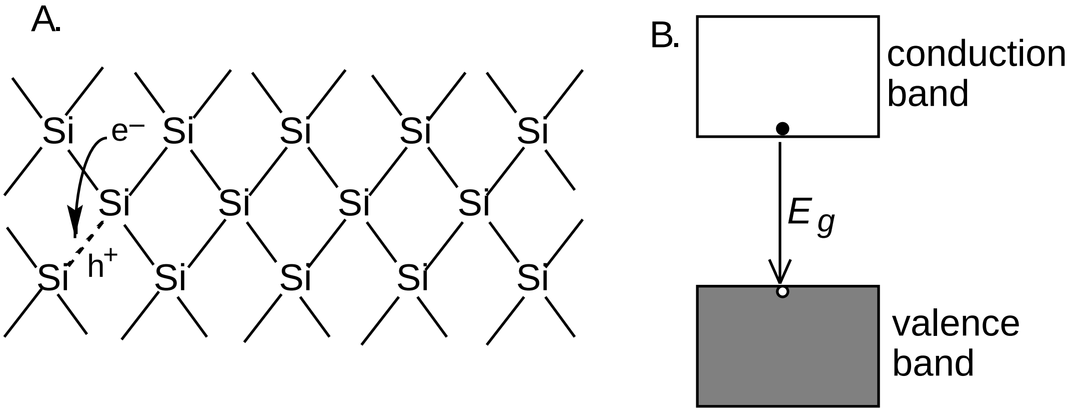


Figure 8.4. Recombination of the electron–hole pairs annihilates both carriers and releases energy that is roughly equivalent to the band-gap energy. This process may be viewed (A) as a free electron encountering a one-electron bond, a hole (localized picture); or (B) as an electron falling from the conduction band back to the valence band (delocalized picture).

With silicon, as with water, the rates of dissociation and recombination are equal at thermal equilibrium in the dark (light having greater than band gap energy creates additional electron–hole pairs; *see* Chapter 7.) The processes in equations 1 and 2 may be replaced by an equilibrium double arrow.

How are these processes quantified? In water, the equilibrium constant K_W is used as a measure of the extent of ionization at equilibrium,

$$K_W = [H^+]\,[OH^-] \tag{3}$$

At room temperature K_W is 1×10^{-14} M^2, which corresponds to 4×10^{27} ions/cm^6, when concentrations are given as numbers of ions per cubic centimeter. The concentrations $[H^+]$ and $[OH^-]$ are, of course, equal to one another and to the square root of K_W, yielding values for them of ~1 × 10^{-7} M or ~6 × 10^{13} ions/cm^3 at room temperature.

The origin of the small value of K_W (corresponding to a large, positive value of $\Delta G^o = \Delta H^o - T\Delta S^o$; $K = e^{-\Delta G^\circ/RT}$, where ΔG^o, ΔH^o, and ΔS^o are the standard free energy, enthalpy, and entropy for a reaction with equilibrium constant K) is noteworthy: The dissociation reaction is endothermic with a strongly positive ΔH^o value (the exothermic nature of the reverse reaction, the neutralization reaction, is commonly demonstrated in discussions of thermochemistry) and has a substantial negative ΔS^o value, reflecting the fact that water molecules order themselves in solvation spheres around these ions. The autoionization that does occur at room temperature is due to the high entropy of a *dilute* solution of protons and hydroxide ions.

In extending the analogy between water and a semiconductor, measurements of electrical conductivity can be used to establish concentrations, in units of reciprocal cubic centimeter, of valence band holes, denoted p or $[h^+]$, and conduction band electrons, denoted n or $[e^-]$. In the pure solid "solvent," $p = n$, and the product of the two is also governed by chemical equilibrium:

$$K = [h^+]\,[e^-] = p \times n \tag{4}$$

The value of K, the equilibrium constant for the autoionization of silicon at room temperature, has been determined to be about 2×10^{20} cm^{-6}, meaning that $p = n = K^{1/2} \sim 1 \times 10^{10}$ cm^{-3}. These values of n and p correspond to a very small degree of autoionization in silicon (eq 2), as can be seen by comparing them to the density of atoms in silicon, which is on the order of 10^{22} cm^{-3}: ionization occurs only for about one silicon–silicon bond in 10^{12}! Room temperature values of K for several other semiconductors are given in Table 8.1.

Table 8.1 Values of K at 300 K for Semiconductors

Semiconductor	K (cm^{-6})[a]	Band Gap
GaAs	4.0×10^{12}	138 kJ/mol (1.43 eV)
Si	2.2×10^{20}	107 kJ/mol (1.11 eV)
Ge	6.2×10^{26}	66 kJ/mol (0.68 eV)

[a] Equilibrium constant for autoionization.
SOURCE: Data are taken from references 2 and 3.

As with water, the dissociation is endothermic, and what little autoionization there is in the semiconductors of Table 8.1 arises because of the entropy increase associated with the creation of a dilute "solution" of electrons and holes; there is no counterpart in semiconductors analogous to the ordering of solvent molecules that occurs in the aqueous autoionization reaction.

The direction of energy flow in the semiconductor autoionization reaction can be appreciated by considering the reverse reaction: Recombination of electrons and holes (Figure 8.4), like the neutralization reaction in water, yields energy, which can be released in the form of heat and/or light (*see* the discussion of light-emitting diodes (LEDs) in Chapter 7 and following herein). Table 8.1 shows that a decrease in the band-gap energy, a measure of the energy cost associated with autoionization, corresponds to an increase in K (K is proportional to $e^{-E_g/RT}$; the band gap E_g is an internal energy).

The endothermicity of the semiconductor autoionization reaction is also established from the dependence of the equilibrium constant or carrier concentration ($n = p = K^{1/2}$) on temperature. Figure 8.5 makes a direct comparison between the autoionization equilibria of water and the semiconductors silicon, germanium, and gallium arsenide by showing the value of the carrier concentration ($[H^+] = [OH^-]$ for water; $n = p$ for the semiconductors) as a function of reciprocal temperature. The negative slopes demonstrate that these are endothermic reactions that can be used as illustrations of Le Chatelier's principle: Increased temperature will shift the autoionization equilibria to the right, as the system tries to relieve the stress from the additional thermal energy by creating more charge carriers.

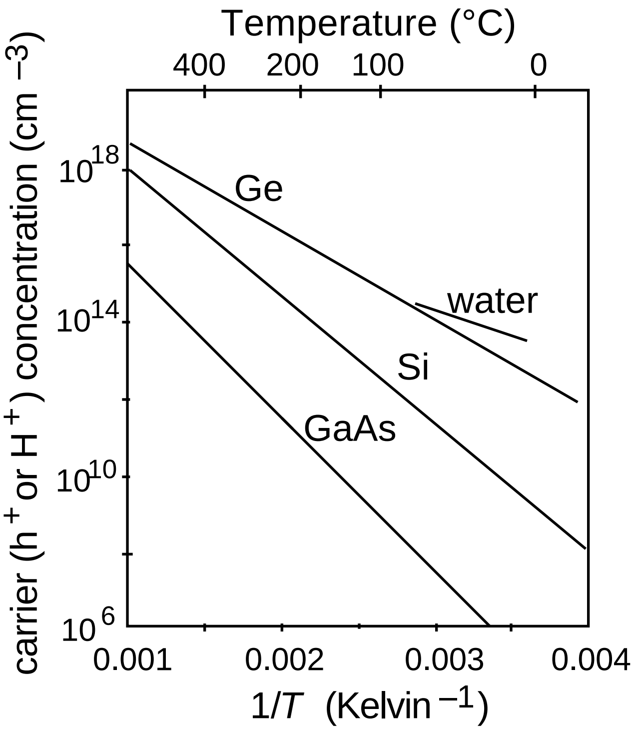


Figure 8.5. A comparison of semiconductor hole concentration, p, and $[H^+]$ in pure water versus $1/T$. (Adapted from references 2 and 3.)

Doping with Electron Donors and Acceptors

Given the analogy between pure water and pure semiconductors as equilibrium-governed solvents, it is natural to wonder whether the relative concentrations n and p can be altered. Bases and acids are routinely added to water to increase $[OH^-]$ or $[H^+]$, respectively, at the expense of the other: The analogous behavior in semiconductors involves adding atoms having additional valence electrons relative to the host crystal atoms or adding acceptor atoms having fewer valence electrons relative to the host crystal atoms.

Deliberately adding impurity atoms, called "dopants," to substitute for atoms that normally comprise the crystal can often be accomplished by incorporating the dopant atoms during the growth of the solid, or afterward, by heating the solid in the presence of a volatile source of the dopant; diffusion of the dopant into the material is enhanced at high temperatures. Because of the small degree of autoionization, often only very small amounts of the dopant, on the order of parts per million, are needed to significantly alter the electrical properties of the solid.

The simplest cases of control of p and n involve covalent tetrahedral semiconductors like silicon. In choosing a dopant that might increase the concentration of conduction-band electrons n at the expense of the concentration of valence-band holes p (recall eq 4, that $p \times n = K$, a constant at a given temperature), a logical strategy is to choose a dopant that is about the same size as the atom to be replaced, so it readily fits into the structure, and that has an additional valence electron. Inspection of the periodic table suggests that phosphorus and arsenic would be good choices.

The localized bonding model of semiconductors may be used to explain the effects of doping. The Lewis structure of silicon doped with a phosphorus atom, shown in Figure 8.6A, suggests qualitatively why phosphorus is a donor atom. The extra valence electron of phosphorus is easily ionized, because it is not needed to bond the phosphorus atom to its four neighboring silicon atoms in the tetrahedral geometry of the atoms in the crystal. Instead, these electrons are free to roam throughout the solid, increasing n. The reaction may be generally written as

$$D \rightarrow D^+ + e^- \qquad (5)$$

where D represents a donor atom in a semiconductor. A mobile electron and an immobile cation are produced by each ionization event.

In the delocalized band picture, this ease of ionization is described by the introduction of a donor energy level near the conduction-band edge. (A quantitative estimate of the energy of the donor level relative to the conduction-band edge is given in the next section.) Consequently, thermal energy is sufficient to promote a large fraction of these donors' excess electrons into the conduction band. This situation is illustrated in Figure 8.6B.

In a similar manner, atoms like aluminum or gallium, having one fewer valence electron than silicon but of similar size, are logical acceptor-type dopants for increasing the valence-band hole concentration p at the expense of n. Again, the localized bonding picture may be used to explain the effects of doping with aluminum. In the localized picture, Figure 8.6C, an aluminum atom, with three valence electrons, fits into the silicon lattice by making three two-electron bonds to each of three neighboring silicon atoms; but must make a one-electron bond to its fourth silicon neighbor. This one-electron bond can be converted to a two-electron bond by an electron from a neighboring two-electron silicon–silicon bond, leading to a mobile hole. The reaction may be written

$$\mathrm{A} \rightarrow \mathrm{A}^- + \mathrm{h}^+ \tag{6}$$

where A represents an acceptor atom in a semiconductor. Thus, a mobile hole and immobile anion result from the ionization process.

In the delocalized picture, the unfilled orbitals on aluminum lie just above the filled valence band. As such, thermal energy is sufficient to promote electrons out of the filled valence band into these energy levels, simultaneously producing valence-band holes. This process is illustrated in Figure 8.6D.

The Hydrogen Atom Model for Estimating Dopant Ionization Energies

Figures 8.6A and 8.6C suggest a simple model for quantitatively estimating the ionization energies of dopants. The extra valence electron of a phosphorus-donor dopant atom that is not used for covalent bonding is held to the phosphorus atom through electrostatic attraction in much the way that the electron of a hydrogen atom is held to the nucleus; in both cases, ionization corresponds to freeing the electron and leaving behind a center of positive charge. For the hydrogen atom, allowed energies for the electron, determined from the Schrödinger equation (or from the earlier Bohr model), are commonly presented in introductory courses to illustrate quantization. The models may be applied to give a rough estimate of dopant ionization energies in semiconductors, as well.

Equation 7 describes the allowed energies for the hydrogen atom, where e is the charge on an electron, m is the mass of an electron, ε_o is the vacuum permittivity, ε_r is the relative permittivity of the medium ($\varepsilon_r = 1$ for a vacuum), n is the principal quantum number, and h is Planck's constant.

$$E = \frac{-e^4 m}{8 \varepsilon_o^2 \varepsilon_r^2 h^2 n^2} = \frac{-2.18 \times 10^{-18}\ \mathrm{J}}{n^2} \tag{7}$$

In most introductory chemistry texts this equation appears as $E = -(\text{constant})/n^2$, because in the hydrogen atom, all of the terms except n are constants and can be combined into one constant. Equation 8 is the equation for the Bohr radius, the most probable distance from the nucleus for finding the electron.

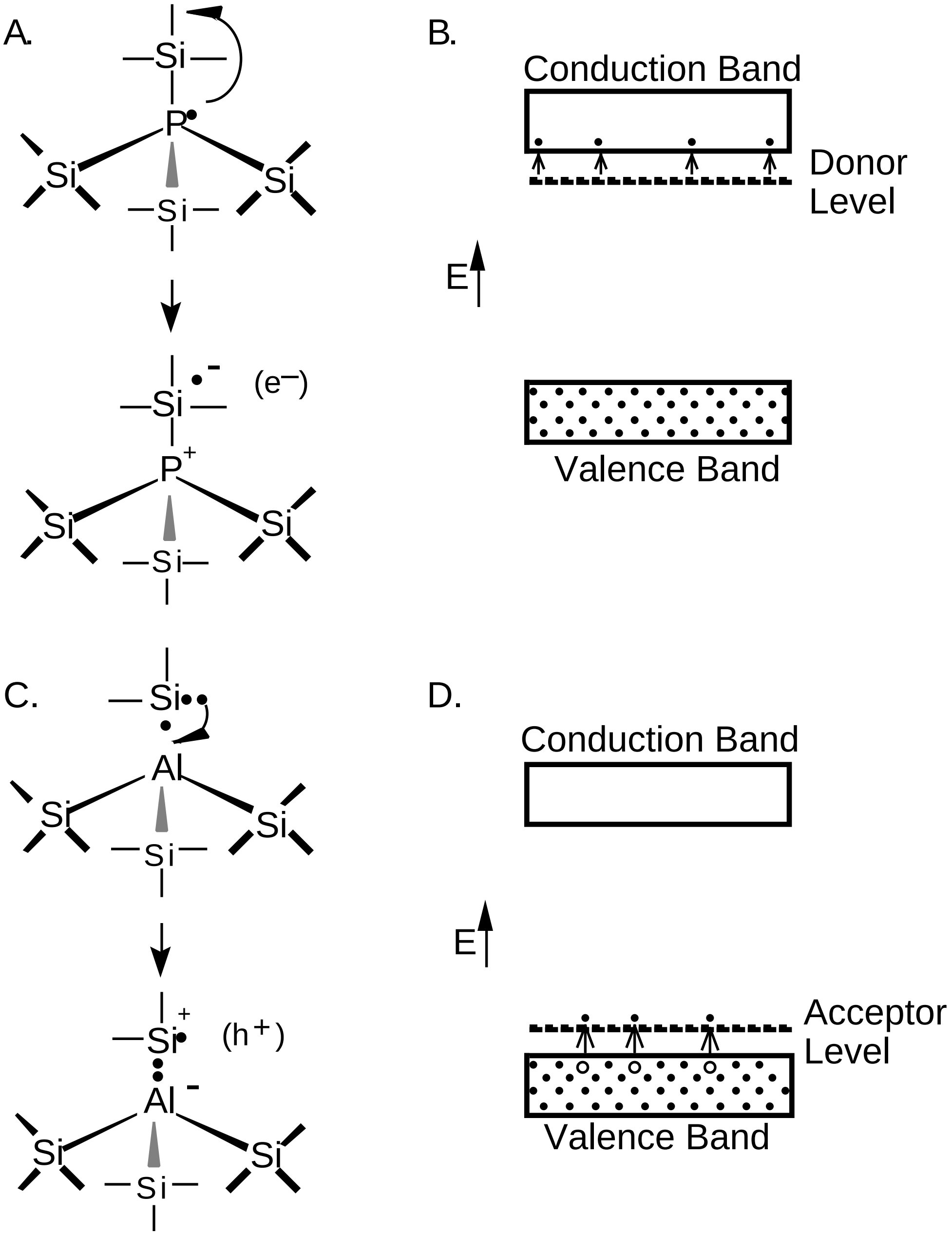


Figure 8.6. A: A localized bonding picture showing the effect of adding phosphorus to a silicon crystal. B: The addition of a donor atom such as phosphorus introduces electrons in donor levels that are close to the conduction band. As such, the electrons (filled circles) are easily promoted into the conduction band. C: A localized bonding picture showing the effect of adding aluminum to a silicon crystal. D: The addition of aluminum to a silicon crystal introduces acceptor levels that lie just above the valence band. Thermal energy is sufficient to promote electrons from the valence band into these levels, creating holes (open circles) in the valence band.

$$r = \frac{n^2\, h^2\, \varepsilon_o\, \varepsilon_r}{\pi\, e^2\, m} \qquad (8)$$

This equation usually appears as $r = a_o n^2$ (after collection of the constants into a_o, the radius of the first Bohr orbit).

The hydrogen-atom model can be applied to this doped semiconductor with two modifications: First, unlike the vacuum assumed in the space between the proton and electron of the hydrogen atom, the solid has intervening atoms that shield the electron from the nucleus. This shielding reduces the attraction of the nucleus for the electron by the square of the dielectric constant of the medium (the dielectric constant is a measure of how easily the medium is electrically polarized). In a vacuum, ε_o is used ($\varepsilon_r = 1$); in a solid, ε_o is multiplied by the relative dielectric constant of the solid. (The relative dielectric constant, ε_r, is on the order of 12 for silicon.) This approach leads to an approximately hundred-fold reduction in the electrostatic attraction. Second, the kinetic response of electrons to electrical forces indicates that electrons behave as though they have a mass, called the “effective mass,” that is usually somewhat smaller than the value of their mass in vacuum. Consequently, m^*, the effective mass of the electron, replaces m in equation 8. With these two changes, essentially the same equations can be used for this donor-doped semiconductor as for the hydrogen atom.

The combined effect of these two modifications is that instead of requiring 13.6 eV to remove an electron from a hydrogen atom in a vacuum (or 10.5 eV to remove an electron from a phosphorus atom in vacuum), a phosphorus atom doped into a silicon crystal has an ionization energy that is far lower, by more than a factor of 200; the measured value is ~0.044 eV.

The case of aluminum doped into silicon is equivalent, except that a positively charged hole is to be ionized from a negatively charged acceptor: When an electron from a neighboring silicon–silicon bond is trapped at an aluminum atom, the aluminum becomes a center of fixed negative charge with a one-electron silicon–silicon bond, the positively charged hole, electrostatically bound to it (Figure 8.6C). The allowed energy levels and Bohr radius are calculated in the same way, and a similar result is found. Experiments show that only 0.057 eV is needed to ionize the holes provided by aluminum atom dopants in silicon. Moreover, the first Bohr radius typically expands from 0.53 Å in hydrogen to tens of angstroms, spanning many atoms, for common semiconductor dopants *(4)*. Ionization energies of common donors and acceptors in silicon are summarized in Figure 8.7.

Figure 8.7 shows the placement of Group 15 donors like phosphorus near the conduction-band edge and of Group 13 acceptors like aluminum near the valence-band edge. The small amount of energy needed to ionize these dopants means that at room temperature the amount of thermal energy available, ~0.025 eV, is sufficient to ionize a substantial fraction of them.[1]

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[1] Effects due to interactions among dopants at common doping levels can effectively reduce the band gap and bring the dopant levels even closer to the band edge.

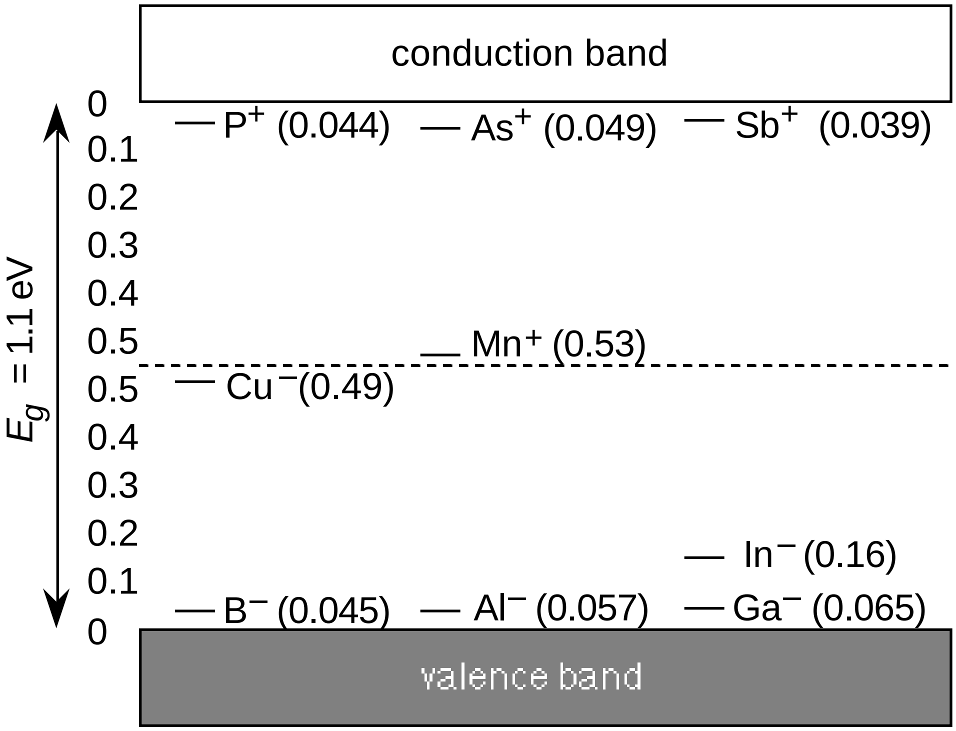

Figure 8.7. Energy levels for isolated impurities in silicon, with the ionization energies in parentheses. The energies are measured from the nearest band edge and are reported in electron volts. Donors are indicated with a plus charge and acceptors with a minus charge, their charges after ionization leading to conduction-band electrons and valence-band holes, respectively. (Adapted from reference 5.)

The celebrated absorption and emission spectra of the hydrogen atom, which arise from electronic transitions between the quantized electronic energy levels of the atom, also have counterparts in doped semiconductors. Similar energy levels in the band-structure diagram for semiconductors, are shown in Figure 8.8 for silicon doped with donor atoms. The energies of the ground state of the dopant (the state corresponding to the principal quantum number n = 1; this is the state shown in diagrams like Figure 8.7) and its excited states (n = 2, 3, etc.) are located relative to the conduction-band edge, which represents n = infinity and corresponds to ionization. Because of the minimal thermal energy needed to ionize the dopants, extremely low temperatures are required to observe these transitions spectroscopically *(6)*.

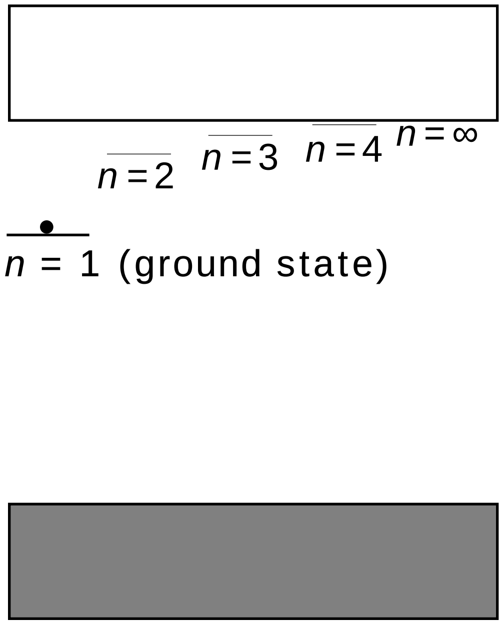

Figure 8.8. A hydrogen-atom analogy may be used to describe dopants in semiconductors. Superimposed on the normal band diagram for a donor-doped semiconductor are several discrete energy levels that correspond to excited states for the donor's bound electron. The ground state is that shown for the donor atom in Figure 8.6B, and promotion of the donor's electron into the conduction band is equivalent to ionization. In this figure, the separation between the energy level of the donor atom and the conduction band has been expanded to show the energies of the excited states more clearly. Like the hydrogen atom, a doped semiconductor would be expected to show narrow spectral bands due to electronic transitions between discrete energy levels; these bands can be observed at very low temperatures. A similar diagram could be drawn for an acceptor-doped semiconductor.

Dopants for Compound Semiconductors

For compound semiconductors like GaAs, the same principles involving dopant size and valence-electron count can be utilized to alter the solid's electrical properties. For example, substitution of a comparably sized Group 16 element like Se or Te for As leads to an n-type material, because the dopant is a donor with one extra valence electron relative to As. Substitution of a comparably sized Group 12 element like Zn for Ga produces p-type material, because the Zn atom, with two valence electrons, is an acceptor relative to Ga. An interesting case is provided by Group 14 dopants, which would be predicted to serve as donors if they substitute for Ga and as acceptors if they substitute for As. Both types of situations occur: in GaAs, C is found to be an acceptor and Sn is found to be a donor.

The Semiconductor as an Acid–Base System

In addition to water, many other solvents autoionize with the formation of cationic and anionic species that are regarded as the strongest acidic and basic species that exist in the medium. For example, NH_3 dissociates into NH_4^+ and NH_2^- ($K \sim 10^{-26}$); and H_2SO_4 into $H_3SO_4^+$ and HSO_4^- ($K \sim 10^{-4}$). A species that increases the characteristic cation concentration of the solvent is regarded as an acid, and a species that increases the characteristic anion concentration as a base. Scales analogous to the pH scale of water can be constructed with the neutral point occurring where the concentrations of the cation and anion are equal.

Applying this kind of definition to a semiconductor like silicon, the mobile hole can be regarded as the acid species and the mobile electron can be regarded as the basic species. Dopants can be classified on the basis of the way they affect the relative concentrations of these electrons, n, and holes, p. In the sections that follow, the analogy will be made that the holes correspond to like-charged protons (h^+ is like H^+); and that the electrons correspond to like-charged hydroxide ions (e^- is like OH^-). An alternative analogy that emphasizes the correspondence of electrons in the semiconductor with protons in water—the species that are physically transferred in the two media—can also be made.

Effect of Doping on Conductivity

We can elaborate on the semiconductor–acid–base analogy by considering species in both media that strongly dissociate. The species in semiconductors that best mimic strong acids and bases, which fully ionize when placed in water, are acceptor and donor dopants whose energy levels lie very near the valence- and conduction-band edges, respectively (Figure 8.7). These so-called “shallow dopants” can be ionized to a substantial extent by thermal excitation at room temperature: Electrons are excited from the donor orbitals into the conduction band to produce carriers in the conduction band; or from the valence band into the acceptor orbitals to create holes in the valence band.

The behavior of silicon illustrates why small concentrations of dopants can have an enormous effect on electrical conductivity, which depends on the density of charge carriers (Chapter 7). As noted, pure silicon has equal but small numbers of electrons and holes carrying charge in the conduction and valence bands, respectively, with $n = p = {\sim}1 \times 10^{10}$ cm^{-3}. If only one in a million silicon atoms is replaced with a phosphorus atom, then at temperatures at which most of the donors are ionized, the value of n leaps to ~10^{17} cm^{-3}, roughly a ten-million-fold increase in charge carrier density and electrical conductivity over pure silicon.[2] Because the chemical equilibrium must satisfy equation 4, the value of p must drop by the same factor, to ~10^3 cm^{-3}. Semiconductors for which $n > p$ are called n-type semiconductors and are analogous to alkaline solutions for which [OH$^-$] > [H$^+$].

Similarly, if aluminum atoms had been introduced at the part-per-million concentration level and were largely thermally ionized, p would be ~10^{17} cm^{-3} and n would drop to ~10^3 cm^{-3} ($= K/p$). Semiconductors for which $p > n$ are called p-type and are analogous to acidic solutions for which [H$^+$] > [OH$^-$].

In semiconducting materials with an imbalance in n and p, whichever particles are in larger concentration are called majority carriers and those in smaller concentration are minority carriers. Thus in n-type materials, electrons are majority carriers and holes are minority carriers, with the reverse the case in p-type materials. The inversely related values of n and p can also be regarded as an analogy for the common ion effect: addition of a donor shifts the equilibrium position of equation 4 so that the concentration of valence-band holes is suppressed; addition of an acceptor likewise suppresses the concentration of conduction-band electrons.

Analogies to Weak Acids and Bases

In addition to aluminum or phosphorus, a variety of other atoms can enter a silicon crystal and introduce energy levels within the band gap in accord with their ionization properties. Figure 8.7 shows, for example, that copper acts as an acceptor and introduces energy levels at 0.49 eV above the valence-band edge. For this so-called “deep acceptor,” thermal energy at room temperature can fill only a small fraction of these states with electrons from the valence band. Thus, copper somewhat increases the hole concentration in the valence band, but by less than if the copper atoms reacted completely to give Cu$^-$ and an equal number of holes. This process is analogous to the ionization of a weak acid in water: the proton concentration is increased but by much less than the stoichiometric number of moles of acid added.

Similarly, manganese serves as a deep donor, characterized by a state lying 0.53 eV below the conduction-band edge. This state is relatively far from the conduction band edge; at room temperature few of the manganese atoms will be thermally ionized to Mn$^+$ and an equal number of conduction-band electrons. This reaction is analogous to the behavior of a weak base in water, which increases the concentration of hydroxide ions but by much less than the stoichiometric number of moles of the base added.

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[2] This number can be calculated by determining the number of atoms per cubic centimeter of silicon (density times Avogadro's number divided by the atomic mass of Si) and then dividing the value obtained by 10^6. The latter factor represents the substitution of one phosphorus atom per million silicon atoms and assumes that they are all ionized. The value obtained is 5×10^{16} charge carriers/cm^3, which was rounded to ~10^{17}/cm^3 in the text.

The Fermi Level and Its Analogy to pH

Irrespective of what species have been added to water, their influence on the solution is described in terms of the concentration of hydrogen ions through the pH value (related to the thermodynamic chemical potential): Both pure water and solutions with a pH of 7 are described as neutral; all solutions with pH less than 7 are acidic and those with pH greater than 7 are alkaline.

The analogous property of interest in characterizing electronic materials is the concentration of electrons. This concentration is reflected in the so-called Fermi level, E_f (the thermodynamic electrochemical potential), which is defined as the energy at which the probability of finding an electron is 1/2, i.e., below the Fermi level it is more likely that the electronic states are occupied with electrons, and above the Fermi level it is more likely that they are not. For a metal at room temperature, the Fermi level occurs at roughly the energy of the highest occupied level in the partially filled band at 0 K[3] (Figure 8.9A).

The position of the Fermi level relative to the band edges provides the analog of the pH scale associated with aqueous solutions. A pure semiconductor for which $n = p$ will have its Fermi level in about the middle of the band gap[4] (Figure 8.9B), an analogy to pure water having a pH of 7, in the middle of the common pH range. As acceptors are added to a neutral semiconductor, increasing the concentration of holes and reducing the concentration of conduction band electrons (making $p > n$) , the Fermi level will shift toward the valence-band edge (Figure 8.9C), reflecting the fact that it is less likely that electrons will be found occupying the higher energy levels of the conduction band. This is analogous to adding acid to a neutral solution, moving the pH to values <7. Conversely, as donors are added to a neutral semiconductor, enhancing the concentration of conduction-band electrons (making $n > p$) and the likelihood that electrons will be found occupying the higher energy levels of the conduction band, the Fermi level will shift toward the conduction-band edge (Figure 8.9D), just as adding base to a neutral solution moves the pH to values >7.

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[3] At 0 K, the electrons will be paired in the lowest energy levels of the solid, and the Fermi level will occur at the top of the occupied energy levels: there is a sharp break between the occupied (probability of occupancy is one) and the unoccupied (probability of occupancy is zero) energy levels at 0 K. As the temperature increases, some of the electrons will be promoted to higher energy levels by absorbing thermal energy, causing the occupation probability to change less abruptly, but leaving the energy at which the occupancy probability is 1/2 (the Fermi level) at about the same energy.

[4] Because of the statistical origin of the Fermi level, there need not be an occupiable energy level at the Fermi level. Occurrence of the Fermi level near the middle of the band gap reflects the fact that the probability of occupancy is very high in the valence band and very low in the conduction band. The exact position of the Fermi level depends on several factors, including the effective masses of the electrons and holes; *see* reference 7.

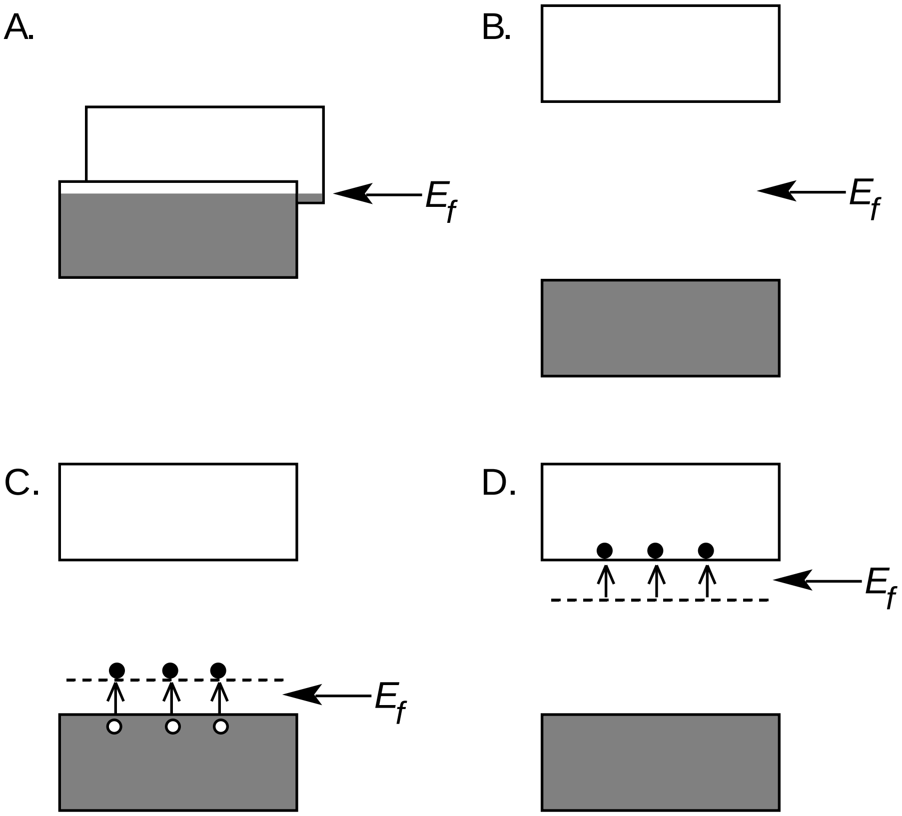

Figure 8.9. The position of the Fermi level (E_f) for (A) a metal, (B) an undoped semiconductor, (C) a p-type semiconductor, and (D) an n-type semiconductor.

Extent of Ionization

The pH of aqueous solutions and the Fermi level in semiconductors play analogous roles in determining the extent of ionization in the two media. Figure 8.10 encapsulates the analogy. For a weak acid, HA, the fraction of molecules in the protonated form depends on the relative values of pK_a and pH: as pH is lowered relative to the pK_a of the acid, a progressively larger fraction of molecules will be in the protonated form, HA; conversely, as pH increases to values exceeding pK_a, a progressively larger fraction of these molecules will be in the deprotonated form, A^-. When pH = pK_a, equal quantities of the protonated and deprotonated species are present. These relationships are easily seen by rearranging the equilibrium constant expression to: $K_a/[H^+] = [A^-]/[HA]$; or, $\mathrm{pH} - \mathrm{p}K_a = \log\{[A^-]/[HA]\}$.

Similarly, for a weak acceptor whose ionization energy is E_I (*see* Figure 8.7), the Fermi level position E_f will dictate the percentage of acceptors that are ionized (formally A^-) or un-ionized (formally A): As the Fermi level moves toward the valence-band edge (analogous to moving to low pH), progressively more of the acceptors will be un-ionized; as the Fermi level moves toward the conduction-band edge (analogous to moving to high pH), progressively more of the acceptors will be ionized. When the Fermi level is at the acceptor energy level, there will be roughly equal numbers of ionized and un-ionized acceptors.[5]

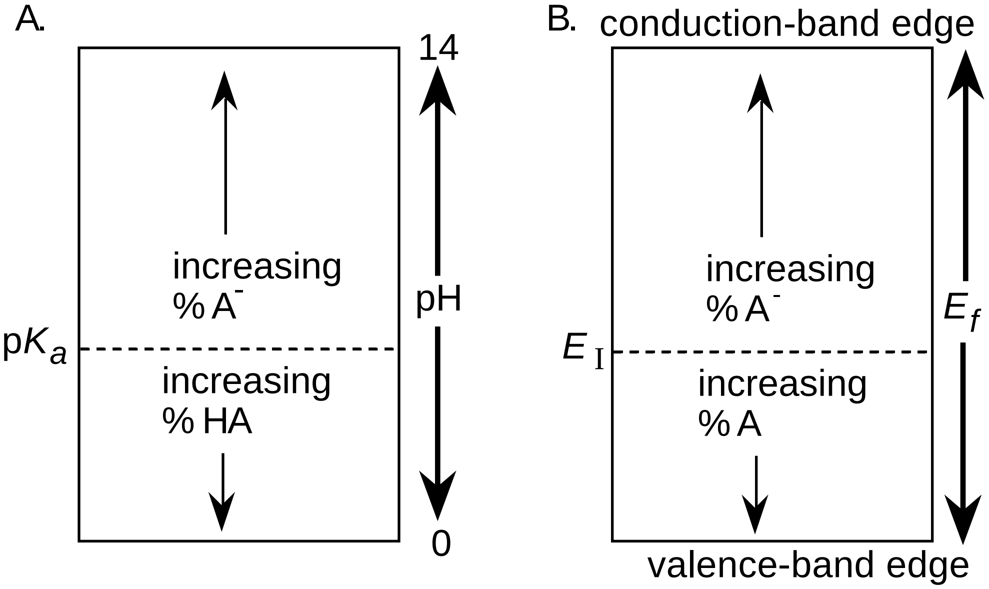

Figure 8.10. A: The relative amounts of HA and A^-, the protonated and deprotonated forms of a weak acid, can be varied by changing the pH relative to pK_a. B: Similarly, the relative amounts of A and A^-, the un-ionized and ionized forms of a weak acceptor, respectively, can be varied by changing the Fermi level, E_f, relative to the ionization energy level of the acceptor, E_I. The separation of the band edges is equal to the band gap, E_g.

Similar analogies can be established for weak bases in water and weak donors in the semiconductor: the ratio of protonated to deprotonated base, BH^+/B, will increase with decreasing pH; and the ratio of ionized to un-ionized donor, D^+/D, will increase as the Fermi level moves toward the valence band.

Neutralization Reactions and Buffers

Neutralization reactions can be established in the solid just as they are in aqueous solution and followed by shifts in the Fermi level in the same way that pH changes would be used to chart the course of titrations in water. As an example, consider a sample of p-type, aluminum-doped silicon with a concentration of acceptors, N_a. As noted, Al readily accepts electrons, a behavior making it analogous to a strong acid, for which the Fermi level will lie near the valence-band edge, as shown in Figure 8.9C.

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[5] The 1:1 ionized:un-ionized concentration analogy is not exact at this energy because of the spin of the electron. *See* reference 3.

The concentration of p should thus be ~N_a, just as [H^+] is taken as the concentration of a strong acid in water.

If the sample is now heated in phosphorus vapor to achieve uniform incorporation, ionizable electrons from these donor phosphorus atoms that are introduced at concentration N_d can combine with these valence-band holes, reducing p to ~ (N_a – N_d) and shifting E_f toward the conduction band. When $N_d = N_a$, the equivalence point has been reached, $n = p$, and E_f should be roughly in the middle of the band gap, analogous to a neutral aqueous solution. Additional phosphorus will increase n and continue to decrease p [$n \sim (N_d - N_a)$; $p \times n = K$] and shift E_f closer to the conduction band, just as adding base past the equivalence point would move the pH into the alkaline regime. A graph of the position of E_f versus $|(N_a - N_d)|$, plotting the course of the so-called “compensation” process, is shown in Figure 8.11. The shape is similar to a strong-acid–strong-base titration. Of course, this same sequence can be run in reverse, beginning with a phosphorus-doped silicon sample to which aluminum is added: In this case, the Fermi level begins near the conduction band and moves toward the valence band.

Similar compensation reactions can occur between a strong donor and weak acceptor, between a strong acceptor and a weak donor, and between a weak acceptor and weak donor. Analogous to titrations between strong bases and weak acids, and between strong acids and weak bases, a buffer region is established: just as pH is roughly constant over large changes in the strong-acid or strong-base concentration because of the interconversion of conjugate weak acid–base forms, the Fermi level is constant over large changes in strong-acceptor or strong-donor concentrations because of the interconversion of conjugate ionized–un-ionized donor or acceptor forms (relative concentrations of ionized and un-ionized forms).

As in aqueous solution, these relations can be understood in light of the equilibria that are involved. Addition of strong donors in the titration of a weak (deep) acceptor A, such as Cu in Figure 8.7, will cause formation of the ionized acceptor, A^-, rather than releasing the donor's electron to the conduction band; the analogy can be made to titrating a weak acid like HF with hydroxide ion:

$$HF + OH^- \rightarrow H_2O + F^- \tag{9}$$

$$A + e^- \text{ (from strong donor)} \rightarrow A^- \tag{10}$$

Similarly, addition of strong acceptors in the titration of a weak (deep) donor D, such as Mn in Figure 8.7, will cause formation of the ionized donor, D^+, rather than increasing the concentration of holes in the valence band; the aqueous analogy is to titrating a weak base like NH_3 with strong acid:

$$NH_3 + H^+ \rightarrow NH_4^+ \tag{11}$$

$$D + h^+ \text{ (from strong acceptor)} \rightarrow D^+ \tag{12}$$

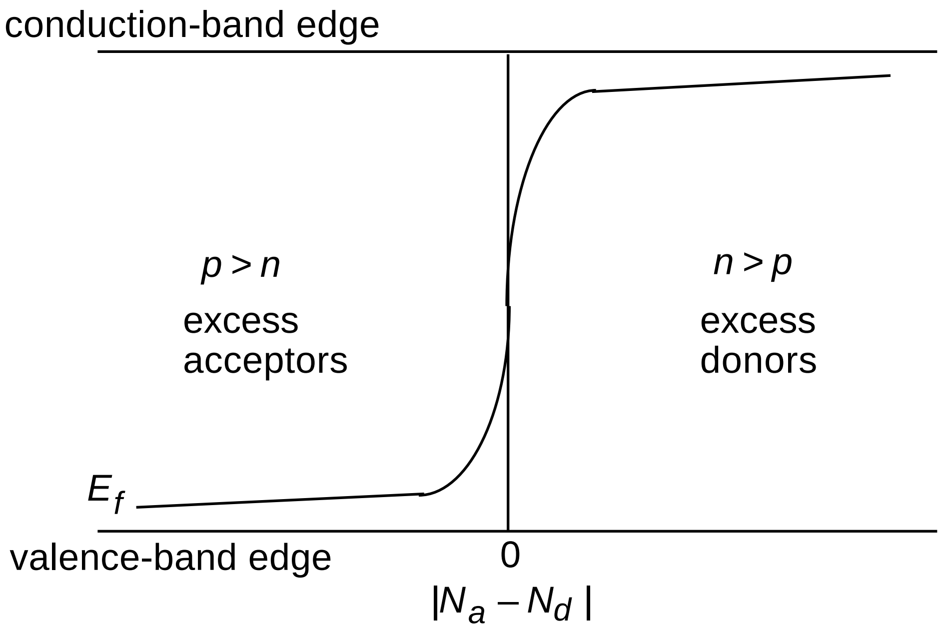


Figure 8.11. A plot of the position of the Fermi level (E_f) as a function of doping. The left side of the diagram corresponds to a p-doped semiconductor, with N_a equal to the number of acceptor atoms. In p-type semiconductors the Fermi level is just above the valence band (*see* Figure 8.9C). Electrons provided by the addition of small amounts of donor atom impurities (N_d) will annihilate some of the valence-band holes in what can be thought of as a neutralization reaction in the semiconductor. The net number of acceptors remaining will be $|N_a - N_d|$. As a result, the Fermi level shifts toward the conduction band. When the number of donors equals the number of acceptors, the "equivalence point" is reached, and the Fermi level is roughly halfway between the valence and conduction bands. As more donor atoms are added to the semiconductor, the Fermi level continues to rise. When the number of donors has exceeded the number of acceptors present initially, the semiconductor has become essentially n-type. This process is analogous to the titration of a strong acid with a strong base. The *x*-axis in this plot, $|N_a - N_d|$, is analogous to the volume of titrant added. (Adapted from reference 8.)

The p–n Junction: A Solid-State Concentration Cell

If acidic and alkaline solutions are mixed, the neutralization reaction is favorable and rapid. Alternatively, it is possible to exploit the difference in concentration of H^+ of these two solutions to create an electrical output by means of a concentration cell. As shown in Figure 8.12, if a couple like

H^+–H_2 is established in the two solutions (hydrogen gas at 1 atm is bubbled over Pt electrodes immersed in the solutions), and the two solutions are connected by a salt bridge, a potential difference (voltage) can be measured. The cell can be written as $H_2|NaOH(aq)||HCl(aq)|H_2$. For solutions that are 1 M in acid and base, a voltage of 0.83 V is realizable. This value is determined from the Nernst equation at 298 K by treating the system as a concentration cell for the reaction

$$[H^+]_{\text{acid side}} \rightarrow [H^+]_{\text{base side}} \tag{13}$$

The Nernst equation for this concentration cell may be written as

$$E = E^{o} - \frac{RT}{nF} \ln Q = \frac{-2.3\ RT}{F} \log \frac{[H^+]_{\text{base side}}}{[H^+]_{\text{acid side}}} \tag{14}$$

where R is the universal gas constant; T is absolute temperature; n is the moles of electrons; F is Faraday's constant, and Q is the reaction quotient. Because $[H^+]_{\text{acid side}} > [H^+]_{\text{base side}}$, E is positive. Of course, if the output energy is recovered as electricity by allowing current to pass, both solutions will eventually have equal values of $[H^+]$, corresponding to pH 7, and the chemicals must be replenished to continue the cell's operation.

If a p-type semiconductor is again regarded as analogous to an acidic solution and an n-type semiconductor to an alkaline one, their juxtaposition as in Figure 8.13 also represents a concentration cell, because the concentrations of electrons, the Fermi levels, in the two phases (high in the n-type material; low in the p-type material) will seek to come to equilibrium by the reaction

$$[h^+]_{\text{p-type side}} \rightarrow [h^+]_{\text{n-type side}} \tag{15}$$

or

$$[e^-]_{\text{n-type side}} \rightarrow [e^-]_{\text{p-type side}} \tag{16}$$

The "built-in" voltage that develops between these two phases that are brought together at what is called a p–n junction is given by the same kind of Nernstian expression, reflecting the analogous equilibrium considerations:

$$E\ (\text{in volts}) = \frac{-2.3\ RT}{F} \log \frac{[h^+]_{\text{n-type side}}}{[h^+]_{\text{p-type side}}} = \frac{-2.3\ RT}{F} \log \frac{[e^-]_{\text{p-type side}}}{[e^-]_{\text{n-type side}}} \tag{17}$$

One means for preparing a p–n junction has been intimated in connection with the neutralization (compensation) experiment (Figure 8.11). If a sample of n-type Si is exposed to a high concentration of aluminum vapor for a short time, the surface region of the solid can be made to become p-type by virtue of now having a higher acceptor concentration than donor concentration. The bulk sample is still n-type, however, because the aluminum atoms are not given time to diffuse into

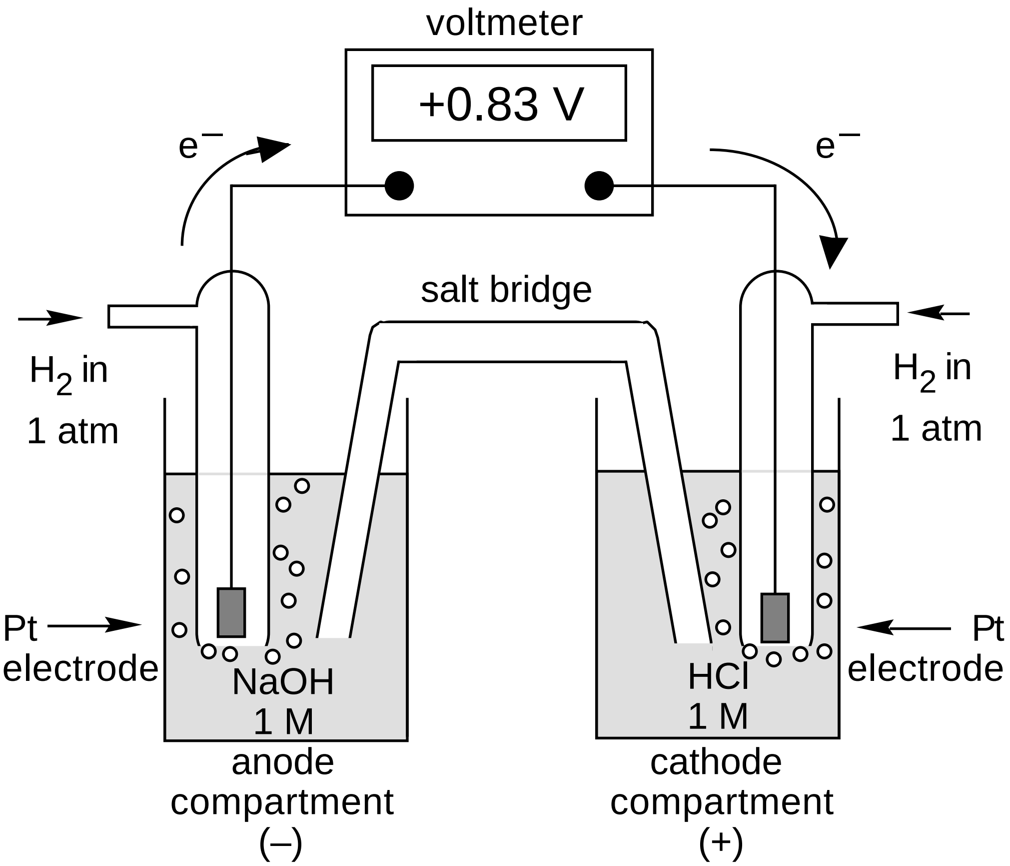


Figure 8.12. An electrochemical cell. The right compartment is the standard hydrogen electrode (1 M HCl, 1 atm H_2) and the left compartment contains 1 M NaOH and 1 atm H_2. This cell will produce a potential of +0.83 V at 298 K and may be thought of as a concentration cell in which the right compartment has $[H^+]$ = 1 M and the left compartment has $[H^+] = 1 \times 10^{-14}$ M.

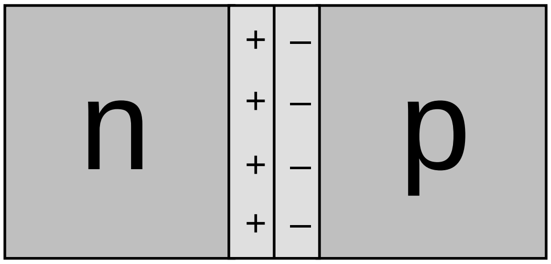


Figure 8.13. A p–n junction. Electrons spontaneously flow from the n-type side to the p-type side until equilibrium is reached. This leaves a small region with a net positive charge on the n-type side of the junction and a region with a net negative charge on the p-type side, opposing the additional net flow of charge across the junction.

the bulk at the elevated temperature employed. And at room temperature, diffusion is sufficiently slow for these dopants that it can be neglected. This process will not give an atomically abrupt p–n junction but rather a narrow region over which the conductivity will gradually change from n-type to p-type. With modern growth methods based on chemical vapor deposition (CVD) and molecular beam epitaxy (MBE), junctions that are virtually atomically abrupt can now be prepared (*see* Chapter 10).

The electronic properties of the p–n junction provide an explanation for the operation of LEDs, diode lasers, and photovoltaic (solar) cells. As shown in Figures 8.13 and 8.14, when a junction is formed between an n-type and p-type semiconductor, electrons flow from the n-type semiconductor (at higher electron concentration) to the p-type semiconductor (at lower electron concentration) until the electrochemical potential (Fermi level) is equalized in the two materials. The transfer of charge at the junction leaves a small region of net positive charge at the n-type side and a small region of net negative charge at the p-type side of the junction. The charge separation internally builds up a small difference in potential energy, and thus produces a voltage across the junction.

The bending of the band edges in the equilibrium sketch of Figure 8.14 reflects the distribution of the internal or “built-in” voltage through the junction. The electrochemical potential of electrons in the donor-doped material is lowered because of the buildup of positive charge, while the electrochemical potential of electrons in the acceptor-doped material is raised because of the buildup of negative charge, until the electrochemical potentials have equilibrated. Then there is no further net transfer of charge across the interface.

If a circuit is now prepared by making low resistance (ohmic) contacts with metals, one to the n-type material and one to the p-type material, a variety of energy conversion schemes can be realized once a voltage source or light source is introduced into the circuit.

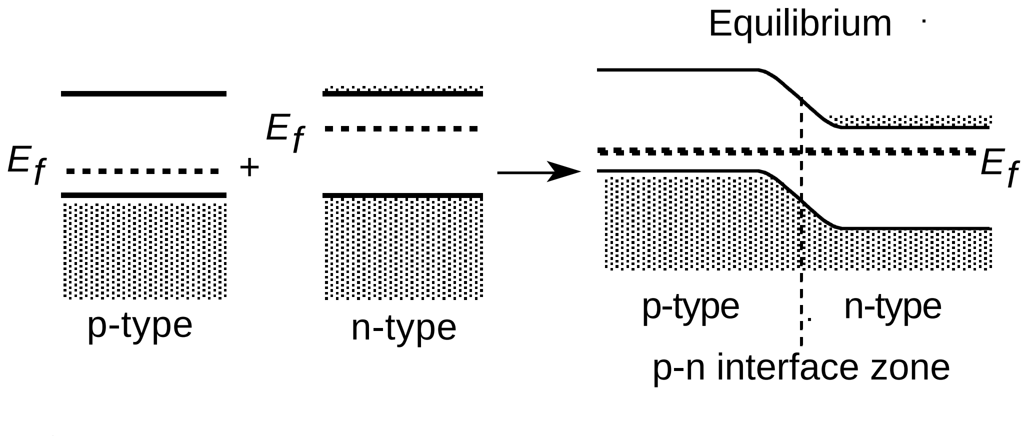


Figure 8.14. A band-energy diagram of a p–n junction. The two semiconductors are in equilibrium with each other and must have their Fermi levels at the same energy. The band-gap energy does not change throughout the solid. Only the top portion of the valence band and the bottom portion of the conduction band are shown.

Biasing the p–n Junction

The introduction of an external voltage source into the circuit (called biasing) to induce a current disturbs the equilibrium situation just described. Substantial current flow through the junction requires that electrons in the conduction band move from the side with more electrons to the side with fewer electrons. Similarly, holes in the valence band must move from the side with more holes to the side with fewer holes. Thus, electrons must be given enough energy to move over the potential energy barrier from the n-type side to the p-type side, while holes must be forced to move under the barrier from the p-type side to the n-type side during current flow (recall from Demonstration 8.1 that hole energies increase downward).

If the voltage applied to the n-type side is negative relative to that applied to the p-type side, the voltage is referred to as forward bias. The energy barrier for electrons and holes to flow through the junction is decreased relative to the equilibrium energy barrier, Figure 8.15A, and substantial current can flow through the junction. Under reverse bias the opposite situation occurs. The applied voltage adds to the internal voltage, Figure 8.15B, making current flow even more difficult. This is the essence of diode behavior: The current increases exponentially with forward bias and is negligible with reverse bias, as sketched in Figure 8.15C.

Under forward bias, the electrons reaching the p-type side and the holes reaching the n-type side are minority carriers in these regions. They can recombine with the majority carriers that are in abundant supply (Figure 8.16). This recombination results in luminescence (emitted light), as electrical energy is converted to light by the p–n junction. A p–n junction used to produce light is called a light-emitting diode, LED, Figure 8.17.

The color of the luminescence can be controlled by varying the band gaps of the junction materials, as noted in Chapter 7. Employing semiconductors that are solid solutions is a particularly effective way to continuously tune the band gap (*see* Chapter 7). Semiconductors with the formulas GaP_xAs_{1-x} (x = 1.00 – 0.40) can be used to tune the bandgap from 1.88 eV (red light) to 2.23 eV (green light) *(9)*.

Laboratory. A laboratory that explores observed properties such as the color, wavelength and energy of light, and excitation voltage for a series of compound semiconductors appears as Experiment 7 of this book.

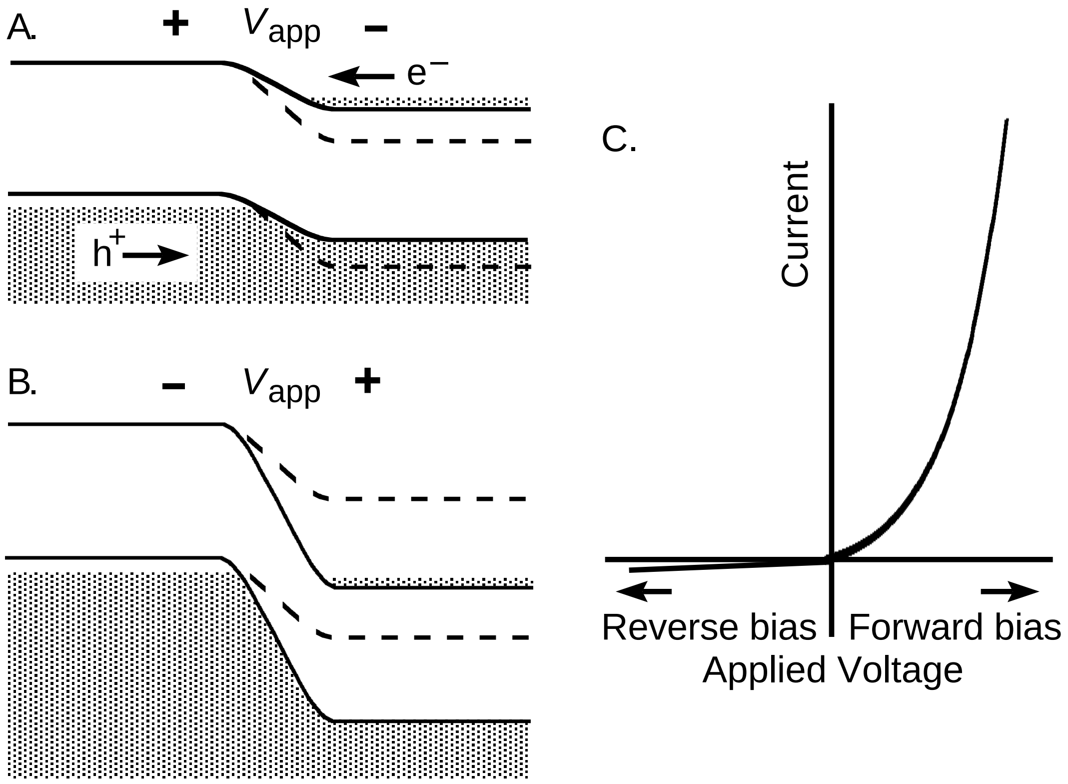


Figure 8.15. A: A p–n junction under forward bias conditions. B: A p–n junction under reverse bias. The dashed lines in A and B show the equilibrium band bending when no bias is applied, Figure 8.14. C: Current through a p–n junction as a function of applied voltage, V_{app}.

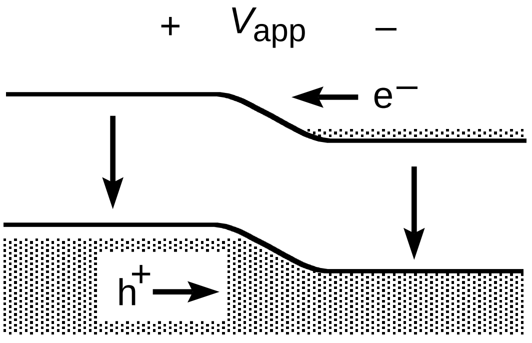


Figure 8.16. A p–n junction acting as a light-emitting diode (LED) under forward bias conditions. As electrons in the conduction band migrate toward the positive potential applied at the p-type side, they can return to the valence band (recombine with the abundant holes) and emit light of the band-gap energy. As holes in the valence band migrate toward the negative potential at the n-type side, they can recombine with the abundant electrons and emit light of the band-gap energy.

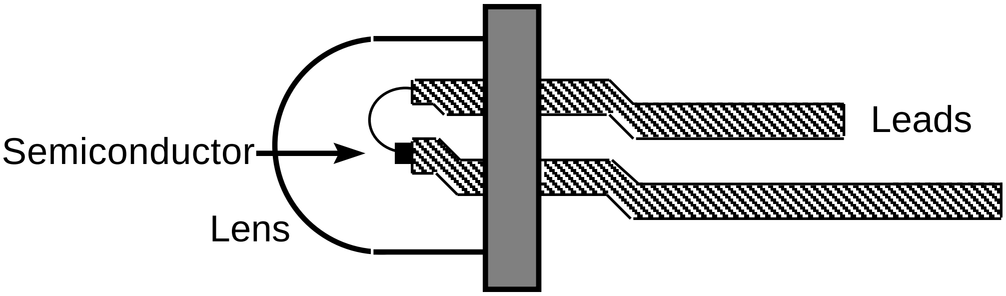


Figure 8.17. Schematic diagram of an LED.

Demonstration 8.3. Biasing and Dissection of an LED

Materials

LED (*see* Supplier Information for Chapter 7)
second LED with the cover removed (prepared before class)
A few milliliters of dichloromethane
LED circuit (containing a 1-kΩ resistor) described in Chapter 7 (*see* Figure 7.22B)
Magnifying lens or Micronta 30× microscope (Radio Shack)
Microscope connected to a television camera (optional)

Procedure

- Connect the LED to the battery in the two possible ways. The LED will light in one way (forward bias) and not in the other (reverse bias).
- Before class, place the second LED in dichloromethane. **CAUTION: Avoid inhalation of the vapors. Perform in a fume hood.** The plastic cover will slowly dissolve.
- Using a magnifying lens, observe that the semiconducting material is very small (~1 mm^2) and rests on a metal plate, which acts as the electrical contact for one side of the p–n junction. The electrical connection between the top of the chip (the other side of the p–n junction) and the electrical lead is made by a very thin piece of gold wire. This setup is shown in Figure 8.17. You may show the LED to the entire class at once using a microscope connected to a television camera. This equipment is often available in biology departments.
- Forward bias the LED by connecting it to a battery. If electrical contact through the gold wire is maintained, the LED will still light with its plastic lens removed.

It is possible to prepare a diode laser from a semiconductor p–n junction by making the structure in the shape of a laser cavity and electrically stimulating the recombination of such large numbers of carriers that lasing action results (Figure 8.18) *(10)*.

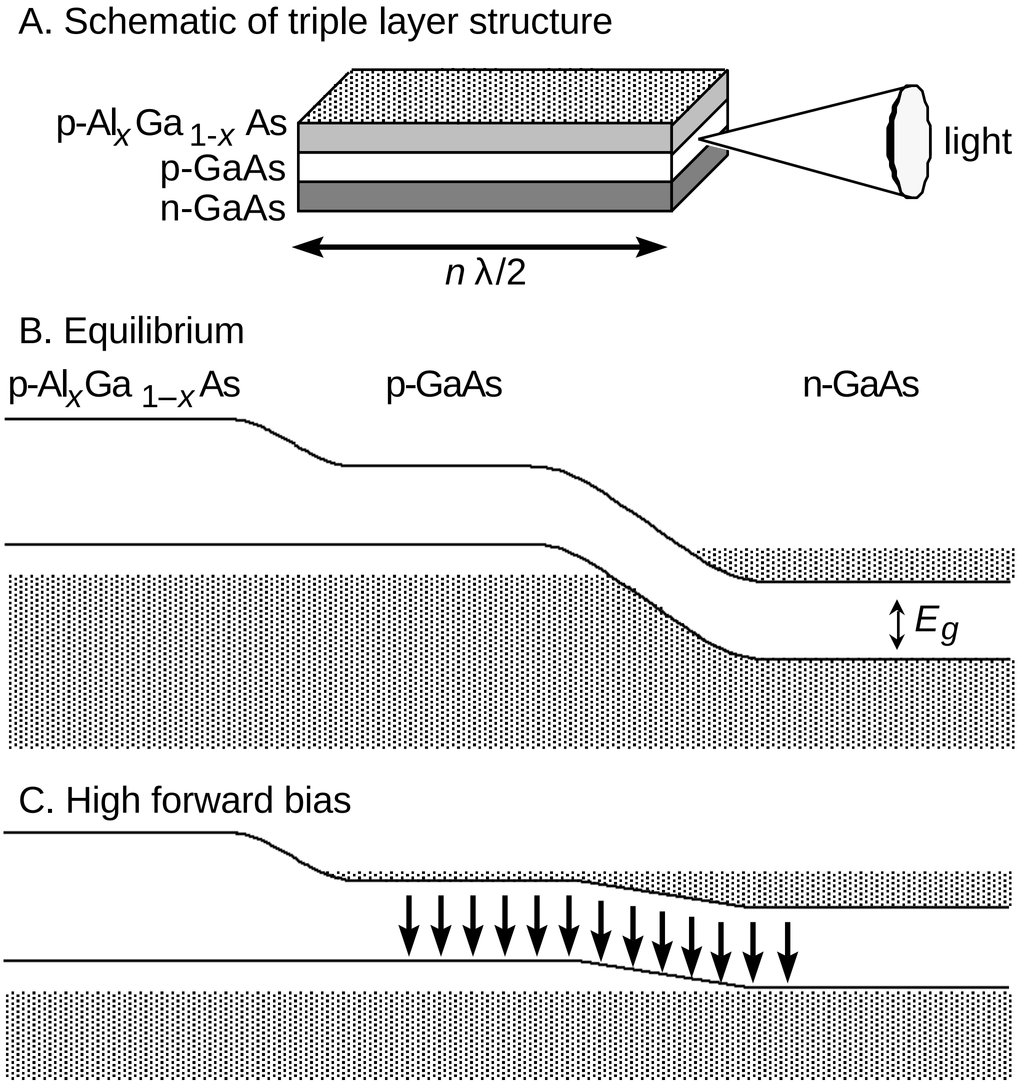


Figure 8.18. A: Schematic of a diode laser. The light is emitted from the p–n junction area. The cavity length itself must be a half-integral number of wavelengths of the light emitted. B: Confinement of the electron–hole pairs within the active lasing area of the solid is accomplished by bounding the active region with another semiconductor whose band gap is larger than that of the first semiconductor. In this case, a solid solution of Al$_x$Ga$_{1-x}$ As is used as the larger band-gap material, and GaAs is used as the narrower band-gap material. C: Under high forward bias, this construction forces electrons to stay within the GaAs region, where they recombine with holes that are present, and emit light in the process.

Finally, if light having an energy above the band gap of the semiconductor shines on the junction, the electron–hole pairs created in the junction region are separated by the electric field therein, as shown in Figure 8.19. This separation leads to an electrical current (at maximum efficiency, each photon absorbed moves one electron through the electric circuit), the basis of the photovoltaic cell in which the energy of light is converted into electricity by this remarkable solid-state concentration cell.

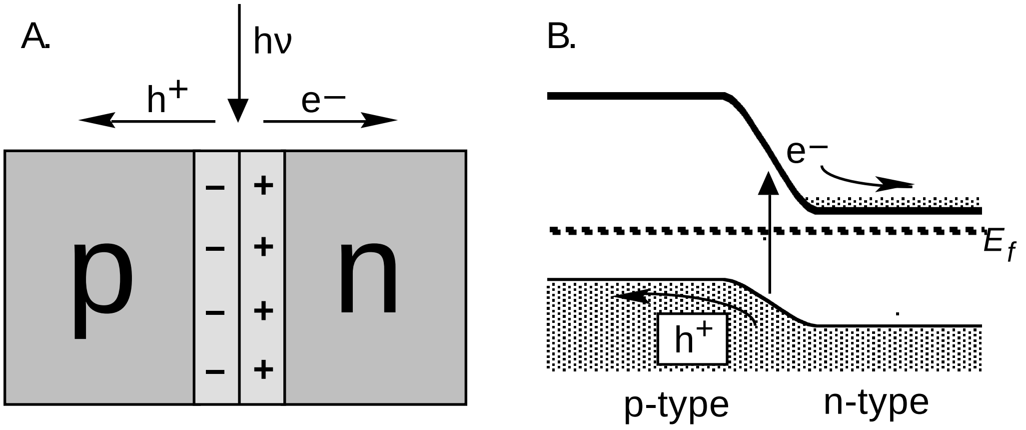


Figure 8.19. Two views of a photovoltaic cell based on the p–n junction. A: If light above the bandgap energy falls on the junction, the semiconductor will absorb the light. Electrons and holes will be generated and move toward opposite ends of the junction. The positive and negative signs represent the charges in the junction region resulting from the formation of the junction. B: A band diagram of the p–n junction. As light above the band-gap energy is absorbed in the junction region, electrons will be promoted from the valence band to the conduction band, leaving holes in the valence band. The slope of the band edge corresponds to the built-in electric field that causes the electrons to migrate toward the right (the n-type side) while the holes move toward the left (the p-type side) to create an electrical current. The magnitude of the current is determined by the absorbed light intensity: each photon can provide one electron to the current flow, but not all of the electrons may be collected. For example, defects in the solid may promote the recombination of the photogenerated electron–hole pairs, and thus lead to smaller electric currents.

Demonstration 8.4 can be used to illustrate how light absorption depends on solution path length and concentration, and thereby to discover or verify the Beer–Lambert law that is a cornerstone of spectroscopy. Use of a diode laser pointer as the light source and a solar cell based on a silicon diode as the light detector demonstrate the versatility of the p–n junction.

Demonstration 8.4. Counting Photons Using a Solar Cell

Materials

Diode laser (670 nm, 5 mW); other lasers (He–Ne, e.g.) and solutions can be substituted for those used here (*see* Supplier Information for Chapter 4)
Solar cell, approximately the size of the laser beam (Radio Shack); instructions for reducing the size of the solar cell are given in Laboratory Experiment 9
Two wires
Digital multimeter
Five or six Plexiglas cells (12 cm × 11 cm × 3.5 cm or 5.0 in × 4.5 in × 1.5 in)
$CuSO_4 \cdot 5\ H_2O$
Red food coloring
Darkened room or a cardboard box to serve as a light shield

Procedure

- Solder two wires to opposite sides of the solar cell in order to accommodate leads from the digital multimeter for measurements of current (*see* Experiment 9).
- Make a 0.01 M solution of Cu^{2+} by dissolving 2.5 g of $CuSO_4 \cdot 5\ H_2O$ in 1 L of water. Add a few drops of sulfuric acid if the solution is cloudy.
- Align the laser to strike the solar cell, allowing space in between for interposing as many of the Plexiglas cells as will be used. It is best to clamp the laser and solar cell in place, and to fix the laser in the “on” position. (See the diagram in Experiment 9.) **Caution: Do not look into the laser; its beam can damage the eye!** Try to set up the system so that there is only a small background current (minimal ambient light).
- *Uncorrected* relative numbers of photons transmitted by the copper solutions can be obtained by recording the solar cell current as a function of path length (here, the number of identical solution cells interposed in the path of the laser beam). Typical values are shown as in Figure 8.20A for zero to five solution cells. The fraction of light transmitted by a given solution or set of solutions is the current measured in their presence divided by the current measured in their absence. If time permits, a more accurate measurement can be made by correcting for reflective losses at the air–Plexiglas and Plexiglas–solution interfaces: the fraction of light transmitted is the current measured in the presence of the copper solutions divided by the current measured when the same cells are filled with water instead of cupric ion solution.

As each solution cell is added, providing a linear increase in path length, the same fractional decrease in transmitted light should be observed. Thus a semilogarithmic plot of the current versus the number of solution cells should be linear, as shown in Figure 8.20B.

- Make a 0.05 M cupric ion solution and dilute to 0.04 M, 0.03 M, 0.02 M, and 0.01 M concentrations. This step can either be done ahead of time or as part of the presentation of the demonstration. Again, add a few drops of sulfuric acid if the solutions are cloudy.
- Measure the current transmitted by each solution to estimate the fraction of transmitted light as a function of concentration. Data can again be corrected as described. A plot of the current versus cupric ion concentration or a semilogarithmic plot of the current versus cupric ion concentration can be prepared (Figures 8.20C and D). As was found for increases in path length, linear increases in concentration will decrease the transmitted light by the same fraction. Collected data should be well fit by the Beer–Lambert law: $-\log_{10}$ (fraction of light transmitted) = absorbance = absorptivity × concentration × path length
- Fill a cell with water and place enough red food coloring in it to make the solution color extremely dark. Despite the intense absorption in the visible spectrum, there should be little effect on the intensity of the transmitted laser light, a result illustrating the lack of absorbance by this solution at the monochromatic laser wavelength of 670 nm. Conversely, if a cell containing the visibly very pale cupric ion solution intercepts the beam, a significant decline in current will be seen, corresponding to the much stronger absorptivity at this wavelength of the cupric ions.

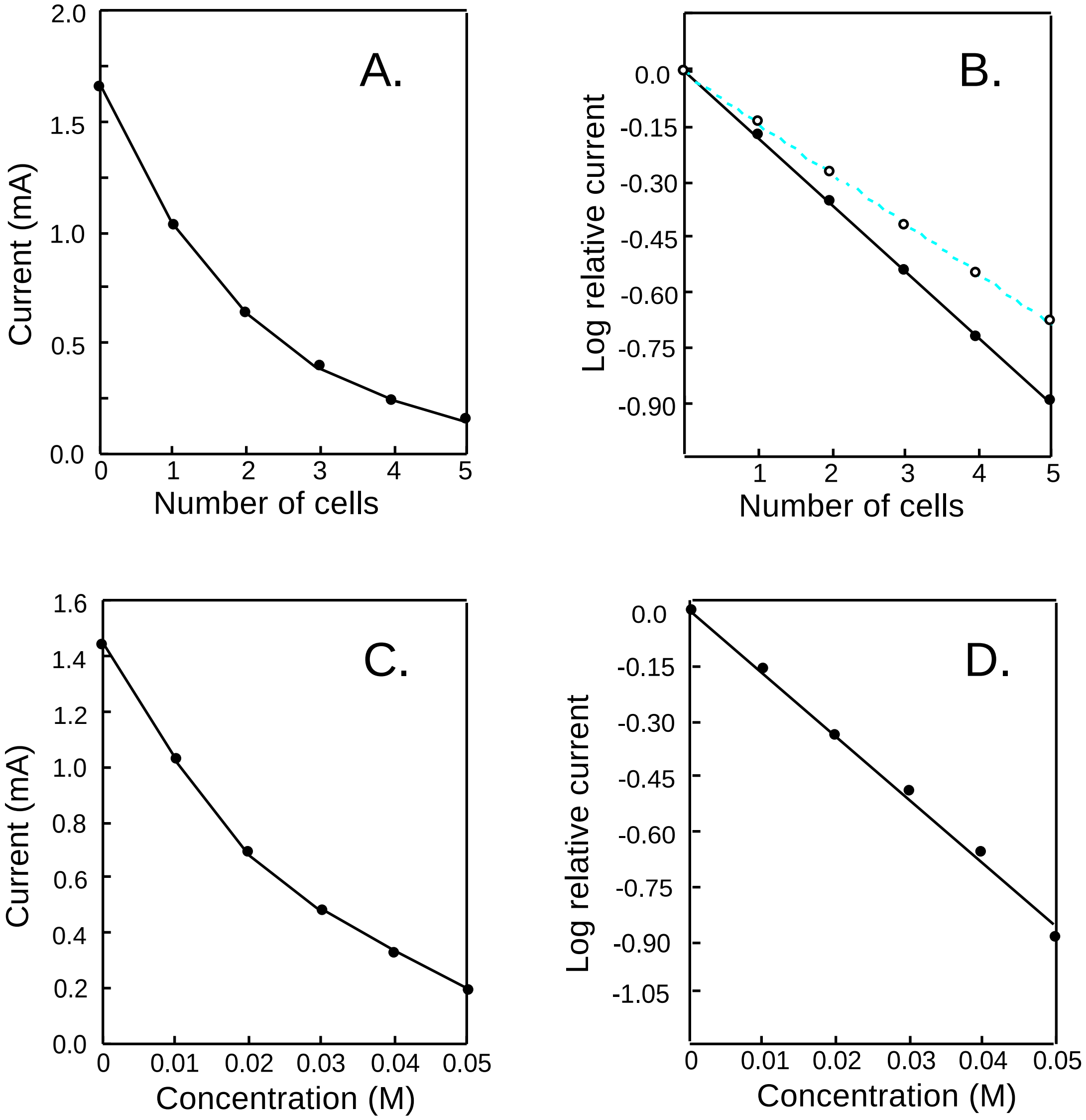
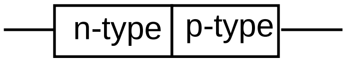


Figure 8.20. Data from Demonstration 8.4. A: Plots of photocurrent (uncorrected; see text) versus the number of cells, each of which contains 0.01 M copper sulfate. B: Plots of the logarithm of the relative photocurrent versus the number of cells used. The closed circles are for uncorrected data, while open circles represent data that have been corrected for reflective losses (*see* text). C: Plots of photocurrent versus copper sulfate concentration using a single cell. D: Plots of the logarithm of relative photocurrent versus the copper sulfate concentration. The same result was obtained with or without the correction for reflective losses.

The analogies between semiconductors and aqueous solution chemistry are summarized in Table 8.2.

Table 8.2 Parallels Between Aqueous Solution Chemistry and Semiconductors

Chemical Reaction	Aqueous Example	Silicon Example
Solvent autoionization	$H_2O \rightarrow H^+ + OH^-$ $K_w = [H^+][OH^-]$ $[H^+] \approx 10^{14}$ ions/cm^3	$Si_{(crystal)} \rightarrow h^+ + e^-$ $K = [h^+][e^-] = p \times n$ $[h^+] \approx 1.5 \times 10^{10}$ cm^{-3}
Strong acid–acceptor, strong base–donor	$HCl \rightarrow H^+ + Cl^-$ $NaOH \rightarrow Na^+ + OH^-$	$Ga \rightarrow h^+ + Ga^-$ $As \rightarrow As^+ + e^-$
Weak acid–acceptor; base–donor	$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$ $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$	$Cu \rightleftarrows h^+ + Cu^-$ $Mn \rightleftarrows Mn^+ + e^-$
Common ion effect	adding base (acid) suppresses the concentration of H^+ (OH^-)	adding a donor (acceptor) suppresses the concentration of h^+ (e^-)
Concentration cell[a]	H_2 ½NaOH½½HCl ½H_2 $E = \frac{-2.3RT}{F} \log \frac{[H^+]_{\text{base side}}}{[H^+]_{\text{acid side}}}$	 $E = \frac{-2.3RT}{F} \log \frac{[h^+]_{\text{n-side}}}{[h^+]_{\text{p-side}}}$

[a] Cell is treated as a concentration cell $[H^+]_{\text{acid side}} \rightarrow [H^+]_{\text{basic side}}$.

SOURCE: Adapted from reference 11.

Ionic Concentration Cells

Oxygen Sensors

Another kind of solid-state concentration cell is employed to control the ratio of air to exhaust gas in catalytic converters *(12)*. It is based on ZrO_2 that has been doped with CaO. Crystals of ZrO_2 doped with CaO have the fluorite structure (Chapter 5): the zirconium atoms form a face-centered cubic arrangement and the oxygen atoms fill all eight tetrahedral holes in the structure. If some of the Zr^{4+} is replaced by Ca^{2+}, oxygen vacancies must be created in order to maintain electroneutrality. The presence of vacancies in the tetrahedral holes now allows migration of oxide ions through these vacancies, and CaO-doped ZrO_2 acts as an ionic conductor in the solid state.

The oxygen sensor shown in Figure 8.21 acts in the following way: Oxygen molecules from the exhaust gas are adsorbed by platinum electrodes in the cell and converted into oxygen atoms. If the concentration of oxygen atoms in the other compartment (air, which has a constant oxygen content) is different, the oxygen atoms will have a tendency to migrate through the doped ZrO_2 solid as oxide ions. On the side with the higher oxygen content the following reactions are occurring:

$$O_2\,(g) + Pt\,(s) \rightarrow 2O\text{ (on the Pt surface)} \tag{18}$$

$$O\text{ (on the Pt surface)} + 2e^- \rightarrow O^{2-}\text{ (migrating through }ZrO_2) \tag{19}$$

The reverse reactions are occurring on the side with the lower oxygen concentration. (This behavior is analogous to the reactions 2 $H^+ \rightarrow H_2$ and $H_2 \rightarrow 2\ H^+$ in a concentration cell based on the standard hydrogen reaction.) The concentration on one side is known, so the measured potential difference can be related to the unknown oxygen concentration through the Nernst equation.

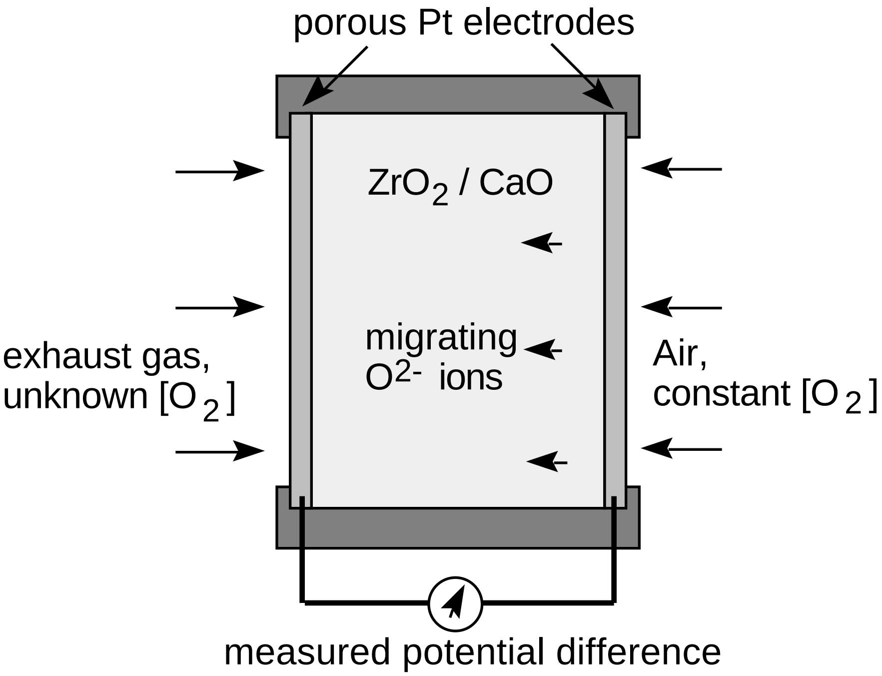


Figure 8.21. An oxygen sensor based on CaO-doped ZrO_2. Oxide ions are created at the platinum electrodes from O_2. If the concentration of O_2 is different in the two compartments, a potential develops. If the concentration in one compartment is known, the concentration in the other can be calculated using the Nernst equation. (Adapted with permission from reference 12.)

The Fluoride-Selective Electrode

Crystals of lanthanum fluoride (LaF_3) have provided the basis for a fluoride selective electrode, first developed in 1966 *(13, 14)*. Pure LaF_3 is conductive because of the mobility of the fluoride ions through the crystal; however, in the commercially available fluoride electrode, the samples are doped with EuF_2. Doping with a divalent cation creates fluoride vacancies for reasons described in the previous section and further increases the conductivity. A slice from a single crystal of the doped material serves as the electrode membrane.

At the interfaces of the membrane, ionization creates a charge on the membrane surface that depends of the fluoride concentration in solution, as follows:

$$LaF_3(\text{solid}) \rightleftarrows LaF_2^+(\text{solid}) + F^-(\text{solution}) \qquad (20)$$

and the cell potential becomes

$$E_{\text{cell}} = \text{constant} - \frac{2.3RT}{nF} \log a_{F^-}, \qquad (21)$$

where the constant depends on the reference electrodes and a_{F^-} is the activity of fluoride ions in solution.

Commercially available fluoride electrodes are very selective, with only the hydroxide ion interfering, and then only above a pH of 8. Below pH 5, protonation of fluoride to form hydrogen fluoride, to which the electrode does not respond, also causes error in total fluoride determinations. The LaF_3 fluoride-selective electrode has found applications in the analysis of minerals, fertilizers, drinking and waste water, teeth and bones. Solid-state electrodes are available that sense the other halides, CN^-, S^{2-}, SCN^-, Cd^{2+}, Cu^{2+}, Pb^{2+}, and Ag^+.

Laboratory. Experiment 12 involves the synthesis and study of Cu_2HgI_4, a compound that is an ionic conductor.

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Additional Reading

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- *Semiconductors*; Hannay, N. B., Ed.; Reinhold: New York, 1959.
- Streetman, B. G. *Solid State Electronic Devices,* 3rd ed.; Prentice Hall: Englewood, NJ, 1990.

Acknowledgments

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Exercises

1. At room temperature, which pure semiconductor would give rise to more electron–hole pairs, Ge or Si? GaAs or Si? Explain your answers based on Table 8.1.

2. Use Figure 8.5 to answer the following questions.
   a. Estimate the value of the autoionization equilibrium constant K for Si at 300 °C.
   b. From the temperature dependence of all of the substances shown, is autoionization a heat-absorbing or heat-releasing process? How do you know?
   c. At 20 °C, roughly how many times more positively-charged carriers does water have than GaAs?

3. Sketch a plot of Fermi level versus added dopant for a situation in which
   a. P is added as a dopant to In-doped Si
   b. Al is added as a dopant to Sb-doped Si

4. Show that the voltage in the cell shown in Figure 8.12 is 0.83 eV using either
   a. standard reduction potentials , or
   b. a concentration cell calculation

5. Determine whether the following are n- or p-type semiconductors:
   a. CdS in which silver substitutes for some cadmium atoms
   b. CdS in which bromine substitutes for some sulfur atoms

6. For the element Ge, which has the diamond crystal structure, the autoionization equilibrium constant at 300 K is 6×10^{26} cm^{-6}.
   a. What are the values of n and p at 300 K? Which elements might serve as dopants to increase n; to increase p. Why?
   b. If a donor is added that makes $n = 3 \times 10^{18}$ cm^{-3}, what is the corresponding value of p?
   c. The band gap for Ge is 0.7 eV. Sketch the band diagram, and indicate on it the positions of strong and weak acceptors and donors. Indicate where the Fermi level is for the three cases of $n = p$, $n > p$, and $n < p$.
   d. Compare the K value with that of Si (2×10^{20} cm^{-6}) and account for the difference qualitatively.
   e. Characterize In and Sb as donors or acceptors, explain why they have this characteristic in Ge, give the equations for their ionization, and describe their effect on the electron and hole concentrations.
   f. Predict what happens to the Fermi level if you begin with only In-doped Ge and then add Sb until the Sb concentration is much higher than the In concentration. What aqueous reaction is this like?
   g. When gold, Au, is doped into Ge, it is a weak acceptor, with an energy level of 0.2 eV. Where would it be placed on the band diagram and why?

7. Consider a solar cell (photovoltaic cell) made of GaAs, which has a band gap of 1.4 eV at room temperature.
   a. A rough absorption spectrum for GaAs is shown in Figure 8.22A. Explain its qualitative shape.
   b. A p–n junction is made from GaAs by starting with Se-doped GaAs (Se substitutes for As) and heating the solid in an atmosphere of Zn, which substitutes for Ga. Explain why this makes a p–n junction. With which semiconductor containing only a single kind of atom is GaAs isoelectronic?
   c. Each photon absorbed by a GaAs solar cell creates one conduction-band electron and one valence-band hole that contribute to electrical current in the solar cell. The efficiency of a solar cell (defined as electrical energy produced divided by the photon energy absorbed) is greatest for photons having roughly the band-gap energy. Why?
   d. Shown in Figure 8.22B is the solar output at the earth's surface. Why is GaAs a good choice for a solar cell material?

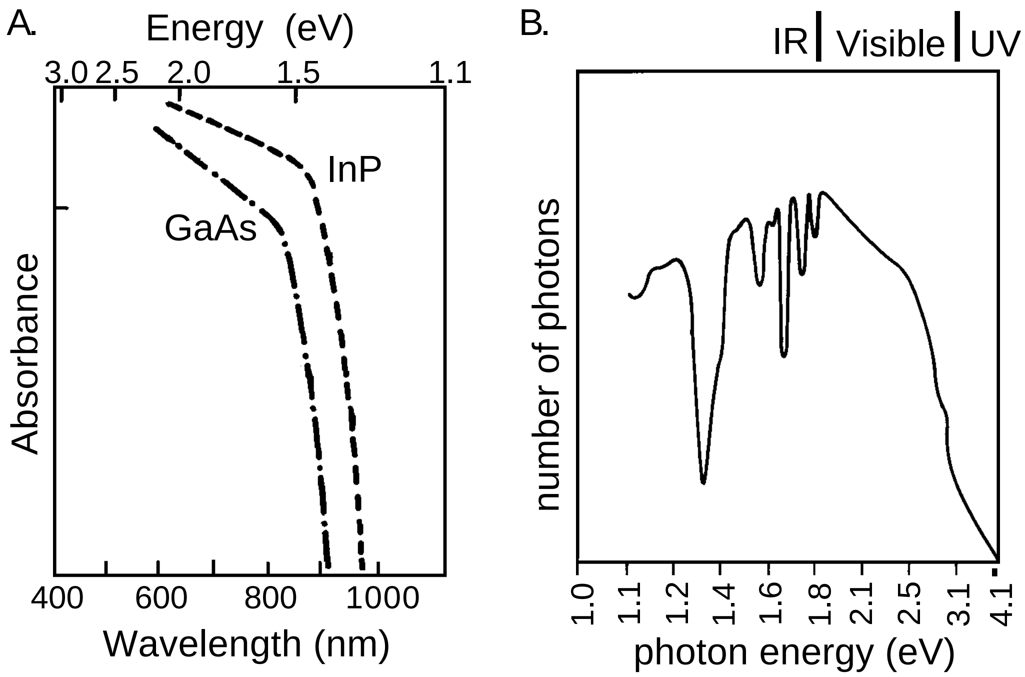


Figure 8.22. A: Absorption spectra of GaAs and InP semiconductors. B: The solar energy spectrum as measured at the earth's surface under average weather conditions. (Adapted with permission from references 15 and 16.)

8. Explain why the semiconductivity of pure silicon is strongly temperature-dependent while that of doped silicon is much less so.
9. An electrochemical cell is to be used to run a LED.
   a. Sketch all the components of an electrochemical cell that consists of Ag and Mg electrodes and suitable 1 M electrolytes (identify what they are).
   b. What voltage will this cell generate if the E^o values are as follows:

$$Ag^+ + e^- \rightarrow Ag \qquad E^o = 0.80\ V$$

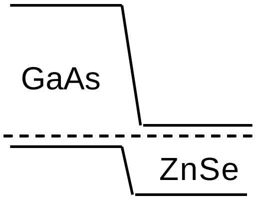
$$Mg^{2+} + 2e^- \rightarrow Mg \qquad E^o = -2.37\ V$$

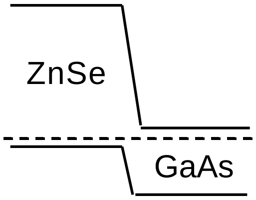
   c. If the voltmeter is removed, sketch the direction in which electrons will spontaneously flow in the wire and describe the net chemistry that will take place in each cell compartment.
   d. An InP LED is connected between the electrodes. Does it matter which side of the p–n junction is connected to which electrode and, if so, how do you connect it to make it glow?
   e. Suggest dopants that will substitute for In to make the p-type region of the LED and for P to make the n-type region. Explain your choices.
   f. Use the sketch shown in Figure 8.22A to predict the energy of the LED's light output, and explain your prediction.
   g. Discuss how long the LED can remain lit by the electrochemical cell by analyzing qualitatively what happens to the cell voltage over time. What energy conversions are taking place?

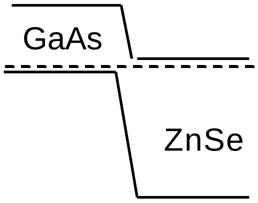
10. The ionization of a weak donor might be written as $D \rightarrow D^+ + e^-$; or as $D + h^+ \rightarrow D^+$. Interpret these two equations with an aqueous analogy.

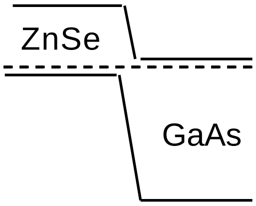
11. In this chapter it is stated that doped semiconductors will give rise to narrow spectra like that of the hydrogen atom. Calculate the energies for the following transitions in phosphorus-doped silicon. For each calculated energy, determine in what region of the electromagnetic spectrum these transitions will fall. (Take $0.3m_{e-}$ for the effective mass of the electron and $\varepsilon_r = 12$.)
    a. $n = 4$ to $n = 3$
    b. $n = 4$ to $n = 1$
    c. $n = 3$ to $n = 2$
    d. These spectra are often obtained at liquid helium temperature, 4.2 K. What is the ambient thermal energy at this temperature (kT, or RT on a molar basis) and how does it compare to the energies associated with these transitions?

12. Which of the following represents a junction between p-type ZnSe (band gap 2.7 eV) and n-type GaAs (band gap 1.4 eV) at equilibrium? The dashed line is the Fermi level.









13. In problem 12, which color light will pass through both semiconductors without being absorbed?
    a. ultraviolet light of 3.0 eV
    b. green light of 2.4 eV
    c. red light of 1.7 eV
    d. near-infrared light of 1.1 eV

14. If zinc is doped into germanium, it can contribute two holes to the valence band. Explain. Can you make an analogy to a particular kind of aqueous acid?

15. Using the Nernst equation, calculate the voltage that could be obtained from a silicon p–n junction where the majority carriers in the n- and p- type regions have a concentration of 10^{17} cm^{-3} ($K \sim 10^{20}$ cm^{-6}).

16. A 5-mW diode laser with output at 670 nm is directed at a solar cell.
    a. To how many moles of photons/second does this power correspond (1 W = 1 J/s)?
    b. If all of these photons are absorbed by the solar cell and each photon produces one electron in the solar cell circuit, how much current in amperes (1 A = 1 coulomb/sec) would be measured ?