

## Chapter 12: Water as Solvent; Acids and Bases

### Preview

We turn from water as a resource, to the properties of water as a solvent, and consider

- Hydrogen bonding, and the formation of clathrates and of biological structures
- Dissolved ions
- Strong and weak and bases acids
- Acid rain

### 12.1 Unique Properties of Water

Water is the most commonplace of substances, and yet its properties are unique among chemical compounds. Perhaps most remarkable are its high melting and boiling temperatures. **Table 12.1** lists the melting and boiling points for the hydrides from carbon to fluorine, all of which are elements in the first row of the periodic table. Compared to the neighboring hydrides, water has by far the highest melting and boiling points. One characteristic that makes Earth uniquely suitable for the evolution of life is its surface temperature which, over most of the planet, lies within the liquid range of water.

**Table 12.1** Liquid Temperature Range for Water and Neighboring First-Row Element Hydrides

	<b>CH<sub>4</sub></b>	<b>NH<sub>3</sub></b>	<b>H<sub>2</sub>O</b>	<b>HF</b>
Melting point (°C)	-182	-78	0	-83
Boiling point (°C)	-164	-33	100	20

#### 12.S1 Hydrogen bonding

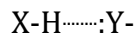
The high temperature required for boiling implies that liquid water has a high cohesive energy; the molecules associate strongly with one another. One source of this cohesion is water's high dipole moment (1.85 Debye\*). The O-H bonds are highly polar; negative charge builds up on the oxygen end while positive charge builds up on the hydrogen end. The dipoles tend to align with one another, increasing the cohesive energy. But if the dipole-dipole interaction were the only factor, then HF would have a higher boiling point than water, because it has a higher dipole moment (1.91 Debye). The greater cohesion of water derives, in addition, from its ability to form a network of hydrogen bonds (H-bonds).

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\*The dipole moment,  $\mu$ , is defined as the charge times the distance separating the charge. 1 Debye (D) =  $3.336 \times 10^{-30}$  coulomb (C) x meters (m). For example, for one electron ( $1.60 \times 10^{-19}$  C) separated from a proton by 1 Å ( $10^{-10}$ m),  $\mu = 1.6 \times 10^{-29}$  C x m = 4.80 D.

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H-bonds are the strong electrostatic interaction between an H atom on an *electronegative* atom, X [one which has a strong attraction for electrons] and a lone pair on another atom, Y. We use a dotted line to represent the H-bond:

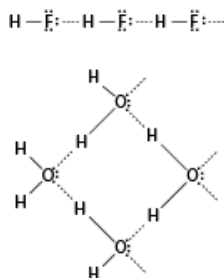


The electronegativity of X is important, since it determines the extent to which the bonding electrons are pulled toward X and away from H. Thus hydrocarbons do not form H-bonds to a significant extent, because C and H have similar electronegativities, resulting in an essentially neutral H atom. The elements to the right of carbon in the periodic table – N, O and F – are increasingly electronegative, because their increasing nuclear charge draws the valence electrons closer to the nucleus. They are the ones that can donate H-bonds, and they are also the elements that retain lone pairs when they form compounds.

The same principles apply to elements of the second and higher rows of the periodic table, but H-bonding is weaker for these elements [e.g. P, S and Cl] since they are less electronegative than those in the first row [because the nucleus is farther from the valence electrons]. The most important H-bonds in nature are those in which X and Y are N and/or O.

H-bonding is very important in biological molecules, for which N and O atoms occur at key points in the structure. The H-bonds help maintain the three-dimensional shape of these molecules, and are responsible for determining how they interact with one another. Perhaps the most important H-bonds are those which establish complementarity of the bases in the DNA double helix [see p?], and thereby determine the genetic code.

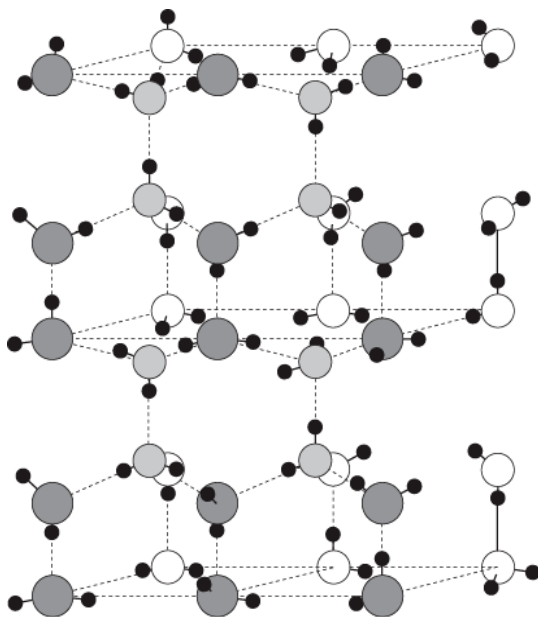
Water is able to donate two hydrogen bonds, one from each of its H atoms, while simultaneously accepting two hydrogen bonds, one to each of the electron lone pairs on the oxygen atom. Thus liquid water forms a three-dimensional network of H-bonds, whereas HF, having only one donor site, is limited to forming linear H-bond chains (**Figure 12.1**).



**Figure 12.1** Linear H-bonding in HF versus network H-bonding in H<sub>2</sub>O.

The H-bond network of water is demonstrated strikingly by the crystal structure of ice, in which each water molecule is H-bonded to four other molecules in connected six-membered rings (**Figure 12.2**). These six-membered rings produce a very open structure, which accounts for another unusual property of water, its

expansion upon freezing. Most substances contract upon solidification because the molecules take up more room in the chaotic liquid state than they do in the close-packed solid. The liquid continues to expand as it is heated due to the increased motion of the molecules. When ice melts, however, the open lattice structure collapses on itself and the density *increases*. H-bonded networks still exist, but they fluctuate very rapidly, allowing the individual water molecules to be mobile and closer together. As liquid water is heated from 0°C, the H-bonded network is further disrupted and the liquid water continues to contract. When the temperature reaches 4°C, the density of liquid water reaches a maximum. As the temperature rises above 4°C, the water slowly expands, reflecting the increasing thermal motion. The lower density of ice relative to water is of great ecological significance to the world's temperate-zone lakes and rivers. Because winter ice floats on top of the water, it protects the aquatic life below the surface from the inhospitable climate above. If ice were denser than water, the lakes and rivers would freeze from the bottom up, creating arctic conditions.

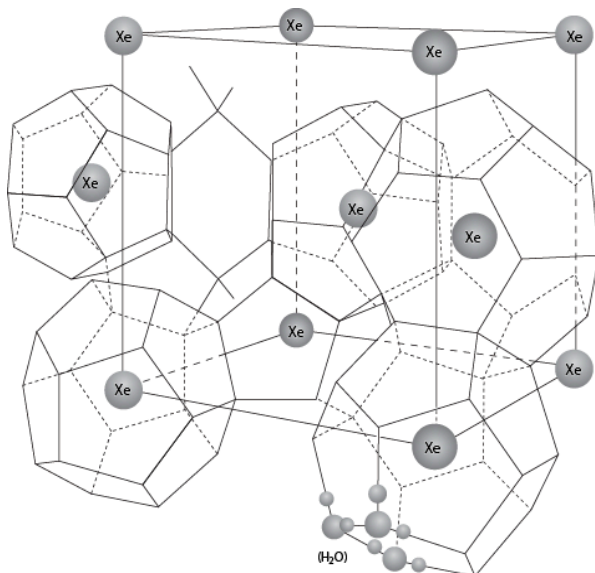


**Figure 12.2** The crystal structure of ice. The larger circles and smaller circles represents oxygen atoms and hydrogen atoms, respectively. Oxygen atoms with the same color shading indicate they lie in the same plane.

### **12.S2. Clathrates and water miscibility**

The ability of water molecules to hydrogen bond to one another accounts for the existence of crystalline *clathrates* [also called *hydrates*], compounds in which water molecules can pack themselves around non-polar molecules by forming ordered arrays of H-bonds. The structure of xenon hydrate,  $8\text{Xe} \bullet 46\text{H}_2\text{O}$ , is shown in **Figure 12.3**. The crystals consist of arrays of dodecahedra formed from 20 water molecules H-bonded together. Within the dodecahedra are the Xe atoms, or

nonpolar molecules of similar size, such as CH<sub>4</sub> or CO<sub>2</sub>. By filling the voids, the guest molecules stabilize the clathrate H-bond network. The clathrates are stable to temperatures appreciably higher than the melting point of ice. For example, methane hydrate melts at 18 °C at atmospheric pressure. Clogging of natural gas pipelines by methane hydrate was once a problem for gas distribution. It was solved by removing water vapor before the gas was fed into the lines.



**Figure 12.3** The structure of a clathrate crystal, xenon hydrate; the xenon atoms occupy cavities (eight per unit cube) in a hydrogen-bonded three-dimensional network formed by water molecules (46 per unit cube).

As discussed earlier (p?) it has come to be appreciated that methane hydrates occur very widely in nature, principally in ocean sediments or in the arctic permafrost. Anaerobic microbes in sediments or in swamps decompose organic matter to methane [see p. ?]. When methane is released into the surrounding water, it forms methane hydrate, provided the temperature is low enough, and/or the pressure is high enough.

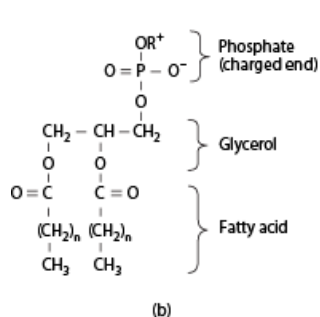
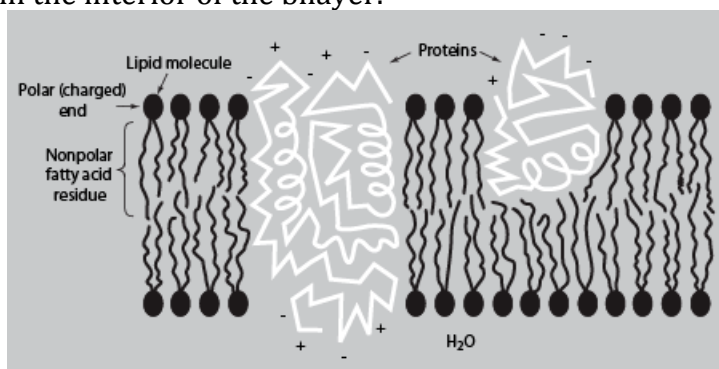
The ability of water to form extended H-bond networks around nonpolar molecules also explains why oil and water do not mix. Water molecules actually attract hydrocarbon molecules; as shown in **Table 12.2**, the enthalpy of dissolution in water is negative for simple hydrocarbons, meaning that the molecular contact releases heat. The heat release reflects an attractive force created by the interaction between water and the guest molecule. Nevertheless, the free energy values are positive; the reaction is disfavored by large negative entropy changes ( $\Delta G = \Delta H - T \Delta S$ ). The negative entropy implies that mixing increases molecular order, consistent with the water molecules packing around the nonpolar solute, as they do in the clathrate structures. Thus, oil and water do not mix because the packing tendency of the water inhibits it.

**Table 12.2** Free Energy, Enthalpy, and Entropy of Solution in Liquid Water at 298 K

Process	$\Delta G$ (joules/mol)	$\Delta H$ (joules/mol)	$\Delta S$ (joules/K/mol)
CH <sub>4</sub> in benzene → CH <sub>4</sub> in water	+10,878	-11,715	-75
C <sub>2</sub> H <sub>6</sub> in benzene → C <sub>2</sub> H <sub>6</sub> in water	+15,899	-9,205	-84
C <sub>2</sub> H <sub>4</sub> in benzene → C <sub>2</sub> H <sub>4</sub> in water	+12,217	-6,736	-63
C <sub>2</sub> H <sub>2</sub> in benzene → C <sub>2</sub> H <sub>2</sub> in water	+7,824	-795	-29
Liquid propane → C <sub>3</sub> H <sub>8</sub> in water	+21,129	-7,531	-96
Liquid <i>n</i> -butane → C <sub>3</sub> H <sub>10</sub> in water	+24,476	-4,184	-96
Liquid benzene → C <sub>6</sub> H <sub>6</sub> in water	+17,029	0	-59
Liquid toluene → C <sub>7</sub> H <sub>8</sub> in water	+19,456	0	-67
Liquid ethyl benzene → C <sub>8</sub> H <sub>10</sub> in water	+23,012	0	-79

Source: W. Kauzmann (1959). Some factors in the interpretation of protein denaturation. *Advances in Protein Chemistry* 14:1-63.

This tendency of water and nonpolar molecules to separate is responsible for many important structures in biology. For example, proteins keep their shape in water by folding in such a way that *hydrophobic* (“water-hating”) alkyl and aryl groups of the amino acids are in the interior, away from the water, while *hydrophilic* (“water-loving”) polar and charged groups face the exterior, where they contact the water. Likewise, biological membranes are bilayers of lipid molecules (**Figure 12.4**), with the hydrocarbon chains of the lipids packed together away from the water in the interior of the bilayer.



**Figure 12.4** a) The hydrophilic-hydrophobic bilayer structure of a biological membrane; b) molecular structure of a lipid molecule.

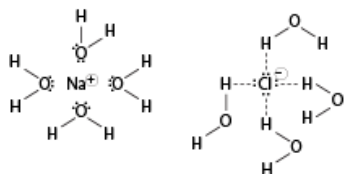
The solubility of organic molecules in water increases when they have functional groups capable of forming H-bonds with water. Thus alcohols, ethers, acids, amines and amides are all significantly soluble in water, the extent of solubility depending on the size of the hydrocarbon portion of the molecule. The smaller the hydrocarbon portion the higher the solubility. Small alcohols, like methanol and ethanol, are completely miscible with water. The -OH group can both donate and accept H-bonds with water molecules, providing a strong impetus for mixing. Ethers are not completely miscible, since the -O- atom substituent can accept but not donate an H-bond. However, the solubility is considerably enhanced by the H-bond acceptance, relative to the solubility of a comparable hydrocarbon. Thus the solubility of the gasoline additive MTBE [methyl tertiarybutyl ether – **see p?**] is 4700 mg/l, compared to only 24 mg/l for the equivalent hydrocarbon, 2,2'-dimethylbutane. This is why MTBE is a far more serious groundwater contaminant than the gasoline to which it has been added.

## 12.2 Acids, Bases, and Salts

### 12.3.3. Ions, autoionization, and pH

Another unique property of water is the ease with which it dissolves ionic compounds. The forces between ions of opposite charge in a crystal are very strong, and cost a good deal of energy to disrupt. This can be seen in the high melting point of an ionic crystal, such as ordinary table salt. Yet salt dissolves readily in water, because the water molecules strongly *solvate* both the positive sodium ions and the negative chloride ions. The strong interionic forces are replaced by equally strong solvation forces.

The strong solvation forces stem from water's large dipole moment and H-bonding ability. Anions interact with the positive end of the dipole via H-bonds, while cations interact with the negative end via coordinate bonds from the oxygen lone-pair electrons (**Figure 12.5**).



**Figure 12.5** Solvation of ions in water.

Among the ions that are stabilized in water are the hydrogen and hydroxide ions. Strong acids such as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> release H<sup>+</sup> ions when dissolved in water, while strong bases such as NaOH or KOH release OH<sup>-</sup>. These ions are special because they react together to form water



Reaction [12.1] is a *neutralization* reaction; the strong base neutralizes the strong acid and vice versa. The reverse of this reaction is *autoionization*; the water

can ionize itself because the ions are stabilized by other water molecules. This reverse reaction does not proceed to any great extent; the position of equilibrium for reaction [12-1] lies far to the right. Nevertheless, autoionization is a key factor in acid-base chemistry because it sets the range of available acid and base strengths in water.

In contrast to reactions in the gas phase, reactions in aqueous solution are usually rapid. The water molecules are in continuous contact with one another, and the H-bonds and coordinate bonds are broken and reformed rapidly. There are some metal ions for which the coordinate bonds to water are long-lived for special electronic reasons, as in the complex ion  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . But for most ions, the bonds are broken and reformed very rapidly, producing an averaged solvation environment for the ion. Consequently the extent of reaction is generally set by the equilibrium constant, rather than the kinetics, even if the position of equilibrium lies far to the right or to the left. We can use the experimentally determined equilibrium constant to calculate the extent of reactions from various starting conditions. This is a particularly useful capability in acid-base reactions, which are fundamental to the chemistry of the aqueous environment.

### 12.S4 The pH Scale

For solutions of a strong acid, HX, the concentration of  $\text{H}^+$  ions is the same as the *analytical* concentration ( $C_{\text{HX}}$ ), i.e. the number of moles per liter [symbolized  $M$ ] of dissolved HX. We write

$$[\text{H}^+] = C_{\text{HX}} M$$

Likewise for solutions of a strong base, MOH

$$[\text{OH}^-] = C_{\text{MOH}} M$$

Because  $[\text{H}^+]$  is generally less than 1 M, and frequently much less, it has become standard to express the concentration as the negative logarithm, symbolized by “p”:

$$\text{pH} = -\log[\text{H}^+]$$

For example, when the HX concentration is  $10^{-3}$  M [i.e. 1 millimolar], the pH is 3, and when it is twice this much, the pH is 2.7 [because  $-\log[2 \times 10^{-3}] = 0.3 - 3 = 2.7$ ]. In the same way

$$\text{pOH} = -\log[\text{OH}^-]$$

If we now consider the autoionization reaction [reverse of equation [12.1]]



we can write the equilibrium expression as

$$K = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}] \quad [12.3]$$

We see that  $[H^+]$  and  $[OH^-]$  are reciprocally related

$$\begin{aligned} [H^+] &= K[H_2O]/[OH^-] \\ \text{or } pH &= -\log (K[H_2O]) - pOH \end{aligned} \quad [12.4]$$

In an aqueous solution the concentration of the water molecules is essentially constant; a liter of water weighs 1000 g, and contains  $1000 \text{ g}/18 \text{ g mol}^{-1} = 55.5$  moles. [The added weight from the dissolved ions is a small fraction of 1000 g, unless the solution is very concentrated]. Therefore it is customary to include  $[H_2O]$  in the 'effective' equilibrium constant. For the autoionization equilibrium, the effective constant,  $K[H_2O]$ , is called  $K_w$ ; its experimental value is  $10^{-14} \text{ M}^2$ . Substituting this value in eq. [12-4], we see that

$$pH = 14 - pOH \quad [12.5]$$

In other words, the autoionization equilibrium requires that the pH and pOH add up to 14.

In pure water there is no source of  $H^+$  or  $OH^-$  other than the autoionization reaction itself, which requires that one  $H^+$  be produced for every  $OH^-$ . In that case  $[H^+] = [OH^-]$ , and plugging this condition into the equilibrium expression [12-3] gives

$$[H^+]^2 = 10^{-14} \text{ M}^2, \text{ or } [H^+] = 10^{-7} \text{ M}$$

Thus the autoionization reaction requires that pure water have a pH of 7. This is also the pH of a solution in which a strong acid has been exactly neutralized by a strong base. A pH of 7 defines neutrality; pH values below 7 are acidic, while pH values above 7 are basic, or *alkaline*.

### **12.55 Weak acids and bases; buffers**

Because water dissolves so many different substances, the only place in the environment where pure water is found is at the start of the hydrological cycle, in water vapor. Even raindrops include other substances; as detailed in Part II, the formation of raindrops in saturated air is nucleated by atmospheric particles, especially nitrates and sulfates. In addition, the water in cloud vapor and raindrops is in equilibrium with other constituents of the atmosphere, especially carbon dioxide. These substances tend to lower the pH of rainwater significantly below neutrality.

Strong acids transfer a proton completely to water, but many acidic substances hold the proton more or less tenaciously, and the transfer to water may be incomplete. For a generalized acid, HA, the extent of the transfer depends on the equilibrium constant,  $K_a$ , for the *acid dissociation* reaction



$$K_a = [H^+][A^-]/[HA] \quad [12.7]$$

$K_a$  is often referred to as the *acidity constant*. If  $K_a$  is small, then only a small fraction of HA will be dissociated, creating a considerable difference between the concentration of acid molecules and the concentration of hydrogen ions.

Worked Problem 12.1: pH of a Weak Acid

Q: What is the pH of a 0.1 M solution of acetic acid, which has a  $K_a$  of  $10^{-4.75}$  M<sup>2</sup>?

A: Dissociation of HA produces an equal number of H<sup>+</sup> and A<sup>-</sup> ions, and therefore  $[H^+] = [A^-]$ . Substituting this equality in eq. [12-7], and rearranging, gives

$$[H^+]^2 = K_a[HA] \quad [12.8]$$

If only a small fraction of HA is dissociated, then  $[HA]$  is essentially the same as the analytical concentration,  $C_{HA}$  [this will be the case provided  $K_a \ll C_{HA}$ ], and therefore

$$[H^+]^2 \sim K_a C_{HA} \quad [12.9]$$

In this problem  $C_{HA} = 0.1$  M, and  $K_a = 10^{-4.75}$  M<sup>2</sup> (which is much smaller than  $C_{HA}$ \*) so  $[H^+]^2 = 10^{-4.75} \times 10^{-1.0} = 10^{-5.75}$

$$[H^+] = 10^{-2.88} \text{ M or pH} = 2.88$$

Therefore, a 0.1 M solution of acetic acid has a pH close to 3.0.\*

[footnote: \*Since the value of  $[H^+]$  is only 1% of the value of  $C_{HA}$ , the approximation that  $(HA) = C_{HA}$  is a good one in this case. When this approximation is poor, then allowance must be made for the lowering of HA due to the ionization reaction. Since every molecule of HA that ionizes produces one H<sup>+</sup> ion,  $C_{HA} = [HA] + [H^+]$ , or  $[HA] = C_{HA} - [H^+]$ . Substituting this into equation [12-7] and rearranging, we have

$$[H^+]^2 + K_a[H^+] - K_a C_{HA} = 0$$

which may be solved with the quadratic formula.]

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If HA holds its proton tenaciously, then the anion, A<sup>-</sup>, will have some tendency to remove a proton from water. Thus if a salt of A<sup>-</sup> is added to water, the reaction



which is called a *hydrolysis*, or a *base dissociation* reaction, will proceed to some extent. Since OH<sup>-</sup> is produced, A<sup>-</sup> is acting as a base. Assuming that the equilibrium does not lie completely to the right, A<sup>-</sup> is a weak base. The equilibrium constant, called the *basicity constant*, is

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad [12.11]$$

[As in the case of the autoionization reaction the water concentration,  $[H_2O]$ , being constant, is lumped into the equilibrium constant.]

The acid and base dissociation reactions are linked by the autoionization reaction. This can be seen by adding reaction [12-6] to reaction [12-10] to yield reaction [12-2]. When reactions are added, the equilibrium constants multiply, i.e.

$K_a K_b = K_w$  [This result can be checked by substituting the equilibrium expressions, eq. [12-7], [12-11] and [12-3].] Thus determining  $K_a$  also specifies  $K_b$ .

Worked Problem 12.2: pH of a Weak Base

Q: What is the pH of a 0.1 M solution of sodium acetate?

A: Since base dissociation produces one  $\text{OH}^-$  for every HA [eq. [12-10], then  $[\text{OH}^-] = [\text{HA}]$  for a salt of  $\text{A}^-$  dissolved in water. Then  $[\text{OH}^-]$  can be calculated by substitution in eq. [12-11] and rearranging,

$$[\text{OH}^-]^2 = K_b[\text{A}^-] \sim K_b C_{\text{A}^-} \quad [12.12]$$

provided that  $K_b \ll C_{\text{A}^-}$ , so that the difference between  $[\text{A}^-]$  and  $C_{\text{A}^-}$  is negligible.

In this problem  $C_{\text{A}^-} = 0.1 \text{ M}$ , and  $K_b = K_w/K_a = 10^{-14}/10^{-4.75} = 10^{-9.25} \text{ M}$  (which is much less than  $C_{\text{A}^-}$ ), so that

$$[\text{OH}^-]^2 = 10^{-9.25} \times 10^{-1.0} = 10^{-10.25}$$

or  $[\text{OH}^-] = 10^{-5.12} \text{ M}$ . Since  $[\text{H}^+] = K_w/[\text{OH}^-]$ , then  $\text{pH} = 14 - 5.12 = 8.88$ . Thus a 0.1 M sodium acetate solution has a pH close to 9, a fairly alkaline value.

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**12.S6 Conjugate Acids and Bases; Buffers**

A weak acid, HA, and its anion,  $\text{A}^-$ , constitute a *conjugate acid-base pair*. The two are the same molecular entity, differing only by one proton. The actual charge is unimportant in this context. The base could equally well be neutral, and then its conjugate acid would have a positive charge. For example, the ammonium ion and ammonia,  $\text{NH}_4^+$  and  $\text{NH}_3$ , constitute a conjugate acid base pair.

An important characteristic of a conjugate acid-base pair is that a mixture of the two partners has a pH that is close to the negative logarithm of the acidity constant, called the  $\text{p}K_a$ . This can be seen by rearranging the equilibrium expression, eq. [12-7]

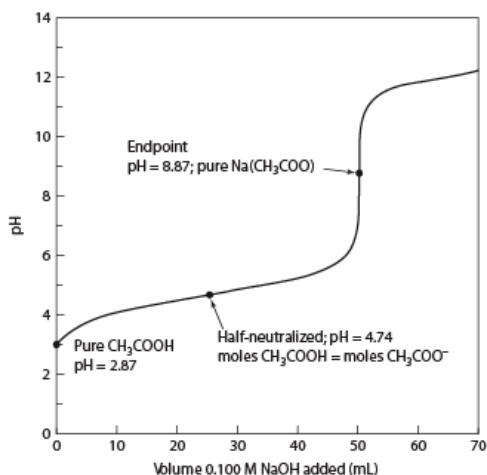
$$[\text{H}^+] = K_a[\text{HA}]/[\text{A}^-]$$

$$\text{or } \text{pH} = \text{p}K_a - \log[\text{HA}]/[\text{A}^-] \quad [12.13]$$

If  $[\text{HA}] = [\text{A}^-]$ , then the pH is exactly  $\text{p}K_a$ . Moreover, the pH will be close to the  $\text{p}K_a$ , as long as  $[\text{HA}]/[\text{A}^-]$  is not far from unity. Even if this ratio reaches a value of 10 or 0.1, the pH will deviate from  $\text{p}K_a$  by only one unit. Thus the pH is *buffered* against large changes. A mixture of HA and  $\text{A}^-$  constitutes a *buffer* solution, because it resists large pH changes when small amounts of other acids or bases are added to the solution.

The buffering effect is best illustrated by a *titration* curve of the acid. **Figure 12.6** shows a titration curve for a 0.1 M acetic acid solution, to which successive amounts of a strong base [e.g. NaOH] are added. At the start of the titration the pH is close to 3, while at the end point, when all of the HAc has been converted to NaAc, the pH is close to 9. At the halfway point  $[\text{HAc}] = [\text{Ac}^-]$ , and  $\text{pH} = \text{p}K_a = 4.74$ . From the 10% to the 90% points of the titration, the pH varies only by minus and plus one

unit from this value. But as the endpoint is approached, the *buffer capacity* of the  $\text{HAc}/\text{Ac}^-$  mixture is used up, and the pH shoots up to 9 and beyond. With only a 10% excess of the base titrant  $[\text{OH}^-] = 10^{-2} \text{ M}$ , the pH reaches 12.



**Figure 12.6** The change in pH during the titration of a weak acid with a strong base; 50.0 mL of 0.100 M acetic acid is titrated with 0.100 M NaOH.

### 12S.7 Water in the Atmosphere: Acid Rain

Although pure water is neutral, and has a pH of 7.0, rainwater is naturally acidic because it is in equilibrium with carbon dioxide. When dissolved in water, carbon dioxide forms carbonic acid, a weak acid:



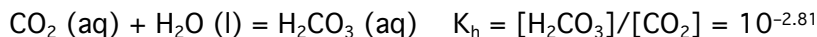
We can gauge the amount of carbonic acid from the equilibrium constant for reaction [12-7]

$$K_s = [\text{H}_2\text{CO}_3] / P_{\text{CO}_2} = 10^{-1.5} \text{ M/atm} \quad [12.15]$$

where  $P_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$ , in atmospheres.\*

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[footnote: \*Actually, dissolved  $\text{CO}_2$  is mostly unhydrated; only a small fraction exists as  $\text{H}_2\text{CO}_3$  molecules:



The total concentration of dissolved  $\text{CO}_2$  is:

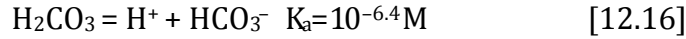
$$[\text{CO}_2]_T = [\text{CO}_2] + [\text{H}_2\text{CO}_3] = [\text{H}_2\text{CO}_3][1 + K_h^{-1}] = 10^{2.81} [\text{H}_2\text{CO}_3]$$

Most equilibrium measurements are made with respect to total dissolved  $\text{CO}_2$ , and  $[\text{H}_2\text{CO}_3]$  is to be understood as  $[\text{CO}_2]_T$ .

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Since the atmospheric concentration of CO<sub>2</sub> is currently 379 ppm, P<sub>CO<sub>2</sub></sub> = 379 x 10<sup>-6</sup> or 10<sup>-3.4</sup> atm (at sea level), and therefore [H<sub>2</sub>CO<sub>3</sub>] = K<sub>s</sub>P<sub>CO<sub>2</sub></sub> = 10<sup>-1.5</sup> ∞ 10<sup>-3.4</sup> = 10<sup>-4.9</sup> M.

Rainwater is thus a dilute solution of carbonic acid. The acid dissociates partially to hydrogen and bicarbonate ions:



From K<sub>a</sub> we can calculate [H<sup>+</sup>], as in Worked Problem 12.1

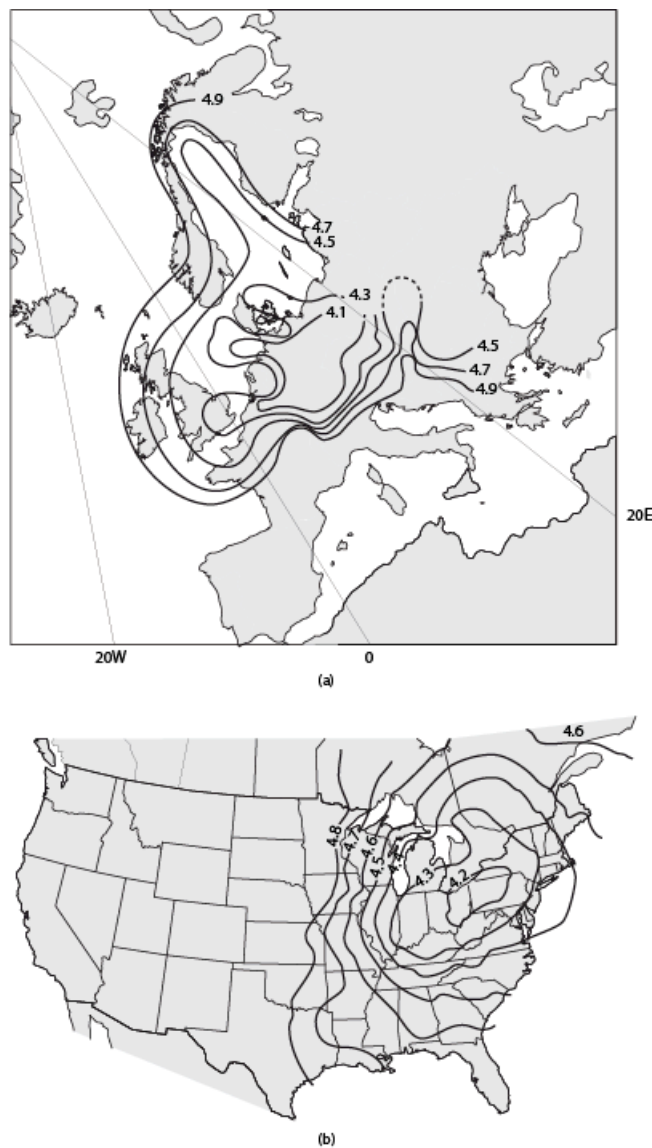
$$[\text{H}^+]^2 = K_a[\text{H}_2\text{CO}_3] = 10^{-6.4} \times 10^{-4.9} = 10^{-11.3}$$

$$[\text{H}^+] = 10^{-5.7} \text{ and pH} = 5.7$$

Thus, atmospheric CO<sub>2</sub> depresses the pH of rainwater by 1.3 units from neutrality. Even in the absence of anthropogenic emissions, rainwater is naturally acidic (although it can occasionally be neutral or alkaline as a result of contact with alkaline minerals in windblown dust, or with gaseous ammonia from soils or from industrial emissions).

To the acidifying effect of carbon dioxide must be added the contributions from other acidic constituents of the atmosphere, particularly HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. These acids can both be formed naturally: HNO<sub>3</sub> derives from NO produced in lightning and forest fires, while H<sub>2</sub>SO<sub>4</sub> derives from volcanoes and from biogenic sulfur compounds. At the natural background concentrations, these acids rarely influence rainwater pH significantly.

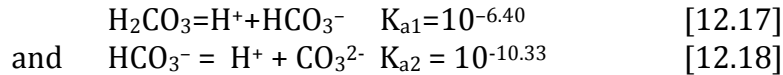
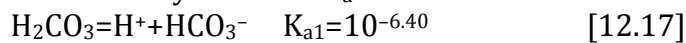
In polluted areas, however, the concentrations of these acids can be much higher and can reduce the pH of rainwater substantially over extended regions, producing what is known as *acid rain*. It is not uncommon in polluted areas to find the pH of rainwater in the pH 5–3.5 range. Some fogs, which can be in contact with pollutants over many hours, have had pH readings as low as 2.0, a degree of acidity equivalent to a 0.01 M solution of a strong acid. Moreover, the acid rain can fall quite far from the sources of pollution, due to long-range atmospheric transport. In particular, acid rain is a pressing problem for areas downwind of coal-fired power plants, whose tall smokestacks ameliorate local pollution by lofting SO<sub>2</sub> and NO emissions high into the air. Thus, power plants in western and central Europe affect the rain falling on Scandinavia, and power plants in the U.S. Midwestern industrial belt similarly affect rain falling on northeastern regions of the United States and on southeastern Canada (**Figure 12.7**), although emissions of SO<sub>2</sub> have been reduced in recent decades (see Figure 2. x, p.?). While acid rain is a phenomenon in the hydrosphere, it depends upon atmospheric conditions—the extent of acidic emissions and the prevailing weather patterns.



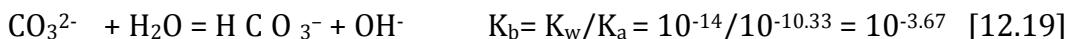
**Figure 12.7** Contour lines of long-term, volume-weighted averages of pH in precipitation in a) Europe, 1978-1982, and b) eastern North America, 1980-1984. *Sources:* EMEP/CCC (1984). *Summary Report*, Report 2/84 (Lillestrøm, Norway: Norwegian Institute for Air Research); National Acid Precipitation Assessment Program (NAPAP) (1987). *NAPAP Interim Assessment* (Washington, DC: U.S. Government Printing Office).

### 12.58 Polyprotic Acids

Carbonic acid actually has two ionizable protons, but they dissociate successively, and with very different  $K_a$  values:



Because the bicarbonate ion is negatively charged, it holds its proton more tenaciously than does carbonic acid, and the second dissociation reaction makes no significant contribution to the  $H^+$  concentration of a carbonic acid solution or to that of a  $H_2CO_3/HCO_3^-$  buffer. However, we can neutralize both protons on  $H_2CO_3$  with a strong base, or equivalently start with a solution of a carbonate salt, and then the basic properties of  $CO_3^{2-}$  come into play:



For a solution which is 0.1 M in a carbonate salt (just as in Worked Problem: 12.2 for acetate)

$$[OH^-]^2 = K_b[CO_3^{2-}] \sim 10^{-3.67} \times 10^{-1} = 10^{-4.67}$$

and  $[OH^-] = 10^{-2.34}$ , giving pH = 11.66, a highly alkaline value.

Also, a buffer having equimolar  $HCO_3^-$  and  $CO_3^{2-}$  has

$$pH = pK_a - \log [HCO_3^-]/[CO_3^{2-}] = 10.33$$

However, if only one of the two  $H_2CO_3$  protons is neutralized, or, equivalently, if we start with a solution of a bicarbonate salt, then things are slightly more complicated, since  $HCO_3^-$  is both a conjugate base [of  $H_2CO_3$ ] and a conjugate acid [of  $CO_3^{2-}$ ]. To the extent that  $HCO_3^-$  dissociates a proton [via reaction 12-18], the proton is taken up by another  $HCO_3^-$  ion [via the reverse of reaction 12-17]. Consequently the main acid-base reaction in a bicarbonate solution is



This reaction is obtained by subtracting reaction [12.17] from reaction [12.18], and consequently the equilibrium constant is given by

$$K_{a2}/K_{a1} = [H_2CO_3][CO_3^{2-}]/[HCO_3^-]^2$$

From equation [12-20],  $[H_2CO_3] = [CO_3^{2-}]$  for a solution containing only bicarbonate initially. Then

$$K_{a2}/K_{a1} = [H_2CO_3]^2/[HCO_3^-]^2 \text{ or } [HCO_3^-]/[H_2CO_3] = [K_{a1}/K_{a2}]^{1/2}$$

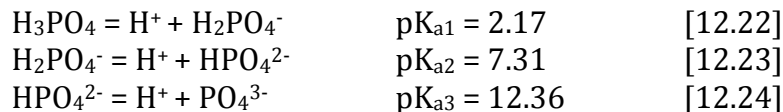
To calculate the pH, we can insert this ratio into the equilibrium expression for reaction [12-17]:

$$[H^+] = K_{a1}[HCO_3^-]/[H_2CO_3] = K_{a1}[K_{a2}/K_{a1}]^{1/2} = [K_{a1}K_{a2}]^{1/2}$$

$$\text{or } pH = [pK_{a2} + pK_{a1}]/2 = [10.33 + 6.40]/2 = 8.36 \quad [12.21]$$

Equation [12-21] can be generalized to any diprotic acid: the pH of a solution of the monoprotic form is just the geometric mean of the two  $pK_a$  values.

There can also be more than two ionizable protons. For example, phosphoric acid has three:



As in the case of carbonic acid, the pH of a solution of  $\text{H}_3\text{PO}_4$  or of  $\text{PO}_4^{3-}$  can be calculated just as it would be for a monoprotic acid or base, while for solutions of the diprotic and monoprotic forms, the pH is the geometric mean of the bracketing  $\text{pK}_a$  values, i.e. for  $\text{H}_2\text{PO}_4^-$

$$\text{pH} = [\text{pK}_{a1} + \text{pK}_{a2}]/2 = 4.74$$

while for  $\text{HPO}_4^{2-}$

$$\text{pH} = [\text{pK}_{a2} + \text{pK}_{a3}]/2 = 9.83$$

The phosphoric acid system has three buffer zones, corresponding to the three  $\text{pK}_a$  values, i.e. solutions having comparable concentrations of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$ , or of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ , or of  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .

### Worked Problem 12.3: Phosphate Protonation

Q: Given the  $\text{pK}_a$  values above, what is the dominant form of the phosphate ion in a) a lake with  $\text{pH} = 5.0$ , and b) seawater with  $\text{pH} = 8.0$ , and what is the ratio of this form to the next most abundant form?

A: The lake pH is higher than  $\text{pK}_{a1}$  but lower than  $\text{pK}_{a2}$ , so most of the phosphate will be present as  $\text{H}_2\text{PO}_4^-$ . For the seawater  $\text{HPO}_4^{2-}$  dominates, because the pH is between  $\text{pK}_{a2}$  and  $\text{pK}_{a3}$ . Since the lake pH is closer to  $\text{pK}_{a2}$  than  $\text{pK}_{a1}$ , the next most abundant form is  $\text{HPO}_4^{2-}$ , while for the seawater  $\text{H}_2\text{PO}_4^-$  is the next most abundant form, since the pH is closer to  $\text{pK}_{a2}$  than to  $\text{pK}_{a3}$ . The ratios can be obtained from the equilibrium expression for the second ionization, [12.23]

$$[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = K_{a2}/[\text{H}^+]$$

At  $\text{pH} = 5.0$ , this ratio is  $10^{-7.31}/10^{-5.0} = 10^{-2.31} = 0.0049$ , while at  $\text{pH} = 8.0$ , the ratio is  $10^{-7.31}/10^{-8.0} = 10^{0.69} = 4.9$  [or  $[\text{H}_2\text{PO}_4^-]/[\text{HPO}_4^{2-}] = 0.20$ ].

### Problems:

1.  $\text{H}_2\text{S}$  boils at  $-61^\circ\text{C}$ ,  $\text{H}_2\text{Se}$  at  $-42^\circ\text{C}$ , and  $\text{H}_2\text{Te}$  at  $-2^\circ\text{C}$ . Based on this trend, at what temperature would one expect water to boil? Why does water boil at a much higher temperature?
2. The pH of aqueous 0.20 M chlorous acid ( $\text{HClO}_2$ ), a weak acid, was measured to be 1.1. What are the values of  $K_a$  and  $\text{pK}_a$  of chlorous acid?
3. The pH of aqueous 0.20 M propylamine ( $\text{C}_3\text{H}_7\text{NH}_2$ ), a weak base, was measured to be 11.96. What are the values of  $K_b$  and  $\text{pK}_b$  of propylamine?

4. Calculate the initial concentration of an aqueous solution of the weak acid hydrocyanic acid (HCN), with a pH of 6.4. The  $pK_a$  of hydrocyanic acid is 9.31.
5. Calculate the initial concentration of an aqueous solution of the weak base hydrazine,  $NH_2NH_2$ , with a pH of 10.20. The  $pK_b$  of hydrazine is 5.77.
6. A solution made of equal concentrations of lactic acid and sodium lactate was measured to have a  $pH = 3.08$ . a) calculate the  $pK_a$  and  $K_a$  of lactic acid. b) Calculate the pH of the solution if there was twice as much acid as salt in the solution.
7. Calculate the ratio of molarities of  $PO_4^{2-}$  and  $HPO_4^-$  ions in a buffer solution with a pH of 11.0.
8. If the concentration of atmospheric  $CO_2$  were to double from its current value of 370 ppm, what would be the calculated pH of rainwater (assuming that  $CO_2$  were the only acidic input)? With respect to rising  $CO_2$  levels, do we have to be concerned about enhanced acidity of rain in addition to potential climate warming?
9. Write the stepwise proton transfer equilibria for the deprotonation of the following chemical species:  
a) hydrosulfuric acid;  $H_2S$   
b) arsenic acid;  $H_3AsO_4$   
b) succinic acid;  $(CH_2)_2(COOH)_2$
10. Selenous acid,  $H_2SeO_3$ , is a diprotic acid with  $pK_a$  values of 2.46 and 7.31. Estimate the pH of 0.200 M  $NaHSeO_3$  (aq).